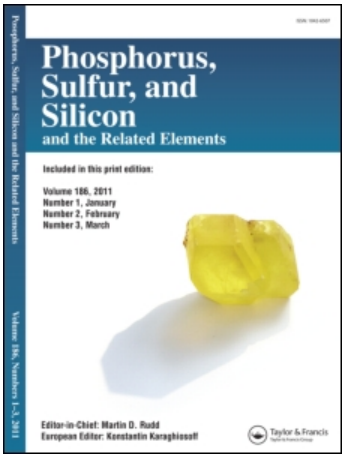

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Microstructure in the Ring Opening Polymerization of Cyclotetrasilanes

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MICROSTRUCTURE IN THE RING OPENING POLYMERIZATION OF CYCLOTETRASILANES

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Abstract Cyclotetrasilanes with methyl and phenyl substituents $Si_4Me_nPh_{8-n}$ (n=3,4,5,6) have been prepared by dearylation of octaphenylcyclotetrasilane and subsequent nucleophilic displacement with methylmagnesium bromide. All monomers are sufficiently strained to be polymerized to high molecular weight linear polysilanes. Ring Opening Polymerization, ROP, of cyclotetrasilanes proceeds with considerable stereoselectivity and regioselectivity. Silylcuprates lead to two inversions of configuration at both the attacked Si atom and at the newly developed active center. The assignment of ^{29}Si NMR signals for poly(methylphenylsilylene) to heterotactic (-38.5 ppm), syndiotactic (-39.0 ppm) and isotactic (-41.0 ppm) triads has been determined based on the polymerization of various mixtures of stereoisomers

INTRODUCTION

Some properties of polysilanes are affected by chain conformation. For example, absorption spectra of poly(dialkylsilylenes) change significantly on passing from all trans ($\lambda \approx 370$ nm) to random trans/gauche ($\lambda \approx 310$ nm) structures.[1,2] These changes can be induced by a variation in temperature, pressure, and sometimes by solvents and/or concentration.[3] All trans segments have high persistence ratios and behave like rigid rods affecting both the mechanical and solution properties of the polymers.[1,4] It has also been predicted that chain conformation and electronic/mechanical properties should depend on chain configuration (tacticity) for asymmetrically substituted polymers.[5,6] However, up to now, it is very difficult to control the tacticity of polysilanes. In an earlier report, the three signals in the ^{29}Si NMR spectrum of poly(methylphenylsilylene) were assigned to three different triads.[7] It was demonstrated that neither the temperature of the reductive coupling process nor the synthetic procedure (thermal reductive coupling with sodium, sonochemical reductive coupling, decomposition of silylmercuric intermediates) significantly affected the microstructure of the final polymers.[7] Thus, it seems that the stereochemistry of propagation is solely governed by the steric and electronic effects of

the substituents during the chain growth, disabling any manipulation of the microstructure and chain conformation.

One possibility for microstructural control is based on the ring opening polymerization (ROP) of selected stereoisomers of cyclic compounds, in which some stereocenters have fixed configurations.[8] Of course, the stereochemistry of the ring opening process (retention/inversion) affects the configuration at the broken and newly formed bonds. Nevertheless, at least some stereocenters can be controlled in the ROP process. The main, and most basic requirement for the ROP process is the thermodynamic and kinetic polymerizability of the cyclic monomers. In this paper, ROP polymerization of some cyclosilanes will be reviewed and the stereochemistry of ROP under various conditions discussed.

Polymerizability of Cyclosilanes

Ring opening polymerization, as with most chain growth processes, is accompanied by a significant loss of entropy, because each monomer molecule loses three degrees of translational freedom. In order to compensate the unfavorable change in entropy, ROP must be accompanied by a release of the ring strain. Therefore, nearly all ROPs are strongly exothermic and only strained three, four and some five, six, seven and larger rings can be polymerized. Because polymerization can occur only when the overall free energy is reduced, a successfull ROP occurs below a certain temperature called the ceiling temperature.

$$T_c = \frac{\Delta H_p^o}{\Delta S_p^o + R\ln[M]_e}$$

This is especially important for weakly strained rings. For example, the recently reported polymerization of nonamethylphenylcyclopentasilane has been successful only at very low temperatures (T≈-70 °C).[9] There are a few exceptions to this rule; in systems with a significant reduction in rotational and vibrational entropy, such as in polymerization of eight membered sulfur and selenium compounds, the overall entropy is increased during ROP and no ring strain is released. In such cases, instead of a ceiling temperature, a floor temperature exists, and elemental sulfur can only be polymerized above T_f≈160 °C.

The effect of temperature should be clearly separated into thermodynamic and kinetic effects. In addition to the previously discussed thermodynamic factors,

polymerization should occur with a sufficient rate, which may require elevated temperatures. Of course, the polymerization rate may be significantly influenced by the catalysts and initiators, as will be discussed later.

Thermodynamic polymerizability depends not only on the ring size, but also on the structure of substituents. Generally, larger substituents stabilize smaller rings because the repulsive interactions between bulky substituents are better tolerated in the monomer than in the polymer chain. Thus, some monomers with bulky substituents (not only rings, but also unsaturated compounds) can not be polymerized. For example, ceiling temperature for polymerization of styrene is above 300 ^{o}C, that for α-methylstyrene ≈70 ^{o}C but that for 1,1-diphenylethylene <-100^{o}C and the latter monomer can not be homopolymerized but only copolymerized with other monomers.

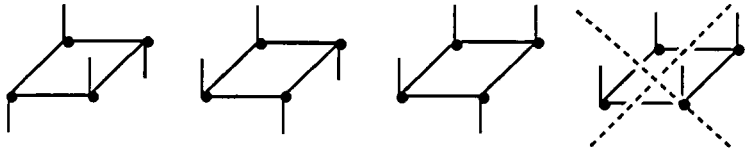
The concept of bulky substituents has been very successfully employed in the preparation of very reactive silanes such as disilenes and cyclotrisilanes. Compounds with very bulky tert-butyl and/or mesityl groups are very stable whereas the analogous species with smaller substituents can only be isolated in argon matrices at very low temperatures (<<-100 ^{o}C).[10,11] Cyclotrisilane, with six mesityl groups is very stable and can not be polymerized. The same is true for cyclotetrasilanes with eight n-hexyl and/or eight phenyl groups. Decreasing the substituent's size to either mixed hexyl/methyl or methyl/phenyl makes the four membered ring sufficiently strained, and the five membered ring is non-polymerizable. Five membered rings with exclusively methyl substituents are strained, and the permethylated six membered ring becomes non-polymerizable.[9,12] Thus, most cyclosilanes available directly from the reductive coupling process, such as $(SiMe_2)_6$, $(SiMePh)_5$, $(SiHex_2)_4$, $(SiPh_2)_4$, $(SiMes_2)_3$ can not be polymerized due to enthalpic factors. In fact, the severe conditions of the reductive coupling of dichlorosilanes with alkali metals usually lead to the equilibration of Si-Si bonds and the formation of strainless rings. Si-Si bonds are especially labile in the presence of excess alkali metals in polar solvents. In non polar solvents Si-Si bonds are more stable, and sometimes strained polymerizable rings can be formed, especially under high dilution when an end-biting process may result in the formation of smaller strained rings.

Monomer Synthesis

The overall enthalpy of polymerization depends on the ring size and bulkiness of substituents. Therefore, we have considered the replacement of bulky substitents by smaller ones in the four-membered rings. This preserves the angular strain, but reduces

the repulsive interactions between bulky substituents. The displacement process should be selective without cleavage of Si-Si bonds. Two candidates have been considered: a three-membered ring with mesityl substituents and a four-membered ring with phenyl substituents. The synthetic process was based on dearylation with strong protonic acids (protodesilylation) and subsequent nucleophilic substitution with organolithium and Grignard reagents. Triflic acid is a very efficent dearylating reagent, especially for polysubstituted silanes.[13] Reaction of triflic acid with octaphenylcyclotetrasilane leads to the clean displacement of four phenyl groups, one at each Si atom in the ring without any ring cleavage.[14] An attempt to remove a fifth phenyl group was unsuccessful and was accompanied by ring opening. On the other hand, hexamesitylcyclotrisilane reacted with triflic acid slowly, but ring opening and some rearrangement processes were observed. Thus, the latter precursor was not successful for the substituent exchange.

We have previously reported detailed studies on the dearylation of octaphenylcyclotetrasilane with triflic acid and the stereo- and regiochemistry of this process.[14] A mixture of three stereoisomers of 1,2,3,4-tetramethyl-1,2,3,4-tetrakis(triflate) cyclotetrasilane was formed, the most hindered all cis isomer was not observed. After treatment of the tetrakis(triflate) derivatives with methylmagnesium bromide in benzene three strained and polymerizable isomers were detected. As in the previous case, the all cis isomer was not observed. Recently,[15] we have assigned ^{1}H and ^{29}Si NMR signals to the isomers of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane with ttt, ttc and tct structures:



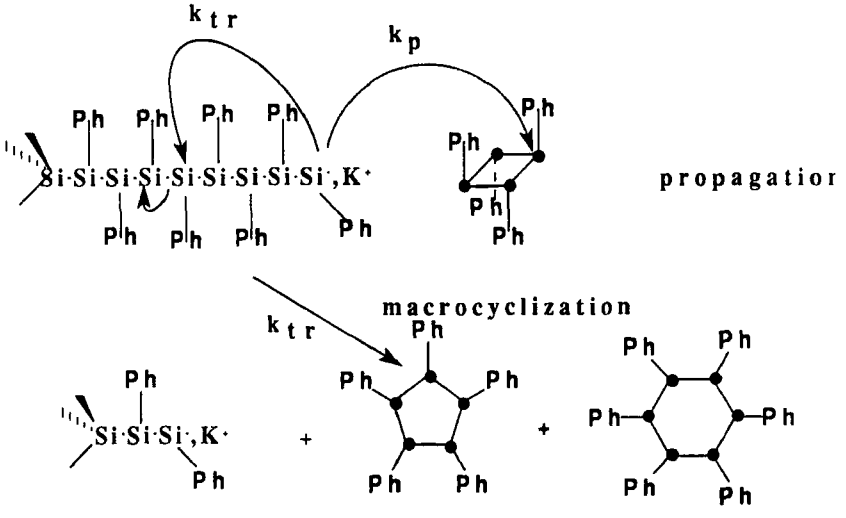
ttt tct ttc ccc

The all trans isomer is sterically least strained and is formed in the largest amount. It can be obtained at ≈95% purity by recrystallization from cold hexane. This compound can be used for the synthesis of poly(methylphenylsilylene) with a microstructure different from the polymers prepared by the reductive coupling process.

RING OPENING POLYMERIZATION OF CYCLOSILANES

The ring opening process requires the cleavage of bonds in the strained rings and formation of linear chains. Si-Si bonds can be cleaved by variety of reagents but at ambient temperatures the most efficient and most selective are nucleophilic species.[16,17] Electrophiles cleave not only Si-Si but also Si-C bonds.[18] Photochemical cleavage of Si-Si bonds is accompanied by extrusion of silylenes and formation of rather unselective silyl radicals.[19] Transition metals can be also considered as potential catalysts for ROP because they are known to metathesize Si-Si bonds,[20,21,22] although they are quite sensitive to steric effects.[23]

The anionic ring opening process of cyclotetrasilanes is represented schematically below:



The ring opening process, favored by enthalpy (ring strain), leads to an increase of molecular weight. However, entropy favors unimolecular Si-Si bond cleavage, resulting in chain degradation to strainless cycles. Depending on the the solvent, temperature, and initiating system either linear polymers or cyclics can be obtained.[8,24] Polymerization initiated by n-BuLi in the highly polar THF is very rapid (<1 min), but is followed by polymer degradation to strainless five and six membered rings. In the absence of THF, n-BuLi is not active enough to polymerize four membered rings with methyl/phenyl substituents. However, polymerization in the presence of a controlled amount (1 mol%)

of THF, crown ethers, or cryptands leads to relatively rapid polymerization (<1 h) and degradation starts only after 3 h.

Figure 1 presents ^{29}Si NMR spectra of poly(methylphenylsilylene) produced by the reductive coupling process and by anionic ring opening polymerization of the all trans isomer.

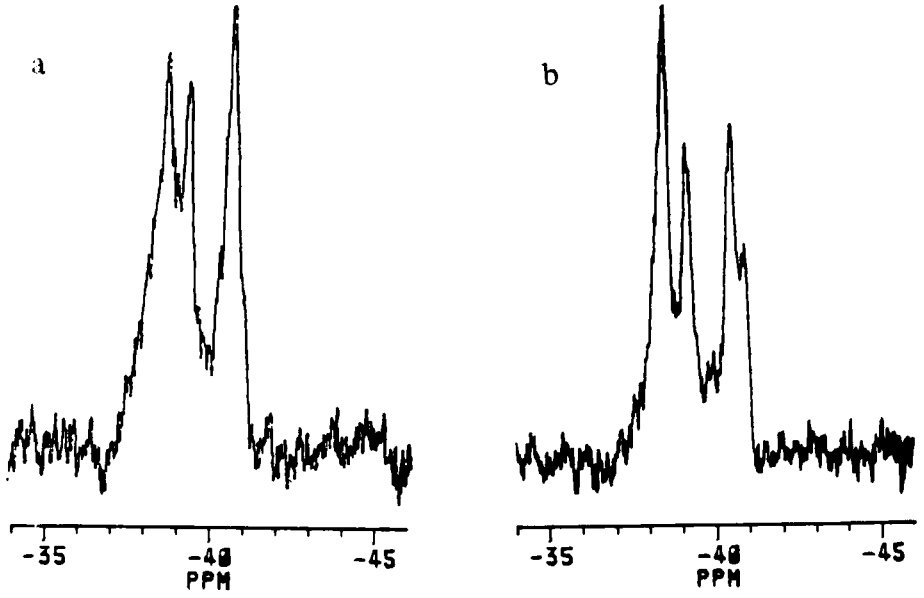


FIGURE 1. ^{29}Si NMR spectra of PMPS (in C_6D_6) prepared by a) the reductive coupling of $PhMeSiCl_2$ and b) ROP of the all-trans isomer of $Me_4Ph_4Si_4$ in C_6H_6 initiated with n-BuLi/[2.1.1] cryptand.

In the latter case, initiated by $[n\text{-BuLi}]_o$=0.01 mol/L / $[\text{cryptand } 2.1.1]_o$=0.01 mol/L. differences in the intensities of the three peaks, previously assigned to isotactic (-39.0 ppm), syndiotactic (-38.5 ppm), and heterotactic (-41.0 ppm) triads,[7] can be seen. Nevertheless, the stereochemical control is very poor, indicating a large degree of racemization.

In order to improve the stereoselectivity of ROP several initiating systems were tested and it was determined that silyl cuprates[25] provide the best results. Fig. 2 depicts the ^{29}Si NMR spectra of the stereorandom polymer prepared by the reductive coupling together with those formed by the silylcuprate initiated polymerization of the mixture of stereoisomers and of the all trans four-membered ring.

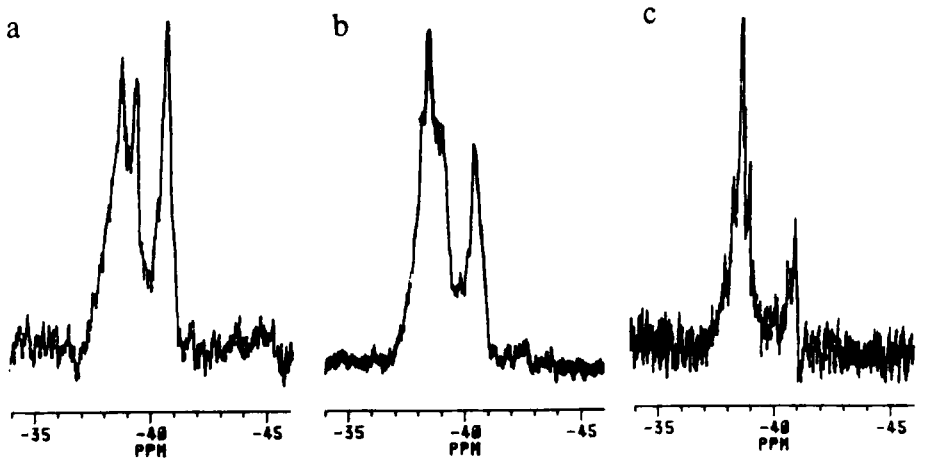
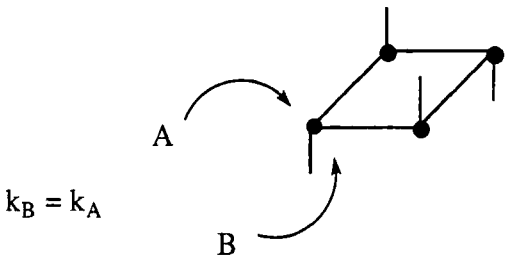
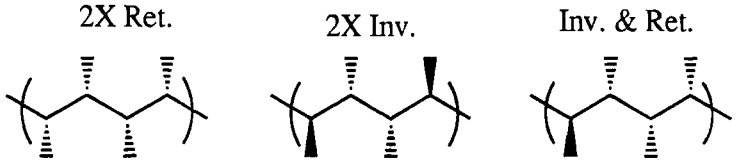


FIGURE 2 ^{29}Si NMR spectra of PMPS (in C_6D_6) prepared by a) the reductive coupling of $PhMeSiCl_2$, the silyl cuprate initiated (THF solution) polymerizations of b) a mixture of stereoisomers of $Me_4Ph_4Si_4$ and c) the all-t rans isomer of $Me_4Ph_4Si_4$.

In the latter case a dramatically different spectrum indicates a large degree of stereocontrol in the ROP. Two peaks at -38.5 ppm and -41.0 ppm are present in a 3:1 ratio.

Scheme II





$[(rrr)r/m]_n$ $[(mrm)m/r]_n$ [(mrr)m/r]n

	2 X RET	2 X INV	INV & RET.
% syndio (rr)	75	-	37.5
% iso (mm)	-	25	12.5
% atact (mr=rm)	25	75	50

The ring opening process of the all trans ring may occur in three different modes: with two retentions of configuration, with two inversions of configuration and with one retention and one inversion of configuration. Additional possibilities may involve retention/racemization, inversion/racemization, etc., but they will not be analyzed in detail here.

Scheme II shows the predicted proportion of syndiotactic, isotactic, and heterotactic triads formed with different stereochemistries, assuming that both prochiral faces of the ring are attacked with equal probabilities. Results presented in Fig. 2c (3:1 ratio) fit the mechanism with either two retentions or two inversions. Nevertheless, the assignment of signals previously reported[7] does not fit either option.

In order to solve the discrepancy between the inversion or retention processes, a mixture of stereoisomers (28% of 1a, 14% of 1b, 58% of 1c) was polymerized using a silyl cuprate (Fig. 2b). The analysis of the content of syndiotactic, isotactic and heterotactic triads for two different stereomechanisms is shown in Table 1. The abundancies of triads were calculated assuming similar reactivities of all Si-Si bonds and similar probabilities of attacking all prochiral faces.

TABLE 1 Expected Tacticities for cuprate polymerization of a mixture of isomers (28% ttt, 14% tct, 58% tcc)

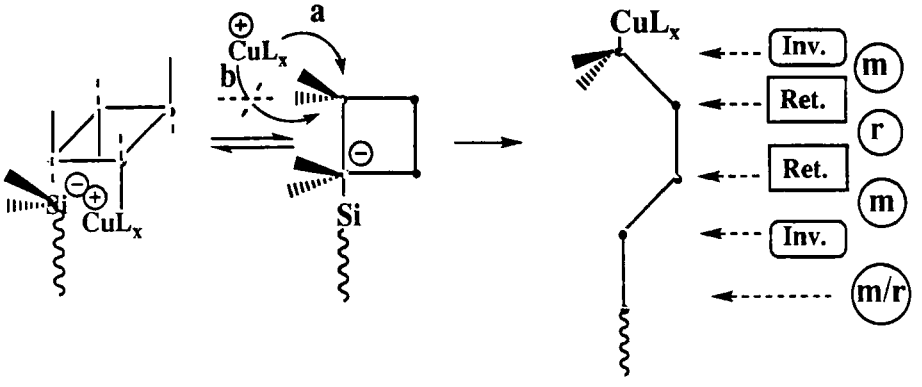
Route	% syndio.	% hetero.	% iso.
2 X RET	37.25	46.5	16.25
2 X INV	19.75	53.5	26.75
OBSERVED	15.0	58.0	27.0

The experimentally observed and calculated signal intensities are best fit by the mechanism with two inversions of configuration. This also means that the low field signal, dominating in Fig. 2c, belongs to the heterotactic triad and the high field signal to the isotactic triad. The center signal is assigned to the syndiotactic triad.

Two inversions of configuration at both attacked Si atom and at the newly developed active center are explained in Scheme III. The propagation may involve the slowly formed pentacoordinated intermediate followed by the rapid ring opening. The slow formation of the intermediate is required to explain the observed first order kinetics

in monomer. Pentacoordinated intermediates have two long apical and three short equatorial bonds.

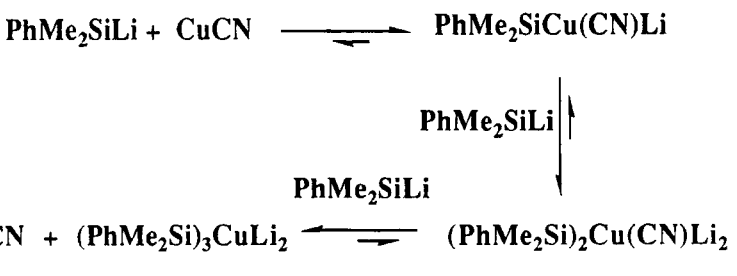
Scheme III



Only the weak apical bonds can be cleaved. The bulky substituents are preferentially located in the apical position. Strained rings, such as cyclotetrasilanes can not be located in two equatorial positions and one of the bonds must be present in the apical position. Taking all of the available information on the pseudoration process into account[26,27] leads to the conclusion that the bulky polymer chain and one of the bonds from the monomer must be in apical positions. This results in an inversion of the configuration at the attacked Si atom during nucleophilic ROP. The inversion at the second Si atom, which becomes a new growing center, can be due to the bulky nature of the silylcuprate species.

Higher order silyl cuprates have two silicon atoms attached to Cu:

Scheme IV



In addition, organocuprates and silyl cuprates tend to aggregate. It is possible that aggregation may lead to the observed stereochemistry at the second Si atom.

Analysis of the ^{29}Si NMR signal intensities for the polymer prepared from the all trans monomer, but with cryptated Li counterion, indicates that ROP proceeds with one inversion and one racemization process. This result is in a good agreement with Scheme 3. The attack occurs with inversion of configuration, but the smaller Li cation may attack both sides of newly developed anionic species. An alternative explanation takes into account fast racemization of the silyl anion which is not bound strongly to the counterion (cryptated Li). Racemization in the less reactive, and more tighly bound silyl cuprates must be much slower and does not proceed before the next propagation step.

In the polymer prepared by the reductive coupling the isotactic triads dominate over syndiotactic and heterotactic triads. As shown in Figure 3, for the zig-zag projection, the steric repulsions between substituents in the isotactic polymer are much lower than in the syndiotactic one. This may help to explain the observed signal intensities.

Poly(phenylmethylsilylene)

Isotactic Syndiotactic

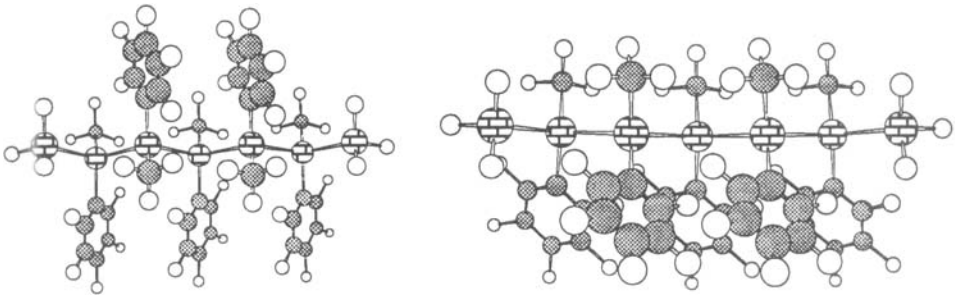
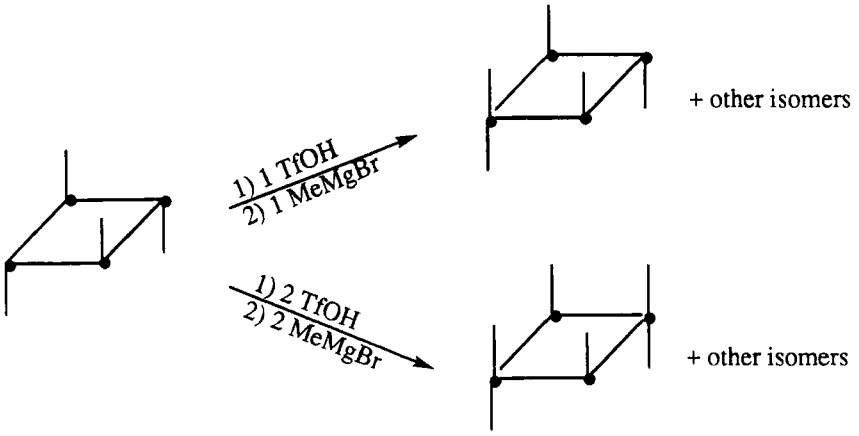


FIGURE 3. Schematic representations of isotactic and syndiotactic segments of PMPS viewed looking down on the backbone existing in the planar zig-zag conformation.

Regiochemistry of Cyclotetrasilanes with Methyl and Phenyl Substituents.

Dearylation of octaphenylcyclotetrasilane with triflic acid can be chemoselective only up to the four acid equivalents. Therefore, the synthesis of pentamethyl and hexamethyl derivatived requires a two-step process. In the first step 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane is prepared and then only treated with either one or two equivalents of triflic acid followed by the reaction with the Grignard reagents as shown in Scheme V.

Scheme V.



The polymerization of cyclotetrasilanes with three (III), four (IV), five (V) and six (VI) methyl groups was initiated by silyl cuprates. The ^{29}Si NMR spectra of the resulting polymers are shown in Fig. 4. The low field signal in poly III can be ascribed to $SiPh_2$ units. It can be noted that no isotactic triads for SiPhMe units at -41.0 ppm is observed. This indicates regioselective opening of the ring and the absence of long SiPhMe segments. The same is true for poly VI. However, in poly V, high field signals at - 41.0 ppm suggest some contribution of isotactic triads and lower regioselectivity.

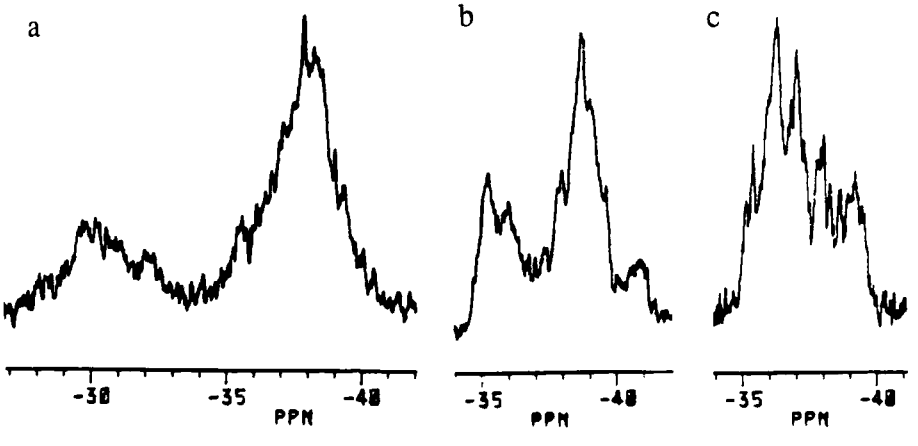


FIGURE 4 ^{29}Si NMR spectra (in C_6D_6) of a) poly III, b) poly V, and c) poly VI prepared by the silyl cuprate polymerizations of $Me_3Ph_5Si_4$, $Me_5Ph_3Si_4$, and $Me_6Ph_2Si_4$, respectively, in THF solution.

Molecular weights, polydispersities and optical properties of the polysilanes are presented in Table 2. Absorption and emission maxima shift to lower energies with an increased content of phenyl substituents.

TABLE 2. Molecular weight, absorbance, and emission data for polymers prepared by the silyl cuprate polymerization of $Me_3Ph_5Si_4$, $Me_4Ph_4Si_4$, $Me_5Ph_3Si_4$, and $Me_6Ph_2Si_4$.

Polymer	$\overline{M_n}$	$\overline{M_w}/\overline{M_n}$	Absorbance λ_{max} (nm)	Emission λ_{max} (nm)
$Me_3Ph_5Si_4$ III	25,000	1.5	353	376
$Me_4Ph_4Si_4$ IV	36,000	1.6	338	365
$Me_5Ph_2Si_4$ V	10,500	2.0	332	360
$Me_6Ph_2Si_4$ VI	12,000	1.6	328	355

Conclusions.

Cyclotetrasilanes with methyl and phenyl substituents $Si_4Me_nPh_{8-n}$ (n=3,4,5,6) have been prepared by the dearylation of octaphenylcyclotetrasilane and the subsequent nucleophilic displacement with methylmagnesium bromides. All monomers are sufficiently strained to be polymerized to high molecular weight linear polysilanes. ROP of cyclotetrasilanes proceeds with considerable stereoselectivity and regioselectivity. Silylcuprates lead to two inversions of configuration at both attacked Si atom and at the newly developed active center.

References.

1. R.D. Miller; B. L. Farmer; W.W. Fleming; R. Sooriyakumaran; J. F. Rabolt *J. Am. Chem. Soc.* 109, 2509 (1987).
2. F.C. Schilling; A. J. Lovinger; D.D Davis; F.A. Bovey; J.M. Zeigler *Macromolecules* 22, 3055 (1989).
3. J. Michl; R.D. Miller *Chem. Rev.* 6, 1359 (1989).
4. W. E. Rochefort; G.W. Heffner; D.S. Pearson; R.D. Miller; P.M. Cotts *Macromolecules* 24, 4861 (1991).
5. P.R. Sundararajan *Macromolecules* 21, 1256 (1988).
6. W.J. Welsh; J.R. Damewood Jr.; R.C. West *Macromolecules* 22, 2947 (1989).
7. J. Maxka; F.K. Mitter; D.R. Powell; R. West *Organometallics* 10, 660 (1991).
8. K. Matyjaszewski *Makromol. Chem. Macromol. Symp.* 42/43, 269 (1991).

9. M. Suzuki; J. Kotani; S. Gyobu; T. Kaneko; T. Saegusa *Macromolecules* 27, 2360 (1994).
10. T. Tsumuraya; S.A. Batcheller; S. Masamune *Angew. Chem. Int. Ed. Eng.* 30, 902 (1991).
11. G. Raabe; J. Michl *Chem. Rev.* 85, 419 (1985).
12. L. F. Brough; R. West *J. Organomet. Chem.* 194, 139 (1980).
13. Y.L. Chen; K. Matyjaszewski *J. Organomet. Chem.* 340, 7 (1988).
14. J. Chrusciel; M. Cypryk; E. Fossum; K. Matyjaszewski *Organometallics* 11, 3257 (1992).
15. E. Fossum; S. W. Gordon-Wylie; K. Matyjaszewski *Organometallics* 13, 1695 (1994).
16. M. Ishikawa; M. Kumada Chem. Commun. 612 (1970).
17. H. Sakurai; I. Imoto; N. Hayashi; M. Kumada *J. Am. Chem. Soc.* 87, 4001 (1965).
18. C. Eaborn *J. Organomet. Chem.* 100, 43 (1975).
19. J. Michl; J.W. Downing; T. Karatsu; A.J. McKinely; G. Poggi; G.M. Wallraff; R. Sooriyakumaran; R.D. Miller *Pure Appl. Chem.* 60, 959 (1988).
20. K. Tamao; T. Hayashi; M. Kumada *J. Organomet. Chem.* 114, C19 (1976).
21. N. P. Reddy; H. Yamashita; M. Tanaka *J. Am. Chem. Soc.* 114, 6596 (1992).
22. J. Chrusciel; M. Cypryk; E. Fossum; K. Matyjaszewski *Makromol. Chem. Macromol Symp.* 73, 167 (1993).
23. T.D Tilley *Acc. Chem. Res.* 26, 22 (1993).
24. M. Cypryk, Y. Gupta; K. Matyjaszewski *J. Am. Chem. Soc.* 113, 1046 (1991).
25. S. Sharma; C. Oehlschlager *Tetrahedron* 45, 557 (1989).
26. R.P. Holmes *Chem. Rev.* 90, 17 (1990).
27. R.J.P Corriu; J.C. Young in The Silicon Heteroatom Bond S. Patai and Z. Rappoport Eds. Wiley (New York) 1 (1991).