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Synthesis and Characterization of Atactic Poly(*p*-tolylsilane) via the Catalytic Dehydrocoupling of *p*-Tolylsilane[1]

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The primary silane *p*-TolSiH$_3$ (*p*-Tol = *p*-CH$_3$C$_6$H$_5$) can be polymerized to poly(*p*-tolylsilane) with 1.0 mol % of both the chiral and achiral zirconocenes Cp$_2$ZrCl$_2$, Cp(Cp^{Si}*)ZrCl$_2$, and (Cp^{Si}*)$_2$ZrCl$_2$ (Cp = C$_5$H$_5$, Cp^{Si}* = C$_5$H$_4$Si(CH$_3$)$_2$-(1*R*)-*endo*-(+)-OC$_{10}$H$_{17}$) in combination with 2.0 mol % of *n*-BuLi. Generally, higher molecular weight linear polymers were obtained when using the substituted zirconocenes in comparison to the parent zirconocene, which in turn produced larger quantities of low-molecular-weight cyclic products. Each polysilane sample was analyzed by ^{29}Si{^{1}H} DEPT and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. Deconvolution of selected regions of the ^{29}Si{^{1}H} DEPT and the ^{1}H NMR spectra for higher molecular weight linear polymers indicated that these catenates were predominantly atactic, on the basis of a triad level Bernoullian statistical model. The data suggested that, in this case, chiral substitution of the zirconocene rings had no effect on the stereogrowth of the polysilane chain.

Introduction

Polysilanes are macromolecules comprised solely of Si−Si covalent bonds. One property of these polymers is $\sigma-\sigma^*$ electron delocalization which extends throughout the backbone of the polysilane chains.[2] This unusual feature is believed to be responsible for many of the useful physical properties of polysilanes and has led to investigations of their potential technical applications.[2] Polysilanes can be utilized as photoresists in microlithography, as additives for the stabilization of polypropylene, and as precursors to SiC ceramics.

Polysilanes are most commonly synthesized by thermal,[3] sonic,[4] or electrochemical[5] Wurtz-type coupling of organochlorosilanes in the presence of an alkali metal. However, the reliable production of a polysilane with exact molecular weight properties from this method has met with limited success. Generally, the average molecular weight properties cannot be adequately controlled; polymers of high polydispersity and variable degrees of polymerization (D_p) are obtained. Furthermore, when using a prochiral monomer, effective stereoregulation of the resulting polysilane microstructure has not yet been achieved.[6]

An alternative methodology introduced by Harrod involves the catalytic dehydropolymerizion of primary silanes in the presence of a catalytic amount of a group 4 metallocene.[7] Catalytically active species can be obtained from a number of metallocene precatalysts in the presence of the silane monomer, the most common being Cp$_2$M(CH$_3$)$_2$ (M = Ti, Zr),[8] CpCp*M[Si(SiMe$_3$)$_3$]R (M = Zr, Hf; R = Me, Cl),[9] Cp$_2$MCl$_2$/2 *n*-BuLi (M = Ti, Zr, Hf),[10] and Cp$_2$MCl$_2$/2 *n*-BuLi/2 B(C$_6$F$_5$)$_3$ (M = Zr, Hf).[11] Polysilanes with D_p < 80 have been generated

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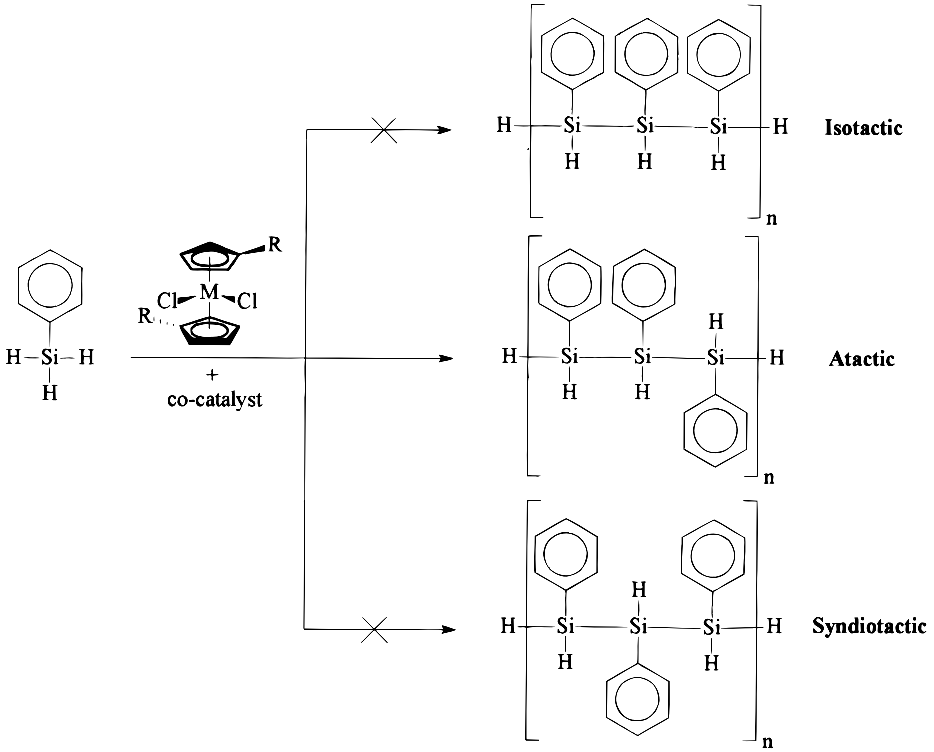
Scheme 1



from group 4 metallocene catalysts depending on the nature of the catalyst system, with Zr-based catalysts most commonly generating higher order polymers. Additional preliminary work has shown that other transition-metal systems can be used as dehydrocoupling catalysts. The combination catalyst systems $Cr(CO)_6$/Red-Al[12a] and $(1\text{-MeInd})(PPh_3)NiCl_2$/MAO (1-MeInd = 1-methylindenyl; MAO = methylaluminoxane)[12b] have both proven to be successful catalysts for the dehydropolymerization of primary silanes.

Recently, group 4 metallocenes have been successfully used for the polymerization of prochiral olefins to stereoregular polyolefins with controlled average molecular weight properties.[13] Thus, transition-metal-mediated procedures offer a possibility for the efficient synthesis of polysilanes. By the implementation of such catalysts to generate polysilanes from prochiral monomers, such as $PhSiH_3$, it may be possible to regulate the stereochemistry of a propagating chain and produce syndiotactic or isotactic polymers.[14] Previous reports by Waymouth et al.[15] and Tanaka and co-workers[16] suggested that the substituted-zirconocene catalysts $(EBTHI)ZrCl_2$/2 *n*-BuLi and $Cp^*(Cp^N)ZrCl_2$/2 *n*-BuLi (EBTHI = ethylenebis(tetrahydroindenyl); $Cp^* = C_5(CH_3)_5$, $Cp^N = CH_2CH_2NMe_2$) produced syndiotactic polyphenysilane $H(PhSiH)_nH$. This assignment was made upon analysis of fractionated polymer samples by $^{29}Si\{^1H\}$ DEPT NMR spectroscopy. However, continued investigation of the $^{29}Si\{^1H\}$ DEPT NMR spectra for similarly prepared polyphenylsilane (PPSi) samples by Corey and Grimmond[17] and by Harrod et al.[18] indicated that the spectrum originally proposed to represent a syndiotactic polymer was in fact that of the atactic polyphenylsilane [*a*-PPSi]. These investigations demonstrated that the group 4 metallocenes which have currently been reported as dehydropolymerization catalysts produced only *a*-PPSi (Scheme 1)

This report discusses the extension of metallocene-catalyzed dehydropolymerization in an attempt to influence the stereogrowth of a polysilane chain through the alteration of the structure of the monomer as well as the catalyst (Scheme 2). The dehydropolymerization of

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(14) For pseudochiral polysilanes, such as poly(*p*-tolylsilane), each silicon atom of the polymer chain is a stereogenic center. The stereochemical arrangement of adjacent Si centers dictates the degree of stereoregularity (also called tacticity) of the polymer chain. Isotactic and syndiotactic stereoregular polysilanes respectively arise from the repeating and alternating arrangement of adjacent Si centers. An atactic polysilane refers to the random arrangement of adjacent Si centers. See ref 23 for a complete description.

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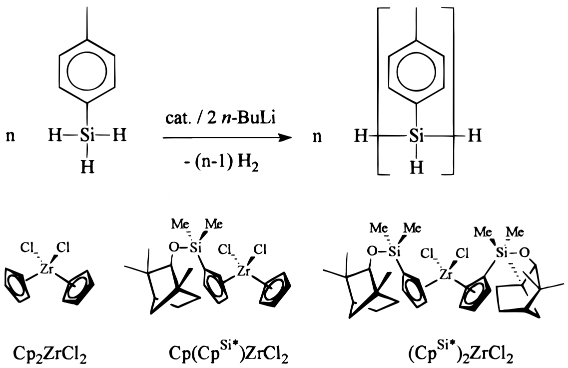
Scheme 2



p-TolSiH$_3$ (*p*-Tol = *p*-CH$_3$C$_6$H$_4$) rather than PhSiH$_3$ was expected to improve the solubility of the polysilane product in common non-chlorinated solvents such as benzene and thus facilitate the spectroscopic studies of the polymer.[19] Furthermore, the inclusion of the *p*-Tol methyl group offered a potentially convenient analysis of polymer tacticity via ^{1}H and ^{13}C{^{1}H} NMR spectroscopy rather than the current route of ^{29}Si{^{1}H} NMR spectroscopy, which requires high sample concentration and extensive periods of data collection. The determination of the general applicability of the ^{29}Si{^{1}H} deconvolution techniques, which had been successfully used to identify *a*-PPSi, to the related poly(*p*-tolylsilane), PTSi, was also anticipated. The chiral functionalized zirconocenes (Cp^{Si*})$_2$ZrCl$_2$ and Cp(Cp^{Si*})ZrCl$_2$ (Cp^{Si*} = C$_5$H$_4$Si(CH$_3$)$_2$-(1*R*)-*endo*-(+)-OC$_{10}$H$_{17}$)[20] were examined as catalyst precursors in comparison to the corresponding parent zirconocene dichloride combination [(Cp)$_2$ZrCl$_2$/2 *n*-BuLi] (Scheme 2). Sequential substitution of the catalyst framework with enantiopure chiral substituents (Cp^{Si*}) was intended to determine the impact of chiral catalysts on the propagating polymer tacticity as well as the steric effects of catalyst functionalization on the molecular weight properties of the polymer obtained.

Results and Discussion

Dehydropolymerization of *p*-TolSiH$_3$ to PTSi. A series of chiral and achiral zirconocenes were investigated as dehydropolymerization catalysts for the synthesis of PTSi. This generally involved activation of the precatalyst (1.0 mol %) at ambient temperature in neat, distilled, degassed *p*-TolSiH$_3$ by addition of *n*-BuLi (2.0 mol %). Stirring for up to 72 h provided an immobile gum, at which point the catalyst was deactivated by exposure to the atmosphere. The crude polymer sample was then isolated from the catalyst residue by dissolution in THF followed by filtration through Celite. Removal of the volatiles afforded an off-white gum in high yield (>80%). PTSi could be purified by washing with cold pentanes and drying in vacuo to afford a glasslike solid in lower yield (ca. 60%). Pentanes removed impurities such as Bu(*p*-Tol)SiH$_2$ and any residual (*p*-Tol)SiH$_3$ monomer, but a portion of the polymer product, which is moderately soluble in hydrocarbon solvents, was also lost during this process. Low-molecular-weight polysilanes were obtained as colorless oils upon purification by this method. Both *a*-PPSi and PTSi are soluble in ethereal solvents such as THF, but only PTSi is significantly soluble in hydrocarbon solvents such as pentanes.

Table 1. GPC Molecular Weight Data for the Catalytic Dehydropolymerization of *p*-TolSiH$_3$ to *a*-LPTSi

entry[a]	M_w[c]	M_n	PD	D_p[c]	L/C	time (h)	λ_{abs} (nm)	convrsn (%)[d]
Cp$_2$ZrCl$_2$[b]	2300	1600	1.4	20	2.3	24	292	100
Cp(CpSi*)ZrCl$_2$[b]	3000	1700	1.8	21	4.0	72	292	100
(CpSi*)$_2$ZrCl$_2$[b]	2200	1600	1.4	21	2.0	24	290	94
(CpSi*)$_2$ZrCl$_2$[b]	4000	2000	2.0	25	5.6	72		100

[a] Catalyst loading of 1.0 mol %. [b] Catalyst activated with 2.0 mol % of *n*-BuLi. [c] $D_p = 2[M_n/104][r(C)/r(Si)]$.[9a] r(C) = 77.3 pm, r(Si) = 117.0 pm. Cf.: Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press; Ithaca, NY, 1960; p 260. [d] Conversion of the monomer.

The molecular weight properties of the PTSi polymerizates obtained using the precatalysts (Cp)$_2$ZrCl$_2$, Cp(Cp^{Si*})ZrCl$_2$, and (Cp^{Si*})$_2$ZrCl$_2$ were analyzed by GPC relative to polystyrene standards, the results of which are presented in Table 1. In all cases, a bimodal molecular weight distribution was observed, which is indicative of the presence of linear and oligocyclic PTSi. This was also confirmed by ^{1}H NMR spectroscopy, where the Si−H protons of the linear and cyclic products could be distinguished by chemical shift (see below). The parent zirconocene catalyst produced PTSi (M_w = 2275, PD = 1.4) with the lowest degree of polymerization (D_p = 20) due to the relatively large amount of low-molecular-weight oligocyclic materials which were present (linear/cyclic ratio (L/C) = 2.3). The average molecular weight of the PTSi obtained can be moderately increased by employing a substituted catalyst, which serves to suppress the formation of oligocyclic PTSi and thereby increases the amount of higher M_w linear poly(*p*-tolylsilane) (LPTSi) generated. This is illustrated by comparison of the molecular weight properties of the PTSi samples obtained using the functionalized catalyst systems Cp(Cp^{Si*})ZrCl$_2$ (M_w = 2979, L/C = 4.0) and (Cp^{Si*})$_2$ZrCl$_2$ (M_w = 4000, L/C = 5.6). Thus, progressive substitution of the catalyst framework (i.e. monosubstituted to heteroannular disubstituted) served to promote the formation of longer chain linear polymers but did so at the expense of the rate of dehydrocoupling, since extended reaction times (72 h) were necessary when using substituted catalysts. It should be noted that, for the parent zirconocene system, reaction times beyond 24 h did not produce higher M_w PTSi than that obtained at 24 h. These results illustrated the dependence of polysilane molecular weight properties on the degree of catalyst substitution.

The samples of PTSi with D_p > 18 were isolated as white glassy solids whose predominantly amorphous nature was established by X-ray powder diffraction. Differential scanning calorimetry (DSC) of several PTSi samples with D_p > 18 revealed no phase transitions from 25 to ~200 °C, where the polymers were subject to decomposition over a 30 °C range.[21]

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[19] The polymerization of *p*-TolSiH$_3$ has been very briefly described using Cp$_2$Zr(Si(SiMe$_3$)$_3$)Me[19a] and Cp$_2$ZrMe$_2$:[19b] (a) Banovetz, J. P.; Suzuki, H.; Waymouth, R. M. *Organometallics* **1993**, *12*, 4700. (b) Hashimoto, H.; Obara, S.; Kira, M. *Chem. Lett.* **2000**, 188.

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[21] Representative XRD and DSC spectra of PTSi are provided in the Supporting Information.

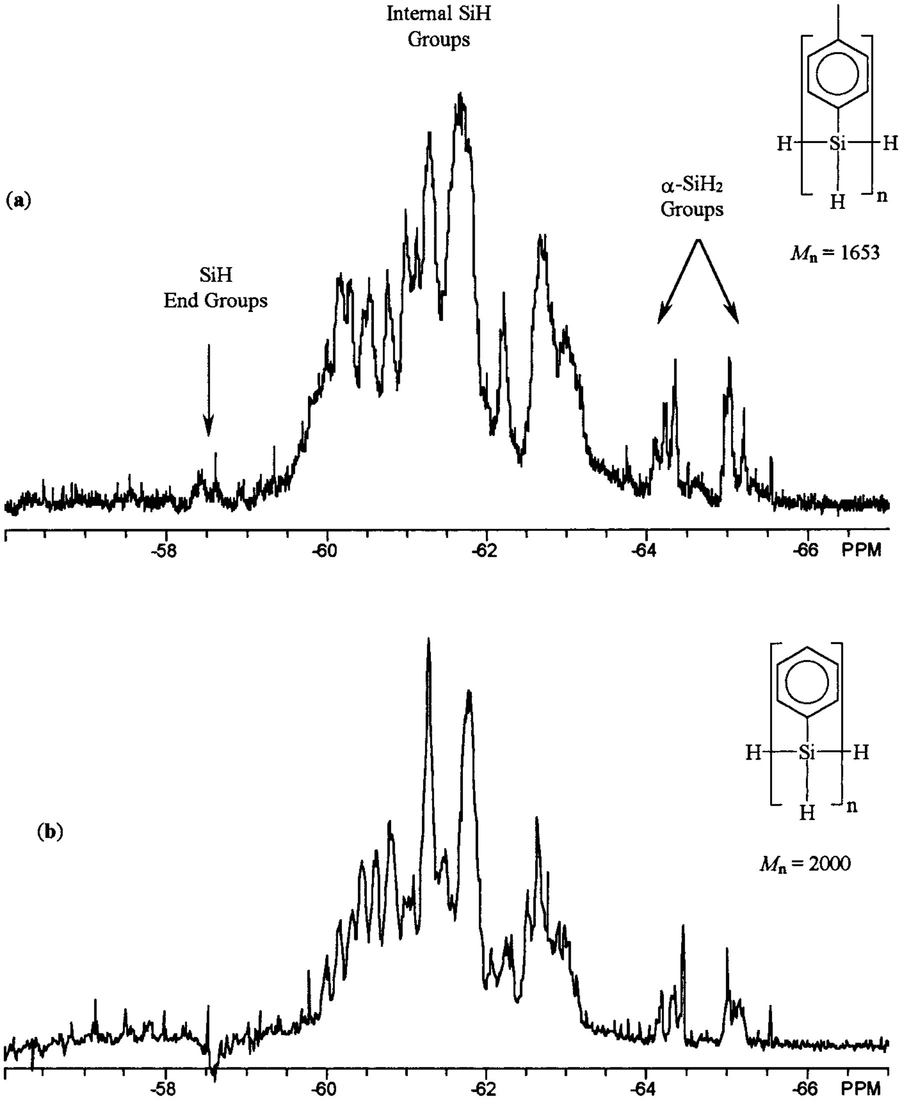

Figure 1. (a) $^{29}Si\{^1H\}$ DEPT NMR spectrum (99 MHz, 298 K) of linear PTSi ($M_n = 1653$) obtained from Cp(Cp^{Si}*)ZrCl$_2$/2 *n*-BuLi. The resonances for the SiH$_2$ end groups, α-SiH end groups, and internal SiH silicon centers are indicated with arrows. (b) $^{29}Si\{^1H\}$ DEPT NMR spectrum (99 MHz, 298 K) of *a*-PPSi ($M_n = 2000$). The atactic polysilane was generated using (Cp^R)$_2$ZrCl$_2$ (R = C(CH$_3$)$_2$CH(CH$_3$)$_2$ as the precatalyst.

Analysis of PTSi Polymer Morphology by NMR Spectroscopy. A predominantly linear PTSi sample ($M_w = 2979$, $M_n = 1654$) which was obtained from the precatalyst Cp(Cp^{Si}*)ZrCl$_2$ was analyzed by NMR spectroscopy in order to determine the polymer microstructure. A higher molecular weight LPTSi sample with low oligocyclic content was used for these experiments because oligomeric species tend to overly complicate the spectra obtained and make meaningful spectral analysis difficult.[17,18] A ^{29}Si CP-MAS (TOSS) solid-state spectrum revealed one broad Lorentzian peak (δ −50 ppm) and is provided in the Supporting Information. This was consistent with the presence of one major type of silicon environment and is proposed to represent the tertiary silane ($R^1R^2R^3SiH$) centers throughout the body of the PTSi chain. The secondary silane end groups were not detected by this method, and the observation of a single resonance provided no evidence for the presence of quaternary Si centers that would be associated with polymer cross-linking.

The $^{29}Si\{^1H\}$ DEPT 90° NMR solution spectrum (benzene-d_6) of linear PTSi is presented in Figure 1a in comparison to the established spectrum for atactic linear polyphenylsilane (*a*-LPPSi) of similar average molecular weight (Figure 1b).[17] While the two spectra in parts a and b of Figure 1 are not identical, as would be expected for two chemically distinct polymers, it is apparent that the spectra contain similar features. Samples of LPTSi contained three types of Si−H functional groups which could be readily detected by $^{29}Si\{^1H\}$ DEPT spectroscopy. As indicated in Figure 1a, the high-intensity region from δ −60.0 to −63.4 ppm contained numerous signals which represented the tertiary Si−H groups populating the main body of the PTSi chain. The tertiary Si−H centers in a position α to the SiH$_2$ polymer end groups (i.e. the α-Si−H groups) appeared characteristically upfield (δ −64.2 to −65.3 ppm) with respect to the remaining resonances and have been previously identified independently by Jones, Harrod, and West.[6,18] The chemical shift region for the SiH$_2$ end groups (δ −55.9 to −56.5 and −58.4 to −59.4 ppm) was most readily established by a $^{29}Si\{^1H\}$ DEPT 135° experiment for a second low-molecular-weight polymer sample of PTSi. In this case, the SiH$_2$ end group

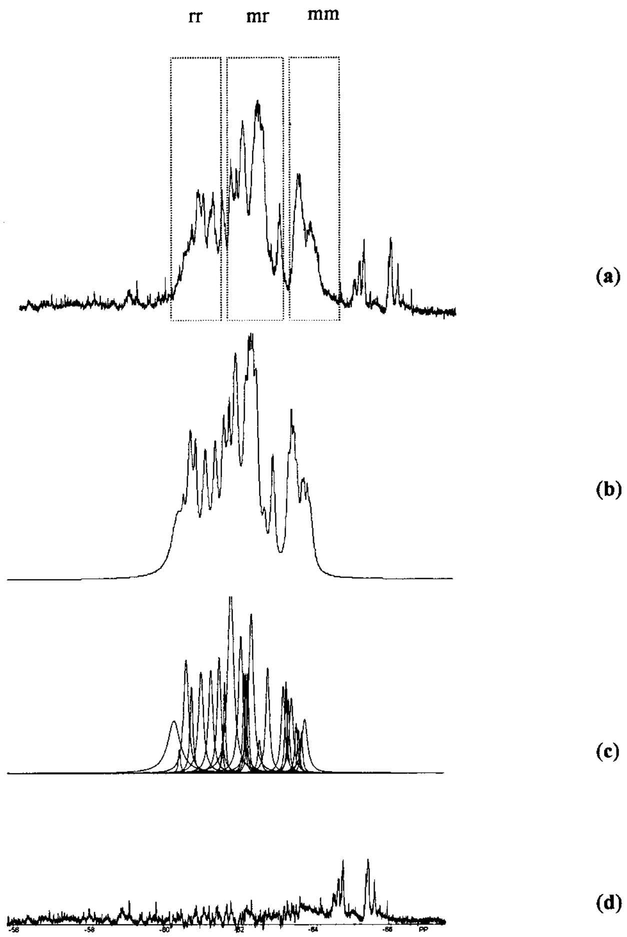

Figure 2. (a) ^{29}Si{^{1}H} DEPT NMR spectrum of linear PTSi (M_n = 1653) obtained from Cp(Cp^{Si}*)ZrCl$_2$/2 *n*-BuLi. For the tertiary SiH centers, the chemical shift regions corresponding to *rr*, *mr*, and *mm* triad level stereosequences are indicated. (b) Calculated tertiary SiH region of the ^{29}Si{^{1}H} DEPT NMR spectrum. (c) The 26 constituent peaks used to simulate the tertiary SiH region of the ^{29}Si{^{1}H} DEPT NMR spectrum. The intensity of the constituent peaks within each stereodomain (Figure 1a) were summed to obtain a triad level parent peak intensity for each stereodomain. The *rr* (0.28):*mr* (0.50):*mm* (0.22) ratio indicated that the polymer was effectively atactic (Pm = 0.47, 1-Pm = 0.53). (d) Difference spectrum of the real (a) and calculated (b) spectra, illustrating the good fit between the real and simulated data. The fitted spectrum matches the actual spectrum to within 0.5%.

chemical shifts appeared phase-shifted by 180° with respect to the remaining tertiary Si−H resonances and with greater relative signal intensity due to the lower degree of PTSi polymerization.

The degree of stereoregulation in LPTSi was estimated using deconvolution techniques which were identical with those previously described for *a*-LPPSi.[17a] For LPTSi, the tertiary Si−H region of the ^{29}Si{^{1}H} DEPT 135° spectrum consisted of a mixture of multiple overlapping signals which were deconvoluted to a series of 26 constituent peaks (Figure 2c). Upon optimization of the spectrum calculated from the composite peaks, the calculated spectrum matched the real spectrum to within 0.5%, as illustrated in Figure 2d by the difference spectrum of the two. Shown in Figure 2a, the Si−H region can be partitioned into three sections which contain the resonances associated with *rr*-, *mr*-, and *mm*-based stereodomains (triads).[22] The range of chemical shifts assigned to each triad region for LPTSi were adapted from the chemical shift ranges which were used previously in the analysis of poly(phenylsilane). Summation of the intensities of the constituent peaks which reside within an individual region provided a parent peak intensity for each region representing one of the three triad level stereosequences (i.e. *rr*, *mr*, *mm*). The information concerning the constituent deconvolution peaks is given in the Supporting Information. Table 2 provides a summary of the data pertaining to the calculated triad level parent peaks reflecting the contribution of each stereoarrangement to the overall microstructure of PTSi. The *rr*:*mr*:*mm* triad peak ratio of 0.28:0.49:0.23 closely followed the Bernoullian statistical pattern that would be expected for a largely atactic LPTSi sample.[23] With a meso stereoreplication probability (Pm) of 0.47 and a corresponding probability of racemic stereoreplication (1-Pm) of 0.53, the predicted PTSi triad ratio of 0.28:0.50:0.22 was in good agreement with the data obtained from the deconvolution of the actual LPTSi spectrum. The diad ratio [*r*]:[*m*] suggested that there was a 6% excess of [*r*] diads, which is slightly less than that observed for *a*-LPPSi. It was therefore concluded that the LPTSi microstructure contained no significant domains of stereobias and that the spectrum in Figure 1a was that of a predominantly atactic polysilane (*a*-LPTSi) with a small (∼6%) syndiotactic bias. The ^{29}Si{^{1}H} NMR spectrum of the PTSi sample obtained on use of the (Cp^{Si}*)$_2$ZrCl$_2$ precatalyst was also recorded and found to be practically identical with that obtained for the Cp(Cp^{Si}*)ZrCl$_2$ case. Deconvolution of this spectrum confirmed that the zirconocene bearing a chiral substituent in each Cp ring also produced *a*-PTSi.

Table 2. Triad Assignments and Peak Intensity Ratios of *a*-LPTSi

entry	chem shift range (ppm)	parent peak intens	unit ratio	Bernoullian predicted ratio	Pm (1-Pm)
rr	−60.20 to −61.34	238.93	0.28	0.28	0.47 (0.53)
mr	−61.4 to −62.56	421.65	0.49	0.50	
mm	−62.95 to −63.34	192.95	0.23	0.22	

Samples of *a*-LPTSi were also examined by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy in order to determine their applicability as alternative spectroscopic means for assessing the microstructure of a polysilane chain. The benzene-d_6 ^{1}H NMR spectrum of an *a*-LPTSi sample (as established by ^{29}Si{^{1}H} NMR spectroscopy) which was obtained from Cp(Cp^{Si}*)ZrCl$_2$/2 *n*-BuLi is shown in

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[22] The triad model of the polysilane chain describes the diastereomeric relationship between three adjacent Si stereogenic centers. For an isotactic polysilane, the diastereomeric relationship of the central Si atom to both neighboring Si centers is mesoid, labeled *mm*. For a syndiotactic polysilane, the diastereomeric relationship of the configuration of the central Si atom to both neighboring Si centers is racemic, labeled *rr*. For an atactic polysilane, the diastereomeric relationship of the configuration of the central Si atom to one neighboring Si centers is mesoid and racemic to the second neighboring center, labeled *mr*. In terms of NMR spectroscopy, separate resonances for the *rr*, *mr*, and *mm* stereoequences can be detected and thereby used as a gauge of polymer stereoregularity. See ref 23 for a complete description.

[23] (a) Bovey, F. A. In *Chain Structure and Conformation of Macromolecules*; Academic Press: New York, 1982. (b) Bovey, F. A. *High-Resolution NMR of Macromolecules*; Academic Press: New York, 1972. (c) Bovey, F. A. In *Polymer Conformation and Configuration*; Academic Press: New York, 1969.

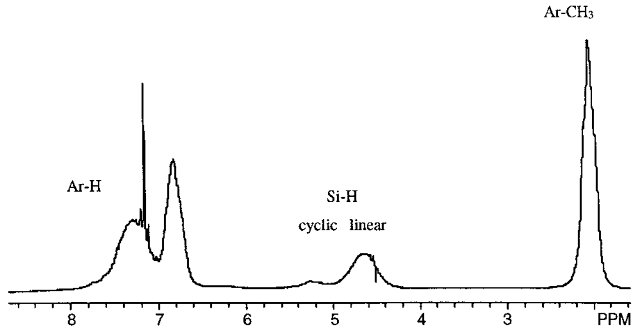

Figure 3. ^{1}H NMR spectrum (500 MHz, 298 K) of *a*-PTSi obtained from Cp(Cp^{Si*})ZrCl$_2$/2 *n*-BuLi with the Ar−H, Si−H, and Ar−CH$_3$ regions indicated. As shown, the Si−H region contains two broad signals, representing the linear (δ <5.0 ppm) and cyclic (δ >5.0 ppm) polysilanes.

Figure 3. The spectrum contained the three characteristic resonances for the aryl, Si−H, and methyl protons of the *a*-LPTSi in the appropriate ratio of 4.1:1.0:3.0, respectively. The resonance for Si−H protons of *a*-PTSi indicated that the polymer was mostly linear with a minor cyclic content (resonance appearing at δ >5.0 ppm), while the relative intensity of 1.0 suggested that there was no significant level of polymer cross-linking. The methyl group resonance was intended to be a probe of polymer tacticity and, at ambient temperature, demonstrated a broad central signal flanked by two lower intensity shoulder signals. This pattern was consistent with the presence of *rr*, *mr*, and *mm* type triad resonances, although the nearly coincident nature of the signals made it difficult to extract reliable information concerning their relative intensities by deconvolution techniques. However, at 346 K the inequivalent methyl resonances were sufficiently resolved that the hybrid signal could be replicated as a collection of three deconvolution peaks. A diagram of the methyl region for *a*-LPTSi at 346 K and the constituent deconvolution peaks is presented in Figure 4, with the corresponding data summarized in Table 3. The optimized calculated peak matched the actual hybrid peak to within 0.5% error, and the intensities of the three constituent signals were used as a gauge of the stereoarrangement within the *a*-LPTSI backbone. The three individual resonances shown in Figure 4 were assigned to the methyl groups of the *mm*, *mr*, and *rr* triad level stereoenvironments throughout the polymer microstructure. The unit ratio of the relative intensities for the triad resonances was 0.24:0.51:0.25, which closely matched the predicted ratio of 0.25:0.50:0.25 in the case where meso and racemic stereoreplication probabilities were equivalent; i.e., Pm = 1-Pm = 0.50. Therefore, assessment of the ^{1}H NMR spectrum for PTSi indicated that the polymer microstructure was completely atactic. This was in good agreement with the information obtained from the analysis of the polymer microstructure by ^{29}Si{^{1}H} NMR spectroscopy.

Attempts to characterize the atactic nature of the polysilane by ^{13}C{^{1}H} NMR spectroscopy were not successful. The methyl region of the *a*-PTSi spectrum for the sample analyzed by ^{1}H and ^{29}Si{^{1}H} NMR spectroscopy was composed of several overlapping peaks, including two major peaks of approximately equal intensity (a typical ^{13}C{^{1}H} NMR spectrum is included in the Supporting Information). This did not represent the established triad distribution of stereocenters within the polymer framework and suggested that ^{13}C{^{1}H} NMR spectroscopy could not be used for microstructural characterization of PTSi in this case.

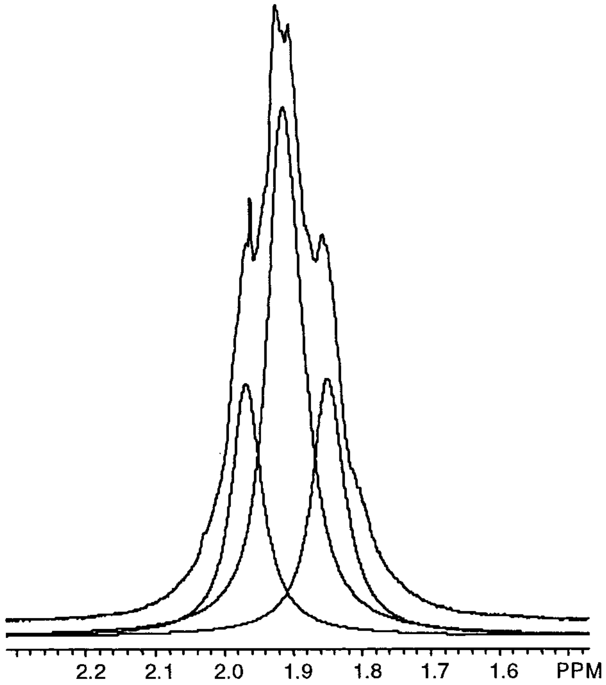

Figure 4. Selected Ar−CH$_3$ region of the ^{1}H NMR spectrum (500 MHz, 346 K) of *a*-PTSi obtained from Cp(Cp^{Si*})ZrCl$_2$/2 *n*-BuLi. The methyl resonance consists of three overlapping signals, which were proposed to correspond to the *rr*, *mr*, and *mm* stereosequences. The intensity of each stereodomain was approximated by deconvolution of the actual resonance using three constituent peaks as shown. The 0.24:0.50:0.26 ratio of the three constituent peaks obtained indicated that the polymer was atactic (Pm = 1-Pm = 0.5).

Table 3. ^{1}H NMR Data and Deconvolution of the Methyl Region in *a*-LPTSi

entry[a]	δ (ppm)	rel peak intens	unit ratio	Bernoullian predicted ratio	Pm (1-Pm)
rr[b]	1.85	40.02	0.24	0.25	0.50 (0.50)
mr	1.91	83.94	0.51	0.50	
mm[b]	1.97	40.87	0.25	0.25	

[a] The triad distribution predicted from the ^{1}H NMR spectrum at 298 K failed to replicate the ^{29}Si{^{1}H} data. The data provided were recorded at 346 K. [b] The *rr* and *mm* resonances were arbitrarily assigned as shown. These resonances could be switched without affecting the conclusions drawn from these data.

Conclusion

The zirconocene dichloride/2 *n*-BuLi combination catalysts (Cp)$_2$ZrCl$_2$, Cp(Cp^{Si*})ZrCl$_2$, and (Cp^{Si*})$_2$ZrCl$_2$ were active in the dehydropolymerization of *p*-TolSiH$_3$ to PTSi. Substitution of the catalyst Cp rings with chiral functional groups resulted in an increase in the average molecular weight properties of the linear polysilane product by inhibiting the formation of low-molecular-weight oligocyclic species. The tacticity of the linear polymer chains obtained was determined by deconvolution of the LPTSi ^{1}H and ^{29}Si{^{1}H} NMR spectra and was found to be atactic (*a*-LPTSi) for all polymer samples. The inclusion of the chiral functional groups within the zirconocene dichloride precatalyst was intended to modify the steric environment of the catalyst system and ultimately direct the stereogrowth of the polymer chain. However, the spectroscopic analysis of the resulting atactic polymer indicated that polymer propagation failed to occur by a mechanism of enantiomorphic site control.[24] The *p*-TolSiH$_3$ monomer proved to be a useful alternative to PhSiH$_3$ for the study of dehydropolymerization reactions. For example, the polymer generated, *a*-PTSi, was noted to be significantly more soluble in common solvents than *a*-LPPSi, making polymer characterization more convenient. Additionally, the methyl group of the *p*-Tol substituent was used as a marker to examine the polymer tacticity by ^{1}H NMR spectroscopy, although further exploration of the study reported here is necessary to confirm that the resonances for the Me probe correspond to the triad stereodomains. However, the main goal of this monomer choice was to establish if the choice of aryl ring affected the degree of stereocontrol of the ensuing polymer chain during dehydropolymerization. The rate of transition-metal-mediated reactions involving arylsilanes has previously been found to be dependent on the type of aryl group employed: e.g., phenyl vs *p*-Tol.[19a,25] The same rationale was employed here where a decrease in the rate of the reaction, presumably via the inductive effects of the *p*-Me substituent, would promote a greater level of stereoselection during the formation of each new polymer stereocenter. A similar approach has been employed by Waymouth and co-workers in the dehydropolymerization of functionalized primary arylsilanes with group 4 metallocene based catalysts.[19a] It was found that the degree of polymerization was associated with the choice of arylsilane, although no examination of the ^{29}Si{^{1}H} spectra and therefore polymer microstructure was presented. Zhu and Corey have previously found that aliphatic silanes such as *n*-BuSiH$_3$ encouragingly undergo diastereoselective metallocene-catalyzed dehydrocoupling but only oligomeric products were obtained.[26] Although there is evidence for the perturbation of the electronic character of the silicon center in arylsilanes by para substitution of the aryl ring,[27] it would seem that alterations to the primary aryl silane monomer, *p*-TolSiH$_3$ here, have no significant effect on the stereoregularity of the resulting PTSi.

Experimental Section

General Experimental Considerations. The chemicals *p*-TolSiCl$_3$ (Gelest) and LiAlH$_4$ (Aldrich) were purchased and used without further purification. Solvent purification and *n*-BuLi titration have been described previously. The metallocenes Cp(Cp^{Si*})ZrCl$_2$ and (Cp^{Si*})$_2$ZrCl$_2$ were prepared as previously described.[20]

Polymer samples were 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. Detection of the polymers was carried out using a Linear UV−vis detector set to 254 nm. Proton and silicon-29 (^{1}H, ^{29}Si) nuclear magnetic resonance spectra were recorded using a Bruker ARX500 equipped with a broad-band probe. Polymer ^{1}H spectra were recorded in C$_6$D$_6$ and referenced internally to the residual solvent peak or to TMS. The ^{29}Si{^{1}H} DEPT spectra were also recorded in C$_6$D$_6$ and referenced externally. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hertz. ^{1}H NMR used for accurate determination of signal ratios were run with a delay of 0.5−1.0 s to minimize the effects of the differential relaxation period. Unequal NOE suppression or enhancement of signal intensities was assumed to be negligible, as established for ^{29}Si signals of polysilanes.[28] Deconvolution of the ^{29}Si{^{1}H} DEPT spectrum was carried out using the NMR Utility Transform Software (NUTS) package from Acorn NMR.

Synthesis of *p*-TolSiH$_3$. A sample of *p*-TolSiCl$_3$ (98.5 g, 0.44 mol) was dissolved in Et$_2$O (250 mL) and cooled to 0 °C. Periodic addition of LiAlH$_4$ (5.0 g, 0.13 mol) in ~1 g batches over 1 h provided a gray suspension, which was stirred for 12 h, with gradual warming to room temperature. The reaction mixture was refluxed for 2 h, cooled to ambient temperature, and quenched by the addition of aqueous NH$_4$Cl. The crude reaction mixture was filtered and then washed with aqueous HCl (3 × 20 mL) and H$_2$O (2 × 20 mL). The organic layer was separated and dried over Na$_2$SO$_4$ and decanted to afford a colorless clear solution from which the volatiles were removed under reduced pressure. Kugelrohr distillation of the resultant yellow oil gave *p*-TolSiH$_3$ as a colorless liquid (34.8 g, 65%): bp 57−65 °C/6 mmHg (lit.[29] 59.6 °C/35 mmHg). ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ 7.45 (d, $^3J = 7.6$ Hz, 2 H) Ar *H*, 7.14 (d, $^3J = 7.6$ Hz, 2 H) Ar *H*, 4.17 (s, 3 H) Si*H*$_3$, 2.31 (s, 3 H) C*H*$_3$. ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 298 K): δ 140.04, 136.15, 129.21, 124.63 (Ar), 21.66 (*C*H$_3$). ^{29}Si{^{1}H} DEPT 90° NMR (99 MHz, CDCl$_3$, 298 K): δ −61.04 (s) *Si*H$_3$.

Synthesis of *a*-LPTSi. In a glovebox, a Schlenk tube was charged with Cp(Cp^{Si*})ZrCl$_2$ (0.033 g, 4.6 × 10^{-2} mmol) and transferred to a Schlenk line, where it was evacuated and then back-filled with N$_2$. A sample of *p*-TolSiH$_3$ (0.60 g, 4.6 mmol) was added, and the reaction mixture was degassed by three freeze−pump−thaw cycles. After the mixture was stirred for 5 min to provide a homogeneous solution, the precatalyst was activated by addition of 2 equiv of *n*-BuLi (0.037 mL, 9.2 × 10^{-2} mmol, 2.5 M). Bubbling was immediately observed with a gradual orange coloration of the reaction mixture over 12 h. After it was stirred for 48 h, the crude reaction mixture was quenched by exposure to air and dissolved in THF (5 mL). Filtration through Celite provided a clear colorless solution, from which the volatiles were removed under reduced pressure to give a slurry which was washed with cold pentanes (2 × 5 mL). Drying the residue in vacuo afforded *a*-LPTSi as a white glassy powder (0.36 g, 61% yield). ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K): δ 7.6−6.6 (br, 4 H) Ar *H*, 5.4−4.4 (br, 1 H) Si*H*, 2.1−1.7 (br, 3 H) C*H*$_3$ (see Figure 3). ^{13}C{^{1}H} NMR (500 MHz, C$_6$D$_6$, 298 K): δ 136.5 (br) *Ar* H, 128.7 (br) *Ar* H, 21.0 (br), *C*H$_3$. ^{29}Si{^{1}H} DEPT 90° NMR (99 MHz, CDCl$_3$, 298 K): δ −58.6 to −66.1 (m) *Si*H.

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Supporting Information Available: A listing of the deconvolution parameters for LPTSi and figures giving the ^{29}Si CP-MAS TOSS, ^{13}C{^{1}H} NMR (selected *p*-Tol CH_3 region), XRPDF spectra, and the DSC trace of LPTSi. This material is available free of charge via the Internet at http://pubs.acs.org.

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