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, 2cyano-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 welldefined 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 synthesis⁷ provide only oligosilanes. We have recently reported the sonochemical synthesis of polysilanes with low polydispersities⁸ 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 ringopening 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

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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 shifts¹² in three isomers (I, II, III) indicate that they are formed in the approximate ratio 40:35:25 (MeMgBr, benzene/Et₂O 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.

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 ¹H 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) &}lt;sup>1</sup>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). ²⁹Si NMR: -25.9 (I), -27.2 (II), -24.8, -25.2, -25.4 ppm (III).



Figure 1. ¹H 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 silvl 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 ¹H 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 cyclopentaand 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 standards¹⁴) formed by anionic ring-opening polymerization indicates the formation of polymers with molecular weights up to $M_{\text{peak}} =$ 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 (TiCl₄, 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



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