Structural Characterization of Poly(silylenemethylene)

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ABSTRACT: The molecular structure of the monosilicon analog of poly(ethylene), poly(silylenemethylene), $CH_3[SiH_2CH_2]_nSiH_3$, or poly(silaethylene) (PSE), was characterized by means of high-resolution ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. The average molecular weight of this polymer was also determined from the NMR spectra by integration of the $-SiH_3$ and $-CH_3$ end groups, relative to the main-chain $-SiH_2-CH_2-$ units. All of the peaks in the NMR spectra were assigned with the help of a model compound, $CH_3SiH_2CH_2SiH_3$, and PSE with added $SiCH_2SiH_3$ or $SiCH_3$ side groups. In addition to the main-chain $-SiH_2CH_2-$ species, the $-CH_3$ and $-SiH_3$ end groups and a small concentration (ca. 1 per 200 Si atoms in the polymer chain) of $-SiHCH_3-$ branch sites were evidenced in the NMR spectra of the "parent" PSE. These $-SiHCH_3-$ groups were concluded to arise from a small amount of dimethyldichlorosilane in the methyltrichlorosilane starting material used in the synthesis of the 1,1,3,3-tetrachloro-1,3-disilacyclobutane monomer.

1. Introduction

Polycarbosilanes have attracted increasing attention in recent years, partly due to their potential applications as precursors to silicon carbide ceramics.[1] Among the investigated polycarbosilanes, the all-hydrogen-substituted "poly(silaethylene)" (PSE), $[SiH_2CH_2]_n$ (or poly(silylenemethylene)), with its 1:1 Si:C ratio is a particularly attractive candidate for a SiC precursor. The initial claim for the synthesis of a $[SiH_2CH_2]_n$ polymer was made in a patent by Smith in 1986.[2a] This polymer was prepared by the ring-opening polymerization (ROP) of 1,3-disilacyclobutane (DSCB). It was described as having a linear structure and was reported to give a 85% ceramic yield of SiC on pyrolysis; however, subsequent work[2b] has raised some doubt about the linear structure of this product. In this paper,[2b] we reported an improved synthesis for PSE which involves the ROP of 1,1,3,3-tetrachloro-1,3-disilacyclobutane (TCDSCB) followed by reduction with $LiAlH_4$. The ^1H, ^{13}C, and ^{29}Si NMR spectra observed for this PSE consisted essentially of a single line for the (decoupled) $^{13}C\{H\}$ and $^{29}Si\{H\}$ NMR spectra, and, for the ^1H NMR spectrum, two sets of quintets as expected for the $-SiH_2-CH_2-$ repeat unit.

In view of the interest in PSE as a high-yield precursor to stoichiometric SiC,[3] as the parent polymer of a potentially large series of poly(silylenemethylenes),[4] and as the monosilicon analog of polyethylene (PE),[5] we concluded that a more detailed characterization of the PSE molecular structure was needed. The fact that this polymer also exhibits a melting transition which is ca. 100 °C lower than that of PE[5] provided further impetus for such a study, especially in view of the possible consequences of chain branching and/or low molecular weight fractions on the melting transition.

This paper describes the results of our efforts to characterize the molecular structure of PSE by using NMR spectroscopy. The assignments for the end groups and the branch sites were aided by the study of a small molecule analog of the PSE polymer and polymers containing deliberately added side groups. With a complete assignment of the NMR spectra in hand, it was also possible to determine the average molecular weight (M_n) by integration of the appropriate NMR resonances relative to those of added organosilane internal standards.

2. Experimental Section

General Procedures. All NMR spectra were obtained by using a Varian XL-500 NMR spectrometer. C_6D_6 was utilized as the solvent and the internal reference for all of the proton and ^{13}C NMR spectra. ^{29}Si NMR spectra were referenced to TMS externally. Both proton-gated decoupling ^{13}C and ^{29}Si NMR spectra for PSE were measured on solutions containing 0.1 mol % of the relaxation reagent, chromium(III) tris(acetylacetonate), and using a pulse delay time of 15 sec to ensure quantitative results for all peaks. All of the ^{13}C and ^{29}Si NMR spectra of PSE were obtained by using more than 5000 transients. The suppressed ^{29}Si NMR spectrum of PSE was obtained by using the BINOM pulse sequence with a 3300 offset.[13] The errors of the integrated intensities of signals in the spectra of PSE were estimated to be 3%. The mass spectra were recorded on a Hewlett-Packard 5987A GC/MS spectrometer. GC analyses were performed on a Shimadzu GC chromatograph equipped with a Hewlett-Packard recorder-integrator unit. GPC measurements of the polymer samples were performed with a Waters 600 solvent delivery system, a 410 RI detector, and a 745 data processing unit. Helium-sparged HPLC grade toluene at a flow rate of 0.6 mL/min was used as the eluent. Average molecular weights were obtained from a 15-point calibration curve by using polystyrene standards from 200 to 470 000. Benzene, diethyl ether, and pentane solvents were distilled from appropriate drying agents[6] before use. $LiAlH_4$ pellet, $LiAlD_4$ powder, anhydrous $FeCl_3$, and H_2PtCl_6 hydrate were obtained from Aldrich. Air-sensitive materials were manipulated under N_2 using oven-dried glassware and standard inert-atmosphere techniques.[7]

2.1. Synthesis of PSE ($[SiH_2CH_2]_n$). 1,1,3,3-Tetrachloro-1,3-disilacyclobutane (TCDSCB)[8a] (15 g, 0.066 mol) and chloroplatinic acid (0.015 g, 0.027 mmol) were placed in a 250 mL two-necked round-bottom flask equipped with a reflux condenser and a rubber septum. Then 15 mL of benzene was added via a syringe. The solution was stirred and heated at 90 °C under N_2. The solution gradually became viscous during the heating. When the stirbar had stopped stirring after heating for 2.5 h, the heating was terminated and the reaction mixture was allowed to cool to room temperature. Then 150 mL of diethyl ether and 10 g (0.256 mol) of $LiAlH_4$ were added, and the mixture was refluxed for 48 h in a 60 °C oil bath. The solution was then cooled to room temperature, resulting in the precipitation of the inorganic salts. A mixture of 600 mL of 4 M HCl solution and 150 mL of ether was cooled in an ice-water bath with stirring. The liquid phase of the reaction mixture was added dropwise to the dilute acid solution with stirring over 1 h. The resultant solution was stirred for another hour

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in the ice-water bath. After the stirring was stopped, an ether layer formed above the aqueous phase. This ether layer was separated and dried with anhydrous Na_2SO_4 over 1 h. A rotatory evaporator was employed to remove the ether and a very viscous liquid was left. This polymer was redissolved in 20 mL of pentane. The pentane solution was then filtered through a 0.45 μm HPLC filter. Finally, the pentane was removed by a rotatory evaporator. The polymer was further dried under vacuum for 2 h at room temperature. About 3.5 g (yield 60.3%) of polymer was obtained. ^{1}H NMR (ppm): −0.13 (quintet, CH_2), 0.03 (multiplet, CH_3 end groups), 0.17 (doublet, CH_3 side groups), 3.7 (multiplet, SiH_3 end groups), 4.10 (quintet, SiH_2). ^{13}C{H} NMR (ppm): −8.9 ($SiCH_2Si$), −6.2 (CH_3 end groups), −4.6 (CH_2SiH), −2.0 (CH_3 side groups). ^{29}Si{H} NMR (ppm): −62.8 (SiH_3 end groups), −34.4 ($CSiH_2C$), −13.5(SiH). M_n=24 500 and M_w = 133 400.

2.2. Synthesis of Deuterio-PSE($[SiD_2CH_2]_n$). The same procedure was utilized as in the preparation of $[SiH_2CH_2]_n$, except that $LiAlD_4$ was employed as the reducing agent. ^{1}H NMR (ppm): −0.15 (CH_2), 4.10 (vw SiHD); ^{13}C{H} NMR (ppm): −9.4 (CH_2).

2.3. Synthesis of 1,3-Disila-*n*-butane ($CH_3SiH_2CH_2SiH_3$). (a) Synthesis of $CH_3Si(OCH_3)_2CH_2Si(OCH_3)_3$. THF (250 mL) and magnesium powder (24.3 g, 1.0 mol) were mixed in a 1 L three-necked round-bottom flask fitted with a mechanical stirrer, a reflux condenser, and a dropping funnel. Next, a mixture of $(CH_3O)_3SiCH_2Cl$[8b] (85 g, 0.5 mol) and $CH_3Si(CH_3O)_2Cl$[8b] (130 g, 0.92 mol) was added dropwise over 2 h. The resulting mixture was refluxed for 24 h. Hexane (300 mL) was added to the reaction solution to precipitate the magnesium salt. The liquid was transferred to another flask via pressure filter−cannulation. Both the hexane and THF were removed by means of atmospheric pressure distillation. The product (48 g, 0.2 mol, 40% yield) was collected at 50−51 °C/0.5 Torr. ^{1}H NMR (ppm): 3.4 (singlet, 15H, OCH_3), 0.45 (singlet, 3H, CH_3), 0.13 (singlet, 2H, CH_2); ^{13}C{H} NMR (ppm): 51 (OMe), 5.6 (CH_3), 0.8 (CH_2).

(b) Synthesis of $CH_3SiCl_2CH_2SiCl_3$. The product (45 g, 0.187 mol) obtained by procedure **2.3(a)** was added to a stirred mixture of acetyl chloride (90 g, 1.15 mol) and $FeCl_3$ (1 g) over 1 h at room temperature. The resultant mixture was heated to reflux for 16 h. The byproduct methyl acetate and the excess acetyl chloride were removed by distillation at atmospheric pressure. The product was isolated as a clear liquid at 32−33 °C/0.5 Torr in 90% yield (44.2 g, 0.16 mol). ^{1}H NMR (ppm): 0.94 (singlet, 3H, CH_3), 1.58 (singlet, 2H, CH_2); ^{13}C{H} NMR (ppm): 7.28 (CH_3), 20.06 (CH_2).

(c) Synthesis of $CH_3SiH_2CH_2SiH_3$. $CH_3SiCl_2CH_2SiCl_3$ (40 g, 0.152 mol) was mixed with 200 mL of THF in a 500 mL two-necked round-bottom flask. Pellets of $LiAlH_4$ (8 g, 0.2 mol) were then added gradually to the THF solution while stirring at room temperature. The resulting mixture was stirred at room temperature until all the $LiAlH_4$ pellets had dissolved. The mixture was further heated to gentle reflux for 24 h. The solvent and product were evaporated under vacuum and condensed into another flask cooled in liquid nitrogen. The product (9.6 g, 0.106 mol, 69% yield) was collected at 42−43 °C by distillation of the transferred liquid through a spinning band fractionation column. ^{1}H NMR (ppm): −0.40 (sextet, 2H, CH_2), 0.01 (triplet, 3H, CH_3), 3.66 (triplet, 3H, SiH_3), 3.9 (sextet, 2H, SiH_2); ^{13}C{H} NMR (ppm): −6.5 (CH_3), −15.2 (CH_2); ^{29}Si{H} NMR (ppm): −34.02 (SiH_2), −62.5 (SiH_3).

2.4. Preparation of a 1,1,3,3-Tetraethoxy-1,3-disilacyclobutane and 1-Methyl-1,3,3-triethoxy-1,3-disilacyclobutane (MTEDSCB) Mixture. Following the procedure for the preparation of 1,1,3,3-tetraethoxy-1,3-disilacyclobutane (TEDSCB),[8a] 125 g of a 9:1 molar mixture of $Cl(EtO)_2SiCH_2Cl$ and $Cl(EtO)Si(Me)CH_2Cl$ was mixed with 280 g of THF in a 1 L three-necked round-bottom flask. Magnesium powder (24.3 g, 1 mol) was then added over 2 h. The reaction was very exothermic during the addition of the magnesium powder, requiring the cooling of the reaction mixture occasionally with a cold water bath. The obtained mixture was maintained under gentle reflux with stirring for 10 h. Hexane (400 mL) was then added to precipitate the magnesium salt. The solution was transferred under pressure to another flask through a cannula fitted with a paper filter. The hexane and THF solvents were removed by simple distillation. Vacuum distillation gave 24.8 g of a mixture of the products (TEDSCB and MTEDSCB) at 70−80 °C/0.5 Torr. GC analysis indicated that the ratio of both compounds was 87:13 (NMR measurement gave an 86:14 ratio). The mixture was characterized by NMR and mass spectrometry. ^{1}H NMR (ppm): 3.72 (quartet, OCH_2), 1.13 (triplet, $CH_2CH^*_3$), 0.74 (singlet, $SiCH_2Si$), 0.30 (singlet, CH_3); ^{13}C{H} NMR (ppm): 59.36 (OCH_2), 18.84 (CH_2-CH^*_3), 8.06 ($SiCH_2Si$), 8.70 ($SiCH_2Si$ in MTEDSCB), 0.30 (singlet, CH_3 in MTEDSCB); ^{29}Si{H} NMR (ppm): −19.4 [Si-$(OEt)_2$], 3.78 [Si(OEt)Me]; MS peaks attributed to MTEDSCB (EI): *m/e* (relative intensity) 234 (4%), 219 (2%), 206 (6%), 175 (5%), 163 (10%), 153 (15%), 135 (100%), 119 (60%), 103 (23%), 89 (14%); MS peaks attributed to TEDSCB (EI): *m/e* (relative intensity) 264 (6%), 236 (6%), 209 (10%), 192 (10%), 179 (11%), 153 (26%), 135 (100%), 119 (58%), 105 (57%), 89 (70%).

2.5. Synthesis of 1,1,3,3-Tetrachloro-1,3-disilacyclobutane (TCDSCB) and 1-Methyl-1,3,3-trichloro-1,3-disilacyclobutane (MTCDSCB). Following the procedure for preparing TCDSCB,[8a] acetyl chloride (40 g, 0.51 mol) and ferric chloride (0.2 g) were placed in a 250 mL two-necked round-bottom flask equipped with a reflux condenser and a dropping funnel. Then 24 g of the TEDSCB and MTEDSCB mixture (obtained from procedure 2.4) was added through the funnel over 30 min. The resultant mixture was stirred at room temperature for 1 h and further stirred under reflux for 24 h. The byproduct ethyl acetate and the excess acetyl chloride were removed by atmospheric pressure distillation. A total of 17 g of product (a mixture of TCDSCB and MTCDSCB) was obtained by vacuum distillation at 56−58 °C/5 Torr. This mixture (about 9:1 ratio from NMR analysis) was found to give the following NMR resonances. ^{1}H NMR (ppm): 1.32 (singlet, CH_2), 0.13 (singlet, CH_3); ^{13}C{H} NMR (ppm): 27.33 (CH_2 in TCDSCB), 22.24 (CH_2 in MTCDSCB), 3.67 (CH_3 in MTCDSCB); ^{29}Si{H} NMR (ppm): 17.28 (Si(Me)Cl in MTCDSCB), 15.96 ($SiCl_2$ in MTCDSCB), 12.70 ($SiCl_2$ in TCDSCB).

2.6. Synthesis of a $[SiH_2CH_2]_m[SiHMeCH_2]_n$ Copolymer from TCDSCB and MTCDSCB. A portion (2.45 g) of the TCDSCB and MTCDSCB mixture from procedure **2.5** and chloroplatinic acid (2.5 mg, 0.0045 mmol) were placed in a 100 mL round-bottom flask along with benzene (2.5 mL). The solution was stirred and heated to reflux for 24 h. The resultant very viscous solution was cooled to room temperature, and 50 mL of diethyl ether was added, followed by 1 g of $LiAlH_4$. This $LiAlH_4$ ether solution was stirred at room temperature and then heated to reflux for 48 h. The workup and the separation steps were the same as for the PSE homopolymer given in section 2.1. ^{1}H NMR (ppm): 4.27 (multiplet, SiH), 4.12 (quintet, SiH_2), 3.7 (triplet, SiH_3), 0.18 (doublet, CH_3 side groups) −0.13 (quintet, $SiCH_2Si$); ^{13}C{H} NMR (ppm): −8.9 ($SiCH_2Si$), −4.6 (SiC^*H_2SiHMe), −2.0 (CH_3 side group); ^{29}Si{H} NMR (ppm): −13.41 (SiH), −34.42 (SiH_2).

2.7. Synthesis of Methyl-Branched PSE. After TCDSCB (2 g, 8.85 mmol) had been polymerized by heating to reflux with H_2PtCl_6 (2 mg, 0.0036 mmol) in 2 mL of benzene, 50 mL of diethyl ether and then 1 mL (3 mmol) of 3 N MeMgBr solution in diethyl ether were added. This solution was refluxed for 4 h. After the mixture was cooled to room temperature, 1 g of $LiAlH_4$ was added and stirred at room temperature for 2 h. The resulting solution was refluxed for 48 h. The workup procedure and the separation of the reduced polymer were the same as described for the PSE homopolymer in section 2.1. ^{1}H NMR (ppm): −0.12 (quintet, CH_2), 0.19 (doublet, CH_3 side groups), 4.1 (quintet, SiH_2), 4.26 (multiplet, SiH); ^{13}C{H} NMR (ppm): −8.87 (CH_2SiH_2), −4.6 (CH_2SiH), −2.0 (CH_3 side groups); ^{29}Si{H} NMR (ppm): −34.5 (SiH_2), −13.5 (SiH).

2.8. Synthesis of a 1,1,3-Trichloro-3-((trichlorosilyl)-methyl)-1,3-disilacyclobutane (TCMSDSCB) and 1,1,3,3,5,5-Hexachloro-1,3,5-trisilacyclohexane (HCTSCH) Mixture. A ca. 1:1 mixture of the two possible trimeric byproducts, 1,1,3-triethoxy-3-((diethoxychlorosilyl)methyl)-1,3-disilacyclobutane and 1,3,5-hexaethoxy-1,3,5-trisilacyclohexane, were isolated in 20% yield from the synthesis of TEDSCB.[8a] A 20 g portion of this mixture was added to a solution of acetyl chloride (30 g, 0.382 mol) and $FeCl_3$ (0.2 g) at room temper-

ature. After refluxing for 24 h, the reaction mixture was cooled to room temperature. The byproduct ethyl acetate was removed by distillation at atmospheric pressure. Vacuum distillation at 116−118 °C/0.5 Torr gave 14 g of a liquid product, which was a mixture of TCSMDSCB and HCTSCH in about a 1:1 ratio (by NMR spectroscopy). This mixture was employed in the following polymerization without further separation. The mixture was found to exhibit the following NMR peaks. ^{1}H NMR (ppm): 0.65 (strong singlet, CH_2 units in HCTSCH), 0.2−1.4 (multiplet, CH_2 units in TCSMDSCB); ^{13}C{H} NMR (ppm): 16.8 (all the carbons in HCTSCH), 16.5 ($SiCH_2SiCl_3$), 23.2 (Cl_2SiCH_2SiCl); ^{29}Si{H} NMR (ppm): 20 (all $SiCl_2$ units in HCTSCH), 15.5 (SiCl), 11.7 ($SiCl_2$, TCSMDSCB), 6.00 ($SiCl_3$).

2.9. Synthesis of PSE with CH_2SiH_3 Side Groups. Using the same procedure described in section 2.1, TCDSCB (2 g, 8.85 mmol) and a ca. 1:1 mixture (0.5 g, 1.47 mmol) of TCMSDSCB and HSTSCH (obtained via procedure 2.8) were copolymerized by using 3 mg (0.0058 mmol) of H_2PtCl_6 in 3 mL of benzene (HSTSCH is unreactive under these conditions). After reduction and workup as described in procedure 2.1, a viscous liquid was obtained. ^{1}H NMR (ppm): −0.38 (CH^*_2-SiH_3 side groups), −0.11 (quintet, CH_2), 3.8 (SiH_3 side groups), 4.17 (quintet, SiH_2), 4.26 (multiplet, SiH); ^{13}C{H} NMR (ppm): −10.6 (CH_2 in the CH_2SiH_3 side group), −8.9 (CH_2-SiH_2), −4.8 (CH_2SiH); ^{29}Si{H} NMR (ppm): −64.2 (SiH_3 side groups), −34.5 (SiH_2), −10.7 (SiH).

3. Results and Discussion

Unlike poly(ethylene), which can be obtained from the corresponding olefin, PSE is available only through the ROP of a disilacyclobutane (DSCB) monomer. Due, apparently, to the activation of the Si−H groups by the reaction catalyst, chloroplatinic acid,[2,5] 1,1,3,3-tetrachloro-1,3-disilacyclobutane (TCDSCB) is the preferred monomer for making this polymer rather than DSCB. The mechanism of the Pt-catalyzed ROP of 1,3-disilacyclobutanes is not known in detail; however, it has been postulated to involve the formation of a, presumably Pt-stabilized, zwitterion intermediate $^+SiR_2CH_2SiR_2CH_2^-$, followed by propagation by attack of either the siliconium or carbanion end on the disilacyclobutane.[9] The polymer that results from the ROP of TCDSCB, after reduction with $LiAlH_4$, is expected to possess two different end groups, i.e., CH_3 and SiH_3. A regular alternation of the two different chain units, CH_2 and SiH_2, is also anticipated, based on the structure of the monomer and the presumed polymerization mechanism. Therefore, the expected structure for this polymer is $CH_3[SiH_2CH_2]_nSiH_3$.

Our preliminary ^{29}Si NMR studies of this polymer showed evidence for a R_3SiH structure,[2b] suggesting a small proportion of branch sites along the PSE main chain. It is well known in the case of PE that appreciable chain branching, especially when the branching involves relatively long side chains, can lead to a lowering of the melting transition temperature, as well as a reduction in the degree of crystallinity of the solid polymer.[10] Thus, we turned our attention to the question of what side groups were actually present in this PSE by carrying out a detailed comparison of the NMR spectra of this polymer with the spectra obtained for copolymers of PSE that were deliberately "doped" with certain potential side chain groups.

3.1. Preparation and NMR Studies for CH_3-$SiH_2CH_2SiH_3$. To aid the assignment of the NMR spectra for PSE, we selected 1,3-disila-*n*-butane, CH_3-$SiH_2CH_2SiH_3$ (n-DSB), as a model compound. The molecular structure of n-DSB makes it particularly suitable for this purpose, as the CH_3 and SiH_3 groups should closely resemble the polymer end groups and the CH_2 group in this compound should be quite similar to the CH_2 groups next to the terminal SiH_3 in PSE. In 1977, n-DSB was reported as an unexpected byproduct from the reduction of 1,1,3,3-tetraethoxy-1,3-disilacyclobutane in a 20% yield, and only ^{1}H NMR data were reported for it.[11] The synthetic procedure described in this paper[11] was not a satisfactory approach to make n-DSB because of its low yield. Following the procedure indicated in Scheme 1, we were able to prepare this compound in good yield from easily obtainable starting materials. The overall yield from the methoxy-substituted silanes, $MeSi(OMe)_2Cl$ and $ClCH_2Si(OMe)_3$, was about 24%.

Scheme 1. Synthesis of 1,3-Disilabutane

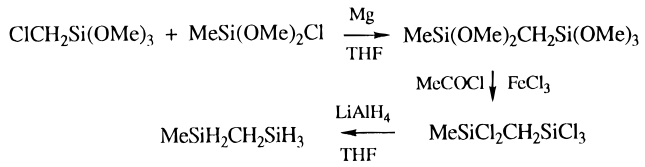


Table 1. Chemical Shifts (ppm) for 1,3-Disila-*n*-butane

n-DSB	^{1}H	^{13}C{H}	^{29}Si{H}
$CH_3SiH_2CH_2SiH_3$	0.01 (triplet)	−6.5	
$CH_3SiH_2CH_2SiH_3$	3.9 (sextet)		−34.0
$CH_3SiH_2CH_2SiH_3$	−0.40 (sextet)	−15.2	
$CH_3SiH_2CH_2SiH_3$	3.66 (triplet)		−62.5

The methoxy-substituted 1,3-disilabutane $(MeO)_3$-$SiCH_2Si(OMe)_2Me$ was obtained through a Grignard coupling reaction between $Cl(MeO)_2SiMe$ and $(MeO)_3$-$SiCH_2MgCl$. The Cl group in $Cl(MeO)_2SiMe$ is a better leaving group than MeO. Thus the in-situ-prepared Grignard reagent $(MeO)_3SiCH_2MgCl$ couples primarily with the SiCl groups, resulting in the primary formation of the desired coupling product. The yield of this coupling reaction was ca. 40%. Following the same procedure as used for chlorinating the alkoxy-substituted ring compounds,[8] this linear methoxy-substituted carbosilane was chlorinated by acetyl chloride under the catalysis of $FeCl_3$. After reduction by $LiAlH_4$, the chlorocarbosilane was converted to n-DSB. The IR and ^{1}H NMR spectra of the reduced product are consistent with the previous results.[11] The chemical shift values for n-DSB are summarized in Table 1.

3.2. NMR Assignments for the Main Structure in PSE. A deuterio-PSE, $[SiD_2CH_2]_n$, was obtained by the ROP of TCDSCB, followed by reduction with $LiAlD_4$. Its ^{1}H NMR spectrum is shown in Figure 1a. In comparison to the two major peaks (quintets) observed in the ^{1}H NMR spectrum of $[SiH_2CH_2]_n$ (Figure 1b), only one major peak is seen in $[SiD_2CH_2]_n$. This observation confirms the assignment of the 4.1 ppm resonance to the SiH_2 protons and that at −0.13 ppm to the CH_2 protons. The residual peak at 4.1 ppm in Figure 1a is attributed to the residual protons in the reducing agent $LiAlD_4$.

3.3. Identification of the End Groups and Branch Site in PSE. In order to search for the end groups in PSE, we expanded the height and width of all peaks in the CH_2 and SiH_2 regions of the ^{1}H NMR spectrum as shown in Figures 2a and 3. In Figure 3, we can see two quintets (3.9 and 4.3 ppm), which we have assigned to ^{29}Si−H coupling of the main Si−H groups ($^1J_{Si-H}$ = 193 Hz). The triplet at 4.02 ppm is a spinning sideband. Thus, this set of peaks shifted in position when the spinning rate was varied, and when the sample was examined without spinning, they disappeared entirely. In Figure 3, a weak multiplet can be seen at 3.7 ppm. Based on the chemical shift of the SiH_3 groups in the model compound n-DSB (Table 1), this peak can be

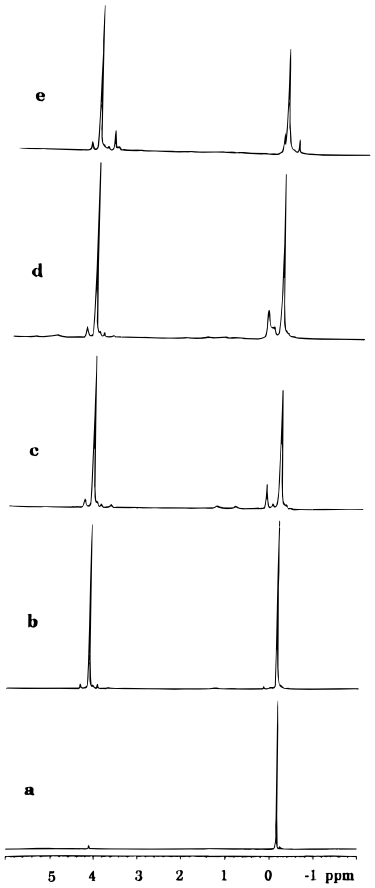


Figure 1. (a) ^{1}H NMR spectrum of $[SiD_2CH_2]_n$. (b) ^{1}H NMR spectrum of PSE, $[SiH_2CH_2]_n$. (c) ^{1}H NMR spectrum of a PSE with Me side groups made by copolymerization. (d) ^{1}H NMR spectrum of a PSE with Me side groups made by means of a substitution reaction. (e) ^{1}H NMR spectrum of a $[SiH_2CH_2]_m[SiH(CH_2SiH_3)CH_2SiH_2CH_2]_n$ copolymer.

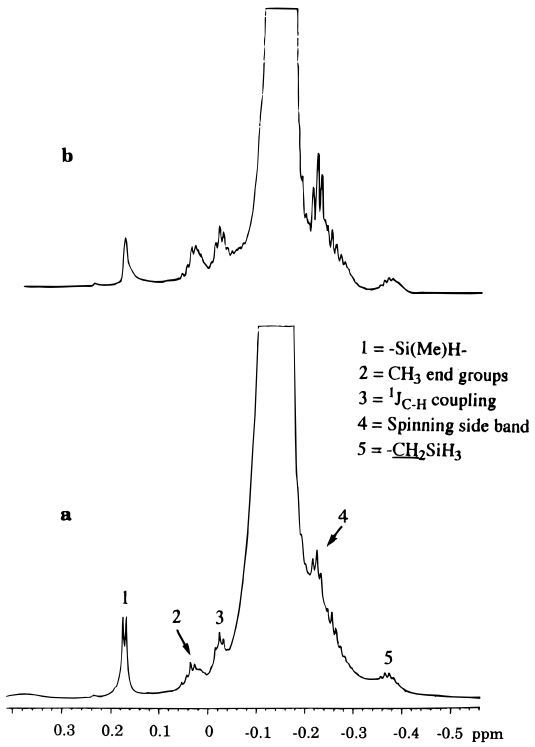


Figure 2. (a) ^{1}H NMR spectrum of the CH_2 region of PSE. (b) ^{1}H NMR spectrum of the CH_2 region of PSE decoupled from the Si−H at 4.3 ppm.

assigned to the SiH_3 end groups in PSE. The multiplet at −0.02 ppm in Figure 2a is attributed to ^{13}C−H coupling ($^1J_{C-H}$ = 116 Hz). The absence of this multiplet in the carbon-decoupled ^{1}H NMR spectrum confirmed this assignment. Similar to the triplet at 4.02 ppm, the multiplet at −0.22 ppm was also shown to be a spinning sideband. The remaining unassigned resonances are those at 0.17, 0.03, and −0.38 ppm. From the chemical shift of the CH_2 group in n-DSB, we can assign the mutiplet at −0.38 ppm with reasonable confidence to the CH_2 immediately next to the SiH_3 end group. The multiplet at 0.03 ppm could be due to the CH_3 end groups, judging from the approximate correspondence to the chemical shift of the CH_3 group in the model compound as shown in Table 1. The apparent doublet peak at 0.17 ppm could not be assigned to any portion of the ideal $CH_3[SiH_2CH_2]_nSiH_3$ structure.

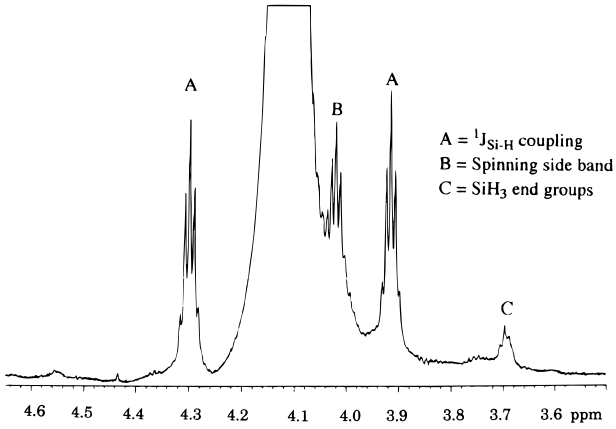


Figure 3. ^{1}H NMR spectrum of the SiH_2 region of PSE.

The proton-decoupled ^{13}C NMR spectrum of PSE is shown in Figure 4a with expanded amplitude. The major resonance at −8.9 ppm is due to the carbons in the polymer main chain. The two symmetric peaks (at −8.68 and 9.03 ppm) around the major one are attributed to Si−C coupling ($^1J_{Si-C}$ = 43.7 Hz). The small peak at −14.8 ppm can be assigned to the CH_2 groups next to the SiH_3 end groups, based on the assignments of the CH_2 group for n-DSB. The tiny peak at −6.2 ppm is very close to the chemical shift of the CH_3 group in n-DSB as is shown in Table 1. Therefore, it was assigned to the CH_3 end groups for the polymer. There are still two small unassigned peaks, at −2 and −4.7 ppm, on the left side of the major peak in the ^{13}C{H} NMR spectrum.

The proton-decoupled ^{29}Si NMR spectrum of this polymer is given in Figure 5a. The major peak at −34.4 ppm is assigned to the SiH_2 groups in the main chain. The symmetric peaks at −32.4 and −36.2 ppm in Figure 5a is attributed to C−Si coupling ($^1J_{C-Si}$ = 475 Hz). The SiH_3 end groups are also observable and appear at −62.8 ppm. In addition, there is another small peak at −13.5 ppm. Usually, silanes with one (Si)H show up in this range,[12] which suggests that a R_3SiH structure exists in this polymer. As is demonstrated below, it turns out that the remaining unassigned peaks in the ^{1}H and ^{13}C NMR spectra can also be assigned to such a group. It is also possible that the R_3SiH branch site makes its neighbor SiH_2 groups, i.e., $-SiH_2CH_2SiH(Me)CH_2SiH_2-$, have slightly different chemical shift, such as the peaks near −36 ppm in the ^{29}Si NMR spectrum (Figure 5a).

Based on the current understanding of the ROP mechanism for the disilacyclobutanes,[10] it is difficult to explain the formation of R_3SiH branch sites in the context of the polymerization of TCDSCB alone. A more likely source of such side groups would be other sub-

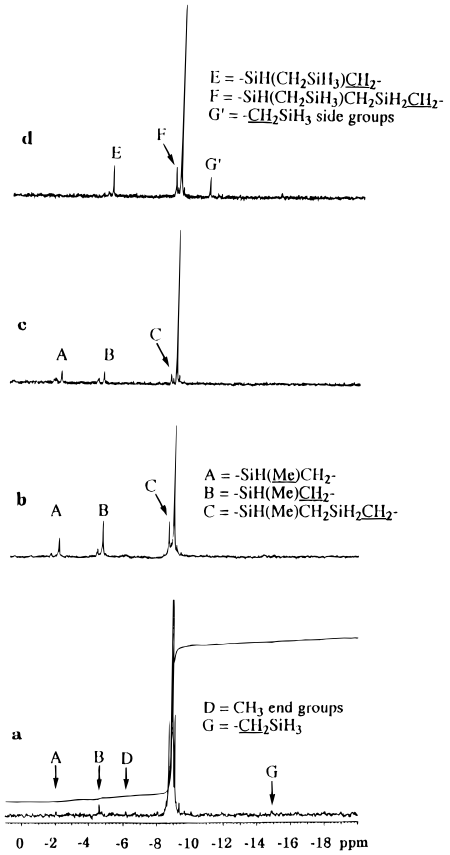


Figure 4. (a) $^{13}C\{H\}$ NMR spectrum of PSE. (b) $^{13}C\{H\}$ NMR spectrum of PSE with Me groups made by copolymerization. (c) $^{13}C\{H\}$ NMR spectrum of PSE with Me side groups made by means of a substitution reaction. (d) $^{13}C\{H\}$ NMR spectrum of a $[SiH_2CH_2]_m[SiH(CH_2SiH_3)CH_2SiH_2CH_2]_n$ copolymer.

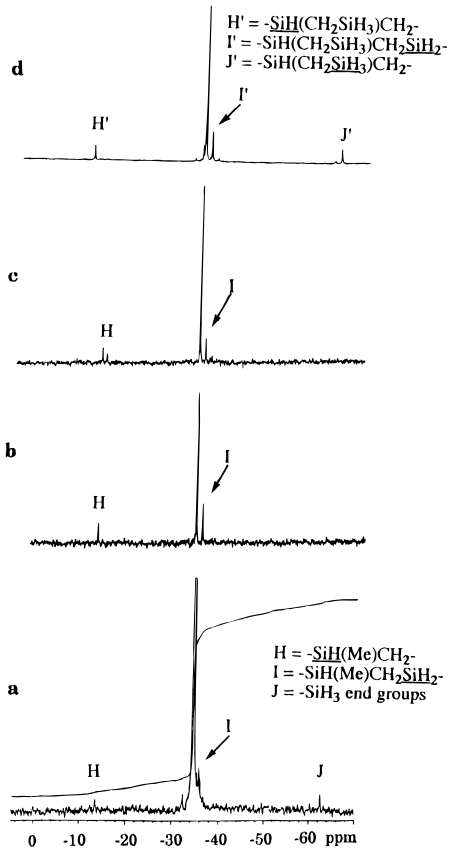
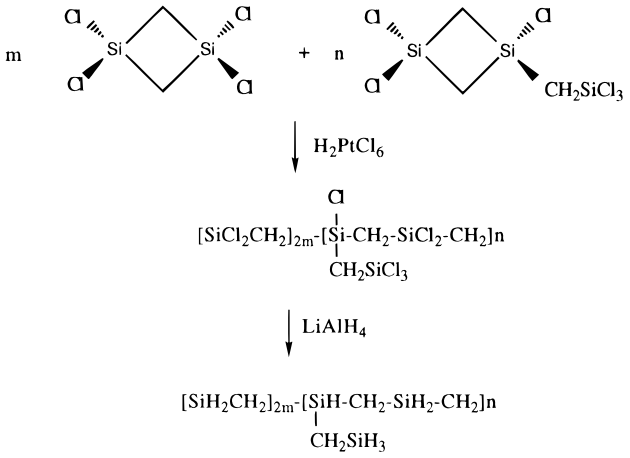


Figure 5. (a) $^{29}Si\{H\}$ NMR spectrum of PSE. (b) $^{29}Si\{H\}$ NMR spectrum of PSE with Me groups made by copolymerization. (c) $^{29}Si\{H\}$ NMR spectrum of PSE with Me side groups made by means of a substitution reaction. (d) $^{29}Si\{H\}$ NMR spectrum of a $[SiH_2CH_2]_m[SiH(CH_2SiH_3)CH_2SiH_2CH_2]_n$ copolymer.

stituted disilacyclobutanes present as impurities in the monomer employed for this synthesis. The TCDSCB[8] monomer employed for the synthesis of PSE was obtained from 1,1,3,3-tetraethoxy-1,3-disilacyclobutane (TEDSCB) by chlorination with acetyl chloride and $FeCl_3$. The TEDSCB was in turn prepared by the Grignard coupling of $Cl(EtO)_2SiCH_2Cl$.[8] This coupling reaction has been confirmed to lead to trimeric products as well as the predominant alkoxy-substituted disilacyclobutane.[8] Due to their very similar boiling points, two trimeric compounds were actually isolated after distillation as a 1:1 mixture. After chlorination, these two trimeric products were identified as a mixture of 1,1,3-trichloro-3-((trichlorosilyl)methyl)-1,3-disilacyclobutane (TCSMDSCB) and 1,1,3,3,5,5-hexachloro-1,3,5-trisilacyclohexane (HCTSCH). The latter compound was found to be inactive as a monomer in the ROP process;[9b] however, TCSMDSCB, if present in the TCDSCB monomer, would be expected to participate in chain formation, leading to a copolymer that contained, after reduction, SiH units and CH_2SiH_3 side groups as shown in Scheme 2.

Another likely disilacyclobutane impurity in the TCDSCB monomer is 1-methyl-1,3,3-trichloro-1,3-disilacyclobutane (MTCDSCB), which would lead to the formation of SiH units and CH_3 side groups as indicated in Scheme 3. This could arise from the presence of some $(CH_3)_2SiCl_2$ in the CH_3SiCl_3 which was utilized as the starting material for the synthesis of the TCDSCB. Indeed, this compound is known to be present at the level of a few percent in the commercial CH_3SiCl_3 product which we used to prepare the $Cl(OEt)_2SiCH_2Cl$ for the synthesis of TEDSCB.[8] Chlorination of this $(CH_3)_2SiCl_2$ by Cl_2, followed by alcoholysis with ethanol,

Scheme 2. Synthesis of PSE with CH_2SiH_3 Groups

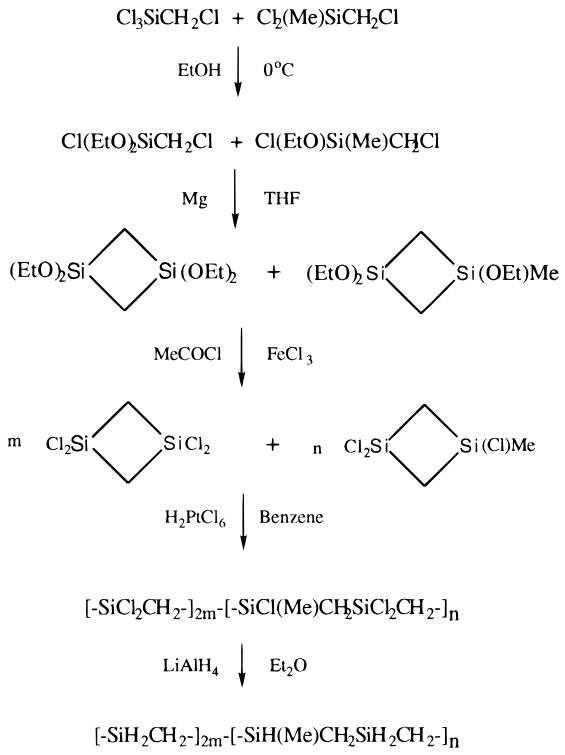


could give rise to $Cl(OEt)(CH_3)SiCH_2Cl$, which, in turn, would yield a methyl-substituted disilacyclobutane in the Grignard coupling reaction with $Cl(OEt)_2SiCH_2Cl$. The substitution of the ethoxydisilacyclobutanes by acetyl chloride would generate the corresponding chlorodisilacyclobutanes, in which MTCDSCB could occur as a byproduct.

Although either of the above two hypotheses could lead to the formation of a SiH structure in PSE, only one of these, the one which yields a polymer containing the $-SiH(Me)CH_2-$ structure, can account for the doublet at 0.17 ppm in the ^1H NMR spectrum as well as the other NMR resonances observed for the as-synthesized PSE.

3.4. NMR Assignment from ^1H Homodecoupling Experiments for PSE. In order to check for the

Scheme 3. Postulated Sequence of Reactions Leading to the Formation of a PSE with Methyl Branches



presence of a $-CH_2Si(Me)H-$ linkage in PSE, we performed the following ^1H homodecoupling experiment. From the previous NMR study of a series of silane compounds,[12] we know that the peak position of the SiH groups in the ^1H NMR spectrum is near 4.3 ppm. Thus, the decoupling position was set at 4.3 ppm, although we did not see the SiH peak because of the overlapping SiH_2 peak from Si−H coupling. The resultant spectrum is shown in Figure 2b. We find that the doublet peak at 0.17 ppm turns into a singlet, as would be expected for a Me group in a $-Si(Me)HCH_2-$ linkage.

3.5. Origin of the Methyl Side Groups in PSE. Based on the decoupling experiment, it is very likely that $-SiH(Me)CH_2-$ groups are present in the PSE homopolymer. As hypothesized above, the methyl side groups in PSE could be due to the existence of a small amount of dimethyldichlorosilane in the starting material. Dimethyldichlorosilane could form various intermediate compounds which may coexist with the reaction products derived from methyltrichlorosilane, as illustrated in Scheme 3, but the identification of them by spectroscopic means would be difficult because of their low content. Therefore, in order to increase the concentrations of these intermediates for characterization purposes, a 9:1 molar mixture of (chloromethyl)trichlorosilane and (chloromethyl)methyldichlorosilane was used as the starting material in the series of reactions employed for the preparation of PSE (Scheme 3).

The reaction of ethanol with (chloromethyl)trichlorosilane and (chloromethyl)methyldichlorosilane should give rise to $Cl(EtO)_2SiCH_2Cl$ and $Cl(EtO)Si(Me)CH_2Cl$, respectively.[8] All of the silane products from this reaction were used for the ring-closure reaction without separation. The product isolated from the ring-closure reaction by vacuum distillation was examined first by GC. Two components were observed in a 13:87 ratio. The major component was TEDSCB and the small one was the methyl-substituted disilacyclobutane.

Identification of the minor component was carried out by mass spectrometry and NMR spectroscopy. Mass spectrometry (EI) showed that the largest peak was 234, after all of the peaks from TEDSCB were subtracted. The observed peak at 234 corresponds to the molecular ion peak from 1-methyl-1,3,3-triethoxy-1,3-disilacyclobutane (MTEDSCB). The NMR spectra of the methyl-substituted disilacyclobutane plus TEDSCB mixture are given in Figure 6. The observed peaks can be assigned with the aid of the NMR results from the pure TEDSCB[8a] and 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane[14] samples. The carbon atoms of OCH_2CH_3 in both four-membered rings appear at 59.3 and 18.8 ppm, respectively, in the $^{13}C\{H\}$ NMR spectrum (Figure 6a). The CH_2 units in the ring structure of TEDSCB appear at 7.86 ppm as observed in the pure TEDSCB sample.[8a] In the $^{13}C\{H\}$ NMR spectrum, the CH_2 units in the methyl-substituted ring MTEDSB are found at 8.70 ppm, while the Me group attached to the Si atom in MTEDSCB is observed at 0.81 ppm, based on the NMR assignment of 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane.[14] Two peaks, shown at −19.5 and 3.8 ppm in the ^{29}Si NMR spectrum of the mixture of two disilacyclobutanes, can be assigned to the $Si(OEt)_2$ and Si(OEt)Me groups according to the chemical shifts of TEDSCB[8a] and 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane,[14] All of these observations suggest that the methyl substituted ring MTEDSCB was created along with TEDSCB.

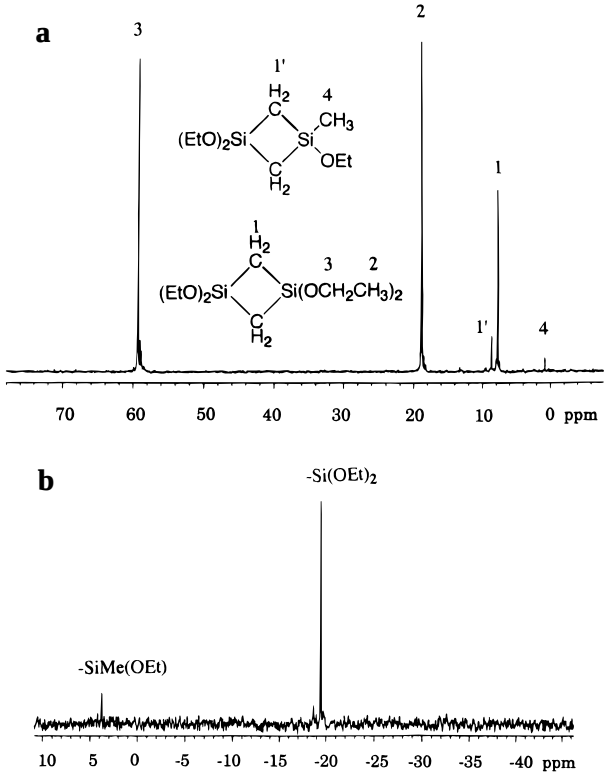


Figure 6. (a) $^{13}C\{H\}$ NMR spectrum of a mixture of TEDSCB and MTEDSCB. (b) $^{29}Si\{H\}$ NMR spectrum of a mixture of TEDSCB and MTEDSCB.

Following the procedure to make the "pure" TCDSCB,[8] the mixture of TEDSCB and MTEDSB was treated with acetyl chloride and $FeCl_3$. The obtained product should be a mixture of TCDSCB and 1-methyl-1,3,3-trichloro-1,3-disilacyclobutane (MTCDSCB). This mixture was characterized by NMR spectroscopy. As shown in Figure 7a in the ^1H NMR spectrum, the major peak at 1.62 ppm is attributed to the CH_2 units in both 1,3-disilacyclobutanes, whereas the small peak at 0.13 ppm should correspond to the methyl group in MTCDSCB.

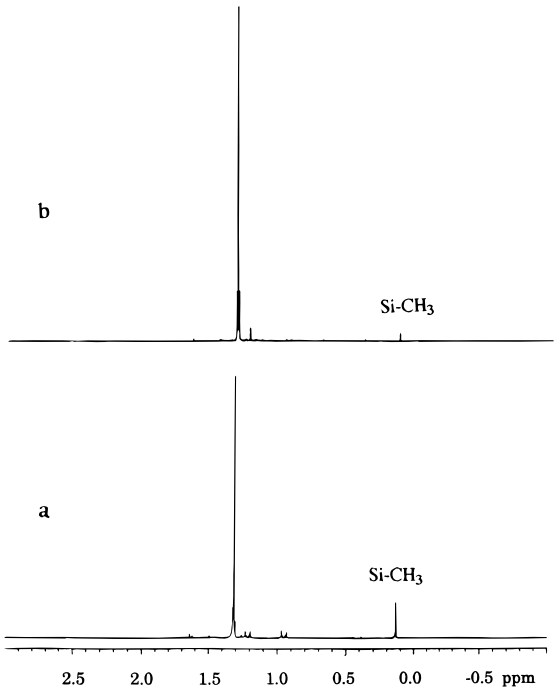


Figure 7. (a) ^{1}H NMR spectrum of a mixture of TCDSCB and 1-methyl-1,3,3-trichloro-1,3-disilacyclobutane. (b) ^{1}H NMR spectrum of TCDSCB.

Table 2. NMR Assignments for the Methyl-Branched PSE Obtained from the Copolymerization of TCDSCB and MTCDSCB

structural units	^{1}H (ppm)	^{13}C (ppm)	^{29}Si (ppm)
$-SiH_2CH_2-$	4.12 (quintet)		−34.4
$-SiH_2CH_2-$	−0.13 (quintet)	−8.9	
$-SiH(CH_3)CH_2-$	4.27 (multiplet)		−13.4
$-SiH(CH_3)CH_2-$	0.18 (doublet)	−2.0	
$-SiH(CH_3)CH_2-$	−0.13 (multiplet)	−4.6	
$-SiH_2CH_2SiHMe-$			−36.0

When the ^{1}H NMR spectrum of the "pure" TCDSCB that was used for the synthesis of the PSE homopolymer is enlarged (Figure 7b), a small peak at 0.13 ppm becomes visible. This peak is located at the same chemical shift as the methyl group observed in the mixture, confirming that the methyl monomer was indeed formed and survived in the "pure" TCDSCB monomer after the indicated series of reactions.

The mixed monomers made from Cl_3SiCH_2Cl and $Me(Cl)_2SiCH_2Cl$ were then copolymerized and reduced as was done for the homopolymer. The expected structure of the copolymer is $[SiH_2CH_2]_m[SiH(Me)CH_2]_n$. The NMR spectra of the sample obtained from the copolymerization are shown in Figures 1c, 4b, and 5b. The assignments of the main resonances in these figures are listed in Table 2.

As is shown in Table 2, the SiH_2 and CH_2 groups are observed at 4.12 and −0.13 ppm in the ^{1}H NMR spectrum, the SiH groups from the copolymer appear at 4.27 ppm, and the CH_3 side groups give rise to a doublet at 0.18 ppm. Three major peaks, attributed to the CH_3 side groups, CH_2 units attached to −Si(H)Me− directly, and CH_2 in the main chain, show up at −2, −4.6, and −8.9 ppm in the ^{13}C{H} NMR spectrum. As also indicated in Table 2, the SiH and major SiH_2 groups in the ^{29}Si NMR spectrum occur at −13.4 and −34.4 ppm. The peak at −36 ppm in the ^{29}Si NMR spectrum (Figure 5b) can be assigned to the SiH_2 groups in the $-SiH_2CH_2SiH(Me)-$ units. All of these peaks in the copolymer made from the TCDSCB and MTCDSCB monomers are perfectly overlapped with the corresponding peaks in the homopolymer, suggesting that the origin of the methyl groups in PSE is, indeed, the byproduct dimethyldichlorosilane in the starting methyltrichlorosilane.

Scheme 4. Synthesis of PSE with Me Side Groups by Substitution

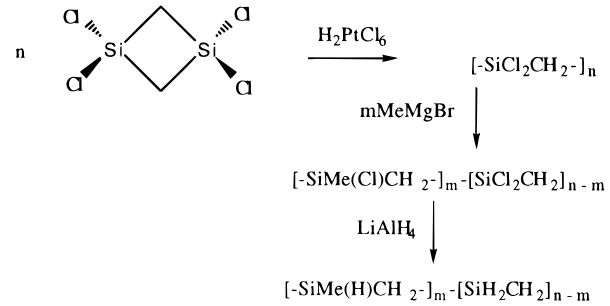


Table 3. NMR Assignments for the Methyl-Substituted PSE Made by the Grignard Reaction

structural units	^{1}H (ppm)	^{13}C (ppm)	^{29}Si (ppm)
$-SiH_2CH_2-$	4.10 (quintet)		−34.5
$-SiH_2CH_2-$	−0.12 (quintet)	−8.9	
$-SiH(CH_3)CH_2-$	4.26 (multiplet)		−13.5
$-SiH(CH_3)CH_2-$	0.19 (doublet)	−2.0	
$-SiH(CH_3)CH_2-$	−0.12 (multiplet)	−4.6	
$-SiH_2CH_2SiHMe-$			−36.0

In addition to these major peaks, we can also see extra peaks that appear in the copolymer due to the higher content of the methyl groups than that in the homopolymer. It is well known that in the branched form of polyethylene, the structural units on the neighboring α and β positions of the branch sites have slightly different chemical shifts than the main-chain units.[15] We can reasonably expect that the neighboring α and β groups of the branch sites in PSE will also show different chemical shifts, compared to the main-chain units. In Figure 4b, the peak at −8.6 ppm in the ^{13}C NMR spectrum can be assigned to the italicized CH_2 groups in the $-CH_2SiH_2CH_2SiH(Me)-$ units; the small peaks at −4.3 and −1.6 ppm can be attributed to the CH_2 and CH_3 groups in the −Si(Me)HCH$_2$Si(Me)H− units, which could originate from the polymerization of two $Cl_2Si[CH_2]_2SiCl(Me)$ monomers so as to form a $-SiCl_2CH_2-SiCl(Me)CH_2SiCl(Me)CH_2SiCl_2-$ sequence. The ^{13}C chemical shifts for both the Me and CH_2 groups in the −SiMe(H)CH$_2$SiMe(H)− units would be expected to lie slightly upfield relative to those of the main branch sites ($-SiH_2CH_2SiMeHCH_2SiH_2-$), based on previous observations for related model compounds.[12]

3.6. Preparation of a PSE with Methyl Side Groups by a Si−Cl Substitution Reaction. To further confirm the assignments of the methyl-branched PSE, a methyl-substituted polymer was also prepared by adding MeMgBr to the chloro polymer made from the ROP of TCDSCB as shown in Scheme 4.

After the reduction by $LiAlH_4$, the isolated polymer should have a $[SiMe(H)CH_2]_m[SiH_2CH_2]_n$ structure. The ratio of *m* to *n* is about 1:6, based on the ratio of the starting materials employed and the ^{1}H NMR spectrum. A random distribution of the Me groups is expected in the polymer structure. The reduced polymer was examined by NMR spectroscopy, and the structural units are assigned in Table 3.

If the data in Table 3 are compared with those in Table 2, we can see that the structures in both methyl-branched polymers are the same, although these two polymers were prepared by quite different routes. Therefore, there seems to be little doubt that the branch

Table 4. NMR Assignments for the $[SiH_2CH_2]_m[SiH(CH_2SiH_3)CH_2SiH_2CH_2]_n$ Copolymer

structural units	^{1}H (ppm)	^{13}C (ppm)	^{29}Si (ppm)
$-SiH_2CH_2-$	4.17 (quintet)		−34.5
$-SiH_2CH_2-$	−0.11 (quintet)	−8.9	
$-SiH(CH_2SiH_3)CH_2-$	4.26 (multiplet)		−10.7
$-SiH(CH_2SiH_3)CH_2-$	−0.38 (multiplet)	−10.6	
$-SiH(CH_2SiH_3)CH_2-$	3.8 (triplet)		−64.2
$-SiH_2CH_2SiH(CH_2SiH_3)-$			−36.0
$-SiH(CH_2SiH_3)CH_2-$	−0.10 (multiplet)	−4.8	

sites in the PSE homopolymer are in fact the −SiHMeCH$_2$− units.

Like the copolymer made from TCDSCB and MTCDSCB, it is also possible to form −SiMe(H)CH$_2$SiMe(H)− units in the polymer obtained by the reaction of MeMgBr with the chloro polymer $[SiCl_2CH_2]_n$. Indeed, we find a similar set of NMR peaks (at −1.6 and −4.3 ppm) in the ^{13}C NMR spectrum (Figure 4c) of this polymer as those that were assigned to the CH$_3$ and CH$_2$ groups, respectively, of the units in the ^{13}C NMR spectrum of the copolymer. Similarly, the peak at −8.6 ppm in the ^{13}C NMR spectrum can be assigned to the italicized CH$_2$ groups in $-SiH_2CH_2SiH_2CH_2Si(H)Me-$ units; and in the ^{29}Si{H} NMR spectrum (Figure 5c) of this methyl-substituted PSE, the peaks at −14.5 and −36.0 ppm correspond to the SiH groups in the −SiMe(H)CH$_2$SiMe(H)− units and the SiH$_2$ groups in the $-SiH_2CH_2SiMe(H)-$ units, respectively.

3.7. Preparation and NMR Assignments of a PSE Copolymer with CH_2SiH_3 Side Groups. In addition to the methyl-substituted disilacyclobutanes, another potential four-membered ring-contaminant in the TCDSCB monomer used for the ROP experiments is the trimeric product 1,1,3-trichloro-3-((trichlorosilyl)-methyl)-1,3-disilacyclobutane (TCMDSCB). This compound was, in fact, isolated along with its isomeric, six-membered-ring relative 1,1,3,3,5,5-hexachloro-1,3,5-trisilacyclohexane in low yield from the Grignard coupling reaction (followed by chlorination with acetyl chloride) used to prepare the TCDSCB monomer. If this compound was present in TCDSCB monomer, a copolymer with pendant −CH$_2$SiH$_3$ groups would be expected after reduction of the chloro polymer with LiAlH$_4$.

In order to evaluate this alternative potential source of branch sites for the PSE product and also to determine if such a novel copolymer could in fact be prepared, a copolymerization of TCDSCB with a mixture of TCMDSCB and its six-membered-ring isomer was conducted by using a 12:1 molar ratio of TCDSCB to TCMDSCB (Scheme 2). Based on the starting ratio of monomers, a copolymer of the type $[SiH_2CH_2]_m[SiH(CH_2SiH_3)CH_2SiH_2CH_2]_n$ was expected, where the ratio of *m* and *n* should be 12:1 with a random distribution of the −CH$_2$SiH$_3$ branches. The NMR spectra of this copolymer are shown in Figures 1e, 4d, and 5d, and the peak assignments are given in Table 4.

In comparison with the ^{1}H NMR spectra of the methyl-branched PSE, we can see some obvious changes. The peaks due to the SiH$_3$ groups at 3.7 ppm and the CH$_2$ peaks at −0.38 ppm have increased in intensity as shown in Figure 1e. No peak at 0.17 ppm is seen in the spectrum (Figure 1e) of the PSE containing added CH$_2$SiH$_3$ side groups.

The ^{13}C{H} NMR spectrum of this copolymer is shown in Figure 4d. As indicated in Table 4, the major peak at −8.9 ppm is attributed to the CH$_2$ units in the polymer main chain, the peak at −10.6 ppm can be assigned to the CH$_2$ units in the CH$_2$SiH$_3$ side groups based on a previous NMR study of some related organosilanes,[12] and the peak at −4.8 ppm must also arise from a CH$_2$ unit, because in the proton-coupled ^{13}C NMR spectrum, this peak splits into a triplet. We can attribute this peak to the italicized CH$_2$ unit in the $-CH_2SiH(CH_2SiH_3)-$ structure of the copolymer because of the fact that the −CH$_2$ group in a R$_3$SiH unit generally has a higher chemical shift than that in a R$_2$SiH$_2$ unit.[12] The chemical shift of this peak is very close to the small one at −4.6 ppm observed in the homopolymer PSE; however, we do not find any peak at −2 ppm in the spectrum of the CH$_2$SiH$_3$− doped PSE, which indicates that the assignment of the branch group as −CH$_2$SiH$_3$ fails to account for all of the minor peaks observed in the ^{13}C NMR spectrum of the PSE homopolymer.

The ^{29}Si{H} NMR spectrum of this copolymer is shown in Figure 5d. As is summarized in Table 4, the major peak at −34 ppm is assigned to the SiH$_2$ units in the polymer main chain. The peaks at −62 and −64 ppm are attributed to all the SiH$_3$ groups, while the peak at −10.6 ppm presumably comes from the SiH units. Again, the chemical shift of this peak is not at the same position as the SiH units in the homopolymer.

In summary, these NMR spectra clearly indicate the formation of a copolymer containing −Si(H)(CH$_2$SiH$_3$)− groups; however, the peak positions of the branch sites in the ^{1}H, ^{13}C, and ^{29}Si NMR spectra do not exactly match those in the homopolymer, suggesting that copolymerization of TCDSCB with a small amount of 1,1,3-trichloro-3-((trichlorosilyl)methyl)-1,3-disilacyclobutane was not responsible for the formation of the SiH groups in PSE. Indeed, it seems likely that if this trimeric form was indeed obtained in significant amounts in the Grignard coupling reaction used to prepare the TEDSCB monomer, due to its significantly high boiling point, it was effectively removed during the subsequent synthesis and separation steps in the overall preparation of TCDSCB.

3.8. Quantitative Measurement of the Methyl Side Groups and the Molecular Weight of PSE by NMR Spectroscopy. Having identified specific peaks in the NMR spectra of PSE as arising from either −SiH(Me)− branch sites or the CH$_3$ and SiH$_3$ end groups, we decided to attempt the quantitative determination of both these branch sites and the average molecular weight of the polymer by integration of these peaks relative to the main-chain −SiH$_2$CH$_2$− units. In order to ensure good quantitative accuracy for the NMR peak integration, these measurements were carried out in the presence of a NMR relaxation reagent, chromium(III) tris(acetylacetonate). The obtained ^{13}C{H} and ^{29}Si{H} NMR spectra are shown in Figures 4a and 5a.

A direct comparison of the integrated intensity of the major peaks with those of the small peaks was first used to obtain approximate values for the concentrations of the side and end groups. In the ^{29}Si NMR spectrum, the integrated intensity of the SiH$_2$ peak is about 200 times that of the SiH peak, which means that the concentration of the side groups is about 1 per 200 Si atoms in the polymer chain (the error limits are estimated to be ∼3%). The intensity ratio of the SiH$_2$ to SiH$_3$ peaks was measured as ca. 250:1, which corresponds to a degree of polymerization for PSE of about 250. The ratio of the integrated intensity of the major CH$_2$ units to CH$_3$ side groups in the ^{13}C NMR spectrum is also around 200:1, in good agreement with the ^{29}Si results. From the ^{1}H NMR spectrum, the integrated ratio of SiH$_3$ to SiH$_2$ peaks gave a value of approximately 260 for the degree of polymerization of PSE,

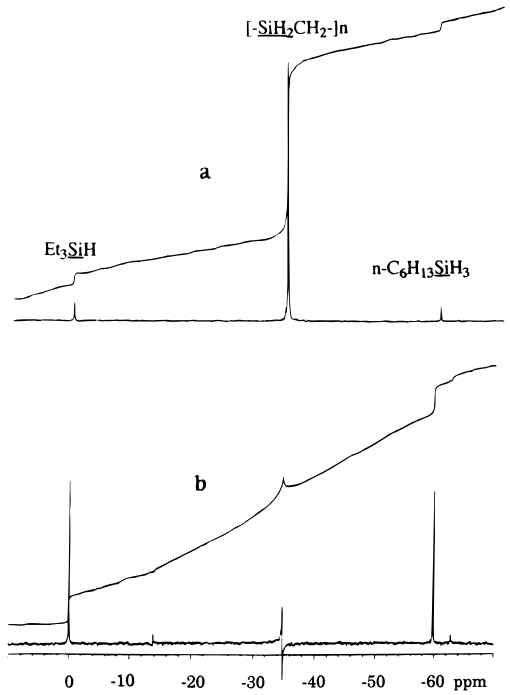


Figure 8. (a) ^{29}Si{H} NMR spectrum of PSE with Et_3SiH and n-$C_6H_{13}SiH_3$ reference peaks. (b) ^{29}Si{H} NMR spectrum of PSE containing internal refererence and employing the BINOM pulse sequence to suppress the main $-SiH_2-$ resonance.

consistent with the result from the ^{29}Si{H} NMR spectrum.

Another, more accurate, approach for quantitative measurement of such widely different NMR intensities involves the use of reference peaks of added standards which lie intermediate in intensity and frequency between the major peaks and the small peaks of interest. Figure 8 shows the ^{29}Si{H} NMR spectrum of PSE with Et_3SiH and n-$C_6H_{13}SiH_3$ added as integration standards. The peak at 0.32 ppm corresponds to Et_3SiH, and the peak at −59.48 ppm is due to the $C_6H_{13}SiH_3$. The central peak at −34.5 ppm is due to the major SiH_2 group of PSE. The Et_3SiH and n-$C_6H_{13}SiH_3$ serve as references for the branched SiH and the end SiH_3 groups in the PSE polymer, respectively. The molar ratio of both compounds to the $-SiH_2CH_2-$ unit in PSE was set at 1:20. Under the same conditions of added relaxation reagent and a relatively long pulse delay time as was used in the initial approximate determination, the measured intensity of SiH_2 groups from PSE to Et_3SiH or n-$C_6H_{13}SiH_3$ was indeed found to correspond to a 20:1 ratio. Next the major SiH_2 peak was suppressed by using the well-known BINOM pulse sequence.[13] The resultant spectrum is shown in Figure 8b. The small SiH and SiH_3 peaks at −14.0 and −62.5 ppm in the PSE polymer are clearly observable, as are the reference peaks from Et_3SiH and n-$C_6H_{13}SiH_3$ at 0.32 and −59.48 ppm. The ratio of the integrated areas of the Et_3SiH peak to that of the SiH branch sites and the n-$C_6H_{13}SiH_3$ to the SiH_3 end groups were measured as ca. 10:1 and 13:1, respectively. After these numbers were multiplied by 20, the contents of the SiH and SiH_3 in PSE polymer were thus calculated as 1/200 and 1/260. The uncertainty of these values is about 3%. These results are in good agreement with those obtained from the unsuppressed measurement without added standards.

The number-average molecular weight (M_n) obtained from GPC analysis (refractive index detector; polystyrene standards) for this particular PSE sample was about 24 000 (M_w = 133 000). Using the value determined above for the degree of polymerization of PSE (260), the calculated average molecular weight for PSE is around 11 400, which is about half that measured by GPC. Given the great deal of uncertainty in the GPC molecular weight, this value of ca. 11 400 must be taken as the best available estimate currently for the M_n of the PSE prepared by this ROP method. Although this value is relatively small compared to that typically found for PE, it is believed to be sufficiently high to lend confidence to the DSC-determined T_m value.[5] Moreover, the measured value for the concentration of the methyl side groups of about 1 in every 200 polymer units should be sufficiently small, particularly in the context of the small size of the CH_3 group, so as not to greatly influence the properties or degree of crystallinity of the PSE homopolymer.

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