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Synthesis, Characterization, and Glass Transitions of Some Asymmetrically Substituted Poly(siloxanes)

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ABSTRACT: A homologous series of poly(*n*-alkylmethylsiloxanes), $[SiMe(R)O]_n$, were prepared by cationic ring-opening polymerization (ROP) of cyclotrisiloxanes containing *n*-alkyl substituents, such as C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *n*-C_5H_{11}, and *n*-C_6H_{13}, on the Si. The resultant polymers were characterized by NMR, GPC, and DSC measurements. All of these asymmetrically substituted polymers were obtained in high molecular weight form and were found to have an atactic configuration. Their glass transitions were found to increase smoothly from Et to *n*-Hex (i.e., −139, −120, −115, −111.9, and −108 °C, for Et to *n*-Hex, respectively). These T_gs are much lower than those of the corresponding polyolefins, $[C(H)(R)\text{-}CH_2]_n$. Moreover, in the case of these polyolefins, the T_gs decrease continuously from R = Me to *n*-Hex. The calculated T_gs for the polysiloxanes that were obtained by using published empirical equations show the same general trend as the experimental values.

1. Introduction

Since the 1960s, it has been generally acknowledged that the addition of flexible *n*-alkyl side groups to the polymer backbone usually decreases the polymer's glass transition temperature.[1] For example, the T_gs of the substituted poly(ethylenes), $[CH(R)CH_2]_n$, where R = Me, Et, *n*-Pr, *n*-Bu, and *n*-Hex, have been found to be: −20, −25, −40, −50, and −65 °C, respectively.[2] Similarly, for the corresponding poly(*n*-alkylmethacrylates), the T_gs for the alkyl = Me, Et, *n*-Pr, *n*-Bu, and *n*-Hex polymers were measured as 105, 65, 35, 20, and −5 °C, respectively.[3] A similar behavior for the T_gs of the *n*-alkyl-substituted poly(styrenes) has also been observed.[4] The detailed understanding of the relationship between the molecular structure of polymers and their T_gs is still a matter of some controversy;[5a] nonetheless, empirical equations have been developed which allow the approximate calculation of the T_gs for a large number of polymers.[5b]

Most of the previous studies of structural effects on T_g have centered on carbon backbone polymers. In the case of the asymmetrically alkyl substituted poly(siloxanes), $[Si(Me)RO]_n$, where R = Et, *n*-Pr, *n*-Bu, *n*-Pen, and *n*-Hex, only the Et- and *n*-Pr-substituted polymers have been mentioned, as gas separation materials, in the literature.[6] The T_gs of both polymers were reported at −135 and −120 °C, respectively, but their preparation or molecular weights were not specified.[6] Other studies which have yielded T_gs for poly(siloxanes) have included the dimethyl,[7] methyl/phenyl,[7] diphenyl,[8] and methyl/$CH_2CH_2CF_3$-[9]substituted poly(siloxanes), because these polymers are important in applications. The symmetrically di-*n*-alkyl-substituted poly(siloxanes) have also been studied because of their unusual mesomorphic behavior.[10a] These are crystalline polymers which undergo partial disordering of the polymer chains prior to melting. Moreover, a series of poly(methylalkylsiloxanes) with *n*-alkyl groups from *n*-ocyl to eicosanyl (n_c = 8−20) were prepared by hydrosilation, and their rheological and thermal properties were studied.[10b] These polymers (M_n = 5400−7180) showed no glass transitions but did exhibit melting transitions (for $n_c \geq 9$) which were attributed to crystallization of the relatively long side chains.[10b]

Our recent work on the asymmetrically *n*-alkyl-substituted poly(silylenemethylenes), $[SiMe(R)CH_2]_n$, has revealed a dependence of the glass transition temperatures on the length of the side chain *n*-alkyl group which is rather different from that which is exhibited by the above-mentioned C−C backbone polymers.[11a] Instead of dropping continuously from R = Me to *n*-Hex as in the polyolefins, the T_gs of the *n*-C_nH_{2n+1}- (n = 2−6) substituted poly(silylenemethylenes), $[SiMeRCH_2]_n$, reach a maximum (at −61 °C) for the R = *n*-Pr substituted polymer. The origin of this different behavior is unclear but may be related to the fact that the backbone of these polycarbosilanes is more flexible than that of the corresponding all-carbon backbone polymers, owing to the longer Si−C bonds.[11b] Since the poly(siloxane) backbone is even more flexible than that of the poly(silylenemethylenes), we were interested in determining how the T_g changes with *n*-alkyl side chain length for these polymers. However, the synthesis and characterization of most of the corresponding siloxane polymers have apparently not been reported; moreover, we have found no reports of the ring-opening polymerization of 1,3,5-trialkyl-1,3,5-trimethylcyclotrisiloxanes, where the alkyl group is a relatively long chain hydrocarbon.

We describe here the results of our efforts to synthesize a series of *n*-alkyl-substituted cyclotrisiloxane derivatives and to employ them as monomers to obtain asymmetrically substituted poly(siloxanes) containing alkyl substituents on Si. The obtained T_gs of these poly(siloxanes) are compared with those of the corresponding C−C and Si−C backbone polymers, as well as some of their symmetrically disubstituted analogs.

2. Experimental Section

2.1. General Procedures. All manipulations involving air-sensitive materials were carried out in oven-dried glassware under nitrogen following standard inert atmosphere procedures.[12] Tetrahydrofuran, diethyl ether, and hexane were distilled under nitrogen from appropriate drying agents.[13] The reagents employed were commercially available from Aldrich, unless otherwise specified. NMR spectra were obtained by using a XL-500 NMR spectrometer using $CDCl_3$ as the solvent and were referenced by TMS externally. GC analyses were performed on a Shimadzu GC Chromatograph equipped with a Hewlett-Packard recorder−integrator unit. Unless otherwise specified, samples separated satisfactorily by using the following parameters: 6-ft SE-30 column, 90−

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250 °C at 6 °C/min, INJ and TCD at 250 °C, and helium at 50 cm^3/min. GPC measurements of the polymer samples were performed on a Waters 600 solvent delivery system, 410 RI detector, and 745 data processing unit. Helium-sparged HPLC grade toluene at a flow rate of 1.0 mL/min was used as the eluent. Molecular weights were obtained from a 15-point calibration curve by using polystyrene standards from 600 to 470 000. All DSC measurements were performed on a TA 2920 instrument by cooling the polymer sample to −155 °C and then warming up to 50 °C at 10 °C/min. The T_g was determined as the inflection point in the heating portion of the DSC curve, after an initial heating/cooling cycle. These transitions were found to be repeatable on subsequent cooling and warming cycles. The sample weights were typically between 6 and 15 mg. Cyclohexane and indium were used to calibrate the instrument.

2.2. Preparation of $R(Me)SiCl_2$. Compounds **2.2b**−**2.2d** were made by the same procedure as described for **2.2a**.

2.2a. Ethylmethyldichlorosilane. Methyltrichlorosilane (105 g; 0.7 mol) was mixed with 200 mL of diethyl ether in a 1 L three-necked round-bottom flask equipped with a reflux condenser and a mechanic stirrer. The flask was cooled by an ice/water bath. Then 350 mL (0.7 mol) of 2 M ethylmagnesium bromide was added to this ether solution dropwise over 1 h. The resultant mixture was heated to reflux for 12 h. After the reaction mixture was cooled to room temperature, the liquid was transferred to another l L flask via a cannula. Two 200 mL portions of diethyl ether were used to extract the product from the magnesium chloride. All of the collected liquid was combined for distillation. After removal of the ether by atmospheric pressure distillation, the product was collected at 100 °C; yield, 81 g (81%). Purity: 98.5% (by GC). ^1H NMR (ppm): 0.75 (singlet 3 H, $SiCH_3$), 1.1 (multiplet, 5 H, $SiCH*_2CH*_3$) $^{13}C\{H\}$ NMR (ppm): 4.38 ($SiCH_3$), 5.92 ($SiC*H_2CH_2-$), 13.77 ($SiCH_2C*H_3$). $^{29}Si\{H\}$ NMR (ppm): 34.5.

2.2b. Methyl-*n*-propyldichlorosilane. Starting materials: $MeSiCl_3$ and *n*-propylmagnesium bromide. Yield: 76%. Bp: 125 °C. Purity: 96%. ^1H NMR (ppm): 0.76 (singlet, 3 H, $SiCH_3$), 1.03 (triplet, 3 H, $SiCH_2CH_2CH*_3$), 1.10 (triplet, 2 H, $SiCH*_2CH_2CH_3$), 1.5 (multiplet 2 H, $SiCH_2CH*_2CH_3$). $^{13}C\{H\}$ NMR (ppm): 5.14 ($SiCH_3$), 16.01 ($SiC*H_2CH_2CH_3$), 16.97 ($SiCH_2CH_2C*H_3$), 23.82($SiCH_2C*H_2CH_3$). $^{29}Si\{H\}$ NMR (ppm): 33.11.

2.2c. *n*-Butylmethyldichlorosilane. Starting materials: $MeSiCl_3$ and *n*-butylmagnesium chloride. Yield: 59%. Bp: 148 °C. Purity: 99% (by GC). ^1H NMR (ppm): 0.76 (singlet, 3 H, CH_3), 0.91 (triplet, 3 H, $SiCH_2CH_2CH_2CH*_3$), 1.12 (triplet, 2 H, $SiCH*_2CH_2CH_2CH_3$), 1.47 (multiplet, 2 H, $SiCH_2CH*_2CH_2CH_3$), 1.49 (multiplet, 2 H, $SiCH_2CH_2CH*_2CH_3$). $^{13}C\{H\}$ NMR (ppm): 5.01 ($SiCH_3$), 13.45 ($SiC*H_2CH_2CH_2CH_3$), 21.24 ($SiCH_2CH_2CH_2C*H_3$), 24.43 ($SiCH_2CH*_2CH_2CH_3$), 25.31 ($SiCH_2CH_2CH*_2CH_3$). $^{29}Si\{H\}$ NMR (ppm): 33.29.

2.2d. Methyl-*n*-pentyldichlorosilane. Starting materials: $MeSiCl_3$ and *n*-pentylmagnesium bromide. Yield: 83%. Bp: 49−50 °C/6 Torr. Purity: 93.8% (by GC). ^1H NMR (ppm): 0.75 (singlet, 3 H, $SiCH_3$), 0.90 (triplet, 3 H, $SiCH_2CH_2CH_2CH_2CH*_3$), 1.11 (triplet, 2 H, $SiCH*_2CH_2CH_2CH_2CH_3$), 1.35 (multiplet, 4 H, $SiCH_2CH*_2CH_2CH*_2CH_3$), 1.51 (multiplet, 2 H, $SiCH_2CH_2CH*_2CH_2CH_3$). $^{13}C\{H\}$ NMR (ppm): 5.04 ($SiCH_3$), 13.73 ($SiC*H_2CH_2CH_2CH_2CH_3$), 21.45 ($SiCH_2CH_2CH_2CH_2C*H_3$), 21.96 ($SiCH_2C*H_2CH_2CH_2CH_3$), 22.04 ($SiCH_2CH_2CH_2C*H_2CH_3$), 34.42 ($SiCH_2CH_2C*H_2CH_2CH_3$). $^{29}Si\{H\}$ NMR (ppm): 33.28.

2.2e. *n*-Hexylmethyldichlorosilane. Starting materials: $MeSiCl_3$ and *n*-Hexylmagnesium bromide. Yield: 79%. Purity: 94%. Bp: 60−61 °C/6 Torr. ^1H NMR (ppm): 0.76 (singlet, 3 H, $SiCH_3$), 0.88 (triplet, 3 H, $SiCH_2CH_2CH_2CH_2CH_2CH*_3$), 1.12 (triplet, 2 H, $SiCH*_2-$), 1.28 (multiplet, 4 H, $SiCH_2CH*_2CH_2CH_2CH*_2CH_3$), 1.37 (multiplet, 2 H, $SiCH_2CH_2CH*_2CH_2-$), 1.49 (multiplet, 2 H, $SiCH_2CH_2CH_2CH*_2-$). $^{13}C\{H\}$ NMR (ppm): 5.04 ($SiCH_3$), 13.93 ($SiCH_2CH_2CH_2CH_2CH_2C*H_3$), 21.54($SiC*H_2-$), 22.29 ($SiCH_2C*H_2-$), 22.38 ($SiCH_2CH_2CH_2CH_2C*H_2CH_3$), 31.26 ($SiCH_2CH_2C*H_2-$), 31.97 ($SiCH_2CH_2CH_2CH_2C*H_2CH_2CH_3$). $^{29}Si\{H\}$ (ppm): 33.17.

2.3. Preparation of 1,3,5-Trialkyl-1,3,5-trimethylcyclotrisiloxanes. Compounds **2.3b**−**2.3e** were made by the same method as described for **2.3a**.

2.3a. 1,3,5-Triethyl-1,3,5-trimethylcyclotrisiloxane. Zinc oxide (53 g, 0.63 mol) and ethyl acetate (180 mL) were placed in a 500 mL three-necked round-bottom flask equipped with a dropping funnel, a mechanical stirrer, and a reflux condenser fitted with a nitrogen gas outlet. Over a period of 1 h, a solution of 60 g (0.42 mol) of ethylmethyldichlorosilane in 120 mL of ethyl acetate was added to the zinc oxide mixture. The temperature of the reaction solution increased to approximately 50 °C during the addition period. After the addition was complete, stirring was continued for 1 h. The mixture was then poured slowly into 250 mL of saturated aqueous sodium bicarbonate solution with vigorous stirring. The organic phase was separated and dried over anhydrous Na_2SO_4. The crude product was purified by distillation. Isolated yield, 12 g (32.4%). Bp: 50−55 °C/2.2 Torr. Purity: 95.1% (by GC). ^1H NMR (ppm): 0.13 (singlet 3 H, $SiCH_3$), 0.56 (doublet of quartet, 2 H, $SiCH*_2CH_3$), 0.97 (triplet, 3 H, $SiCH_2CH*_3$). $^{13}C\{H\}$ NMR (ppm): −1.15($SiCH_3$), 5.92($SiC*H_2CH_3$), 8.90 ($SiCH_2C*H_3$). $^{29}Si\{H\}$ NMR (ppm): −8.16, −8.06.

2.3b. 1,3,5-Trimethyl-1,3,5-tri-*n*-propylcyclotrisiloxane. Starting material: **2.2b** Yield: 31.2%. Bp: 76−80 °C/2.2 Torr. Purity: 95.5% (by GC). ^1H NMR (ppm): 0.13 (singlet, 3 H, $SiCH_3$), 0.59 (triplet, 2 H, $SiCH_2CH*_2CH_3$), 0.97 (triplet, 3 H, $SiCH*_2CH_2CH*_3$), 1.42 (multiplet 2 H, $SiCH_2CH*_2CH_3$). $^{13}C\{H\}$ NMR (ppm): −0.51 ($SiCH_3$), 16.06 ($SiC*H_2CH_2CH_3$), 17.69 ($SiCH_2CH_2C*H_3$), 19.73($SiCH_2C*H_2CH_3$). $^{29}Si\{H\}$ NMR (ppm): −9.11, −9.08.

2.3c. 1,3,5-Tri-*n*-butyl-1,3,5-trimethylcyclotrisiloxane. Starting material: **2.2c**. Yield: 39.3%. Bp: 130−134 °C/2.2 Torr. Purity: 97.5% (by GC). ^1H NMR (ppm): 0.13 (singlet, 3 H, $SiCH_3$), 0.58 (triplet, 2 H, $SiCH*_2CH_2CH_2CH_3$), 0.89 (triplet, 3 H, $SiCH_2CH_2CH_2CH*_3$), 1.37(multiplet, 4 H, $SiCH_2CH*_2CH*_2CH_3$). $^{13}C\{H\}$ NMR (ppm): −0.56 ($SiCH_3$), 13.70 ($SiCH_2CH_2CH_2C*H_3$), 16.85 ($SiC*H_2-$), 24.72 ($SiCH_2CH*_2CH_2CH_3$). 25.99 ($SiCH_2CH_2CH*_2CH_3$). $^{29}Si\{H\}$ NMR (ppm): −8.84, −8.78.

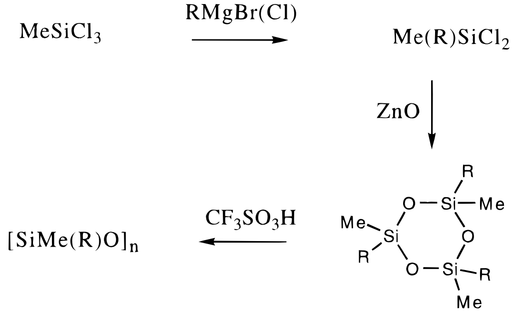
2.3d. 1,3,5-Trimethyl-1,3,5-tri-*n*-pentylcyclotrisiloxane. Starting material: **2.2d**. Yield: 22%. Bp: 145−149 °C/2.2 Torr. Purity: 96.5% (by GC). ^1H NMR (ppm): 0.13 (singlet, 3 H, $SiCH_3$), 0.57 (triplet, 2 H, $SiCH*_2-$), 0.87 (triplet, 3 H, $SiCH_2CH_2CH_2CH_2CH*_3$), 1.30 (multiplet, 4 H, $SiCH_2CH*_2CH_2CH*_2CH_3$), 1.41 (multiplet, 2 H, $SiCH_2CH_2CH*_2CH_2CH_3$). $^{13}C\{H\}$ NMR (ppm): −0.54 ($SiCH_3$), 13.84 ($SiCH_2CH_2CH_2CH_2C*H_3$), 17.12($SiC*H_2CH_2CH_2CH_2CH_3$), 22.19 ($SiCH_2C*H_2CH_2CH_2CH_3$), 22.28 ($SiCH_2CH_2CH_2C*H_2CH_3$), 35.26 ($SiCH_2CH_2C*H_2CH_2CH_3$). $^{29}Si\{H\}$ NMR (ppm): −8.89, −8.86.

2.3e. 1,3,5-Tri-*n*-hexyl-1,3,5-trimethylcyclotrisiloxane. Starting material: **2.2e**. Yield: 30.7%%. Purity: 96% (by GC). Bp: 170−175 °C/2.2 Torr. ^1H NMR (ppm): 0.13 (singlet, 3 H, $SiCH_3$), 0.60 (triplet, 2 H, $SiCH*_2-$), 0.88 (triplet, 3 H, $SiCH_2CH_2CH_2CH_2CH_2CH*_3$), 1.25−1.40 (multiplet, 8 H, $SiCH_2CH*_2CH*_2CH*_2CH*_2CH_3$). $^{13}C\{H\}$ NMR (ppm): 5.04 ($SiCH_3$), 14.0 ($SiCH_2CH_2CH_2CH_2CH_2C*H_3$), 17.20 ($SiC*H_2-$), 22.52 ($SiCH_2C*H_2-$), 22.60 ($SiCH_2CH_2CH_2CH_2C*H_2CH_3$), 31.53 ($SiCH_2CH_2C*H_2-$), 32.73 ($SiCH_2CH_2CH_2CH_2C*H_2CH_2CH_3$). $^{29}Si\{H\}$ NMR (ppm): −8.86, −8.79.

2.4. Polymerization. Polymers **2.4b**−**2.4e** were prepared by the same procedure as described for **2.4a**.

2.4a. Poly(ethylmethylsiloxane). In a typical polymerization setup, a 50 mL two-necked flask, equipped with a nitrogen inlet, septum, and a stirring bar, was charged with 2 g of 1,3,5-triethyl-1,3,5-trimethylcyclotrisiloxane. The monomer was degassed and flushed with nitrogen, and subsequently 1 μL of trifluoromethanesulfonic acid was added via the septum. After 1 h of stirring at room temperature, formation of high molecular weight material became evident by the increase in viscosity. Usually, the mixture was allowed to react for 12 h before workup. The crude polymer was dissolved in 100 mL of toluene and precipitated by adding ethanol (about 30 mL) so as to remove any low molecular weight oligomers. The precipitated sample was dried under vacuum at 110 °C for at least 24 h. A yield of 1.4 g of high molecular weight product was isolated. ^1H NMR (ppm): 0.04 (singlet 3 H,

Scheme 1. Approach Employed for the Synthesis of the *n*-Alkyl-Substituted Cyclosiloxanes and the Corresponding Poly(siloxanes)



$SiCH_3$), 0.47 (quartet, 2 H, $SiCH^*_2CH_3$), 0.93 (triplet, 3 H, $SiCH_2CH^*_3$). ^{13}C{H} NMR (ppm): −1.27 ($SiCH_3$), 6.42 (SiC^*H_2-CH_3), 9.06 ($SiCH_2C^*H_3$). ^{29}Si{H} NMR (ppm): −21.71.

2.4b. Poly(methyl-*n*-propylsiloxane). Starting material: **2.3b**. ^{1}H NMR (ppm): 0.03 (singlet, 3 H, $SiCH_3$), 0.49 (triplet, 2 H, $SiCH_2CH^*_2CH_3$), 0.94 (triplet, 3 H, $SiCH_2CH_2$-CH^*_3). 1.38 (multiplet 2 H, $SiCH_2CH^*_2CH_3$). ^{13}C{H} NMR (ppm): −0.47 ($SiCH_3$), 16.40 ($SiC^*H_2CH_2CH_3$), 17.90 ($SiCH_2$-$CH_2C^*H_3$); 20.09 ($SiCH_2C^*H_2CH_3$). ^{29}Si{H} NMR (ppm): −22.90.

2.4c. Poly(*n*-butylmethylsiloxane). Starting material: **2.3c**. ^{1}H NMR (ppm): 0.04 (singlet, 3 H, $SiCH_3$), 0.50 (triplet, 2 H, $SiCH^*_2CH_2CH_2CH_3$), 0.87 (triplet, 3 H, $SiCH_2CH_2CH_2$-CH^*_3), 1.33 (multiplet, 4 H, $SiCH_2CH^*_2CH^*_2CH_3$). ^{13}C{H} NMR (ppm): −0.56 ($SiCH_3$), 13.65 ($SiCH_2CH_2CH_2C^*H_3$), 17.22 (SiC^*H_2−), 25.11 ($SiCH_2CH^*_2CH_2CH_3$), 26.16 ($SiCH_2CH_2CH^*_2$-CH_3). ^{29}Si{H} NMR (ppm): −22.56.

2.4d. Poly(methyl-*n*-pentylsiloxane). Starting material: **2.3d**. ^{1}H NMR (ppm): 0.03 (singlet, 3 H, $SiCH_3$), 0.48 (triplet, 2 H, $SiCH^*_2$−), 0.87 (triplet, 3 H, $SiCH_2CH_2CH_2CH_2$-CH^*_3), 1.28 (multiplet, 4 H, $SiCH_2CH^*_2CH_2CH^*_2CH_3$), 1.34 (multiplet, 2 H, $SiCH_2CH_2CH^*_2CH_2CH_3$). ^{13}C{H} NMR (ppm): −0.48 ($SiCH_3$), 13.89 ($SiCH_2CH_2CH_2CH_2C^*H_3$), 17.50 ($SiC^*H_2CH_2CH_2CH_2CH_3$), 22.28 ($SiCH_2C^*H_2CH_2CH_2CH_3$), 22.60 ($SiCH_2CH_2CH_2C^*H_2CH_3$), 35.254 ($SiCH_2CH_2C^*H_2CH_2CH_3$). ^{29}Si{H} NMR (ppm): −22.56.

2.4e. Poly(*n*-hexylmethylsiloxane). Starting material: **2.3e**. ^{1}H NMR (ppm): 0.03 (singlet, 3 H, $SiCH_3$), 0.48 (triplet, 2 H, $SiCH^*_2$−), 0.87 (triplet, 3 H, $SiCH_2CH_2CH_2CH_2$-$CH_2CH^*_3$), 1.26−1.30 (multiplet, 8 H, $SiCH_2CH^*_2CH^*_2CH^*_2$-$CH^*_2CH_3$). ^{13}C{H} NMR (ppm): −0.48 ($SiCH_3$), 14.0 ($SiCH_2$-$CH_2CH_2CH_2CH_2C^*H_3$), 17.59 (SiC^*H_2−), 22.56 ($SiCH_2C^*H_2$−), 22.93 ($SiCH_2CH_2CH_2CH_2C^*H_2CH_3$), 31.60 ($SiCH_2CH_2C^*H_2$−), 33.06 ($SiCH_2CH_2CH_2CH_2C^*H_2CH_2CH_3$). ^{29}Si{H} NMR (ppm): −22.57.

3. Results and Discussion

3.1. Syntheses. The *n*-alkyl-substituted methyldichlorosilanes were prepared by the coupling reaction between methyltrichlorosilane and the corresponding Grignard reagents (RMgBr or RMgCl) in ether (Scheme 1). In general, the yield of these coupling reactions was around 80%. The only exception was *n*-butylmethyldichlorosilane, where a slightly lower yield (60%) was obtained. This may be due to the use of *n*-butylmagnesium chloride, rather than the bromide used in the other reactions, as the Grignard regent. Extraction of the products from MgBrCl was found to be much easier than from $MgCl_2$, because the mixed halide salt forms dense particles in ether, whereas the latter occurs as a flocculant material which apparently absorbs some of the product.

The 1,3,5-tri-*n*-alkylcyclotrisiloxanes were synthesized by the reaction of the obtained *n*-alkylmethyldichlorosilanes with 1.5 equiv of zinc oxide in ethyl acetate. This approach was reported to give a 100% yield for the hexaphenylcyclotrisiloxane.[14] In the synthesis of hexa-*n*-alkylcyclotrisiloxanes, the same method provided a 10−48% yield of the various *n*-alkyl products.[10] In our case, moderate yields (20−30%) were obtained for the cyclic trimers. Since the Si atoms are asymmetrically substituted, all of the cyclic products were obtained as mixtures of the corresponding cis and trans isomers. GC and ^{29}Si NMR analyses indicated that the two isomers usually occur in a 1:4 ratio (i.e., slightly greater trans- content than expected from a purely statistical distribution [1:3]). Figure 1 is an example of the typical ^{29}Si NMR spectrum obtained for these trimers. No attempts were made to separate the cis and trans isomers. Apart from the cyclic trimer, higher cyclic compounds such as the tetramer and pentamer were formed in a ratio of approximately 10:4:1 determined by GC, which is in agreement with the previous results.[15] The remainder of the siloxane product consisted of higher oligomers.

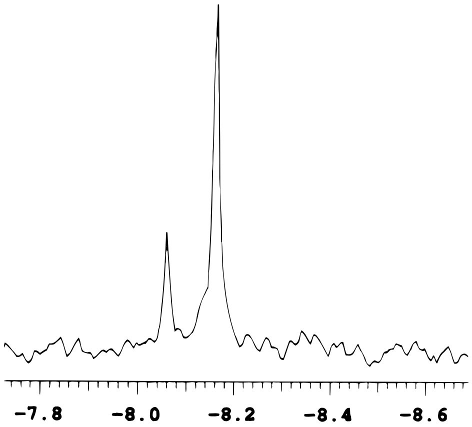


Figure 1. ^{29}Si{H} NMR spectrum of 1,3,5-triethyl-1,3,5-trimethylcyclotrisiloxane.

Table 1. Molecular Weight and T_gs of the $[SiMe(alkyl)O]_n$ Polymers

$[SiMe(R)O]_n$	M_w	M_n	M_w/M_n	T_g (°C)
$[SiMe_2O]_n$[a]	49 350			−126
$[SiMe(Et)O]_n$	66 500	45 800	1.45	−139
$[SiMe(n\text{-}Pr)O]_n$	48 400	37 900	1.28	−120
$[SiMe(n\text{-}Bu)O]_n$	60 700	45 100	1.45	−115
$[SiMe(n\text{-}Pen)O]_n$	161 900	73 500	2.2	−112
$[SiMe(n\text{-}Hex)O]_n$	66 800	42 200	1.58	−108

[a] A commercial sample (trade name: PS044) with M_w = 49 350 from Hüls Petrarch Systems.

Polymerizations were carried out in bulk with trifluoromethanesulfonic acid as a cationic initiator at room temperature. As was reported previously, the polymerization generally gave rise to 70% high molecular weight polymer and about 30% of low molecular weight oligomers.[15] The chemical shifts of the resultant polymers in the ^{29}Si NMR spectrum all appeared between −21 and −23 ppm (listed in the Experimental Section), which are lower than their corresponding monomers, whose chemical shifts were −8 to −9 ppm. This change in chemical shifts from lower field to higher field is attributed to the relief of the strain energy of the 6-membered siloxane ring on formation of the polymer. The molecular weights and the molecular weight distributions obtained by GPC for the fractionated poly(alkylmethylsiloxanes) are listed in Table 1.

Compared to the corresponding symmetrically-disubstituted *cyclo*-hexaalkyltrisiloxanes bearing long alkyl groups,[10] the current methyl-*n*-alkyl-substituted trimers required less time, usually 1 h, to complete the polymerization. This is probably due to the presence of the

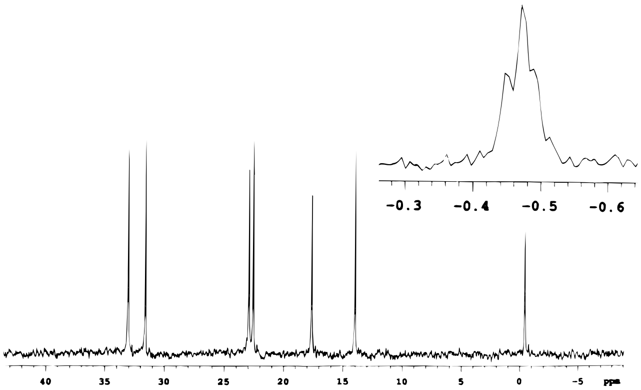


Figure 2. $^{13}C\{H\}$ NMR spectrum of poly(*n*-hexylmethylsiloxane).

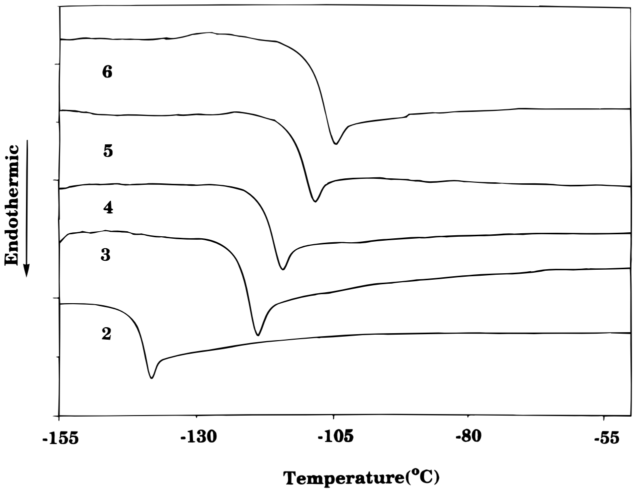


Figure 3. Stack plot of DSC curves for the $[Si(Me)(R)O]_n$ polymers: 2, R = Et; 3, R = *n*-Pr; 4, R = *n*-Bu; 5, R = *n*-Pen; 6, R = *n*-Hex.

small methyl groups, which do not greatly inhibit chain propagation during the ROP process. As was mentioned above, the currently studied monomers contain cis and trans isomers. The resultant polymers are therefore expected to be atactic, as has been observed for poly(methylphenylsiloxane) previously.[16] Figure 2 shows the $^{13}C\{H\}$ NMR spectrum of poly(*n*-hexylmethylsiloxane), which is typical of those obtained for the other polymers. The expanded resonance due to the SiMe carbon was found to be a 1:2:1 triplet, consistent with a completely random arrangement of the various possible triad sequences of chiral centers in an atactic polymer.[17]

3.2. Glass Transitions. All of the polymers studied exhibited clear glass transitions with no evidence of any other thermal transitions. The observed glass transition temperatures are summarized in Table 1 and a stack-plot of the DSC curves is given in Figure 3. A commercial poly(dimethylsiloxane) (PDMS) sample with M_w = 49 350 was also measured for comparison with these other polysiloxanes. The T_gs found for the dimethyl, Me/Et, and Me/*n*-Pr polymers were −126, −139, and −120 °C, which are very close to the values reported in the literature.[6] The T_g of poly(ethylmethylsiloxane) is lower than that of PDMS, probably due to its less symmetrical structure than that of PDMS, whereas the rest of the poly(alkylmethylsiloxanes) have higher T_gs than that of PDMS. Moreover, the T_gs continued to increase for the ethyl to *n*-hexyl substituted poly(siloxanes), as is shown in Table 1. It has been reported that the T_gs of dialkyl substituted poly(siloxanes), such as $[SiEt_2O]_n$, $[Si(n\text{-}Pr)_2O]_n$, $[Si(n\text{-}Bu)_2O]_n$, and $[Si(n\text{-}Pen)_2O]_n$, occur at −138, −110, −116, and −106 °C, respectively.[10] Here, except for the T_g of the di-*n*-butyl polymer, the overall trend of T_gs is similar to what we have observed in the asymmetrically substituted poly(siloxane) system. We note that this behavior is quite different than that typically observed for carbon-backbone polymers with *n*-alkyl side chains, such as the polyolefins and polyacrylics,[2,3] in which a continual decrease in T_g is generally observed as the length of the side chain is increased.

Van Krevelen has proposed some empirical equations to estimate the T_gs for various polymers.[5b] The equation $T_g = Y_g/M$, where $Y_g = Y_{g0} + N(Y_{g9} - Y_{g0})/9$, Y_g is an empirical value called the molar glass transition function, and M is the molar mass of the repeat unit for the polymer, was used to calculate the T_gs for linear polymers with long *n*-alkyl side chains, $[-Z[(CH_2)_N CH_3]-]_n$ (where −Z− stands for the main chain species and $[(CH_2)_N CH_3]$ is the side chain). This study did not list Y_{g0} and Y_{g9} values for siloxane polymers; however, we were able to calculate these based on the data given for the group contributions to Y_g.[5b] The calculated value for Y_{g0} was 11 K kg/mol, according to the group contributions of 7 for $-SiMe_2-$ and 4 for the −O− group. The value calculated for Y_{g9} was about 40 K kg/mol according to the equation $Y_{g9} = 0.2M_9$. Then, by using above two equations, the T_gs for the $[SiMe(R)O]_n$ polymers, where R = Et, *n*-Pr, *n*-Bu, *n*-Pen, and *n*-Hex, were calculated as −111, −102, −95, −89, and −85 °C, respectively. These values do not correspond too closely with those determined experimentally; however, the overall trend of increasing T_g with increasing *n*-alkyl chain size is reproduced reasonably well.

Previously,[11] we reported the synthesis and characterization of various *n*-alkyl-substituted poly(silylenemethylenes) (PSMs), $[SiMe(R)CH_2]_n$, where we found that the T_g first increased from −78.2 °C for $[SiMe(Et)CH_2]_n$ to −61.2 °C for $[SiMe(n\text{-}Pr)CH_2]_n$ and then decreased from R = *n*-propyl to *n*-hexyl. Attempts to apply the empirical equations given above for this case failed to reproduce either the approximate values for the glass transitions temperatures or the trend in T_g with increasing *N*. In a general sense, however, both the relative T_g values observed and the trend with increasing side chain length is understandable in the context of the T_gs obtained for the corresponding *n*-alkyl-substituted poly(siloxanes) and poly(olefins). A comparison of the glass transition temperatures for these three series of asymmetrically *n*-alkyl-substituted polymers is shown in Figure 4.

We can start with the assumption that the poly(silylenemethylene) main chain is more flexible than that of the poly(olefins), due to the longer Si−C bond distance relative to the C−C bond.[11b] Replacing the $-CH_2-$ group in the PSMs by a bridging oxygen atom would clearly increase the main chain flexibility even further; thus, the fact that the T_gs for the PSMs lie intermediate between those of the polyolefins and the polysiloxanes is understandable. In terms of the trend in T_g with the alkyl side chain length, it is also understandable that the PSMs exhibit a behavior which is intermediate between the two extremes of continuously increasing or decreasing T_g with side chain length found for the polysiloxanes and polyolefins, respectively. A more detailed understanding of this behavior must await further theoretical and experimental study; however, we can speculate that the dominant factor that

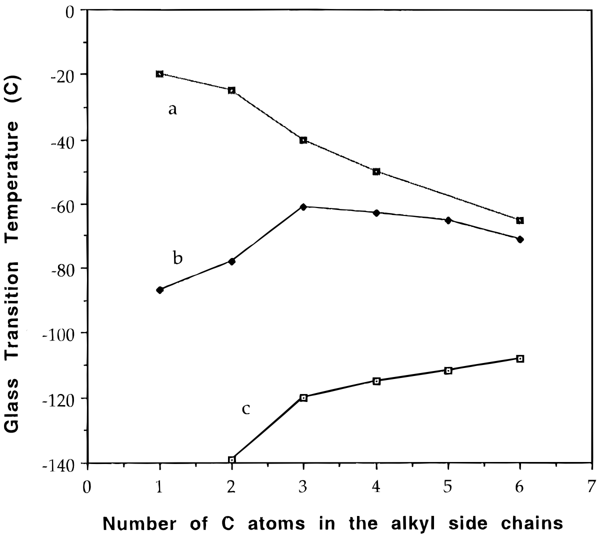


Figure 4. Plot of T_g vs side chain length (m +1) for three series of $\{-Z[(CH_2)_mCH_3]-\}_n$ (Z = (a) $-CHCH_2-$, (b) Si(Me)CH_2-, and (c) Si(Me)O$-$) polymers.

determines T_g in the case of the polysiloxanes is the main chain flexibility, and the effect of adding alkyl groups of increasing size is to reduce this flexibility, and thereby increase the T_g, at least up to *n*-hexyl. On the other hand, for the polyolefins, where the main chain is much less flexible, the dominant effect of adding *n*-alkyl side chains of increasing length is one decreasing the cohesive energy between chains (or, equivalently, increasing the "free volume").[2] The PSMs, with their intermediate chain flexibility may lie in a range where these two effects compete with one another, producing first an increase in T_g from Et to *n*-Pr due to a reduction in the main chain flexibility, and then decreasing T_g beyond *n*-Pr as the effects of the side chain mobility becomes increasingly important in the context of a less mobile main chain.

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References and Notes

(1) Shen, M. C.; Eisenberg, A. *Prog. Solid State Chem.* **1966**, *3*, 407.
(2) Dannis, M. L. *J. Appl. Polym. Sci.* **1959**, *1*, 121.
(3) Rogers, S. S.; Mandelkern, L. *J. Phys. Chem.* **1957**, *61*, 985.
(4) Barb, W. G. *J. Polym. Sci.* **1959**, *37*, 515.
(5) (a) Krause, S; Gormely, J. J.; Roman, N.; Shetter, J. A.; Watanabe, W. H. *J. Polym. Sci., Part A* **1965**, *3*, 3573. (b) Krevelen, D. W. V.; Hoftyzer, P. J. *Properties of Polymers*; Elsvier: Amsterdam, Oxford, England, New York, Tokyo, 1990, Chapter 6, p 129.
(6) Stern, S. A.; Shah, V. M.; Hardy, B. J. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 1263.
(7) Polmanteer, K. E.; Hunter, M. J. *J. Appl. Polym. Sci.* **1959**, *1*, 3
(8) Kuniya, T. *Nippon Kagaku Kaishi* **1989**, *9* 1564.
(9) (a) Paterson, M. S. *J. Appl. Phys.* **1964**, *35*, 176. (b) Alexopoulos, J. B.; Barrie, J. A.; Tye, J. C.; Fredrickson, M. *Polymer* **1968**, *9*, 56.
(10) (a) Out, G. J. J.; Klok, H. A.; Möller, M. *Macromol. Chem. Phys.* **1995**, *196*, 195. (b) Rim, P. B.; Rasoul, H. A. A.; Hurley, S. M.; Orler E. B.; Scholsky, K. M. *Macromolecules* **1987**, *20*, 208.
(11) (a) Shen, Q.; Interrante, L. V. Preparation and Thermal Properties of Some Asymmetrically Substituted Poly(silylenemethylenes). *J. Polym. Sci., Polym. Chem.*, in press. (b) Interrante, L. V.; Wu, H. J., Apple, T.; Shen, Q.; Smith, K. *J. Am. Chem Soc.* **1994**, *116*, 12086.
(12) Shriver, D. F; Drezdon, M. A. *Manipulation of Air-sensitive Compounds*; 2nd ed.; Wiley: New York, 1985.
(13) Gordon, A. S.; Fort, R. A. *The Chemists Companion*; Wiley: New York, 1977.
(14) Takiguchi, T.; Sakurai, M.; Ichimura, J.; Iizuka, Y. *J. Org. Chem.* **1960**, *25*, 310.
(15) Out, G. J. J.; Turetskii, A. A.; Möller, M. *Macromolecules* **1995**, *28*, 596.
(16) Clarson, S. J.; Semlyen, J. A.; Dodgson, K. *Polymer* **1991**, *32*, 2823.
(17) Rushkin, I. L.; Interrante, L. V. *Macromolecules* **1996**, *29*, 3123.

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