Poly(dimethylsilylenemethylene-*co*-dimethylsiloxane): A Regularly Alternating Copolymer of Poly(dimethylsiloxane) and Poly(dimethylsilylenemethylene)

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Organosilicon polymers that contain main-chain silicon atoms bridged by either oxygen or methylene groups have been known for many years, in the form of the polysiloxanes[1] and polysilylenemethylenes,[2] respectively. Polymers that contain both $-C_mH_n-$ and $-O-$ bridging groups, and therefore can be considered as polycarbosiloxanes, are also well-known.[3−5] However, the prototypical polycarbosiloxane copolymer, having a regular −Si−O−Si−C− main chain, has apparently not yet been reported, although both linear[6,7] and cyclic[8] oligomers of this type have been prepared by using various multistep synthetic procedures. In particular, the cyclic compound, 1,1,3,3,5,5,7,7-octamethyl-2,6-dioxa-1,3,5,7-tetrasilacyclooctane (**I**) (Scheme 1), has been obtained as a hydrolysis product of tetramethyldiethoxydisilylmethane[8] and also by reaction of $(ClSiMe_2)_2CH_2$ with $Me_2Si(OK)_2$.[9] Interestingly, in one of these papers,[8] it was noted that the ring-opening polymerization of compound **I** by using "the usual methods" for cyclic siloxanes was unsuccessful.

We report here the successful synthesis of this 1:1 alternating copolymer of poly(dimethylsiloxane) and poly(dimethylsilylenemethylene) by cationic ring-opening polymerization and some preliminary results regarding its physical properties and thermal decomposition in air and in an inert atmosphere. Also reported are the results of preliminary, as yet unsuccessful, efforts to prepare the corresponding all-ethyl-substituted polymer by the same method, which is of interest in connection with its potential mesophase behavior.[10,11]

The methods that have been previously used[4,5] to prepare the eight-membered ring compound **I** suffer from several problems, including difficult to prepare and purify starting materials and low yields of the desired end product. We prepared compound **I** by the reaction of a dichlorocarbosilane, $ClSi(Me)_2CH_2Si(Me)_2Cl$, in ethyl acetate with zinc oxide, a reaction which has been used extensively for the preparation of various cyclic siloxanes (Scheme 1).[12] The dichlorocarbosilane starting material for this synthesis was obtained from the Grignard coupling reaction of methylene chloride and excess dichlorodimethylsilane by using a Mg−Zn mixture.[13] Yields as high as 30% were obtained in the Grignard coupling reaction, and the ring-closure reaction for the formation of the eight-membered ring provided a ca. 50% yield of the cyclic tetramer after fractional distillation at 3 Torr (bp 54−56 °C). The structure of compound **I** was characterized by ^1H, ^{29}Si, and ^{13}C NMR spectroscopy.[14]

After several unsuccessful attempts to polymerize **I** by using anionic catalysts, such as BuLi and KOH,[15] in a manner analogous to that commonly used for cyclic siloxanes,[16] we turned to triflic acid (trifluoromethanesulfonic acid (HOTf)), which is well-known to be an effective cationic catalyst for the ring-opening polymerization of such compounds.[17] Thus, compound **I** (2 g) was mixed with 2 μL of HOTf at room temperature under nitrogen. In less than 30 min, the mixture became quite viscous; the viscous material was stirred at room temperature for 48 h before work-up. The product was then dissolved in chloroform and reprecipitated by adding twice the volume of methanol. The clear, colorless, viscous liquid obtained amounted to ca. 55% of the total product. GPC analysis of this sample[18] showed that the M_n for the high molecular weight fraction was around 50 000 ($M_w/M_n = 1.4-1.8$). Evaporation of the solvents from the methanol/chloroform-soluble fraction gave a clear, low-viscosity, liquid whose GPC trace showed only low molecular weight products (< ca. 500 amu). The ^1H NMR spectra of this fraction showed two different methylene peaks: one for the low molecular weight linear polymer or large rings and one for unreacted monomer. An integration of the relative areas indicated that about 38% of this fraction was unreacted monomer. Therefore, the overall yield of polymeric/oligomeric products from this reaction was about 82%. Characterization of the high molecular weight fraction rests on the results of elemental analyses and ^1H, ^{13}C, and ^{29}Si NMR spectra,[19] which are fully consistent with expectations for the $[SiMe_2CH_2SiMe_2O]_n$ structure (Figure 1).

DSC showed a glass transition for the high molecular weight fraction at −106 °C but no melting transition.[20] The reported glass transition temperatures for poly(dimethylsiloxane) (PDMS) and poly(dimethylsilylenemethylene) (PDMSM) are −127[21] and −100 °C[22] (a glass transition temperature of −87 °C has also been reported for this polymer[11]), respectively. The reduction in T_g on going from the polysilylenemethylene to the polysiloxane is presumably related to the reduced torsional barriers for, and therefore increased flexibility of, the polymer chains on replacement of a $-CH_2-$ group by $-O-$. Thus, the observation of a T_g value for the alternating copolymer that is in between those of its homopolymer analogues is understandable.

The thermal stability of the alternating copolymer was also examined by TGA both in an inert atmosphere (nitrogen) and in air (Figure 2).[23] The results indicate a relatively high thermal stability in an inert atmosphere, with a T_{10} value (the temperature at which 10% weight loss was observed) of 475 °C. In contrast, a 10% weight loss is reached by ca. 245 °C in air, although the char yield by 1000 °C (ca. 17%) is significantly higher than that under nitrogen (ca. 0%).

A comparison of the thermal stability of the two parent homopolymers, PDMS and PDMSM, was reported in 1968 by Levin and Carmichael.[24] They reported the T_{10} values for both polymers and found that in air PDMS (403 °C) is more stable than PDMSM (325 °C), while in helium PDMS (452 °C) is less stable than PDMSM (510 °C). On this basis, the stability of the copolymer in air (T_{10} = 245 °C) is considerably lower than that of either of the two homopolymers, whereas

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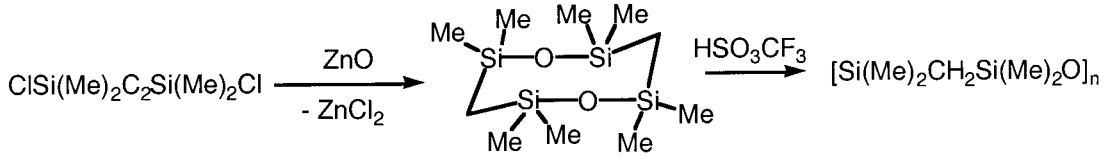
Scheme 1. Synthesis and Polymerization of 1,1,3,3,5,5,7,7-Octamethyl-2,6-dioxa-1,3,5,7-tetrasilacyclooctane (I)



I

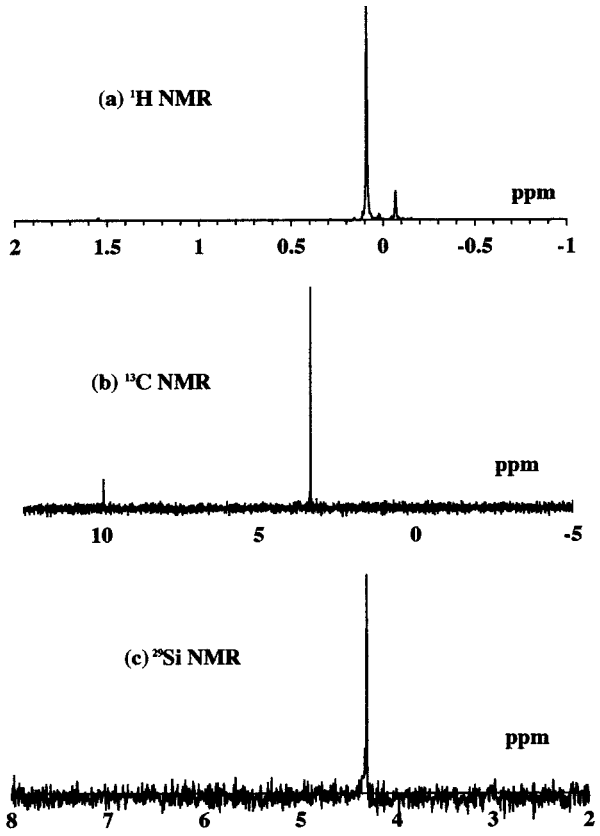


Figure 1. (a) ^{1}H, (b) ^{13}C, and (c) ^{29}Si NMR spectra of $[SiMe_2CH_2SiMe_2O]_n$.

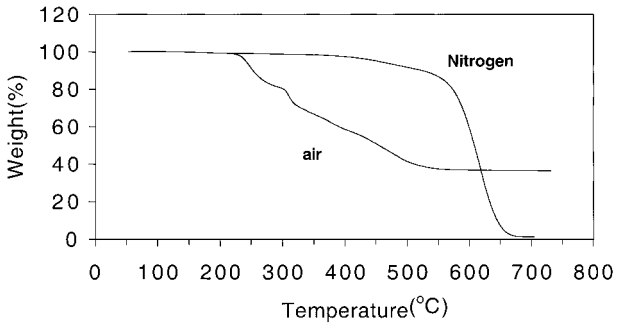


Figure 2. TGA curves for $[SiMe_2CH_2SiMe_2O]_n$ in N_2 and air.

in an inert atmosphere, the copolymer (T_{10} = 475 °C) appears to be intermediate in stability.[25] It is certainly reasonable that the copolymer and the PSM homopolymer are substantially less stable in air than PDMS, due to the likely sensitivity of the bridging methylene groups to oxidation.[23] The considerably lower decomposition onset for the copolymer relative to the PDMSM homopolymer may reflect a greater sensitivity of its methylene groups to oxidation due to the electron-withdrawing effect of the next-nearest-neighbor oxygen atoms. On the other hand, the apparent greater thermal stability of the copolymer (and the polysilylenemethylene homopolymer) in an inert atmosphere suggests that degradation to form small ring compounds, which is the dominant weight loss process for PDMS,[26] may be less facile in this case, presumably owing to the relatively nonpolar character of the Si−C bonds and the decreased frequency of siloxy linkages.

By using the same general procedure, we have also prepared the corresponding all-ethyl-substituted cyclic dimer, $[Si(Et)_2CH_2Si(Et)_2O]_2$.[27] Thus far, our efforts to open this ring so as to form the corresponding $[Si(Et)_2CH_2Si(Et)_2O]_n$ polymer have been unsuccessful.[28] This difficulty in opening the eight-membered ring with ethyl groups on the Si was not unanticipated, based on the known decreased rate of polymerization of octamethylcyclotetrasiloxane (D_4) relative to the more strained hexamethylcyclotrisiloxane (D_3)[29] as well as for the D_3 monomer when Me is replaced by larger alkyl substituents. Our efforts to prepare this R = Et polymer, as well as other poly(silylenemethylene)/polysiloxane copolymers, are continuing, employing both ROP and condensation reactions.

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Supporting Information Available: A summary of the triple detector GPC results (S1) and the DSC trace (S2) for the high molecular weight fraction of the copolymer, $[SiMe_2CH_2SiMe_2O]_n$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) NMR spectra were obtained by using a Varian 300 NMR spectrometer with *d*-chloroform as solvent. Proton-gated decoupling was used in both the ^{13}C and ^{29}Si NMR spectra. Chromium(III) acetylacetonate was used as a relaxation reagent (0.1 mol %) in the ^{29}Si NMR. $[SiMe_2CH_2SiMe_2O]_2$: ^1H NMR: Si−C**H**$_2$−Si −0.14 ppm; Si−C**H**$_3$ 0.10 ppm. ^{13}C NMR: Si−**C**H$_2$−Si 8.82 ppm; Si−**C**H$_3$ 3.39 ppm. ^{29}Si NMR: 5.03 ppm.
(15) The attempted reactions involving KOH and BuLi as an ionic catalysts were carried out both in toluene and by using the neat monomer in each case. After about 20 h reaction at room temperature, chlorotrimethylsilane was added to terminate the reaction. Then the solvent (if used) was removed by evaporation in a vacuum. The ^1H NMR spectrum of the resulting material was identical to that of the starting monomer, and no viscosity change was evident during the reaction.
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(18) GPC was performed by using a Waters 600 pumping system connected to a 60 cm Polymer Labs mixed-D column (mixed bed, bead size: 5A-10A; room temperature: 23−24 °C; flow rate: 1 mL/min). A Viskotec(T60A+LR40) triple detector (refractive index/viscometry/light scattering) system was used to obtain absolute molecular weights, as well as values for the Mark−Houwink constant (a) (solvent: THF, M_n = 50 300, M_w = 79 800, a = 0.749; solvent: toluene, M_n = 55 000, M_w = 79 400, a = 1.435).
(19) $[Si(CH_3)_2OSi(CH_3)_2CH_2]_n$: elemental analysis (Galbraith): Si 37.42% (calc 38.35%), C 41.35% (calc 41.10%), H 9.48% (calc 9.59%). ^1H NMR: Si−C**H**$_2$−Si −0.11 ppm; Si−C**H**$_3$ 0.04 ppm. ^{13}C NMR: Si−**C**H$_2$−Si: 9.60 ppm; Si−**C**H$_3$ 3.04 ppm. ^{29}Si NMR: 4.32 ppm.
(20) A DSC 2920 modulated DSC (TA Instruments) was employed to monitor the thermal transitions at a scan rate of 10 °C/min between −150 and 50 °C; the T_g was recorded on the first heating scan.
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(23) TGA was performed by using a Perkin-Elmer TGA7 thermogravimetric analyzer. Measurements were performed at a heating rate of 10 °C/min in flowing, repurified N_2 and in room air. The polymer sample used was repreciptated from chloroform solution with methanol 3 times and then evacuated at 100−120 °C and ca. 5 Torr for 3−4 h to remove the solvent and any volatile (low molecular weight) constituents.
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(25) A similar conclusion is reached if the T_5 values are used (T_5 = 422 (N_2) and 230 (air), vs 476 (He) and 296 (air) for PDMSM (ref 23) and 386 (air) and 426 (He) for PDMS (ref 25). However, it must be noted that these values provide, at best, only a rough measure of polymer stability and are subject to substantial variation depending on the presence of low molecular weight fractions and the nature of the chain ends, as well as the particular conditions employed in the TGA measurements.
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(27) $[Si(CH_2CH_3)_2OSi(CH_2CH_3)_2CH_2]_n$: ^1H NMR: Si−C**H**$_2$−Si −0.23 ppm; Si−C**H**$_2CH_3$ 0.56 ppm; Si−CH$_2$C**H**$_3$ 0.92 ppm. ^{13}C NMR: Si−**C**H$_2$−Si −0.39 ppm; Si−C**H**$_2$CH$_3$ 6.82 ppm; Si−CH$_2$C**H**$_3$ 8.92 ppm; bp = 145−150 °C/6 mbar.
(28) After treatment with freshly distilled HOTf for 8 h at temperatures up to 200 °C the viscosity of the mixture remained low, and a ^1H NMR spectrum showed no changes relative to the starting monomer.
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