The overall effect is the emergence of a new strategy for the synthesis of macrolides wherein the carbonyl group of the lactone is inserted between the two termini of an acyclic precursor.

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Supplementary Material Available: Characterization data for **3**, **6**, **10**, (10-undecenyloxy)(phenylthio)acetonitrile, **13**, 2-cyano-2-(phenylthio)-1-oxacyclotetradec-4-ene, **14**, **15**, **17**, [(12-hydroxydodecyl)oxy](phenylthio)acetonitrile, and **19–22** (4 pages). Ordering information is given on any current masthead page.

Anionic Ring-Opening Polymerization of 1,2,3,4-Tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane

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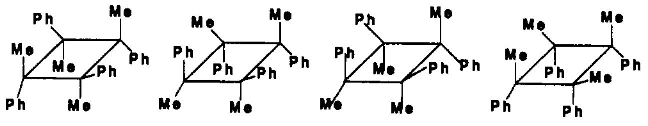
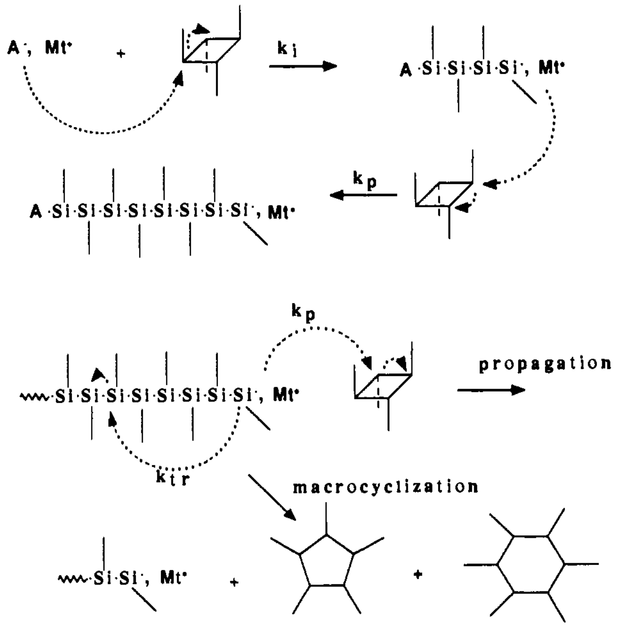
High molecular weight polysilanes are usually prepared by the reductive coupling of disubstituted dichlorosilanes with alkali metals.[1-3] The polymers formed in this process have high polydispersity and are polymodal. Potential applications of polysilanes in microelectronics and integrated optics require well-defined materials[1,2] and stimulate the search for new synthetic routes. The polymerization of masked disilenes,[4] a very promising method, is limited to silanes with two alkyl substituents. Dehydrogenative coupling[5,6] and electrochemical synthesis[7] provide only oligosilanes. We have recently reported the sonochemical synthesis of polysilanes with low polydispersities[8] and the synthesis of substituted polysilanes by polymer modification.[9] In this paper we describe the anionic polymerization of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane (**1**), the first successful ring-opening polymerization of a strained cyclopolysilane.

Cyclopolysilanes are formed during the reductive coupling process. However, these cycles usually cannot be successfully polymerized. For example, octaphenylcyclotetrasilane, a potentially strained ring, only isomerizes to decaphenylcyclopentasilane without formation of a linear polymer. We have previously described displacement of phenyl groups from oligosilanes without cleavage of the Si–Si linkage.[10] The resulting silyl triflates can be converted to various alkyl-, aryl-, and alkoxysilanes.[11] In a similar way, we removed four phenyl groups from octaphenylcyclotetrasilane with 4 equiv of triflic acid and replaced the triflate substituents by methyl groups using methylmagnesium bromide. The resulting 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane (**1**) is the first reported cyclotetrasilane with methyl and phenyl groups at each silicon atom, and the first strained cyclosilane that can be nearly quantitatively polymerized to a high molecular weight product. Triflic acid displaces only one phenyl group at each silicon atom before ring opening; the subsequent displacement, retarded by steric and electronic effects (two triflate groups at the same Si atom), is accompanied by the cleavage of Si–Si bonds. Yields of **1** are above 80%. Tentative assignments of the chemical shifts[12] in three isomers (I, II, III) indicate that they are formed in the approximate ratio 40:35:25 (MeMgBr, benzene/Et$_2$O solvent, ambient temperature). The signal of the all-cis isomer (IV, potentially the most strained) is weak and difficult to distinguish from minor impurities. These monomers have a high affinity toward oxygen and should be stored under inert gas and manipulated in a drybox or under vacuum.



I II III IV

The Si–Si bond is quite labile and can be cleaved by various nucleophilic and electrophilic reagents. A scrambling process (cleavage of Si–Si bonds by silyl anions), although not yet quantitatively studied, has been used as a synthetic tool in preparative organosilicon chemistry.[1] The ring strain of **1** is sufficient for the completion of polymerization before cyclization and back-biting processes become significant:



We used butyllithium and 1,4-dipotassiooctaphenyltetrasilane (**2**) as initiators of the polymerization.

Figure 1 shows the changes in the expanded methyl region in the ^{1}H NMR spectra during polymerization of **1** ($[M]_0 = 0.17$ mol/L) in benzene-d_6, with 1% (mol) of **2** as an initiator. This reaction occurs slowly at ambient temperature, and after 2 h, more than 80% of the monomer remains unreacted. However, after addition of 0.6% (vol) THF, polymerization was accelerated by a factor of 10. This result, typical for anionic polymerization, indicates either replacement of contact ion pairs by loose ion pairs

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(12) ^{1}H NMR chemical shifts of methyl groups in isomers of **1** have been assigned as follows: 0.71 (I), 0.75 (II), 0.73, 0.69, 0.68 ppm (III). ^{29}Si NMR: -25.9 (I), -27.2 (II), -24.8, -25.2, -25.4 ppm (III).

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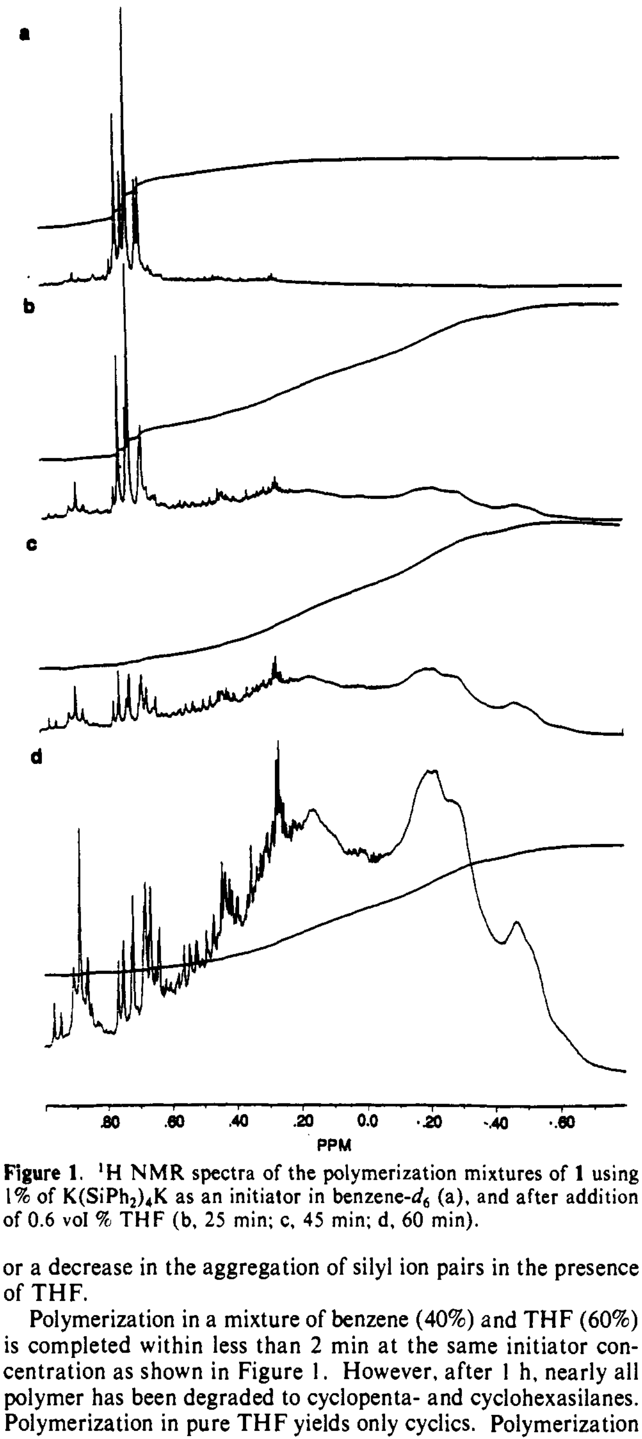

Figure 1. ^{1}H NMR spectra of the polymerization mixtures of **1** using 1% of $K(SiPh_2)_4K$ as an initiator in benzene-d_6 (a), and after addition of 0.6 vol % THF (b, 25 min; c, 45 min; d, 60 min).

or a decrease in the aggregation of silyl ion pairs in the presence of THF.

Polymerization in a mixture of benzene (40%) and THF (60%) is completed within less than 2 min at the same initiator concentration as shown in Figure 1. However, after 1 h, nearly all polymer has been degraded to cyclopenta- and cyclohexasilanes. Polymerization in pure THF yields only cyclics. Polymerization is completed within seconds in benzene in the presence of equimolar amounts of cryptands ([2.2.2] for silylpotassium and [2.1.1] for butyllithium); however, in contrast to THF, no depolymerization was observed within 24 h. Thus, the polarity and solvation power of a reaction mixture influences propagation, macrocyclization, and termination.

There are three important regions in the methyl group area of the ^{1}H NMR spectrum. The most deshielded region (>0.6 ppm) corresponds to four-membered rings. The relative reactivities of the isomers must be similar, since the peak intensities do not change during polymerization. The most shielded region (down to −0.6 ppm) corresponds to poly(methylphenylsilylene). Relative intensities of three broad peaks, assigned to iso-, hetero-, and syndiotactic structures,[13] remain similar during polymerization. The sharp signals in the intermediate region are due to cyclopenta- and cyclohexasilanes. At longer reaction times, the characteristic amber color of silyl anions disappears, due to an unidentified termination reaction.

A GPC analysis of polysilanes (based on polystyrene standards[14]) formed by anionic ring-opening polymerization indicates the formation of polymers with molecular weights up to M_{peak} = 100 000 ($M_w/M_n \approx 2$). The highest molecular weights were obtained in the presence of cryptands. Polymerization degrees up to $DP_n \approx 60$ ($M_n \approx 30\,000$) correspond to the $\Delta[M]/[AC^*]$ ratio; lower than expected molecular weights were obtained at higher ratios, probably due to transfer reactions.

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Supplementary Material Available: Experimental details for the synthesis of **1** and a typical polymerization procedure (1 page). Ordering information is given on any current masthead page.

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Stereoselective Aldol Reactions of Chlorotitanium Enolates. An Efficient Method for the Assemblage of Polypropionate-Related Synthons

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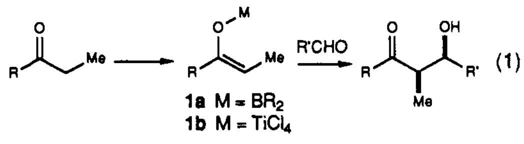
Over the last decade, the stereochemical attributes of the aldol reaction have been improved through the introduction of architecturally refined enolate metal centers.[1] The most efficient of these processes utilizes boron enolates (**1a**, eq 1), which provide a well-ordered transition state leading to predictably high levels of stereoselection. In continuing studies in this area, we have discovered that tetrachlorotitanium enolates (**1b**, eq 1), generated directly from the corresponding ketone or carboxylic acid derivative ($TiCl_4$, R_3N, CH_2Cl_2, −78 or 0 °C),[2,3] participate in highly selective aldol reactions.[4,5] The stereoselectivity in these reactions has been found to be comparable to that reported by us and others for the analogous boron-mediated processes.[6]



(1)

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(5) The studies relating to the characterization of these enolates will be reported at a later time.

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