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Stereostructures of Linear and Cyclic Polyphenylsilanes Produced by Dehydrocoupling in the Presence of Group 4 Metallocene Catalysts

Vladimir K. Dioumaev,† Kamyar Rahimian,‡ François Gauvin,§ and John F. Harrod*

Chemistry Department, McGill University, Montreal, Québec, Canada H3A 2K6

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Phenylsilane was polymerized with a number of group 4 metallocene precatalysts, including (*S,S*)-[1,2-bis(η^5-tetrahydroindenyl)ethane]titanium binaphtholate (**1**)/2BuLi, Cp_2HfCl_2 (**2**)/2BuLi/$B(C_6F_5)_3$, and CpCp*$ZrCl_2$ (**3**)/2BuLi/$B(C_6F_5)_3$. With **1**, polymerization proceeds extremely slowly and it is possible to observe the stepwise oligomerization to Si_2, Si_3, Si_4, and Si_5 species. One- and two-dimensional ^1H and ^{29}Si NMR experiments permit the assignment of peaks to the stereoisomers of the Si_4 and Si_5 compounds. For the linear oligomers $PhSiH_2SiHPh(SiHPh)_nSiHPhSiH_2Ph$ ($n \geq 0$), the ^{29}Si NMR resonances group cleanly into the regions δ (ppm) 58−59 ($Ph\mathit{Si}H_2$), 59−63 ($SiHPh\mathit{Si}HPhSiHPh$), and 64−65 ($PhSiH_2\mathit{Si}HPhSiHPh$). The chiral catalyst **1** has little influence on the sterochemical outcome of the coupling reaction. Higher molecular weight polymers synthesized with **2** and **3** or obtained by fractionation of lower molecular weight polymers all have nearly identical ^{29}Si NMR spectra. It is proposed that this spectrum is a reflection of the pentad composition of the polymers and that any deviations from randomness are a result of intrachain interactions at the growing chain end and are unrelated to the structure of the catalyst.

Introduction

Polysilanes of the type $-[SiRR']_n-$ have a stereochemistry analogous to that of vinyl polymers, with the important difference being that every backbone atom is stereogenic, rather than the alternating stereogenic and nonstereogenic centers found in most vinyl polymers.[1] A number of problems enhance the difficulty of deducing the microstructure of polysilanes, including the much longer relaxation times of Si vs C, broader line widths, and insufficient dispersion of resonances. A number of attempts to produce polysilanes stereoselectively have appeared, but the subject is still far from the level of sophistication achieved with C-backbone polymers.

Wolff et al. tentatively assigned the microstructure of poly(methylphenylsilane) and some unsymmetrically substituted poly(methylalkylsilanes), produced by reactive metal coupling of the respective dichlorosilanes. On the basis of their analysis of the ^{29}Si NMR spectra of these polymers, they concluded that the structures are not atactic.[2] Fossum and Matyjaszewski were able to strengthen the assignments for the ^{29}Si NMR spectra of $[PhMeSi]_n$ polymers by studying the spectra of samples made by ring-opening polymerization of sterically defined cyclotetrasilane monomers.[3] They concluded that, for $[PhMeSi]_n$, the three partially resolved peaks are due to the isotactic (−41.2 ppm), syndiotactic (−39.9 ppm), and heterotactic (−39.2 ppm) triads. More recently, these analyses have been extended by Jones et al., who showed (i) that peak integrals of the overlapping ^{29}Si NMR spectra are unreliable measures of tactic content, (ii) that estimates of microtacticity by peak deconvolution agree with a Bernoullian enchainment model, with meso-enchainment probabilities (p_m) in the range 0.6−0.7, depending on the polymer and the method of synthesis, and (iii) that the Fossum and Matyjaszewski assignment is probably correct.[4]

We have a longstanding interest in polymers produced by catalytic dehydrocoupling of primary silanes (eq 1).[5]

$$(n+m)RSiH_3 \xrightarrow{\text{catalyst}} [RSiH]_n + H[RSiH]_mH + (n+m-1)H_2 \quad (1)$$

In an earlier communication, we reported an unusual selectivity in the polymerization of phenylsilane by bis(indenyl)- and bis(tetrahydroindenyl)zirconium dimethyl catalysts.[6] The unusual NMR spectra of the reaction products in that case were mainly the result of a high

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* To whom correspondence should be addressed. E-mail: Harrod@omc.lan.McGill.ca.

† Current address: Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.

‡ Current address: Sandia National Laboratories, Albuquerque, NM.

§ Current address: Chemistry Department, Bishops University, Lennoxville, QC, Canada J1M 1Z7.

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(3) (a) Fossum, E.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 1618. (b) Fossum, E.; Matyjaszewski, K. In *Silicon Containing Polymers*; Jones, R. G., Ed.; Special Publication No, 166; The Royal Society of Chemistry: Cambridge, U.K., 1995; p 115.

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selectivity toward the production of cyclics, and the presence or absence of stereoselectivity could not be firmly established. Banovetz et al. reported what appeared to be steroselectivity in the polymerization of phenylsilane by a number of Cp_2ZrX_2 precatalysts.[7] Their conclusion that the polymers had an enhanced syndiotactic content was based on the similarity of the chemical shifts of ^{29}Si NMR peaks to those of *all-trans*-hexaphenylcyclohexasilane. More recently, Choi et al. have used $(Me_2N(CH_2)_nCp)(C_5Me_5)$Zr- and $(Me_2CH(CH_2)_nCp)(C_5Me_5)$Zr-based catalysts to make poly(phenylsilanes) of moderately high molecular weight and they concluded, using the same reasoning as Banovetz et al., that these polymers were rich in syndiotactic enchainments.[8] We will show below that these assignments are incorrect.

A strong motivation for investigating the stereochemical outcome of metal-catalyzed dehydrocoupling is the expectation that appropriate design of the metal coordination sphere can offer control over the sterics of the enchainment, in much the same way as for the Ziegler–Natta type polymerization of olefins. If the generally accepted σ-bond metathesis mechanism for group 4 metallocene catalyzed dehydrocoupling is valid, this expectation is entirely reasonable.[5d,e] However, we have recently proposed an alternative mechanism for the silane dehydrocoupling reaction in which Si–Si bond formation occurs (at least in part) by coupling of silyl radicals.[9] The radical coupling occurs outside the coordination sphere of the metallocene catalyst and hence is not affected by it. Note that radical coupling does not necessarily lead to completely atactic polymer. The stereochemistry of nascent Si–Si bonds may be contolled by interactions between the substituents of the terminal silicons (Bernoullian statistics) or penultimate silicons (Markovian statistics). The polymer tacticity will then depend on the chain lengh and the type of monomer, but not on the stereochemistry of the metal center. On the other hand, the σ-bond metathesis coupling occurs within the inner coordination sphere of the catalyst and the polymer microstructure should be influenced by the shape of the metallocene wedge. The two mechanisms might therefore be distinguished by the influence (or the lack of it) of metallocene structure on the microstructure of the polymer.

In the present paper we report the results of phenylsilane dehydrocoupling mediated by a number of chiral and achiral group 4 catalysts of quite different steric properties, together with the ^{29}Si NMR spectra of the resulting polymers and oligomers.

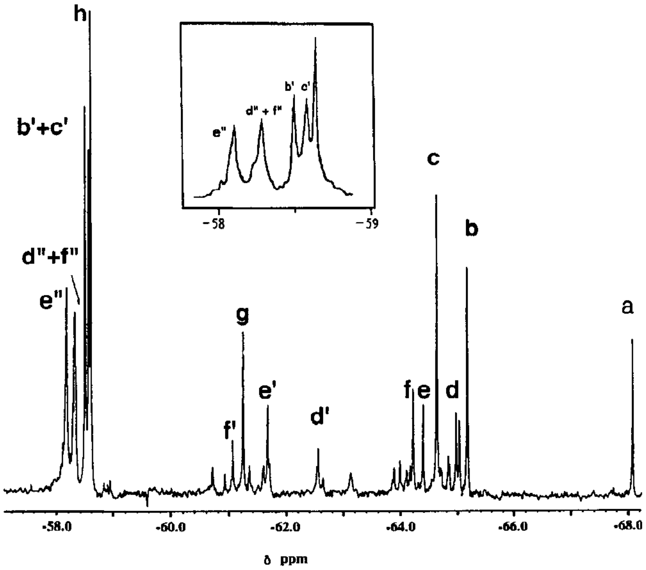

Figure 1. 1D ^{29}Si NMR spectrum of a mixture of oligomers, shown by GPC to contain mainly $Ph_4Si_4H_6$ and $Ph_5Si_5H_7$. Peak assignments: (a) SiH of trimer (T); (b and **c**) SiH of isomers of tetramer (TE); (b′ and c′) SiH_2 of TE; (d–f) penultimate SiH of isomers of pentamer (P); (d′–f ′) internal SiH of P; (d″–f″) SiH_2 of P; (g) SiH_2 of dimer; (h) SiH_2 of T. The inset shows an expansion of the −58 to −59 ppm region.

Results and Discussion

Oligomerization of Phenylsilane with a (*S,S*)-[1,2-Bis(tetrahydroindenyl)ethane]titanium-Based Catalyst. Chiral [1,2-bis(tetrahydroindenyl)ethane]titanium-based catalysts are effective for the stereospecific polymerization of olefins and for the enantioselective catalytic hydrosilylation and hydrogenation of various unsaturated organic substrates.[10,11] In the present study we have used (*S,S,S*)-[1,2-bis(tetrahydroindenyl)ethane]titanium binaphtholate (**1**) activated with BuLi. This precatalyst combination shows high enantioselectivity in the aforementioned organic reactions. Although this catalyst proved to be a very poor one for producing polymers from $PhSiH_3$, its slow production of oligomers allowed the partial assignment of the ^{29}Si and ^{1}H NMR spectra of the tetramers[12] and pentamers, an important key to understanding the corresponding NMR spectra of higher polymers.

A 1D ^{29}Si NMR spectrum of a mixture of linear oligomers obtained with the **1**/2 BuLi precatalyst, determined by GPC to contain mainly $Ph_4Si_4H_6$ and $Ph_5Si_5H_7$, is shown in Figure 1. The assignments indicated were confirmed by a 2D ^{29}Si–^{1}H HMQC-TOCSY experiment. From a ^{29}Si DEPT experiment, all of the peaks in the −58 to −59 ppm range are due to SiH_2 end groups, and all peaks in the −60 to −68 ppm range, with the exception of that of the dimer at −61.23 (g) ppm,

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(7) Banovetz, J. P.; Stein, K. M.; Waymouth, R. M. *Organometallics* **1991**, *10*, 3430.

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(11) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(12) This conclusion is tempered by the fact that peak intensities in ^{29}Si{^{1}H} spectra can be very misleading. We assume, however, that resonances due to chemically identical nuclei at very similar chemical shifts are reasonably comparable.

are due to internal SiH groups. The most intense peaks in the spectrum are two correlated pairs at −65.23 (b) and −58.56 (b′) ppm and at −64.63 (c) and −58.49 (c′) ppm, assigned to the internal and terminal Si's of the two diasteroisomers (*m* and *r*) of the tetramer. A set of three, less intense, correlated triads at (−65.02 (d), −62.55 (d′), −58.32 (d″) ppm), (−64.39 (e), −61.66 (e′), −58.17 (e″) ppm), and (−64.21 (f), −61.05 (f′), −58.32 (f″) ppm) can be confidently assigned to the three stereoisomers (*rr*, *mm*, *rm*) of the pentamer. The remaining unassigned weak lines in the spectrum in Figure 1 are most likely due to the six stereoisomers of the hexamer. It was not possible to extract any correlations between these resonances due to their weakness.

One important piece of information derived from Figure 1 is the fact that the two diasteromers of the tetramer are produced in similar amounts.[12] This in turn indicates that the probabilities of *m* and *r* coupling are roughly equal ($p_m \approx 0.5$); i.e., there is little stereoselection. This is in contrast to the conclusion of Corey and Zhu,[13] who used Cp_2MCl_2/BuLi catalysts (M = Ti, Zr Hf) to polymerize $BuSiH_3$ to low-molecular-weight oligomers. These authors found that one stereoisomer of the tetramer was strongly favored. Whether this difference is due to the different catalyst system, the different monomer, or some other factor remains unknown.

The three sets of peaks assigned to the pentasilane correspond to the expected three inner triads, *rr*, *mr*/*rm*, and *mm*. If the e′ resonance, which has twice the intensity of the d′ and f′ resonances (Figure 1), is assigned to the *mr*/*rm* triad, then little or no stereoselection is indicated. Although the resonances due to the hexasilane isomers could not be assigned, the number of peaks in the regions 60−63.5 and 63.5−65 ppm suggests the presence of a number of stereoisomers in similar abundances and a similar lack of stereoselectivity.[14]

Polymerization of 1,2-Diphenyldisilane with a Cp_2TiMe_2 Precatalyst. We reported earlier the stepwise polymerization of 1,2-diphenyldisilane in the presence of Cp_2TiMe_2 and Cp_2ZrMe_2 precatalysts.[15] We have restudied the Cp_2TiMe_2-catalyzed reaction in detail to extend the interpretation of the ^{29}Si NMR spectra to a slightly higher molecular weight regime. The gel permeation chromatograms of the reaction products with the passage of time are shown in Figure 2. These chromatograms confirm our earlier observation that this reaction proceeds primarily by coupling of dimer to give tetramer, although the amount of trimer resulting from redistribution (Si−Si bond-breaking processes) is in this case somewhat higher than was reported earlier.[15] A series of ^{29}Si NMR DEPT experiments on several of the samples from Figure 2 is shown in Figure 3. These spectra clearly show the dominance of the dimer and tetramer at 40 min reaction time and the appearance of significant amounts of pentamer and hexamer at 60 min, in conformity with the GPC data. By 120 min reaction time the spectral regions of −60 to −62 ppm and −62 to −65 ppm have become very complicated, as expected for a mixture of linear oligomers with no strong selection of particular geometric isomers. However, it should be noted that the massif in the −59 to −66 ppm region already shows the form of the spectrum of the higher polymer seen at 18 h reaction time, which can be recognized as the spectrum of the higher molecular weight polymers to be described below.

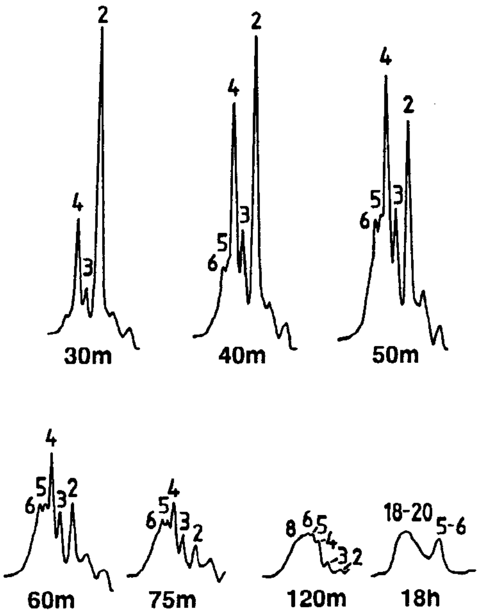

Figure 2. GP chromatograms of products obtained by oligomerizing $Ph_2Si_2H_4$ with a Cp_2TiMe_2 precatalyst, showing evolution of the composition with time. The numbers above the peaks indicate the degree of polymerization of the oligomer(s) at the peak maximum. The reaction was performed at 20 °C in neat reactant with 0.5 mol % catalyst.

Microstructure of Poly(phenylsilanes). Polyphenylsilanes of moderate molecular weight were prepared using several different catalysts. The data shown in Figures 4a and 5a are representative of such polymers.[6] We have also screened a number of other polyphenylsilanes, synthesized with catalysts which give some of the highest molecular weights reported to date. In general, these polymers show very little variation in their ^{29}Si NMR spectra, provided the molecular weight is high enough ($M_n > 4000$, $M_w > 8000$). Two examples of polymers produced with the cation-like catalysts $CpCp^*ZrCl_2/2BuLi/B(C_6F_5)_3$ and $Cp_2HfCl_2/2BuLi/B(C_6F_5)_3$ are shown in parts a and b of Figure 7.[16] In both cases the polymers were subject to a precipitation/purification procedure (see Experimental Section) which results in removal of lower molecular weight linear material and part of the cyclics. Even without the precipitation procedure, the polymers produced with these catalysts only give small amounts of cyclic products (ca. 10%). The main effect of this procedure on the ^{29}Si NMR spectra is to remove the resonances due to terminal and penultimate Si's, which are relatively more concentrated in the low-molecular-weight, linear material. The spectra of these products are dominated by two relatively sharp peaks at −61.0 and −61.5 ppm flanked by lower

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[13] Corey, J. Y.; Zhu, X.-H. *J. Organomet. Chem.* **1992**, *439*, 1.

[14] The six steroisomers of of $Ph_6Si_6H_8$ (*mmm; rmm; mrm; rrm; rmr; rrr*) should give a maximum of eight resonances each for the innermost and penultimate pairs of Si's.

[15] Mu, Y.; Aitken, C.; Coté, B.; Harrod, J. F.; Samuel, E. *Can. J. Chem.* **1991**, *69*, 264.

[16] (a) Dioumaev, V. K.; Harrod, J. F. *J. Organomet. Chem.* **1996**, *521*, 133. (b) Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1994**, *13*, 1548−1550.

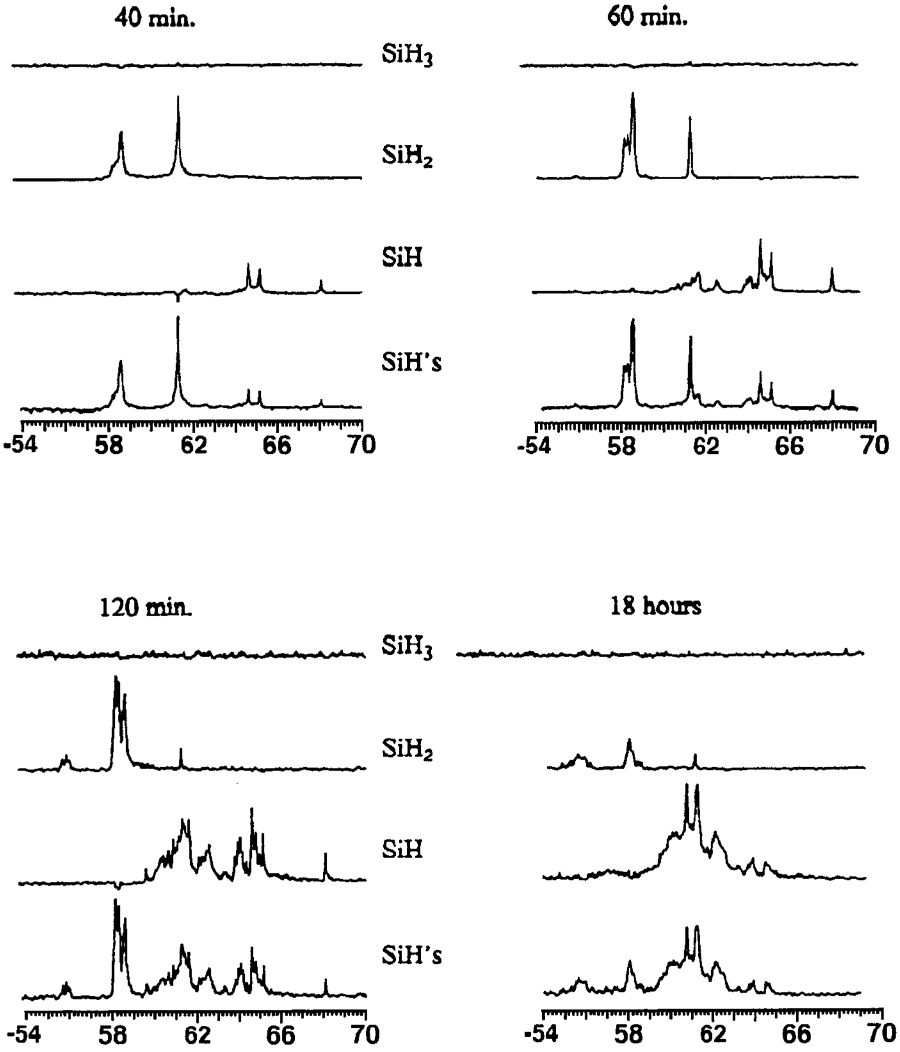

Figure 3. ^{29}Si NMR DEPT spectra of selected samples derived from the reaction of Figure 2.

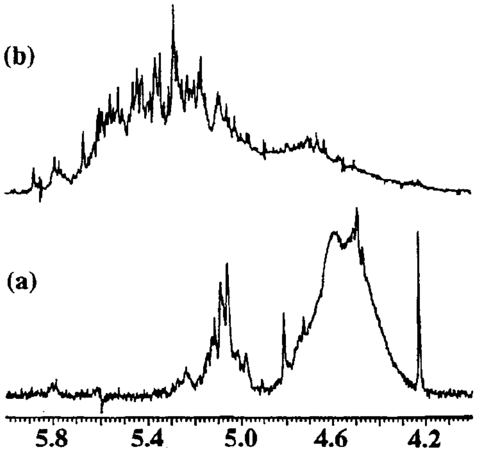

Figure 4. ^{1}H NMR spectra of some oligo(phenylsilylenes) produced with an (Ind)$_2$ZrMe$_2$ precatalyst under different monomer and catalyst concentrations: (a) [catalyst] = 0.049 M, [PhSiH$_3$] = 4.01 M, reaction time 50 h; (b) [catalyst] = 0.104 M, [PhSiH$_3$] = 2.01 M, reaction time 17 h; Reactions were run in toluene at room temperature.

intensity massifs centered at −60.1 and −62.4 ppm. The whole massif occupies the spectral region characteristic of internal PhSiH units and has no significant intensity in the regions assigned above to penultimate PhSiH units, or terminal PhSiH$_2$ units. Judging by the number of ^{29}Si NMR signals, the resolution is at least of the order of pentads, and some pentads appear to be more abundant than others, an expected feature on purely statistical grounds.

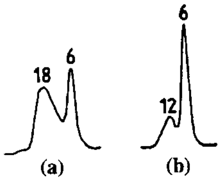

Figure 5. GP chromatograms of the samples (a) and (b) used in Figure 4.

Comparison of the spectra in Figure 7 to those of poly(methylphenylsilanes)[2−4] reveals some similarities. The latter exhibit three resonances at −39.2, −39.9, and −41.2 ppm, previously assigned to the hetero-, syndio-, and isotactic triads, respectively.[4] The polyphenylsilanes (Figure 7) exhibit three prominent peaks centered at −61.0, −61.5, and −62.4 ppm. The chemical shifts of these peaks may be compared to the shifts of the central (PhSiH) units of the three stereoisomers of pentaphenylpentasilane (Figure 1, f′, e′, and d′), which are at −61.05, −61.66, and 62.55 ppm, respectively. The close correspondence between these peaks of the pentamers

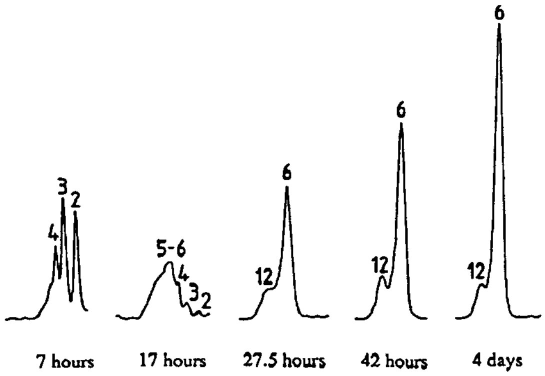

Figure 6. Evolution of the composition of reaction b in Figure 4, as revealed by the GP chromatograms.

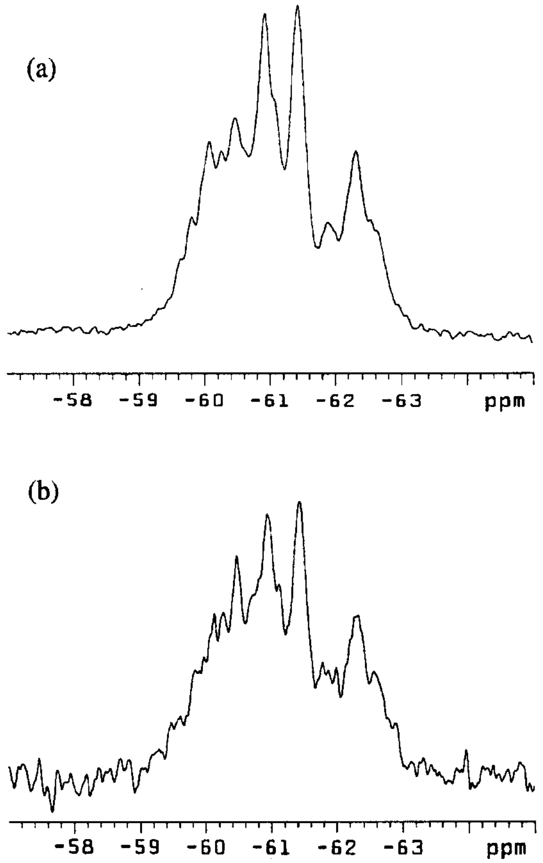

Figure 7. ^{29}Si NMR spectra in C_6D_6 of polysilanes synthesized with (a) $CpCp^*ZrCl_2/2BuLi/B(C_6F_5)_3$ and (b) $Cp_2HfCl_2/2BuLi/B(C_6F_5)_3$.

and the three prominent peaks of the higher molecular weight polymers strongly suggests that they arise from a common stereochemistry.[17] The peaks in the pentamer spectra belong axiomatically to triads, and the intensity ratios of ca. 1:2:1 lead to the conclusion that the central resonance is that of the heterotactic triad (*rm*/*mr*). By analogy, the three prominent peaks of the poly(phenylsilanes) are tentatively assigned to pentads possessing the *rr*, *rm*/*mr*, and *mm* triads as their central units. Although this assignment is in opposition to the assignments made for poly(phenylmethylsilanes), it does conform to the ordering of the triads normally observed for polyolefins.[18]

Prior claims that certain metallocene catalysts give poly(phenylsilanes) with enhanced syndiotactic content were based on the observation of spectra that were essentially identical with those shown in Figure 7.[7,8] From the foregoing, it is obvious that these claims, based on the proximity of the chemical shift of the more intense pair of resonances to that of *all-trans*-hexaphenylcyclohexasilane, is not valid. Even if it were to be shown that the statistical distribution of pentads is not random, this would not be evidence for a stereoselective influence of the catalyst, since free radical and free ion polymerizations do not necessarily give random distributions of stereocenters either.

A final result of interest regarding the reactions from which the spectra in Figure 7 are derived concerns the nature of the cyclic isomers produced in those reactions. In general, we have observed that those catalyst systems which manifest high activity but give large amounts of cyclics and low-molecular-weight linear polymers (DP_n ca. 10), also give broad unresolved massifs in the ^{1}H and ^{29}Si NMR spectra of their products. This is the characteristic of our earliest catalysts, Cp_2MMe_2 ($M =$ Ti, Zr). On the other hand, it has become clear that catalysts which give higher molecular weight polymers ($DP_n > 40$) give small amounts of cyclics whose spectra consist of a limited number of resolved or partially resolved lines that appear within a chemical shift range much narrower than those of the preceding class.

The characteristic differences between the ^{1}H NMR spectra of these two classes of polymer are similar to those in Figure 4. The broad unresolved massif between 5.0 and 6.0 ppm of Figure 4b suggests the presence of a very large number of magnetically different stereocenters and a number of different ring sizes. On the other hand, the narrow chemical shift window (5.0−5.2 ppm) of the cyclics in Figure 4a indicates a much more limited number of stereocenters and ring sizes. In fact, it has been suggested earlier that resonances in this region are due to pentaphenylcyclopentasilane isomers.[13,19] The ^{1}H NMR spectra of the precipitated polymers show the presence of smaller amounts of species resonating between 5.0 and 6.0 ppm than is evident in Figure 4a. It may therefore be concluded that the precipitation procedure removes most, but not all, of the cyclic material. This is not unexpected, since the *all-trans*-cyclohexasilane isomer is very insoluble in most organic solvents, while other isomers are very soluble.

Production of Cyclopolysilanes in Dehydrocoupling Reactions. It has been established that cyclopolysilanes are produced to a greater or lesser extent in all group 4 metallocene catalyzed dehydrocoupling reactions.[20b,21] The relative amounts of cyclic and linear products can depend on virtually every reaction parameter, and it is important to bear this in mind when comparing results for different catalysts, different monomers, or different ratios of reagents and solvents.

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[17] We thank a reviewer for drawing this important fact to our attention.

[18] Bovey, F. A.; Mirau, P. A. *NMR of Polymers*; Academic Press: New York, 1996; pp 181−196.

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[21] Li, H.; Gauvin, F.; Harrod, J. F. *Organometallics* **1993**, *12*, 575.

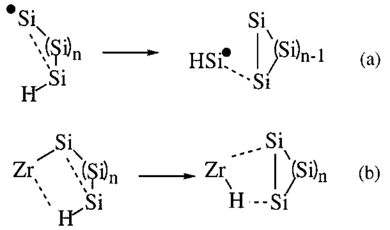
For the moment we are only concerned with the assignments of ^{1}H and ^{29}Si NMR spectra for cyclic oligophenylsilanes. In earlier reports, we compared the GPC behavior of reaction products with their NMR spectra and concluded that, in the ^{1}H NMR spectra, resonances downfield of ca. 5.0 ppm are due largely to cyclic species and resonances upfield of 5.0 ppm are due largely to linear species.[6] We report here some results obtained with a $(Ind)_2ZrMe_2$ (Ind = η^5-indenyl) precatalyst which, under appropriate reaction conditions, gives a very high proportion of cyclic products. The ^{1}H NMR spectra in the Si−H region for some polymer samples produced under two different conditions of precatalyst and monomer concentrations are shown in Figure 4. Attention is drawn to the fact that the precatalyst concentration does not reflect the actual catalyst concentration, since much of the catalyst is usually present in the form of inactive dimers.[6a,20] The spectra in Figure 4 reveal the dramatic influence of reaction conditions on the nature of the product. The gel permeation chromatograms of the samples used in Figure 4 are shown in Figure 5, and they confirm that the difference between spectrum a and spectrum b arises from the presence of a much larger amount of linear, higher molecular weight oligomers in (a), where the monomer/catalyst ratio is higher than in (b).

The evolution of the chromatograms of samples from the reaction in Figure 4b with time is shown in Figure 6. From these chromatograms it is evident that, following a stepwise buildup of chains to ca. 5−6 Si's, further elongation is blocked. We assume that this is due to a facile cyclization of these chains as opposed to further intermolecular coupling to chains of 10−12 Si's. ^{29}Si NMR DEPT experiments on the samples used in Figure 6 detected no SiH_2 groups at and beyond a reaction time of 27.5 h. Very similar results were obtained with a *rac*-[1,2-bis(indenyl)ethane]$ZrMe_2$ precatalyst, except that the stereochemically distinguishable Si's in that case were less numerous than in the case of the bis(indenyl) catalyst.[6] This difference may be due to a difference in ring size distribution and/or a difference in the number of stereoisomers produced. However, what is more important for the present work is the fact that these *cyclic oligo(phenylsilylenes) produce a broad manifold of poorly resolved* ^{29}*Si resonances spanning a range of* δ *from* -45 *to* -65 *ppm,*[6] *which completely overlaps the range of resonances of linear oligomers and polymers.* It is therefore essential that these cyclics be removed as much as possible before interpretation of the NMR spectra of higher polymers is attempted.

Mechanistic Implications. Two broad conclusions can be drawn from the present results. In the first place, the microstructure of higher molecular weight poly(phenylsilanes) is quite insensitive to the structure of the catalyst. In the second place, the nature of the cyclosilane products is very sensitive to the structure of the catalyst and to the specific reaction conditions.

Evidence has been presented to support two mechanistic pathways for zirconocene-catalyzed dehydrocoupling of primary organosilanes. The first is the σ-bond metathesis mechanism, which is the unique pathway under conditions where no reduction of Zr(IV) to Zr(III) occurs.[5d] The second, which we believe is important with BuLi-generated zirconocene catalysts, involves generation of silyl radicals via a Zr(III)/Zr(IV) redox cycle.[9a]

Scheme 1. Schematic Representation of Ring Closure via (a) a Radical and (b) an Intramolecular σ-Bond Metathesis Mechanism



Rings may be formed by closure in the early stages of the chain growth phase of the polymerization, or they may be produced by degradation of longer chains in the later phase of the polymerization. Ring closure in the growth phase could occur by a back-biting radical mechanism (Scheme 1a). On the other hand, it could occur by an intramolecular σ-bond metathesis, as shown in Scheme 1b. The prevalence of this process will be influenced by entropic factors related to the value of n, to the stereochemistry of each silicon, and to the steric constraints of the catalytic site. It will also be affected by kinetic factors, such as concentrations and temperature.

Tilley has thoroughly discussed the influence of steric factors on the various possible σ-bond metathesis transition states involved in the overall polymerization process.[5d,e] He concluded that the lowest energy transition states for a Si−Si bond-forming step are those involving at least one monosilyl species, $RSiH_2X$ (X being either H or metal). This conclusion is supported by the many observations of chain growth by increments of one mer unit in the early stages of polymerization, while there is still a sufficient concentration of monomer in the system. In a situation where this model is operative, the determining factors in ring closure versus chain extension are the relative rates of intramolecular metathesis and intermolecular metathesis between a short chain (ca. Si_4 to Si_6) and monomer. If the extension reaction is fast enough to take the chains past the length(s) at which they are most vulnerable to intramolecular coupling, then the possibility of continued chain growth is assured. However, if the chain extension rates are such as to permit the accumulation of high concentrations of the vulnerable chain length species, and especially if this accumulation coincides with severe depletion of monomer, ring closure will be favored. This seems to be the case with the Ind_2ZrMe_2 precatalyst, which gave the results shown in Figure 6. On the other hand, the titanium analogue gives predominantly linear polymers under similar conditions. This difference may be related to the more sterically constrained cleft in the Ti complexes or to the fact that the catalyst usually remains largely in the oxidation state IV in the case of Zr but Ti easily goes to lower oxidation states.

The highest molecular weights and the most linear polymers reported to date have been obtained with catalysts containing the CpCp*Zr group.[5d,e,16] Although many features of these reactions can be explained by the σ-bond metathesis mechanism, there is also a body of evidence which suggests that the molecular weights of the products are higher in reactions where the Zr is cycling between Zr(IV) and Zr(III).[9b] We have suggested that the coupling of silyl radicals produced during such a cycle could contribute significantly to the formation of Si−Si bonds under conditions where the formation of Zr(III) is favored. In addition, radical coupling is not subject to the severe steric constraints that are characteristic of the σ-bond metathesis transition states involving two polymeric species. The less sterically constrained route of coupling a polysilyl ligand to a $PhSiH_3$ monomer, i.e., stepwise buildup of polymer chains one unit at a time, is not a promising one for producing very long chains, especially when there is only a low concentration of monomer present toward the end of the reaction. The radical coupling hypothesis, however, remains tentative, since no prima facie evidence for specific silyl radicals or of their coupling has been observed. On the other hand, the radical coupling hypothesis accounts for the insensitivity of the microstructure of the higher molecular weight, linear polymers to the structure of the catalyst.

Conclusions

There is no evidence to support the involvement of the metal center in determining the stereochemistry at silicon during the group 4 metallocene catalyzed dehydrocoupling of phenylsilane. The chain stereochemistry of linear higher molecular weight polymers is neither syndiotactic nor isotactic. Whether the polymers are purely atactic or are of some intermediate tacticity will remain unclear until (i) a definitive assignment of ^{29}Si NMR pentad resonances is achieved and (ii) spectra of sufficiently high resolution to measure peak intensities accurately become available. Any deviation from a purely random sequence is most likely due to chain end substituent interactions in the Si−Si bond-forming transition state. The absence of a detectable influence of the catalyst structure on the stereochemical outcome is taken as evidence that radical coupling may play an important role in the buildup of longer polymer chains.

Experimental Section

Materials and Methods. Catalyst preparation and polymerization reactions were performed in Schlenk-type glassware on a dual-manifold Schlenk line, equipped with flexible stainless steel tubing, or in an argon-filled MBraun Labmaster 130 glovebox (<0.05 ppm H_2O; <1 ppm O_2). Argon was purchased from Matheson (prepurified for the glovebox and UHP for the vacuum line) and was used as received. Hydrocarbon solvents (protio- and deuteriobenzene, protio- and deuteriotoluene, pentane, and hexanes) were dried and stored over Na/K alloy, benzophenone, and 18-crown-6 in Teflon-valved bulbs and were vacuum-transferred prior to use. Phenylsilane was degassed and stored over molecular sieves. Cp_2MCl_2 (M = Ti, Zr, Hf), Me_5C_5H, $ZrCl_4$, C_6D_6, PhC(O)Ph, 18-crown-6, and CpNa (2.0 M solution in THF) were purchased from Aldrich and used as received unless stated otherwise. $CpZrCl_3$, *n*-BuLi (1.6 M in hexanes), $CDCl_3$, and $B(C_6F_5)_3$ were purchased from Strem Chemicals Inc.

The compounds $PhSiH_3$,[22] (*S,S*)-[BTHI]Ti(binaphtholate) (BTHIE = η^5-1,2-bis(3-tetrahydroindenyl)ethane),[23] CpCp*-$ZrCl_2$,[24] Ind_2MX_2 (M = Ti, Zr; X= Cl, Me),[25] $(IndH_4)_2MX_2$,[26] (BIE)MCl_2 (BIE = η^5-1,2-bis(3-indenyl)ethane; M = Ti, Zr),[27] and (BTHIE)MCl_2 (M = Ti, Zr)[27] were prepared according to the literature procedures.

Physical and Analytical Measurements. NMR spectra were recorded on Varian Unity 500 (FT, 500 MHz for ^1H) and Varian XL-300 (FT, 300 MHz for ^1H) spectrometers. Chemical shifts for ^1H and ^{29}Si spectra were referenced using internal tetramethylsilane standard. ^{29}Si spectra were acquired with a 3 s preacquisition delay and inverse gated decoupling to obtain decoupled spectra without NOE. A spin relaxation agent, $Cr(acac)_3$, was used.

The molecular weights of the polysilanes were measured with a Waters 510 liquid chromatograph equipped with a Varian RI-4 refractive index detector and Waters Styragel HR1 and HR4 columns in series. The chromatograph was calibrated with polystyrene standards, and THF was used as an eluent. The chromatograms of oligomers in Figures 2, 5, and 6 were obtrained using 500 and 100 Å Ultrastyragel columns in tandem. These columns were calibrated with pure samples of 1,2-$Ph_2Si_2H_4$ and 1,2,3-$Ph_3Si_3H_5$.

Syntheses of (BIE)MMe_2 and (BTHIE)MMe_2 (M = Ti, Zr). These compounds were all prepared by the same procedure, which is a slight modification of the synthesis of Cp_2TiMe_2.[28,29]

Dehydropolymerization with $Cp_2HfCl_2/2BuLi/B(C_6F_5)_3$ and $CpCp^*ZrCl_2/2BuLi/B(C_6F_5)_3$ Catalysts. Polymerization was carried out as previously described.[16a] The high-molecular-weight fractions were separated by fractional precipitation. The product was redissolved in a minimum amount of toluene and precipitated with pentane (3 volumes of pentane/volume of toluene). The dissolution/precipitation cycle was repeated three times to remove the catalyst and its decomposition products and low-molecular-weight cyclics.

GPC (THF): $M_n = 9220$, $M_w = 20\,400$ for $CpCp^*ZrCl_2/2BuLi/B(C_6F_5)_3$ catalyst; $M_n = 7400$, $M_w = 12\,700$ for $Cp_2HfCl_2/2BuLi/B(C_6F_5)_3$ catalyst.

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