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The Coordination Polymerization of Silanes to Polysilanes by a "σ-Bond Metathesis" Mechanism. Implications for Linear Chain Growth

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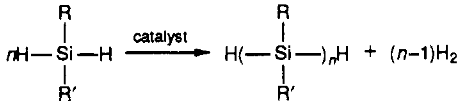
Silicon-containing polymers have a number of potential applications as advanced materials.[1] Much attention is therefore being directed toward development of synthetic routes to silicon-based polymers, including the parent polysilanes $(\text{-SiRR}'\text{-})_n$ which possess an all-silicon backbone.[1] Currently the most practical method for synthesizing polysilanes is a Wurtz-type polycondensation of dihalosilanes with an alkali metal,[1] but other approaches could provide important advantages. For example, coordination polymerizations[2] may provide milder reaction conditions, which allow incorporation of functional groups into the polysilane chain.[3] Also, chemical modification of a metal catalyst could allow fine control over the polymer's molecular weight distribution and substitution pattern.

The coordination polymerization that has attracted by far the most attention is based on the disproportionation of Si–H bonds to Si–Si and H–H bonds (eq 1). Transition-metal catalysts that mediate this disproportionation of σ-bonds have been known for some time, but it was not until 1985 that polysilane chains of significant length (ca. 10–20 Si atoms) were obtained by this method. The latter breakthrough was reported by Harrod and co-workers, who employed titanocene and zirconocene catalysts of the type Cp_2MR_2 ($Cp = \eta^5\text{-}C_5H_5$; M = Ti, Zr; R = alkyl, aryl).[4] Currently, group 4 metallocene complexes provide the most active dehydrocoupling catalysts; however, such polymerizations still appear to be limited to formation of relatively low molecular weight polysilanes, which often contain significant quantities of cyclic oligomers. This Account describes our research on the mechanism of silane dehydropolymerization by zirconocene and hafnocene catalysts. These investigations have led to postulation of a new coordination polymerization mechanism based on "σ-bond metathesis" steps, which involve four-center transition states. Implications of this mechanism as they pertain to prospects for achieving high molecular weights are discussed in light of current information.



$$n\,\mathrm{H{-}\overset{R}{\underset{R'}{Si}}{-}H} \xrightarrow{\text{catalyst}} \mathrm{H(-\overset{R}{\underset{R'}{Si}}-)_nH} + (n-1)\mathrm{H_2} \qquad (1)$$

The σ-Bond Metathesis Mechanism

In our investigations with early-transition-metal silicon compounds, we have observed every possible "σ-bond metathesis" reaction involving a d^0 metal center, silicon, and hydrogen.[2b,5,6] Kinetic studies are consistent with concerted processes in which σ bonds are broken and formed in a four-center transition state. Two examples of observed, stoichiometric processes are shown in eqs 2 and 3. Reactions between d^0 M–Si and Si–H bonds can take place to give Si–Si bond formation (eq 3) or silyl group exchange via the more symmetric transition state.[6]

The observed σ-bond metathesis reactions provide the basis for a new polymerization mechanism that accounts for the catalytic action of d^0 metal complexes in the dehydrogenative coupling of hydrosilanes to

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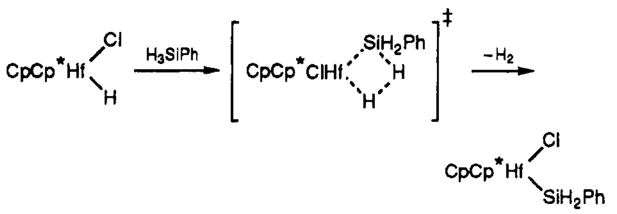

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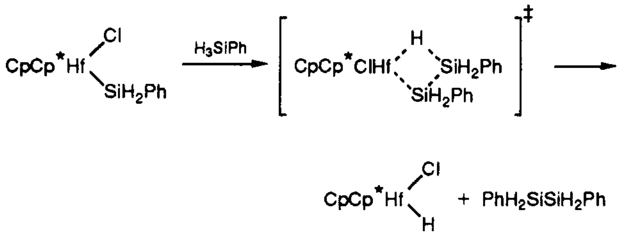


(3)

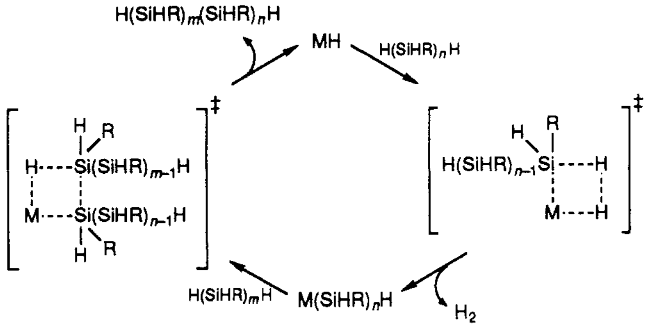
polysilanes. This mechanism, shown in Scheme I, features a coordinatively unsaturated hydride as the active catalyst and is based simply on two steps: (1) the "dehydrometalation" of a silane with a metal hydride and (2) coupling of the resulting metal silyl complex with a hydrosilane to produce a Si–Si bond, with regeneration of the active hydride. An unusual feature of this coordination–polymerization mechanism is that it is step-growth in nature and represents a transition-metal-catalyzed condensation polymerization. Mechanistic studies have produced substantial support for this reaction pathway, including evidence for intermediate species, confirmation of the step-growth nature of chain growth, and evidence that the active form of the catalyst is an unsaturated, d^0 metal hydride.[6,7]

Other studies, particularly with the slower hafnium-based catalysts, have provided more detailed mechanistic insight into fundamental steps in the polymerization and competing side reactions. For example, this step polymerization is "nonideal" in that inequivalent reactivities for different Si–H functional groups in the system are observed, with variations in rates being most dramatic early in the reaction. Thus, disilanes (e.g., PhH_2SiSiH_2Ph) are usually found to be more reactive than the corresponding monosilane.[4j,6b] Beyond disilane formation, the preferred dehydrocoupling reaction appears to involve addition of one silicon at a time to the growing chain, via $MSiH_2R$ intermediates. This selectivity is seen in slow dehydrocoupling reactions, or from examination of model reactions between CpCp*(Cl)Hf$(SiHPh)_nH$ and $H(SiHPh)_mH$ species.[6b,7,8] It is also quite evident that the Si–Si-bond-forming reactions are reversible.[6b,7]

Catalyst Activities

The mechanism in Scheme I provides a basis for the rational design of new catalysts, which are characterized as coordinatively unsaturated, electrophilic metal hydride complexes that readily participate in concerted, σ-bond metathesis processes. The most active catalyst precursors are therefore hydride complexes, or complexes which rapidly convert to hydrides under the polymerization conditions. Because of the high reactivity of d^0 M–Si bonds toward σ-bond metathesis, silyl complexes are rapidly converted to active hydrides in the presence of hydrosilanes. Thus, zirconocene silyl complexes such as $Cp_2Zr[Si(SiMe_3)_3]SiMe_3$ and CpCp*Zr$[Si(SiMe_3)_3]$Me react rapidly with $PhSiH_3$ to produce H_2 and $H(SiHPh)_nH$ polysilanes (in ≥90% yields).[6b] Good catalyst precursors are also obtained via in situ generation of "zirconocene" (from zirconocene dichloride and n-butyllithium), which apparently reacts rapidly with silane via oxidative addition to give a silyl hydride complex.[9,10]

Scheme I



Currently, the most active catalysts are "mixed-ring" zirconocene complexes such as $[CpCp^*ZrH_2]_2$ and CpCp*Zr$[Si(SiMe_3)_3]$Me.[3,6b] With Cp_2Zr derivatives, formation of catalytically inactive hydride-bridged dimers takes place, which removes catalyst from solution. For example, both Cp_2ZrMe_2[4d] and $Cp_2Zr[Si(SiMe_3)_3]Me$[11] are converted during the dehydrocoupling of $PhSiH_3$ to the inactive dimer $Cp_2(PhH_2Si)Zr(\mu\text{-}H)_2ZrCp_2(SiHMePh)$.[4j] The CpCp* ligand set appears to strike a good balance in steric properties, such that inactive hydride dimers are not very stable, but yet sufficient space exists about the metal center to accommodate the four-center transition states. This stabilization of monomeric catalysts leads to long-lived activity. The more crowded catalysts based on the Cp^*_2Zr fragment give slow dehydrocouplings, probably because of steric crowding in the four-center transition states for σ-bond metathesis. Also, as expected, introduction of π-donor ligands, or substitution of zirconium for hafnium, results in slower σ-bond metathesis reactions.[6b]

The proposed mechanism, based on σ-bond metathesis steps that pass through four-center transition states, strongly suggests that lanthanide and actinide complexes might be active catalysts, given their well-known participation in related σ-bond metathesis reactions with hydrocarbons.[12] A number of researchers have investigated scandium group, lanthanide, and

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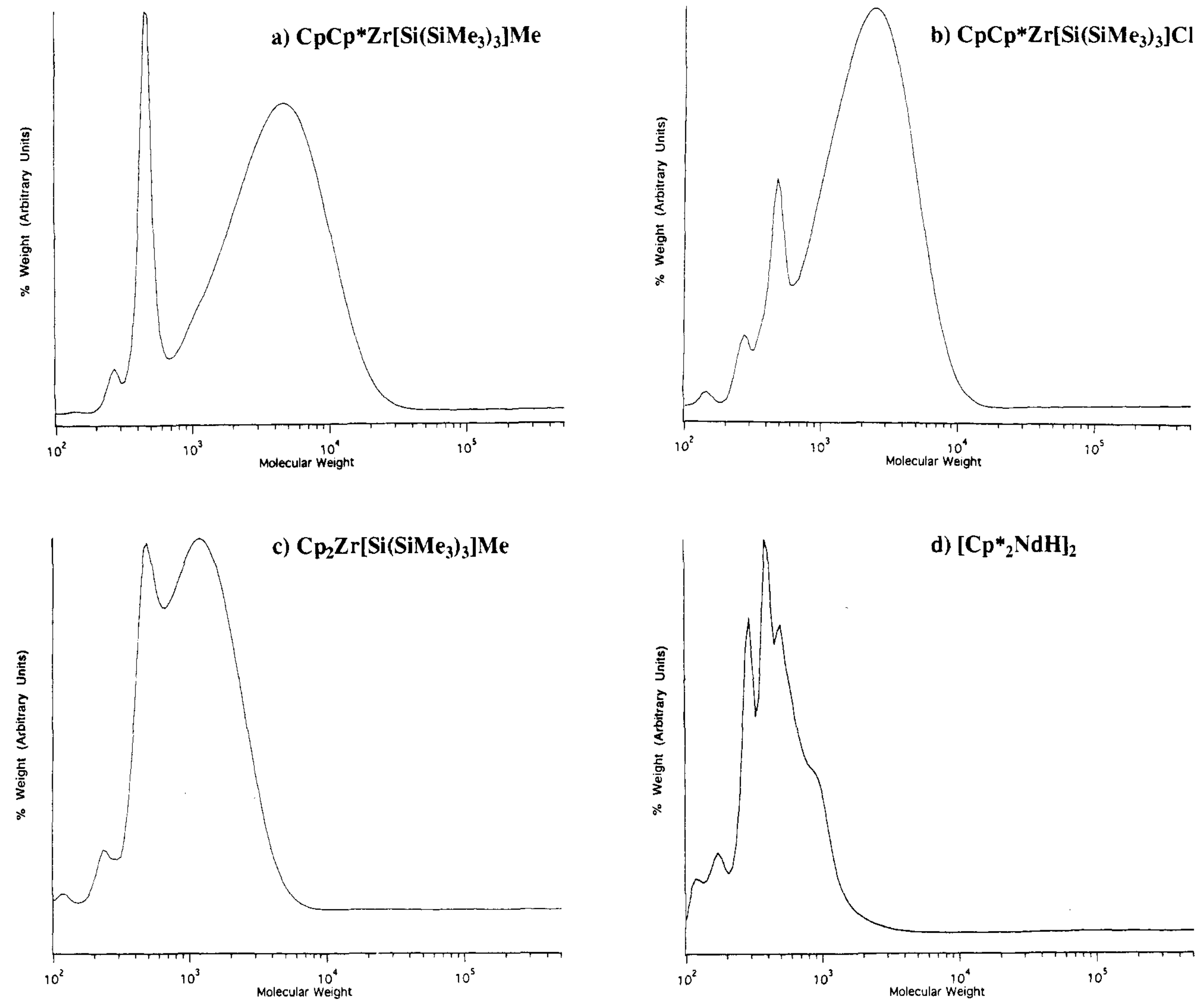

Figure 1. Gel permeation chromatograms for poly(phenylsilylene) samples obtained with the following dehydrocoupling catalysts: (a) CpCp*Zr[Si(SiMe$_3$)$_3$]Me, (b) CpCp*Zr[Si(SiMe$_3$)$_3$]Cl, (c) Cp$_2$Zr[Si(SiMe$_3$)$_3$]Me, and (d) [Cp*$_2$NdH]$_2$. The GPC analyses employed THF solvent, and molecular weight values are based on polystyrene standards.

actinide complexes as catalysts.[13] Although the observed polymerizations are very slow compared to those promoted by mixed-ring zirconium complexes, the participation of these metals in dehydrocoupling lends considerable support to the σ-bond metathesis polymerization mechanism (Scheme I), since other mechanisms involving changes in the metal's valency are highly unlikely.

Evaluation of activities for dehydrocoupling catalysts is complicated by the grossly inequivalent functional group reactivities (monomer vs dimer vs trimer, etc.) that build up the polysilane chains. Therefore, initial rates of hydrogen evolution can be misleading as a measure of dehydropolymerization activity.[14] For example, although some lanthanocene catalysts react with phenylsilane to give moderately rapid hydrogen evolution, only very small oligomers are produced.[13b–f] Therefore, these catalysts are effective in the first few stages of the polymerization, but not afterward. Other catalysts have been reported to merely dimerize PhSiH$_3$.[13a] For the same reasons, rates of monomer disappearance also do not necessarily reflect activity toward chain elongation.

We have employed a simple method for evaluation of a catalyst's activity toward *dehydropolymerization*.[15] This somewhat qualitative procedure is based on gel permeation chromatography (GPC) analysis of the polysilane molecular weight distribution, as produced by the catalyst after 15 min of reaction time with PhSiH$_3$ at room temperature, under an atmosphere of vented nitrogen. Generally, conditions of neat monomer (1 g) and a catalyst concentration of 1.0 mol % are employed. Comparisons using this method are illustrated by the GPC traces of Figure 1. Figure 1a gives the GPC trace for (SiHPh)$_n$ polymer produced by CpCp*Zr[Si(SiMe$_3$)$_3$]Me after 15 min. The sharper, lower molecular weight peak corresponds to cyclic pentamers and/or hexamers, and the higher molecular weight species are linear chains. These assignments are made on the basis of correlations with ^{1}H and ^{29}Si NMR spectroscopy, and

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(14) For most zirconocene catalysts, the very rapid rate of hydrogen evolution makes such rates difficult to measure.

(15) Walzer, J. F.; Imori, T.; Radu, N.; Tilley, T. D. Unpublished results.

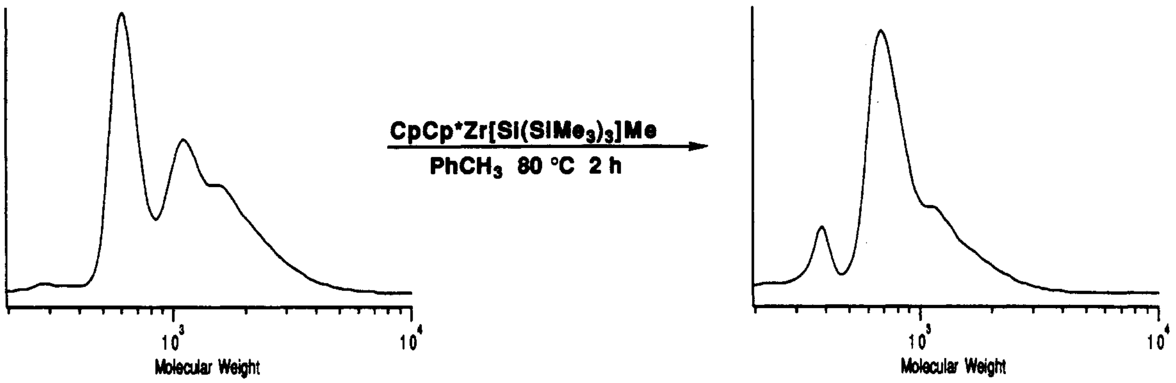

Figure 2. Gel permeation chromatograms that describe the deoligomerization of poly(phenylsilylene) by CpCp*Zr[Si(SiMe$_3$)$_3$]Me. The initial sample of isolated oligomers (a) is ca. 50% cyclic material (highest peak at low molecular weight). Treatment of this sample with more catalyst at 80 °C results in conversion of most of the sample to cyclics (b).

by comparisons to the spectra for independently prepared compounds such as (SiHPh)$_5$ and (SiHPh)$_6$.[10,16-18] The broader, high molecular weight peak corresponds to a number average molecular weight (M_n) value of 3100 and a polydispersity (M_w/M_n) of 1.8. Figure 1b compares the polymer produced under the same conditions by the analogous zirconium chloride CpCp*Zr[Si(SiMe$_3$)$_3$]Cl. The lower molecular weights observed in this case (M_n = 2000 for the high molecular weight fraction) apparently result from the presence of the π-donating chloride ligand, which deactivates the catalyst by making the empty orbital at the metal center less available for substrate-binding. The comparison between parts a and c of Figure 1 illustrates the difference between CpCp*Zr- and Cp$_2$Zr-based catalysts. Finally, a GPC trace for (SiHPh)$_n$ polysilanes produced by [Cp*$_2$NdH]$_2$ is included for comparison (Figure 1d). In this case the oligomers do not exceed the cyclic species in molecular weight, and extended reaction times (over days) do not significantly increase the observed molecular weights. Other lanthanide hydrides give similar results.[15]

For the most active catalysts, a possible problem with the above analysis is that solid polysilane is formed early in the reaction (within 1 min for CpCp*Zr[Si(SiMe$_3$)$_3$]Me), and further increases in molecular weight occur slowly until solvent is added. However, dilution of the reaction mixture promotes deoligomerization to low molecular weight cyclics (vide infra). For reasons discussed later, a better method for evaluating a catalyst's activity toward producing polymer may be via comparisons of rates for specific chain–chain coupling reactions, where the chains are well-defined PhH$_2$Si(SiRR')$_n$SiH$_2$Ph oligomers ($n \geq 4$).

Factors That Impede Elongation of Chains

Transition-metal group 4 metallocene catalysts are quite active toward dehydrocoupling, but the reaction suffers from two principle limitations. First, only short linear chains are produced, and second, there is competing production of low molecular weight, cyclic oligomers. Since for many applications it is desirable to have high molecular weight polymers that display "macromolecular" electronic and/or physical properties,[1] more control over the polymerization would be highly advantageous. At this early stage of investigation, it is clear that the relative amount of cyclic material produced is highly dependent on many variables, including the nature of the catalyst, the R group in the RSiH$_3$ primary silane, and the reaction conditions (solvent, temperature, concentrations, etc.).

A primary limitation to the molecular weights of linear polysilanes produced by dehydropolymerization results from the step-growth nature of the mechanism, which requires extremely high conversion of Si–H to Si–Si bonds (>99%) for production of high polymer.[19] With catalysts employed so far, it appears to be difficult to suppress cyclic formation while achieving a high conversion of Si–H functionalities. Attempts to achieve high conversion to longer H(SiHR)$_n$H chains, via extended reaction times or elevated temperatures, are generally thwarted by competing production of high proportions of cyclic oligomers. This is illustrated by the GPC traces of Figure 2. Figure 2a shows the molecular weight distribution for a poly(phenylsilylene) sample obtained from the room temperature dehydrocoupling of PhSiH$_3$ in toluene with CpCp*Zr[Si(SiMe$_3$)$_3$]Me as a catalyst. An attempt to increase the molecular weight of this polysilane sample via elevated reaction temperature (80 °C, toluene solution, CpCp*Zr[Si(SiMe$_3$)$_3$]Me catalyst) led instead to degradation of linear chains to cyclics, as shown by the GPC trace of Figure 2b. Therefore nearly complete conversion of Si–H to Si–Si bonds is achieved under forcing conditions, but only at the expense of converting the polysilanes to low molecular weight cyclics.[18] Apparently, the cyclic (SiHPh)$_n$ species are more thermodynamically stable than the H(SiHPh)$_n$H linear chains, and some depolymerization–cyclization process is facile. Production of high molecular weight polysilanes via dehydrocoupling will therefore require partitioning of the reaction toward linear chain growth, as well as toward high conversion.

How does the depolymerization of linear chains to cyclics occur? Two processes seem possible. The first (eq 4) involves a classic "back-biting" reaction[19] that proceeds through transition state E. Based on observed steric constraints for related σ-bond metathesis reac-

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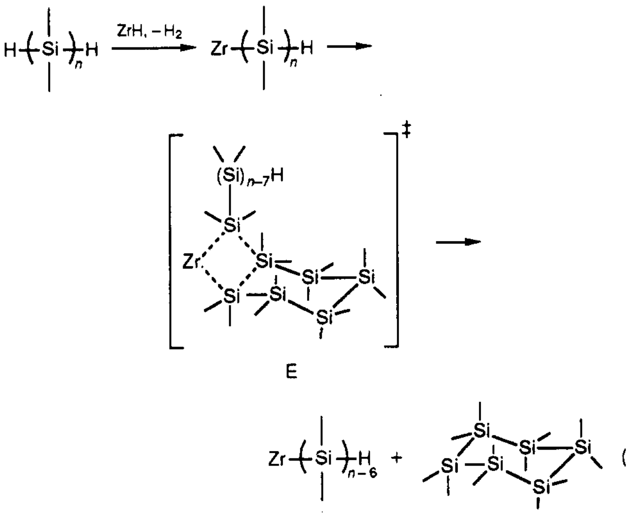

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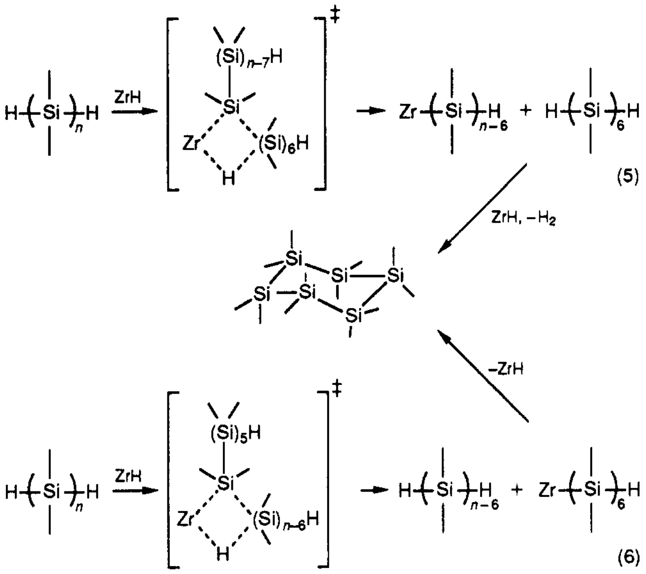
tions,[5,6] this highly substituted four-center transition state does not seem very likely. A more plausible scenario for depolymerization involves the related sequences of eqs 5 and 6, which are based on the observation that Si–Si bond formation is reversible.



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These reactions involve cleavage of chains by metal hydrides, which bite into an internal Si–Si bond thereby passing through the same transition state required for the coupling of silanes. At some frequency, the cleavage reactions will produce short oligomers that can be cyclized to form the thermodynamically preferred rings. Of course, cyclic oligomers can also form kinetically without deoligomerization chemistry, from short $H(SiHR)_nH$ polysilanes as they are formed. It seems possible, then, that conditions which favor the coupling of chains will tend to also favor deoligomerizations via the reactions in eqs 5 and 6, since the same transition states are accessed in the two reactions, and since these reactions may be nearly thermoneutral.[2a,20]

Toward Longer Chains

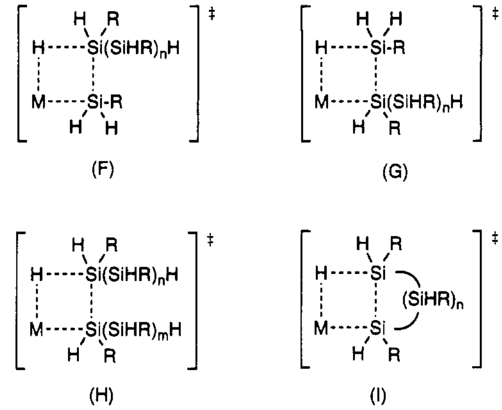
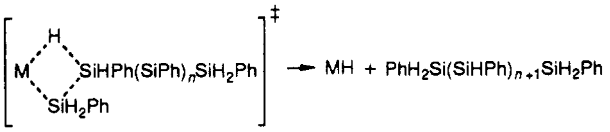


Figure 3. Four-center transition states for Si–Si-bond-forming reactions.

Observed steric constraints for catalysts and silane monomers appear to result from the crowded four-center transition states for σ-bond metathesis. Note that the coupling of silyl groups to form a Si–Si bond (second step of Scheme I) is inherently the most crowded σ-bond metathesis transition state involving a metal center, silicon, and hydrogen. For this reason, primary silanes are in general much more reactive toward dehydrocoupling than secondary or tertiary silanes. It is not too surprising, then, that the most facile Si–Si-bond-forming step in a polymerization involves addition of one silicon at a time to the polysilane SiH_2R end groups, via a monosilyl $MSiH_2R$ derivative (eq 7). This selectivity can be understood in terms of steric hindrance in competing four-center transition states that couple silyl groups together (F–I, Figure 3). The least crowded (and presumably lowest energy) transition state is produced by addition of a $MSiH_2R$ derivative to the end of a polysilane chain, since this places the bulky polysilyl group in the β position relative to the sterically crowded metal center. Therefore, as long as monomer is present, the more important polymerization process corresponds to the case where $n = 1$ in Scheme I, which results in *linear chain growth*. Once monomer is consumed, increases in molecular weight require a catalyst active enough to couple chains together via the higher energy transition state H. However, such conditions will probably also promote cyclizations via transition-state I, given the favorable $\Delta S^{\ddagger}$ term that is expected to contribute to the energy of the latter structure, and intramolecular cyclization may under many conditions occur more rapidly than chain coupling.



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On the basis of the observations and arguments outlined above, we can construct qualitative reaction coordinate diagrams for the competing Si–Si-bond-forming reactions (Figure 4). This analysis suggests two approaches for modification of the dehydrocoupling reaction for production of higher molecular weights. The first strategy is based on the fact that the preferred dehydrocoupling process is addition of one silicon at a time, via transition state F. If conditions exist such that the polymerization is partitioned only along this

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(20) (a) Nolan, S. P.; Porchia, M.; Marks, T. J. *Organometallics* **1991**, *10*, 1450. (b) Schock, L. E.; Marks, T. J. *J. Chem. Soc.* **1988**, *110*, 7701.

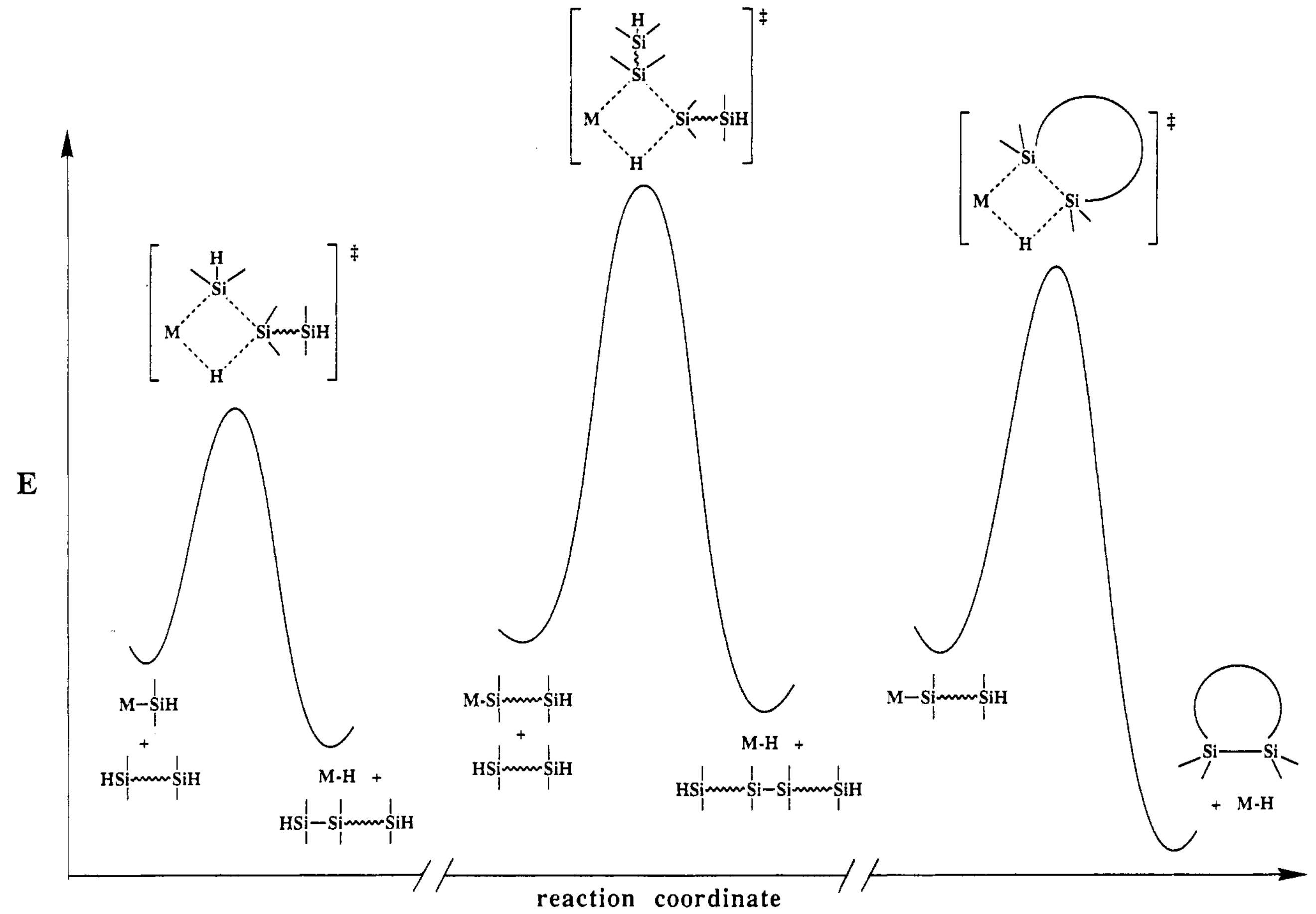

Figure 4. Qualitative reaction coordinate diagrams for competing Si–Si-bond-forming reactions.

lower energy pathway, it should be possible to kinetically grow high molecular weight, linear polysilanes. The higher energy cyclization process leads to more stable polysilanes, but involves two transition states that have a polysilyl group α to the metal center. First, a $M(SiHR)_nSiH_2R$ species must be formed via a transition state with the $(SiHR)_nSiH_2R$ group in the α position (G or H), and second, a heavily substituted four-center transition state (I) is involved in the cyclization (eqs 5 and 6).

The required selectivities appear to be achieved by reduction of the reaction temperature, or by use of slower (and more selective) catalysts which effectively partition the various possible dehydrocoupling processes. We have demonstrated this principle using the $CpCp^*Zr[Si(SiMe_3)_3]Me$ catalyst and neat $PhSiH_3$, by showing that cyclic formation is nearly completely suppressed at 0 °C (Figure 5). Alternatively, linear chain growth by one silicon at a time is favored by use of the more discriminating catalyst $CpCp^*Hf[Si(SiMe_3)_3]Cl$. Figure 6 compares GPC traces for polysilane samples prepared in toluene solution, with both $CpCp^*Zr[Si(SiMe_3)_3]Me$ and $CpCp^*Hf[Si(SiMe_3)_3]Cl$ as catalysts. With the latter catalyst, cyclic formation is completely suppressed, even at 80 °C.[18]

The mechanistic picture described above suggests that cyclizations should also be suppressed by high monomer concentrations, which favor second-order condensations over first-order cyclizations.[19] For dehydropolymerization, such conditions should promote the conversion of metal hydrides to $MSiH_2R$ complexes, which will then be available to increment chains. Oligomers such as $H(SiHPh)_6H$ will then stand a greater chance of growing linearly relative to undergoing cyclizations catalyzed by MH. The influence of initial $PhSiH_3$ concentration on molecular weight distributions, with $CpCp^*Zr[Si(SiMe_3)_3]Me$ as catalyst, is illustrated by the GPC traces in Figure 7. These concentration effects are quite dramatic; note that in the absence of solvent, cyclic formation is greatly suppressed. Also, under conditions that yield few cyclic species, the linear chains achieve higher molecular weights (M_n = 3100 and M_w/M_n = 1.5 for the high molecular weight peak in the last GPC trace of Figure 7).[13e]

An alternative approach to production of higher molecular weight polysilanes is based on use of active catalysts that couple chains. It is apparent from an examination of the rate equations for both chain coupling and depolymerization that chain coupling can compete favorably with depolymerization, given the proper balance of rate constants. Development of this approach may rely heavily on design of new catalysts that display the desired kinetic properties. It is encouraging that, as shown in Figure 6 and as demonstrated by Harrod,[2a,16b] the relative tendency toward chain elongation versus cyclization can be quite sensitive to slight modifications of the catalyst.

On the basis of a likely mechanistic description for the polymerization, we have been able to demonstrate that reaction conditions can be modified in a logical fashion to suppress cyclic formation and achieve longer chains. In particular, it appears that conditions most conducive to monomer–chain coupling lead to preferred linear chain growth and longer chains. However, high polymer is not obtained, and the polymerizations stop

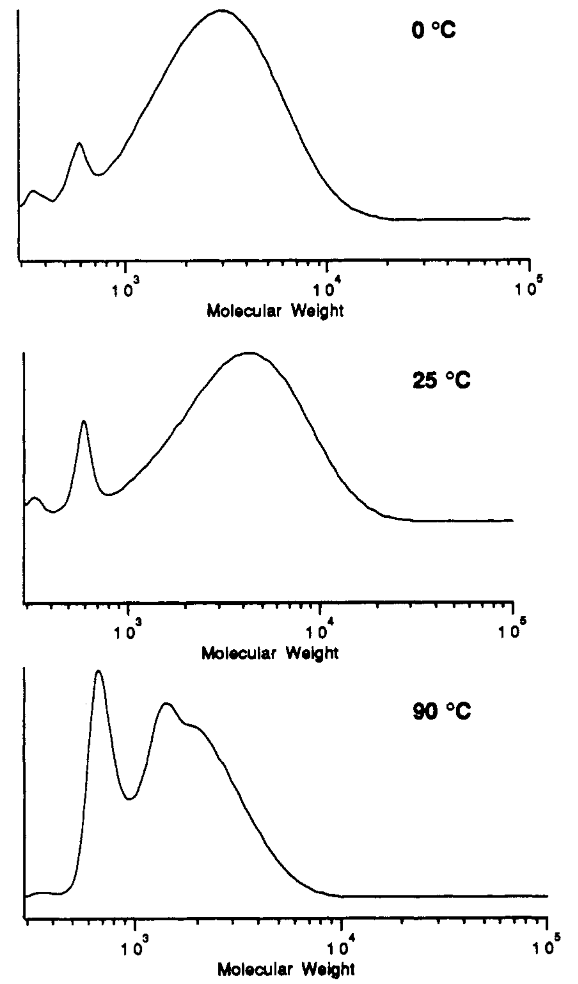

Figure 5. Gel permeation chromatograms, illustrating the influence of temperature on molecular weight distributions for poly(phenylsilylene) samples obtained using CpCp*Zr[Si(SiMe$_3$)$_3$]Me catalyst (0.1 mol %) and neat PhSiH$_3$.

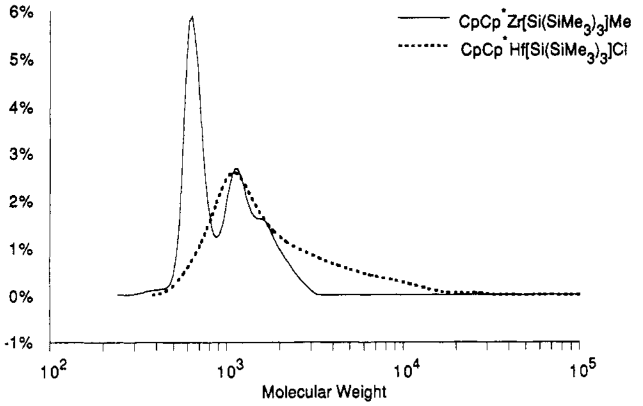

Figure 6. Comparison of gel permeation chromatograms for poly(phenylsilylene) samples obtained with CpCp*Zr[Si(SiMe$_3$)$_3$]Me catalyst at room temperature in toluene (solid line) and with CpCp*Hf[Si(SiMe$_3$)$_3$]Cl catalyst at 80 °C in toluene (dotted line). The polysilanes obtained with the zirconium catalyst are ca. 50% cyclics.

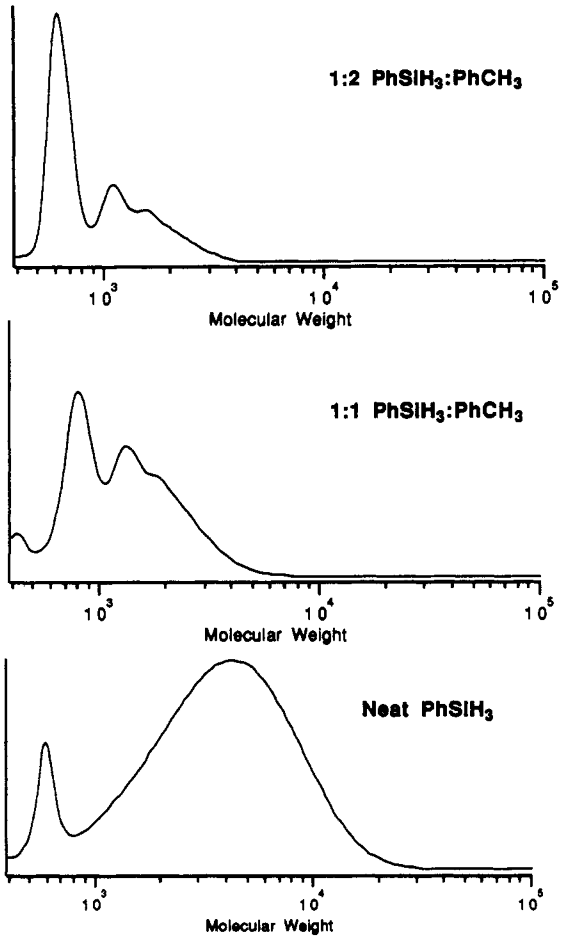

Figure 7. Gel permeation chromatograms, illustrating the influence of PhSiH$_3$ concentration on molecular weight distributions for poly(phenylsilylene) samples obtained using CpCp*Zr[Si(SiMe$_3$)$_3$]Me catalyst (0.1 mol %).

after the number average molecular weight (M_n) has reached a value of ca. 3000 amu (based on polystyrene references). Why do the polymerizations stop at this point? On the basis of the proposed mechanism, polymerization should continue if chain–chain coupling is possible. An explanation for the apparent molecular weight limitation is suggested by the observation that favorable polymerization conditions (active catalyst, neat monomer) lead rapidly to solidified, high-viscosity reaction mixtures. Highly viscous media can severely inhibit condensation polymerizations, since inefficient removal of the small molecular weight product (in this case, hydrogen) slows approach of the reaction to completion.[21] As can be seen by the results of Figure 5, raising the temperature to lower the viscosity can be counterproductive, since cyclic formation becomes competitive at higher temperatures.

It is well-known that the most favorable conditions for polycondensation reactions involve high monomer concentrations, efficient removal of the small molecular weight product (e.g., by evacuation), and temperatures high enough to increase condensation rates without adversely effecting ring–chain equilibria or catalyst stability.[22] Such conditions have been applied in the case of a metal-catalyzed condensation reaction, acyclic diene metathesis (ADMET) polymerization, which couples dienes via olefin metathesis chemistry and elimination of a volatile byproduct, ethylene.[23] We have carried out the dehydrocoupling of PhSiH$_3$ by CpCp*Zr[Si(SiMe$_3$)$_3$]Me (1 mol %) using neat conditions and application of a dynamic vacuum to remove hydrogen. Small quantities of toluene were added dropwise via an

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addition funnel over 5 h, such that the reaction mixture maintained a slight fluidity. With these polymerization conditions, linear poly(phenylsilylene) samples with M_n values of 5300 have been obtained (polystyrene standards; $M_w/M_n = 2.2$), which contain ca. 14% of the low molecular weight cyclics by weight.[24] On the basis of previously reported correlations between GPC data and other measurements, this molecular weight is estimated to correspond to ca. 44 monomer units.[4b] Presumably, further increases in molecular weight would require a catalyst more active toward chain–chain coupling.

Concluding Remarks

It now appears that major factors which limit chain lengths in metal-catalyzed dehydropolymerizations are competing cyclic formation, incomplete conversion of Si–H to Si–Si bonds due to catalyst inactivity, and low-viscosity reaction media resulting in reduced reaction rates. Each of these limitations has been addressed to achieve increases in average molecular weights, but clearly further improvements are needed. Perhaps the most promising approach at this point is based on monomer–chain reactions, which selectively give the desired linear polysilanes. Thus, the slow bleeding of monomer into the reaction mixture should allow the buildup of very long polysilane chains. Development of this approach as a useful method will require discovery of conditions and catalysts which effectively promote monomer–chain relative to monomer–monomer coupling reactions.

Significantly, results so far indicate that there is no inherent limitation to molecular weight control via polymerizations of this type, and in principle it should be possible to identify conditions and catalysts that allow production of high polymers. Even though much progress has been made toward understanding how the dehydropolymerization of silanes is catalyzed by early metal complexes, a more complete mechanistic picture should allow more control over the molecular weight properties. We still lack important information concerning substituent effects and how these might influence relative rates. However, it is apparent that these systems are amenable to modifications that can dramatically influence reactivity. New generations of catalysts may be essential for major advancements in this polymerization chemistry.

The dehydrocoupling of hydrosilanes holds considerable promise as a general route to new polymeric materials. With further improvements, it might serve as a useful alternative to current methods for preparing polysilanes. Perhaps more importantly, dehydrocoupling reactions via σ-bond metathesis could provide approaches to other types of polymerizations,[25] or catalytic conversions of small molecules.

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