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REGIOCHEMISTRY OF POLYSILANES PREPARED BY RING OPENING POLYMERIZATION

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13. ABSTRACT *(Maximum 200 words)*

A series of cyclotetrasilanes bearing varying numbers of methyl and phenyl substituents $Me_nPh_{8-n}Si_4$, have been prepared and characterized using ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. The cyclotetrasilanes were polymerized employing silyl cuprates as initiators resulting in monomodal polysilanes with interesting regiochemistries. The regiochemistry of the polymerizations was studied by ^{29}Si NMR spectra of the polymers. The polymers resulting from ring opening polymerization of $Me_3Ph_5Si_4$, $Me_5Ph_3Si_4$, and $Me_6Ph_2Si_4$ showed absorbance maxima, $\lambda_{max} = 343$, 332, and 328 nm, respectively.

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Regiochemistry of Polysilanes Prepared by Ring Opening Polymerization

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Introduction.

Polysilanes (polysilylenes) are an interesting class of polymers consisting of a linear backbone of silicon atoms with aryl or alkyl substituents.[1,2] The interest in these materials stems from there unusual properties such as sigma-catenation and thermochromism. They have potential applications as photoresists, electro-optical devices, non-linear optical materials, and also as precursors to silicon carbide.[1,2] Polysilanes have been prepared by several methods including: 1) the reductive coupling of dichlorosilanes,[1,2,3] 2) dehydrogenative coupling of hydridosilanes,[4] 3) anionic polymerization of masked diselenes,[5] and 4) ring opening polymerization of cyclotetrasilanes.[6,7] Only the last two routes provide access to polysilanes with controlled microstructures and regiochemistry.

Results and Discussion.

Recent reports have described the synthesis of stereoregular poly(methylphenylsilylene).[7] It is also of interest to study the effects of regiochemistry on polymer properties such as the absorbance and emission spectra. In ring opening polymerization of cyclotetrasilanes, the regio- and stereochemistry of the resultant polymer can be built into the system by synthesizing monomers with known configurations of substituents. A series of cyclotetrasilanes with varying numbers of methyl and phenyl substituents, $Me_nPh_{8-n}Si_4$, have been prepared and polymerized utilizing silyl cuprates as initiators.

Monomer Characterization.

The synthesis of $Me_3Ph_5Si_4$ results in the formation of several isomers which are shown in Figure 1. The isomer possessing an all-trans configuration of the methyl groups is predicted to be the sterically least hindered and therefore present in the highest percentage. If the mixture of isomers is allowed to stand in cold hexane for several days, the predominant isomer crystallizes out and the ^1H NMR spectrum displays two peaks in the methyl region in a 2:1 ratio indicating the all-trans structure. The ^{29}Si and ^{13}C NMR spectra show similar patterns. The all-cis structure (also 2:1 pattern) is sterically more hindered and less probable to form.

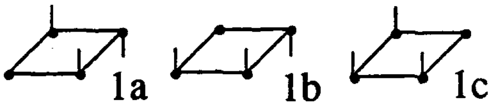


Figure 1. Possible isomers from the synthesis of 1 (phenyl groups are not shown).

Preparation of $Me_5Ph_3Si_4$ starting from only one isomer of $Me_4Ph_4Si_4$ (all-trans) results in the formation of only one stereoisomer which is shown in Figure 2. The reaction mixture also contains 5% $Me_4Ph_4Si_4$ and 5% $Me_6Ph_2Si_4$ which is due to limited chemoselectivity of *triflation.*[9] *The* ^{29}Si *NMR spectrum is shown in Figure 2.* The expected pattern of peaks, 1:2:1, indicates the selective formation of only one isomer.

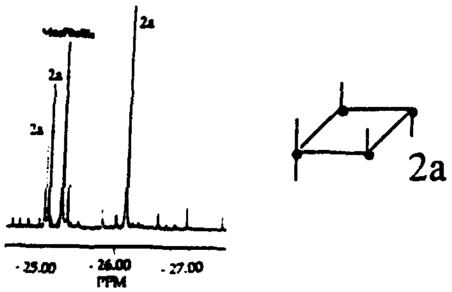


Figure 2. Single stereoisomer resulting from the synthesis of 2. ^{29}Si DEPT NMR spectrum of the product.

Preparation of $Me_6Ph_2Si_4$ *from a mixture of isomers of* $Me_4Ph_4Si_4$, gives rise to a mixture of both geometrical and stereoisomers possessing either a 1,3 or 1,2 arrangement of the Me_2Si units. The possible isomers are shown in Figure 3 along with the ^{13}C spectrum. The ^{13}C NMR spectrum displays six peaks in the methyl region which result from the various methyl groups present in the isomers. Because there are only six major peaks present the reaction appears to proceed preferentially by either the 1,2 or 1,3 arrangement of the triflate groups. The intuitive conclusion would be the sterically least hindered 1,3 arrangement, but differentiating between the two is very difficult.

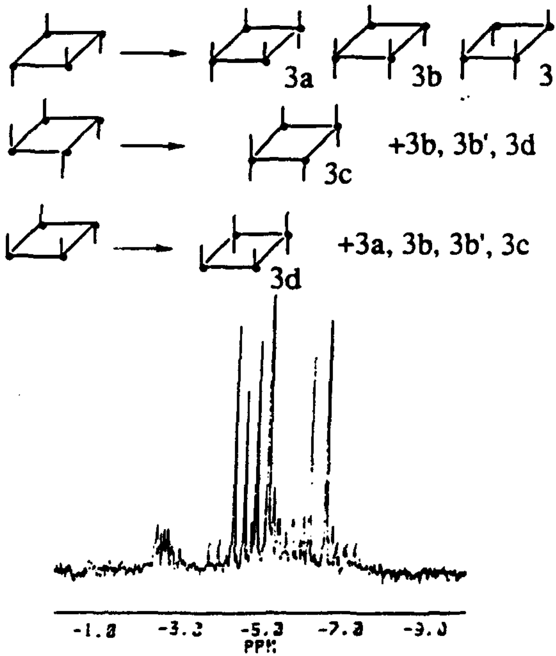


Figure 3. Possible isomers resulting from the synthesis of 3 starting from a mixture of isomers of $Me_4Ph_4Si_4$. ^{13}C NMR spectrum of the products.

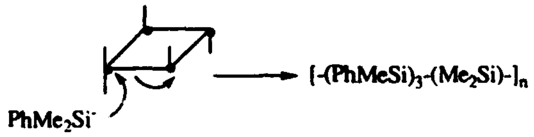
Ring Opening Polymerization.

$Me_5Ph_3Si_4$ In the ring opening polymerization of the all-trans isomer of $Me_4Ph_4Si_4$, there are two peaks present in the ^{29}Si NMR spectrum at -38.5 and -41.0 ppm in the ratio 3:1 corresponding to syndiotactic and heterotactic polymer, respectively. The heterotactic triads result from random junctions between monomer units.

The ^{29}Si NMR spectrum of the polymer obtained from ring opening polymerization of 2 is presented in Figure 4. The peak at -41.0 ppm, corresponding to heterotactic polymer, accounts for only ≈ 10% of the PhMeSi units.

This indicates that ring opening of this monomer is not a random process with regards to regiochemistry. Thus, preferential ring opening of this monomer should occur via the pathway shown in Scheme II. Attack of the initiator and growing chain is expected to occur at the sterically least hindered Me_2Si unit and give rise to the more stable PhMeSi anion.

Scheme I



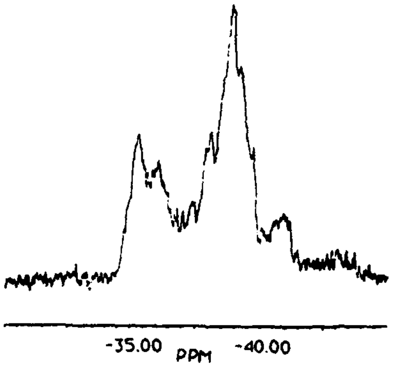


Figure 4. ^{29}Si DEPT NMR spectrum of the polymer obtained from ring opening polymerization of $Me_5Ph_3Si_4$.

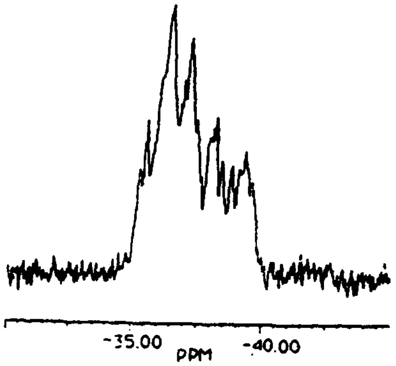


Figure 5. ^{29}Si DEPT NMR spectrum of the polymer obtained from ring opening polymerization of $Me_6Ph_2Si_4$.

$Me_6Ph_2Si_4$ In the 29Si NMR spectrum of the polymer obtained from polymerization of 3 there is no peak present at -41.0 ppm. This confirms its assignment and indicates some additional control over regiochemistry is possible with this monomer. However, a more detailed analysis requires the acquisition of these spectra without using polarization transfer.

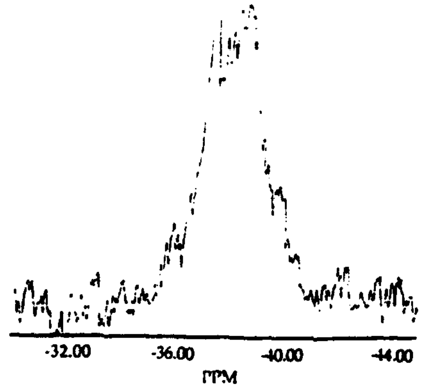
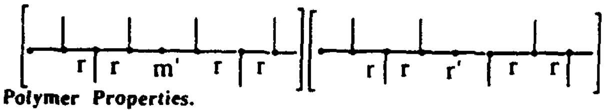


Figure 6. ^{29}Si DEPT NMR spectrum of the polymer obtained upon ring opening of $Me_3Ph_5Si_4$.

$Me_3Ph_5Si_4$ The ^{29}Si NMR spectrum of the polymer prepared by polymerization of **1** is shown in Figure 6. In this DEPT acquired spectrum the most visible peaks are from the PhMeSi units. The absence of the heterotactic peak at -41.0 ppm indicates better control. The sharp, downfield signal may be assigned to the central PhMeSi unit in the syndiotactic triads(rr) which are separated by Ph_2Si units. Because these triads can be coupled in equal probabilities, m' and r' (Scheme II), the signals of the PhMeSi units adjacent to Ph2Si units can absorb at slightly different chemical shifts.



Polymer Properties.

Table 1 gives the relevant molecular weight data and also the absorption maxima for the above polymers. The λ_{max} of the materials shows the expected dependence on the percentage of aromatic groups present in the polymer, as would be expected. No thermal transitions were detected for the materials by differential scanning calorimetry indicating a very low degree of crystallinity.

Table 1. Absorbance data for Polymers 1-3.

Polymer	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$	λmax
2	10,500	2.0	332
3	12,000	1.6	328
1	19,000	2.0	343

Conclusions.

A series of cyclotetrasilanes with varying numbers of methyl and phenyl substituents have been prepared and polymerized using silyl cuprates. The polymerizations of $Me_3Ph_5Si_4$, $Me_5Ph_3Si_4$, and $Me_6Ph_2Si_4$ appear to occur with some regioselectively. The polymers have been analyzed using ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, along with UV spectroscopy. Further work to determine the stereochemistry and a more detailed picture of the regiochemistry of the polymers is in progress.

Experimental. All experiments were performed in a VAC HE dry box under a nitrogen atmosphere with less than 1 ppm of moisture and oxygen. Octaphenylcyclotetrasilane was prepared as reported in the literature.[8] 1,2,3,4-Tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane was prepared by previously reported methods. 1,2,3-Trimethylpentaphenyl cyclotetrasilane was prepared by treating octaphenyl cyclotetrasilane with three equivalents of trifluoromethanesulfonic acid followed by methylation with methylmagnesium bromide. 1,1,2,3,4-Pentamethyl-2,3,4-triphenylcyclotetrasilane, 1,1,2,2-3,4-hexamethyl-3,4-diphenylcyclotetrasilane, and 1,1,2,3,3,4-hexamethyl-3,4-diphenyl-cyclotratsilane were prepared by treating 1,2,3,4-tetramethyl-1,2,3,4-tetraphenyl-cyclotetrasilane with the respective equivalents of triflic acid, followed by methylation. The monomers were polymerized using the silyl cuprate $(PhMe_2Si)_2Cu(CN)Li_2$ in THF.

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