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Catalytic Dehydropolymerization of $PhSiH_3$ to Polyphenylsilane with Substituted Group IV Metallocenes

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Phenylsilane can be converted catalytically to polyphenylsilane using substituted achiral group IV metallocene dichloride precatalysts $(Cp^R)_2MCl_2$ (M = Ti, Zr; $Cp^R = C_5H_4C(Me)_2$-$CH(Me)_2$) and $Cp(Cp^R)MCl_2$ (M = Ti, Zr; Cp = C_5H_5) in combination with 2 equiv of *n*-BuLi. The performance of each precatalyst is described in terms of polymer molecular weight, polydispersity, and polymer microstructure. The polysilanes from each catalyst system were obtained as a mixture of oligocyclic and linear materials with M_w values ranging from 1100 to 4000. Characterization of the crude polymers by ^1H and $^{29}Si\{^1H\}$ DEPT 135° NMR spectroscopy indicated a mostly atactic microstructure with a small syndiotactic bias. A Bernoullian statistical analysis of a typical $^{29}Si\{^1H\}$ polymer spectrum indicated a syndioselective probability (1-Pm) of 0.55 during propagation of the pseudochiral chain. The degree of polymerization was found to be dependent on the metal and the degree of Cp-ring substitution of the metallocene precatalyst.

Introduction

The development of oligomeric and polymeric silane catenates, termed polysilanes, permits investigation of a unique series of molecules. The materials possess a backbone comprised of Si−Si σ bonds which endow them with novel electronic properties by virtue of electron delocalization through the covalent polymer network.[1] This unusual feature is of interest with respect to technical developments in the fields of microlithography[2] and nonlinear optics,[3] although the science involved in synthesizing such compounds remains in its infancy in terms of controlling polymer molecular weight, functionality, and the tailoring of polymer microstructure. One synthetic methodology discovered by Harrod and co-workers and actively pursued by others is the dehydropolymerization of silanes to form polysilanes using a catalytic quantity of a group 4 metallocene.[4−6]

Metallocenes can be used as catalysts for both olefin and silane polymerizations, and the effectiveness of these molecules in mediating and improving all aspects of the silane polymerization is under investigation by several groups. In the current study, the high-yield polymerization of phenylsilane using new hindered monoalkyl- and dialkyl-substituted achiral metallocenes of the titanium triad $(C_5H_4C(Me)_2CHMe_2(C_5H_4R)MCl_2$: R = H, $C(Me)_2CHMe_2$; M = Ti, Zr, Hf) is reported. The effects of modulation of the catalytic architecture and catalyst loading on the polymer properties are also described. Targets for the improvement of polysilane technology include the formation of linear polymers in preference to low-molecular-weight cyclic oligomers and stereocontrol of the pseudochiral polyphenylsilane microstructure. The success of such goals was found in some cases to be dependent on the nature of the catalyst system used.

Generally, metallocene dichlorides are precatalysts, which are activated toward dehydropolymerization upon addition of 2 equiv of *n*-BuLi.[5] The rapid reaction of $PhSiH_3$ with the metal center generates the true catalyst which engages in the stepwise coupling of the silane monomer (eq 1). The mechanism for this dehydrocoupling is believed to be similar to the σ-bond

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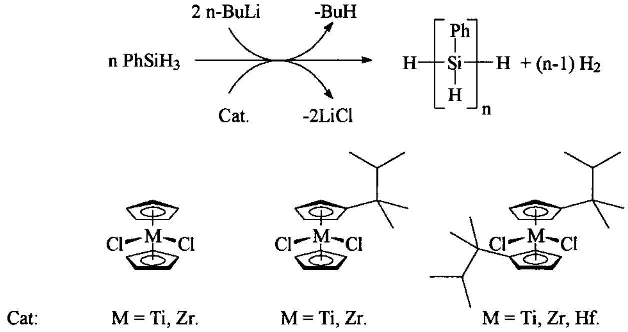

(1)

metathesis route widely accepted as the process which accounts for other Ti triad mediated polysilane syntheses.[6] Simple metallocene dichlorides have been previously used as the precatalysts, although unwanted side reactions such as catalyst deactivation by formation of presumed inert hydride-bridged dimers were suspected to preclude formation of higher molecular weight polymers.[7] The use of catalysts containing bulky alkylcyclopentadienyl substituents was intended to prevent such complications via catalyst–substrate steric control. Furthermore, the addition of a sterically demanding ancillary ligand could act as a probe for the structural features which are necessary to discriminate between the formation of linear and cyclic materials. A possible added advantage of ring-substituted metallocenes was an anticipated influence of the hindered metal environment on the formation of each stereogenic silicon center during the growth of a pseudochiral silicon chain. The metallocenes were synthesized and characterized by standard techniques and are described separately.[8]

Experimental Section

All reactions were run under an atmosphere of dry nitrogen using Schlenk glassware or a glovebox, unless otherwise stated. Reaction vessels were flame-dried under a stream of nitrogen, and anhydrous solvents were transferred by oven-dried syringes or cannula. The molarity of a hexanes solution of *n*-BuLi was confirmed by a titration method.[9] After polymerization experiments were completed, the catalysts were deactivated by exposure to air. An aliquot was extracted and dissolved in freshly distilled THF, and the solution was passed by syringe through a 6000 Series nonsterile 0.45 m PTFE filter before obtaining GPC measurements. GPC data were collected using an SSI 222D HPLC pump to elute the samples through a bank of 10^4, 10^2, and 500 Å Waters 78 × 300 mm Ultrastyragel columns in HPLC grade THF solvent. A Linear UV–vis detector set to 254 nm was used for the detection of the polymers.

Proton and silicon-29 (^{1}H, ^{29}Si) nuclear magnetic resonance spectra were recorded using either a Varian Unity +300 equipped with a multinuclear probe or a Bruker ARX500 equipped with a broad-band probe. Unless otherwise stated, ^{1}H spectra were recorded in C_6D_6 and referenced internally to residual solvent peaks (C_6H_6). ^{1}H NMR spectra used for accurate determination of signal ratios were run with an increased delay (0.5–1.0 s) to minimize the effects of differential relaxation periods. ^{29}Si{^{1}H} DEPT spectra were also recorded in C_6D_6 and referenced externally. Unequal NOE suppression or enhancement of signal intensities was assumed to be negligible, as established by Schilling, Bovey, and Zeigler for ^{13}C and ^{29}Si signals of polysilanes.[10]

Table 1. Polymerization Studies of $PhSiH_3$ using $(Cp^R)_2MCl_2$ (M = Ti, Zr) and $Cp(Cp^R)MCl_2$ (M = Ti, Zr)

precatalyst[a]	amt of cat., mol %	activity[b]	M_w	M_n	polydispersity	L:C[c]
$(Cp)_2TiCl_2$	1.0	0.9	1500	1000	1.5	1.3
$(Cp)_2ZrCl_2$	1.0	2.3	2000	1000	2.0	1.8
$(Cp^R)_2TiCl_2$	0.5	5.3	1100	580	2.0	1.0
$(Cp^R)_2TiCl_2$	1.0	6.3	1200	700	1.7	*d*
$Cp(Cp^R)TiCl_2$	0.5	4.6	2000	1500	1.3	2.0
$Cp(Cp^R)TiCl_2$	1.0	4.3	2100	1500	1.4	2.0
$Cp(Cp^R)ZrCl_2$	0.5	4.1	3000	2000	1.5	4.0
$Cp(Cp^R)ZrCl_2$	1.0	3.8	2500	1500	1.7	9.0
$(Cp^R)_2ZrCl_2$	0.5	1.1	3500	2000	1.8	4.0
$(Cp^R)_2ZrCl_2$	1.0	1.4	4000	2000	2.0	4.0
$(Cp^R)_2HfCl_2$[e]	1.0		3000	2000	2.0	

[a] Activated with 2 equiv of *n*-BuLi. [b] Activity defined as (g of polymer) (mol of cat.)$^{-1}$ (mol of monomer)$^{-1}$ h^{-1}. The activity data can be generally reproduced within 30%, and the values given represent the average of at least two runs per catalyst. [c] L = linear; C = cyclic. [d] Overlap of oligomeric and oligocyclic peaks precluded accurate determination of L:C ratio. [e] Activated with 2 equiv of MeLi.

Deconvolution of the ^{29}Si{^{1}H} DEPT 135° spectrum was carried out using a NMR Utility Transform Software (NUTS) package from Acorn NMR.

A typical experimental procedure is as follows. In a glovebox, a Schlenk tube was charged with $[C_5H_4C(Me)_2CH(Me)_2]_2ZrCl_2$ (0.010 g, 2.2 × 10^{-2} mmol) and transferred to a Schlenk line. On addition of $PhSiH_3$ (0.470 g, 4.35 mmol), the colorless reaction mixture was degassed by two freeze–pump–thaw cycles. The reaction vessel was wrapped in aluminum foil in an unlit fumehood to exclude light. At ambient temperature, the catalyst was activated by addition of *n*-BuLi (0.02 mL, 2.5 M) followed by stirring, resulting in vigorous evolution of gas and formation of a yellow solution. The reaction mixture was stirred for 48 h, to provide a viscous yellow gum which was dissolved in THF and filtered through Celite. The solvent was removed in vacuo to provide the polysilane as an off-white gum (0.439 g, 95%). The results are summarized in Table 1.

Results and Discussion

The polymerizations were carried out under Schlenk conditions in neat distilled phenylsilane with the exclusion of light. Reaction mixtures were initiated at ambient temperature by addition of 2 equiv of *n*-BuLi, at which point formation of colored solutions was observed (pale yellow for Zr systems and dark blue for Ti cases). Initially, vigorous bubbling was noted, followed by gradual thickening of the solution over 2 h until gumlike residues were generated. Aliquots were sampled after 24 and 48 h and polymer molecular weights determined by GPC analysis versus polystyrene standards. Samples of the polymerizates were also analyzed by ^{29}Si{^{1}H} DEPT and ^{1}H NMR techniques in an attempt to assay the extent of polymer tacticity. Linear-to-cyclic ratios were confirmed by integration of the corresponding regions of the GPC chromatograms and the ^{1}H NMR spectra. In the case of $(Cp^R)_2HfCl_2$, addition of 2 equiv of *n*-BuLi failed to generate a catalytically active species,

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although 2 equiv of MeLi resulted in a low yield of polyphenylsilane after 4 days. These findings are summarized in Table 1.

Polymer Molecular Weights. The molecular weight of the polyphenylsilane products obtained appeared to be related to the extent of low-M_w cyclic byproducts formed. As the amount of cyclic products decreased, the average molecular weight of the macromolecules increased. A similar observation was reported earlier when raw polymer was fractionated to remove cyclic oligosilanes.[11] A range of polyphenylsilanes with M_w = 1100−4000 was obtained using the substituted metallocenes. Generally, this represented an increase in M_w in comparison to the materials produced from the corresponding parent metallocene combination catalysts. However, it is likely that the polymer M_w values are still too low for the technical applications of polysilanes. It was observed that zirconocene-based catalysts tended to generate higher molecular weight polysilanes. Furthermore, in agreement with previous results,[5f,12] group IV complexes with two functionalized Cp rings, in this case [$(Cp^R)_2ZrCl_2$], produced polyphenylsilane with 2-fold and 3-fold increases in M_w in comparison to Cp_2ZrCl_2 and Cp_2TiCl_2, respectively.

Alkyl substituents attached to the catalyst cyclopentadienyl ring affected the polymer M_w value obtained. A longer polymer chain was obtained when the monoalkylated zirconocene $CpCp^RZrCl_2$ rather than Cp_2ZrCl_2 was used. This suggested that the alkyl group became involved in the critical stepwise growth polymer mechanism and played an important role in the development of linear polysilanes. A greater increase in polymer M_w was noted with the heteroannular dialkylated analogue $(Cp^R)_2ZrCl_2$. The addition of a second Cp alkyl substituent to the catalyst improved the corresponding polysilane molecular weight to a value approximately twice that obtained using the parent zirconocene. It was also observed that the amount of oligocyclic compounds decreased when the crude polymer M_w was increased. For the parent metallocenes, polymers containing up to 50% low-molecular-weight cyclics in the raw material were observed. However, with the substituted metallocenes, the cyclic oligosilane component could be reduced to between 10 and 20% while the polymer molecular weight, i.e., the amount of larger linear polysilanes, increased. This suggested that substituted zirconocene catalysts in particular disfavored the production of low-molecular-weight cyclic oligosilanes.

Catalyst Loading. Two different catalyst concentrations of 1.0 and 0.5 mol % in neat phenylsilane were examined to determine whether the catalyst loading had any effect on the M_w value and the properties of the polysilane produced. In all cases, both catalyst loadings gave polysilanes of similar molecular weights and the relative monomer consumption remained constant within experimental error. Furthermore, the $^{29}Si\{^1H\}$ NMR profiles (see below), depicting the tacticity characteristics of the silicon framework, were very similar, indicating that the alteration of the catalyst loading had little impact on the performance of the active species in terms of polymer microstructure as well as molecular weights.

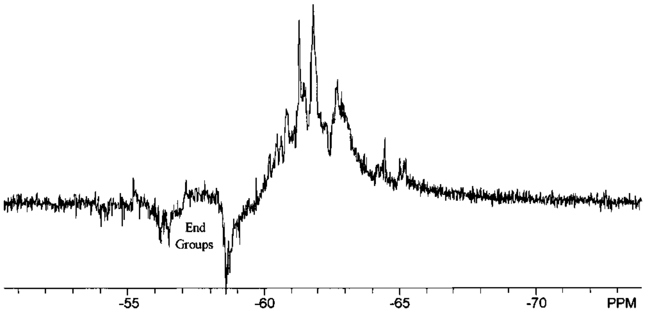

Figure 1. $^{29}Si\{^1H\}$ DEPT 135° NMR of low-molecular-weight atactic polysilane. The spectrum was obtained from a polysilane sample generated using $(Cp^R)_2TiCl_2$ as a precatalyst.

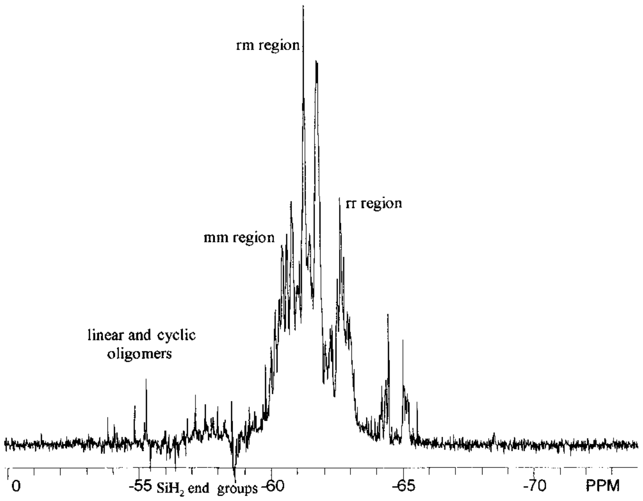

Figure 2. $^{29}Si\{^1H\}$ DEPT 135° NMR of higher molecular weight polysilane. The spectrum was obtained from a polysilane sample generated using $(Cp^R)_2ZrCl_2$ as a precatalyst and is believed to represent a mostly atactic polysilane with a minor syndiotactic bias.

Polymer Microstructure by NMR Analysis. To probe the effects of the various catalysts on the microstructure of the polyphenylsilane, $^{29}Si\{^1H\}$ DEPT 135° spectroscopy of each crude polymer sample was examined with optimization to display secondary silane centers phase-shifted by 180°.[13] The $^{29}Si\{^1H\}$ profile obtained was found to depend mostly on the metal used. Titanium-based catalysts produced phenylsilane polymerizates with broad, poorly defined spectra in which the $R^1-[PhSiH]_n-R^2$ region ranged between −54 and −64 ppm (Figure 1), similar to the results previously established by Harrod et al.[14] However, polymers generated from zirconium catalysts typically displayed a spectrum of significantly greater resolution over two distinct ranges from −59 to −63 ppm and a lower intensity region from −65 to −66 ppm (Figure 2). In a related analysis by Jones, the latter region has been

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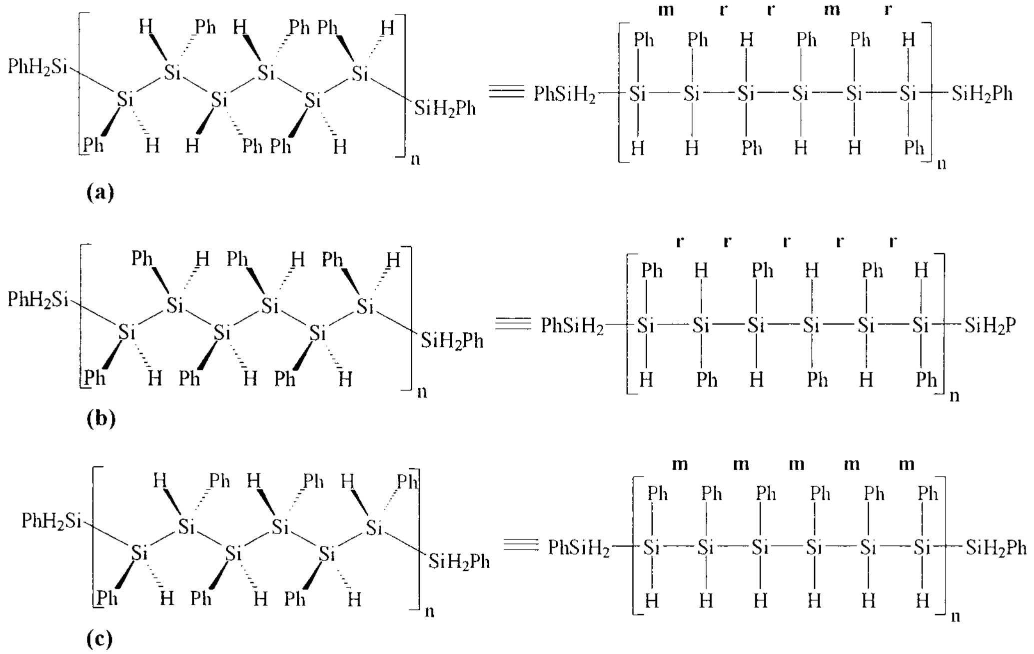

Figure 3. (a) Linear atactic polyphenylsilane. (b) Linear syndiotactic polyphenylsilane. (c) Linear isotactic polyphenylsilane.

associated with β-silyl centers.[15] Additionally, the DEPT sequence highlighted that the out-of-phase SiH_2 end groups of the polymers came into resonance at −56 and −58 ppm, in agreement with the results previously reported by Harrod and Waymouth.[11,14]

In the case of linear polyphenylsilane, three major polymer microstructures are possible, depending on the arrangement of consecutive stereochemical configurations of silicon atoms: atactic (Figure 3a), syndiotactic (Figure 3b), and isotactic (Figure 3c).[16] A random distribution of configurations or atactic backbone would be expected to display a broad $^{29}Si\{^1H\}$ NMR spectrum containing at least three separate areas representing rr, mr, and mm stereodistributions in a ratio of 1:2:1. A stereoregular microstructure would be predicted to display a simplified spectrum with respect to the above distribution or a modified distribution containing enhanced rr or mm intensities which are respectively associated with syndio- and isotactic stereoarrangements.[17] An additional possibility is that each triad region could be separated into a more complicated substructure which represents sensitivity to higher order sequencing of the polymer microstructure: i.e., refinement of the **rr** resonance (a triad level arrangement) to a collection of r**rr**m type resonances (a pentad level arrangement).

In addressing the complexity of the polymer spectra produced from Ti systems, it appeared that the quality of the spectra obtained is dependent on the proportion of oligomeric products present (Figure 1). For Ti-mediated dehydropolymerizations, a large quantity of cyclics and oligomers were formed, as established by GPC analysis. Overall, the more oligocyclic and oligomeric materials present, the lower the definition and the greater the width of the $^{29}Si\{^1H\}$ NMR profile obtained. As a consequence, complete spectroscopic analysis of such a sample is not possible at present, other than to suggest an atactic structure for the polymer morphology on the basis of the large number of ^{29}Si environments indicated to be present. Additionally, the comparison to a 90% linear polymer sample suggests that the higher molecular weight linear materials appear to be responsible for the majority of the upfield resonances (−59 to −63 ppm).

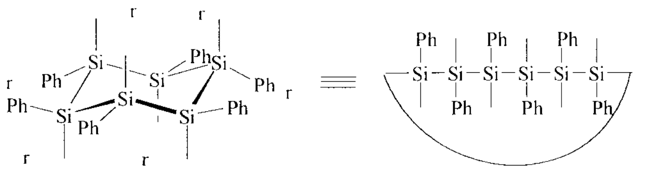

Figure 4. *all-trans*-$Ph_6Si_6H_6$. The equatorial disposition of the phenyl groups on each of the pseudochiral silyl centers generates opposite configurations at adjacent silicon atoms. This racemic relationship between the neighboring atoms results in rrrr stereoregulation throughout the molecule.

One further feature of the cyclic components was that of the sharp singlet at $\delta \sim -61$ ppm which corresponded to that observed in the all-trans conformer of the cyclic silane $(SiPhH)_6$ originally isolated by Hengge.[18] Waymouth suggested that the resonance be assigned to a syndiotactic succession of silicon atom configurations presumably at the pentad (rrrr) level because the six silicon sites in the all-trans cyclic isomer possess a syndiotactic relationship (Figure 4).[11] Upon observation of a polyphenylsilane $^{29}Si\{^1H\}$ trace obtained from metallocene-catalyzed dehydropolymerizations which was essentially identical with that in Figure 2, Waymouth intuitively assigned this spectrum to a syndiotactic polysilane array on the basis that a resonance at $\delta \sim -61$ ppm was obtained. A similar assignment was

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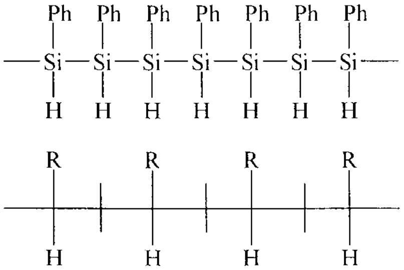

Figure 5. Schematic comparison of poly(phenylsilane) and a poly(olefin).

also made more recently by Tanaka et al. for $PhSiH_3$ condensation using substituted metallocenes.[5i]

The degree of resolution of differing arrangements of chiral centers in $R^1-[PhSiH]_n-R^2$ may be greater than or at least comparable to those associated with polyolefin chemistry ($-[CHRCH_2]_n-$). In contrast to the polyolefin, there is no achiral methylene spacer separating each chiral unit in the polysilane; rather, the chiral units are adjacent to one another (Figure 5). One possible outcome of adjacent chiral centers is that the chemical environment and therefore the chemical shift of each ^{29}Si nucleus throughout the polymer backbone is subject to a greater variation, which ultimately generates a more complicated series of $^{29}Si\{^1H\}$ resonances. Although this could prove beneficial in a more complete study of the stereosequencing, at present it is not possible to designate each of the resonances detected. At the heptad level, a maximum of 36 lines would be predicted, while only 10 resonances would be possible for a pentad tier of resolution.[19] In the polysilane spectrum shown in Figure 2, at least 20 resonances were observed.

GPC and ^1H NMR analysis of the polyphenylsilanes obtained using Zr catalysts indicated that predominantly (80−90%) linear polymers were formed (Table 1). The $^{29}Si\{^1H\}$ NMR spectrum observed from these samples was of a shorter range (−59 to −63 ppm) than polysilanes obtained from Ti-based catalysts. This spectrum has been previously associated with a syndiotactic microstructure solely on the basis of the presence of the presumably all-racemic signal at −61 ppm. However, it is difficult to rationalize the numerous remaining signals purely on the assumption that only rr-based structures are responsible for all of these resonances even at higher levels of resolution: e.g. a heptad level. It appears reasonable to suggest that substructural resonances for each family of stereosequences (mm, rm, rr) are all present and are merely coincident or partially overlapping in chemical shift. As a result, the hybrid signal generated cannot be readily interpreted unless the signals are deconvoluted or the different microstructures somehow separated.

We attempted to establish if any stereochemical runs were present and evaluate the intensity of each stereochemical domain by deconvolution of the polyphenylsilane spectrum obtained when using $(Cp^R)_2ZrCl_2$ as the precatalyst. ^{29}Si deconvolution techniques were also investigated recently by Jones et al. in describing the stereochemistry of unsymmetrical poly(dialkyl)silanes.[15] The spectrum utilized was that of a higher molecular weight polysilane sample ($M_w \approx 4000$) and a linear fraction of greater than 90%. Oligomeric and oligocyclic components tend to overcomplicate the spectrum and need to be removed in order to provide a more accurate gauge of the relevant peak intensities for the polymeric species. The linear portion of the ^{29}Si profile (δ −59 to −63 ppm) was analyzed as the summation of 20 resonances, and the optimized summation spectrum matched to the observed spectrum within 1.30%. The chemical shifts and intensities obtained are listed in Table 3, and a comparison of the real and simulated spectra is presented in parts a and b, respectively, of Figure 6. The individual deconvolution peaks and difference spectrum of the real and simulated spectra are also provided in parts c and d, respectively, of Figure 6.

Table 2. Parameters for the $^{29}Si\{^1H\}$ DEPT 135° Deconvolution Spectrum[a]

line	δ (ppm)[b]	rel intens	line	δ (ppm)[b]	rel intens
1	−59.785	8.999	11	−61.282	74.608
2	−59.977	12.773	12	−61.474	24.095
3	−60.156	18.289	13	−61.768	69.673
4	−60.309	18.580	14	−62.075[c]	9.290
5	−60.437	30.192	15	−62.280[c]	15.386
6	−60.604	29.901	16	−62.523	18.870
7	−60.796	41.116	17	−62.651	40.933
8	−61.000[c]	17.999	18	−62.779	23.515
9	−61.090[c]	17.418	19	−62.894	16.531
10	−61.218	19.450	20	−63.022	16.107

[a] The summation spectrum of the deconvolution peaks matches the actual spectrum to within 1.3%. [b] The actual $^{29}Si\{^1H\}$ 135° DEPT spectrum was obtained in C_6D_6 and referenced externally. [c] Peaks which were varied in assignment.

Table 3. Triad Assignments and Peak Intensity Ratios[a]

entry	chem shift range (ppm)	parent peak intens	unit ratio	Bernoullian predicted ratio	Pm, 1-Pm
rr	−59.79/−60.80	159.85	0.31	0.30	0.45, 0.55
mr	−61.00/−62.28	247.92	0.47	0.50	
mm	−62.52/−63.02	115.96	0.22	0.20	

[a] The values in the table were generated when the four variable peaks were included as mr type resonances. The largest deviation in unit ratios of rr:mr:mm for predicted Bernoulli ratios was 0.37: 0.41:0.22. This corresponds poorly to a Bernoulli ratio of 0.35:0.48: 0.17 with Pm = 0.41 and 1-Pm = 0.59. Parent peak range (intensity): rr, −59.79/-60.80 (159.85); mr, −61.218/−61.77 (187.83); mm, −62.52/−63.02 (115.96). Variable peaks (intensity): a, −61.00 (18.00); b, −61.09 (17.42); c, −62.08 (9.29); d, −62.280 (15.39).

The fit between the real and calculated spectra was sufficiently close, as demonstrated by the difference spectrum of the two (Figure 6d), so that informative quantitative results could be extracted. Initially 16 of the 20 deconvolution peaks were designated to one of the three chemical shift regions, which were assigned from low to high field as mr, rr, and mm domains, on the basis of the original assignment made by Waymouth et al.[11] At present it has not been possible to reliably assign each resonance occurring in the spectrum; consequently, the peak intensities within each region were then summed to generate essentially three simplified “parent” peaks. This would effectively correspond to the triad stereodistribution used previously to evaluate stereoregularity in polysilanes.[15,16]

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(19) (a) Bovey, F. A. In *Chain Structure and Conformation of Macromolecules*; Academic Press: New York, 1982. (b) Bovey, F. A. In *Polymer Conformation and Configuration*; Academic Press: New York, 1969.

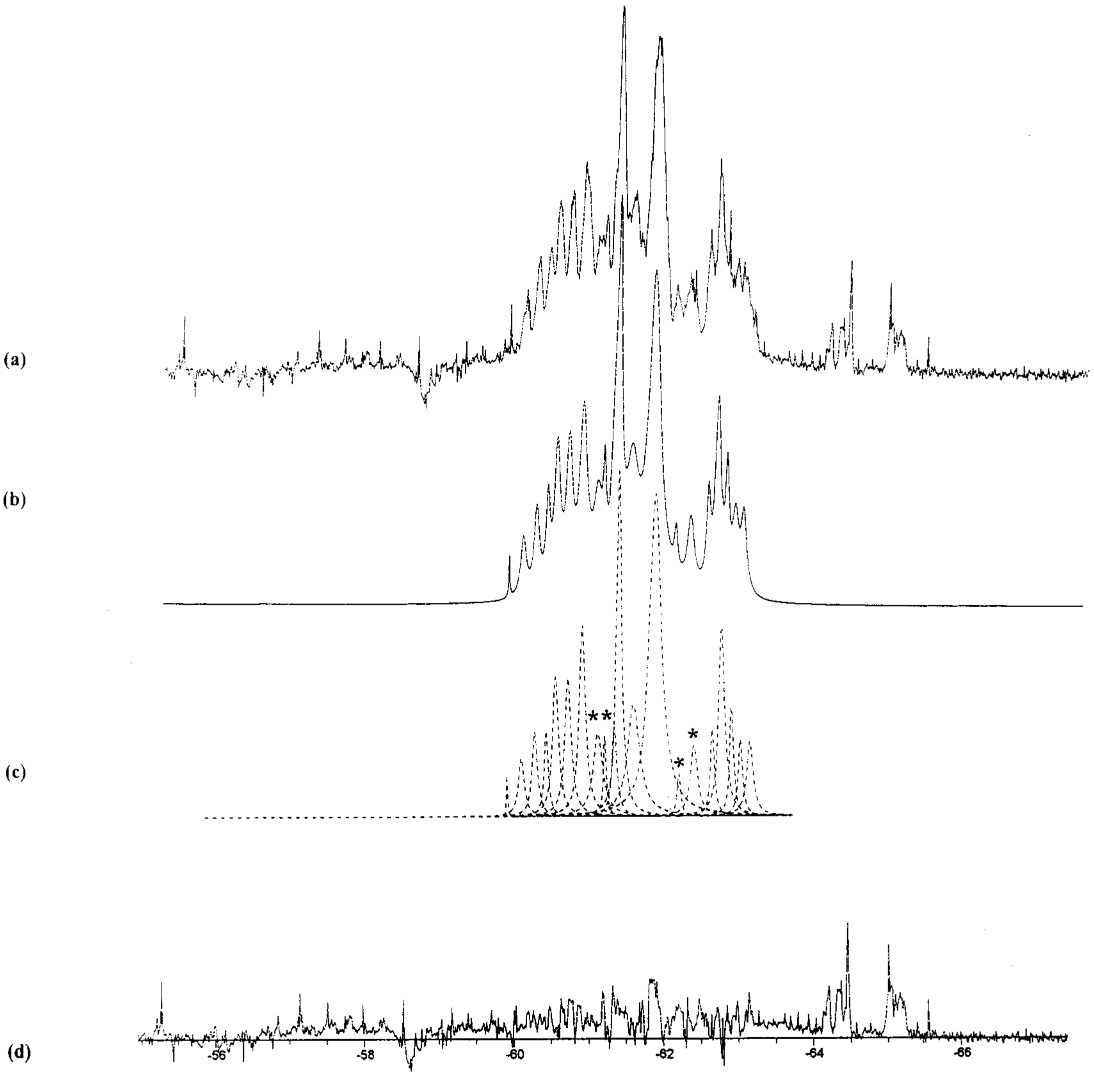

Figure 6. (a) $^{29}Si\{^1H\}$ DEPT 135° NMR of higher molecular weight linear polysilane. The polysilane sample was obtained using $(Cp^R)_2ZrCl_2$ as a precatalyst. The peaks indicated for the SiH_2 end groups appear phase-shifted by 180° and downfield among residual oligomeric signals. The rr, mr, and mm sequences are proposed to be located progressively further upfield throughout the main body of resonances (δ −59 to −63 ppm). (b) Simulated $^{29}Si\{^1H\}$ DEPT 135° spectrum. The simulation was obtained as a summation of 20 separate peaks and matches the actual spectrum in (a) to within 1.30%. (c) Deconvolution peaks of (b). The peaks marked with an asterisk represent the four peaks which were varied in assignment in order to establish the final intensity of each triad region. (d) Difference spectrum. The difference spectrum of (a) and (b) illustrates the close fit between the real data and summation data of the $^{29}Si\{^1H\}$ DEPT 135° polyphenysilane profile.

The four remaining peaks (indicated in Figure 6c and Table 2) were located at the border of each region and were systematically combined with the core peaks to determine a range of possible parent peak intensities. From these data, a range of peak ratios was determined and the ratios were compared assuming a Bernoullian distribution model for stereosequencing, with a mr, rr, mm chemical shift distribution. However, the ratios failed to suitably match a Bernoulli model in any respect; e.g., for addition of all four peaks to the rr block, the ratio obtained is 0.31 (mr):0.47 (rr):0.22 (mm). Thus, it was concluded that either the stereoreplication follows a non-Bernoullian pattern or the peak labeling was incorrect. The peak assignment was then reorganized to conform to the more traditional order developed in polyolefin chemistry, where the atactic triad (mr) is associated with the central resonances of the spectrum. For the polysilane spectrum in Figure 2, this would correspond to the signals from δ −61.22 to −61.77 ppm. The rr sector arbitrarily was assigned between δ −59.79 and −60.80 ppm and the mm to between δ −62.52 and −63.02 ppm. The three regions are labeled in Figure 2 and are omitted in Figure 6 for clarity. Under this regime, the spectrum was then found to conform reasonably well to a Bernoulli statistical pattern. When the four indeterminate chemical shifts were included in the central mr resonance, the overall ratio between the three regions rr:mr:mm was 0.31:0.47:0.22. As indicated in Table 3, the best fit between the observed data and the Bernoulli model occurred with a meso probability (Pm) of 0.45 and thus a racemo probability (Pr = 1-Pm) of 0.55. In this scenario, the expected intensities were 0.30:0.50:0.20, indicating only a slight bias (~10%) in favor of a syndioregular morphology and a mostly atactic polyphenylsilane microstructure.

Significantly, a related treatment was employed by Bovey et al. in the assignment of stereochemistry to poly(methyl-*n*-hexylsilane).[10] With the central bank of mr resonances flanked by the meso and racemic sequences, a Bernoullian propagation model indicated that there was no clear stereoreplication throughout the polymer chain.[17] However, it is also noted that Matyjaszewski and West independently provided evidence for alternative chemical shift assignments.[16]

The arbitrary assignment of rr resonances to the downfield domain and the mm resonances to the upfield area could also be reversed, and thus, an isotactic preference would ensue with 55% isoregulation. However, syndiogrowth is suggested, since this is consistent with the literature[5i,11] and would then require rr resonances to be located downfield, as shown in Table 3 and Figure 2. At any rate, this spectroscopic evidence (Figures 2 and 6) tentatively suggested that one mechanism in effect did lead to a very low degree of stereocontrol of the growing chain. Overall though, it appeared that, at a *triad Bernoullian level*, the polysilane was mostly atactic and that the processes which generate this particular ^{29}Si{^{1}H} spectrum are occurring without significant dictation of *successive* stereochemical centers. It remains possible that more in-depth studies of such spectra would indicate more subtle stereochemical replications that are not detectable by a Bernoullian type analysis. However, these methods will require absolute individual peak assignments which remain outside the scope of this discussion.[17,19]

Conclusion

The substituted metallocene dichlorides $(Cp^{R})_2MCl_2$ ($M = Ti, Zr$) and $Cp(Cp^{R})MCl_2$ ($M = Ti, Zr$) were active in the dehydropolymerization of phenylsilane to polyphenylsilane when combined with 2 equiv of *n*-BuLi. The polymerizates obtained were of moderate molecular weights whose values were dependent on the degree of metallocene substitution and the metal used. Since higher substituted metallocenes produce the more desired linear polysilanes and Zr catalysts give higher molecular weight products than Ti, future work should therefore center on the development of suitably substituted zirconium precatalyst systems.

Substituted zirconocene catalysts gave the largest polysilanes which were proposed to contain a minor syndioregular bias as established by the deconvolution of ^{29}Si{^{1}H} NMR spectrum for the corresponding polyphenysilane. From a Bernoullian statistical analysis, the probability of a racemic stereoreplication (1-Pm) was 0.55, which indicated that the microstructure was mostly atactic. A chain-end control mechanism could account for the small syndioselectivity (~10%) encountered and, if so, the nature of the catalyst (chiral or achiral) would have little or no effect on the stereochemical outcome of the growing chain. The development of an effective stereoselective process for the dehydropolymerization of primary silanes should therefore also focus on areas other than the identity of the catalyst.

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