1240 *Macromolecules* **1997,** *30,* 1240−1242

# Characterization of Poly(1-phenyl-1-silabutane) Tacticity via $^1H/^{13}C/^{29}Si$ Triple-Resonance 3D-NMR

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*Received October 17, 1996*
*Revised Manuscript Received January 9, 1997*

Since the 1980s, poly(carbosilanes) have been the subject of many studies, most often directed toward their use as precursors to silicon carbide.[1] More recently, investigations dealing with the thermal, mechanical, and liquid crystal properties of poly(carbosilane)s have been published.[2] In order to understand the properties of silicon-containing polymers, it is important to characterize their structures. NMR has been a powerful technique for the structure analysis of polymers. This paper demonstrates the combined use of $^1H/^{13}C/^{29}Si$ triple-resonance 3D-NMR methods and pulse field gradients (PFG) for selective detection of signals from $^1H$ atoms coupled to both $^{13}C$ and $^{29}Si$ at low natural abundance. The information which is obtained from 3D-NMR allows resolution and assignment of the resonances from the mm, mr/rm, and rr triad sequences in poly(1-phenyl-1-silabutane) (PPSB) without resorting to the preparation of stereoregular polymer with known relative configuration.

Similar $^1H/^{13}C/^{15}N$ and $^1H/^{13}C/^{31}P$ triple-resonance 3D-NMR techniques have been enormously useful for characterization of biopolymers such as proteins and polynucleotides;[3] however, the biological experiments are usually performed in conjunction with uniform $^{13}C$ and $^{15}N$ isotopic labeling. In polymer chemistry, when isotopic labeling is possible, it is often very difficult and expensive. Recent work[4,5] has shown that triple-resonance 3D-NMR techniques can be tremendously useful for characterizing polymer structure even without labeling.

Those reports involved the use of $^1H$ (100% natural abundance), $^{13}C$ (1.1% natural abundance), and a third nucleus which is present in 100% abundance (e.g., $^{19}F$[4] or $^{31}P$[5]). Performance of $^1H/^{13}C/^{29}Si$ triple-resonance NMR (natural abundance of $^{29}Si = 4.7\%$) is extremely challenging because it requires selective detection of the $^1H-^{13}C-^{29}Si$ spin systems which are present in only 0.05% of the molecules, while suppressing the signals from the remaining 99.95% of the molecules. Nevertheless, with modern instrumentation and a stable instrument environment, such experiments are possible and can produce very useful data.

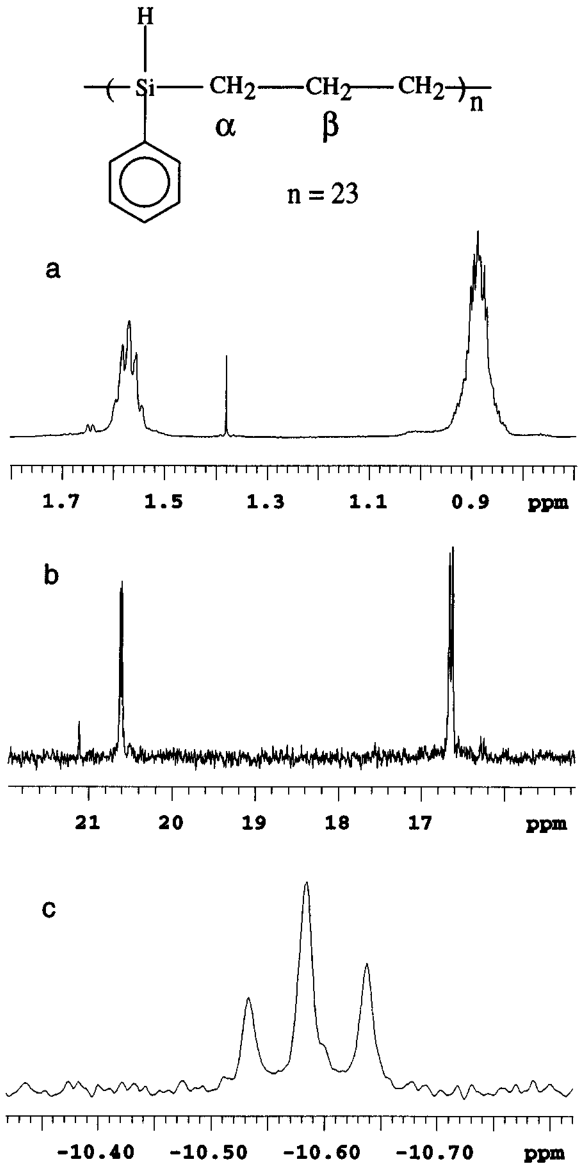

**Figure 1.** One-dimensional NMR spectra of PPSB: (a) expansion of the methylene region from the 600 MHz $^1H$ spectrum; (b) expansion of the methylene region from the 150 MHz $^{13}C$ spectrum; (c) expansion showing the main-chain repeat unit resonances from the 119 MHz $^{29}Si$ spectrum.

The new poly(carbosilane) $[PhSiH(CH_2CH_2CH_2)]_n$ (PPSB) was prepared from PhSi(allyl)ClH in a two-step sequence.[6] Self-hydrosilation of PhSi(allyl)ClH using Karstedt's catalyst[7] gave $[PhSiCl(CH_2CH_2CH_2)]_n$. Reduction with $LiAlH_4$ followed by a nonaqueous workup (to avoid hydrolysis of the Si−H bonds) afforded PPSB in high yield. The 1D-NMR spectra of PPSB are shown in Figure 1. The aliphatic region of the $^1H$ spectrum (Figure 1a) exhibits two broad multiplets at 0.9 and 1.6 ppm from the methylene protons α and $\beta$ to Si, respectively; stereoisomeric effects are not evident. In the aliphatic region of the $^{13}C$ spectrum (Figure 1b), each methylene carbon exhibits two resonances resulting from racemic (r) and meso (m) diad configurations in the polymer chain. The $^{29}Si$ spectrum (Figure 1c) shows three types of resonances that can be attributed to rr, rm/mr, and mm triad stereosequences. Usually, it is possible to distinguish between mm or rr and mr/rm triad stereosequences by the standard NMR experiments based on the higher probability of forming rm/mr sequences. However, it is usually difficult in a random polymer to distinguish between mm and rr sequences. When the polymer is not stereoregular, or its chiral centers are so far apart that the stereochemical influence on shift is small, it becomes difficult to differentiate between stereosequences.

The pulse sequence used to collect the 3D-NMR spectrum is shown in Figure 2. Details of the sequence have previously been described.[5] The experiment involves sequential INEPT-type[8] transfers from $^1H$ to $^{13}C$ to $^{29}Si$ to $^{13}C$ and finally back to $^1H$, using $^1J_{CH}$ and $^2J_{CSi}$,[9] as illustrated on the structure in Figure 2. The last two gradient pulses are applied on the basis of the ratios of the $^1H$ and $^{13}C$ resonance frequencies in order

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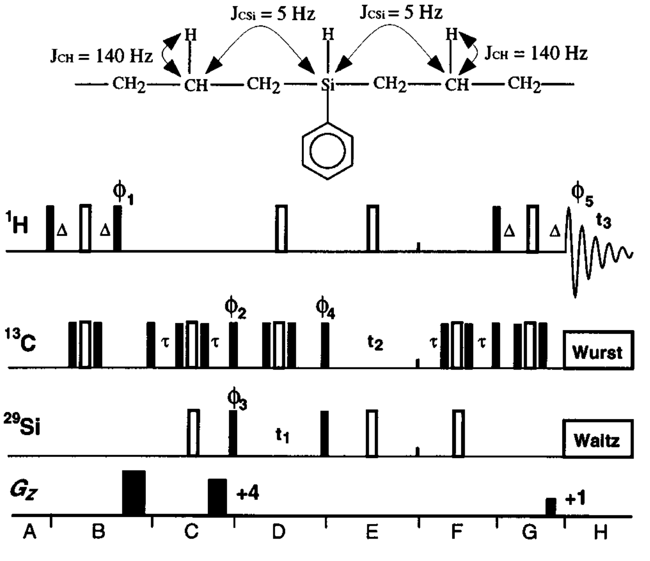

**Figure 2.** Diagram of the pulse sequence used to obtain the $^1$H/$^{13}$C/$^{29}$Si triple-resonance 3D-NMR correlation spectra. Solid and unfilled pulses represent $\pi/2$ and $\pi$ flips with the following phases: $\Phi_1 = \Phi_2 = y$; $\Phi_3 = x, -x$; $\Phi_4 = y, y, -y, -y$; $\Phi_5 = x, -x, -x, x$; $\Phi_3$ is incremented during $t_1$ and $\Phi_4$ is incremented during $t_2$ to provide a hypercomplex phase sensitive 3D data set.[13]

to selectively refocus coherence from mutually coupled $^1$H−$^{13}$C−$^{29}$Si spin triplets and to destroy all other signal components. The sequence produces a correlation spectrum which relates the $^1$H, $^{13}$C, and $^{29}$Si chemical shifts of the atoms connected by the arrows. While the experiment could have been performed more easily using $^1J_{CSi}$ instead of $^2J_{CSi}$ in order to relate the α-methylene $^1$H and $^{13}$C resonances with the signals of directly bound $^{29}$Si, more useful information about the polymer's structure is obtained by relating the β-methylene $^1$H and $^{13}$C resonances with the signals of $^{29}$Si two bonds away. The experiment involves detection of $^1$H (with simultaneous broad-band $^{13}$C Wurst[10] and $^{29}$Si Waltz-16[11] decoupling during the acquisition time), so that all of the advantages associated with detection of a high magnetogyric ratio nucleus are achieved.

Figure 3a shows an expansion from the $^1$H−$^{29}$Si long range ($^3J_{HSi}$ = 9 Hz) PFG heteronuclear multiple quantum coherence (PFG-HMQC)[12] 2D-NMR spectrum of PPSB which relates the β-methylene proton resonances with the resonances of $^{29}$Si atoms which are three bonds away. The corresponding regions from 1D $^1$H and $^{29}$Si NMR spectra are plotted along the vertical and horizontal axes. The 2D-NMR spectrum provides much better sensitivity and resolution than those obtained by direct detection of $^{29}$Si resonances in a 1D

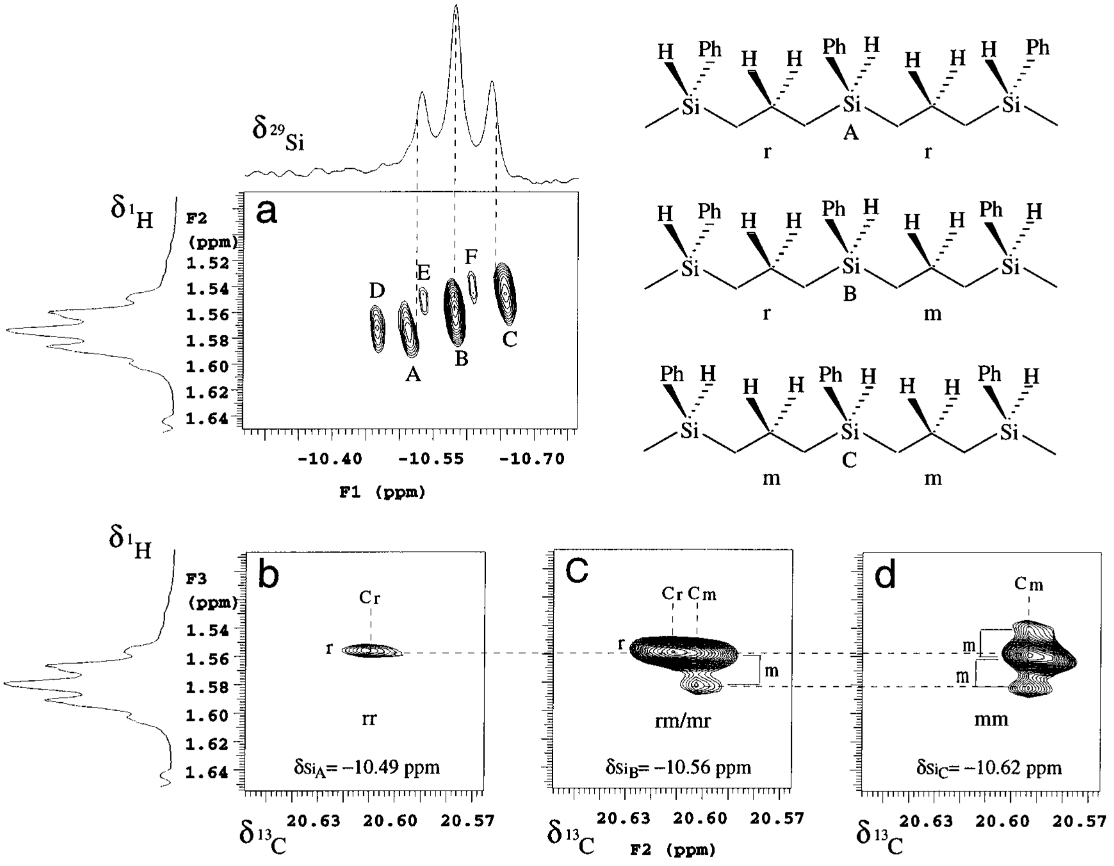

**Figure 3.** $^1$H/$^{13}$C/$^{29}$Si triple-resonance NMR spectra of PPSB (250 mg) obtained in $C_6D_6$: (a) long-range ($^3J_{SiH}$ = 9 Hz) $^1$H−$^{29}$Si HMQC 2D-NMR spectrum showing the $^1$H and $^{29}$Si 1D spectra along the $f_2$ and $f_1$ axes; (b) $f_2f_3$ slice at $\delta^{29}{}_{Si} = -10.49 \pm 0.05$ ppm from the $^1$H/$^{13}$C/$^{29}$Si 3D-NMR; (c) $f_2f_3$ slice at $\delta^{29}{}_{Si} = -10.56 \pm 0.05$ ppm from the $^1$H/$^{13}$C/$^{29}$Si 3D-NMR; (d) $f_2f_3$ slice at $\delta^{29}{}_{Si} = -10.62 \pm 0.05$ ppm. The 3D-NMR spectrum was obtained on a Varian Unityplus 600 MHz spectrometer with a Nalorac 5 mm $^1$H/$^2$H/$^{13}$C/X gradient probe, at 30 °C, with 90° pulses for $^1$H, $^{13}$C, and $^{29}$Si of 10.2, 22.0, and 14.0 $\mu$s, respectively, relaxation delay 1 s, $\Delta = 1.78$ ms ($1/(4x^1J_{CH})$), $\tau = 10$ ms ($1/(4x^2J_{CSi})$, $^2J_{CSi} = 5$ Hz), acquisition time = 0.117 s (with simultaneous $^{13}$C Wurst and $^{29}$Si Waltz-16 decoupling); four transients were averaged for each of 2 × 32 increments during $t_1$ and 2 × 27 increments during $t_2$, 1909.6 Hz spectral window in $f_3$, 357.0 Hz spectral window in $f_1$, and a 100 Hz spectral window in $f_2$ dimensions. The durations and amplitudes of the gradient pulses were 2, 1, and 1 ms and 0.364, 0.243, and 0.064 T/m, respectively. The first gradient pulse serves as a homospoil pulse, so its value relative to the other two is not critical. The total experiment time was 14 h. The data were zero filled to 512 × 512 × 512 and weighted with a shifted sinebell function before Fourier transformation. Digital signal processing was applied to reduce the $f_3$ spectral window to 272.8 Hz during the data processing.

experiment. Three intense crosspeaks (A−C) are observed which corresponds to the three signals detected in the 1D $^{29}$Si NMR spectrum. Additionally, three smaller crosspeaks are observed (D−F), which are attributed to penultimate silicon atoms and are not seen in the 1D-NMR spectrum due to limited chemical shift dispersion.

Three $f_2f_3$ slices from the $^1$H/$^{13}$C/$^{29}$Si 3D-NMR spectrum, at the three different $^{29}$Si chemical shifts of the main-chain repeat units of PPSB, are shown in Figure 3b−d. Each of these slices shows correlations between the $^1$H and $^{13}$C resonances of methylene groups two bonds away from the silicon atoms having that chemical shift. Each slice contains crosspeaks at one (Figures 3b,d) or two (Figure 3c) $^{13}$C chemical shifts depending on whether or not silicon has equivalent methylene carbons two bonds away. Carbons from methylene groups centered in racemic (r) diads are attached to chemically equivalent protons, and therefore, at each $^{13}$C chemical shift, correlations to a single $^1$H resonance are observed (e.g., in Figure 3b). Carbons from methylene groups centered in meso (m) diads are attached to chemically nonequivalent protons, and therefore, at each $^{13}$C chemical shift, correlations to a pair of $^1$H resonances are observed (e.g., in Figure 3d). The slice of the 3D-NMR spectrum from $^{29}$Si with a resonance at −10.49 ppm (Figure 3b) only contains a single correlation between one $^{13}$C resonance from a methylene group centered in an r diad; therefore, both adjoining $\beta$-methylene groups must be centered in r diads and the $^{29}$Si must be centered in an rr triad. The $^{29}$Si with a resonance at −10.56 ppm shows a correlation to a $^{13}$C resonance from a methylene group in an m diad and to a $^{13}$C resonance from a methylene group centered in an r diad (Figure 3c). Consequently, one of the $\beta$-methylene groups adjoining this $^{29}$Si must be centered in an r diad, the second adjoining $\beta$-methylene group must be centered in an r diad, and the $^{29}$Si with resonance at −10.56 ppm must therefore be centered in an mr triad. The $^{29}$Si with a resonance at −10.62 ppm only shows a correlation to a single $^{13}$C resonance from adjoining $\beta$-methylene groups centered in m diads (Figure 3d); therefore this $^{29}$Si must be centered in an mm triad.

The crosspeaks in Figure 3d are more complicated than the simple pair of crosspeaks at a single $^{13}$C chemical shift because of remote tacticity effects (i.e., the CH$_2$ groups on either side can be centered in rmm or mmm tetrads).

Triple-resonance 3D-NMR experiments can be useful for studying polymer structure without resorting to isotopic labeling, even when the nuclei involved are present in low natural abundance. The added chemical shift dispersion permits resolution of resonances, from remote stereosequence effects, which are not evident in 1D-NMR spectra. The simultaneous correlation of three chemical shifts permits assignment of mm and rr resonances without resorting to the synthesis of polymers with known relative configuration. These techniques can be enormously useful for characterizing the structures of star-branched polymers and dendrimers which contain NMR detectable atoms at their branch points.

**Acknowledgment.** We wish to acknowledge the National Science Foundation (DMR-9310642 to P.L.R. and CHE-9412387 to C.T.) for support of this research and the Kresge Foundation and donors to the Kresge Challenge program at the University of Akron for funds used to purchase the 600 MHz NMR instrument used in this work.

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(6) All reactions were conducted using anaerobic techniques. Allylphenylchlorosilane was prepared by the reaction of SiCl$_2$H(allyl) and PhMgBr. Preparation of [PhSiCl(CH$_2$CH$_2$CH$_2$)]$_n$: Karstedt catalyst solution (8 drops of 2.1−2.4% solution diluted in 1 mL of benzene) was introduced dropwise by syringe to a solution of 2.0 g (11 mmol) of allylphenylchlorosilane and 1 mL of benzene. The mixture was stirred at 45 °C for 2 days. Removal of the volatiles at reduced pressure left 2.0 g (100%) of [PhSiCl(CH$_2$CH$_2$CH$_2$)]$_n$. $^1$H NMR (C$_6$D$_6$, ppm): 7.52 (m, 2H), 7.15 (m, 3H), 1.65 (m, 2H), 0.98 (t, 4H). $^{13}$C NMR (C$_6$D$_6$, ppm): 134.9, 134.3, 130.9, 128.8, 20.9, 17.7. $^{29}$Si NMR (C$_6$D$_6$, ppm): 20.3. Preparation of [PhSiH(CH$_2$CH$_2$CH$_2$)]$_n$ (PPSB): A solution of 2.0 g of [PhSiCl(CH$_2$CH$_2$CH$_2$)]$_n$ in 15 mL of diethyl ether was added slowly to an ice-cooled suspension of 0.209 g (5.5 mmol, 100% excess) of LiAlH$_4$ in 20 mL of diethyl ether. The mixture was stirred overnight at room temperature and then refluxed for 1 h. The solution was filtered through Celite, and the volatiles were removed under reduced pressure. The residue was extracted twice with 40 mL of pentane. After removal of volatiles under reduced pressure, the residual aluminum compounds were washed away with 5−10 mL of CH$_3$CN (*carefully, exothermic*); the CH$_3$CN solution was decanted from the insoluble oil. Removal of volatiles under vacuum gave 1.58 g (79%) of PPSB as a waxy viscous liquid. GPC: $M_n = 3392$, $M_w = 9659$ (average $n = 23$). FTIR (neat): 2113 (vs, Si−H). $^1$H NMR (C$_6$D$_6$, ppm): 7.46 (m, 2H), 7.19 (m, 3H), 4.49 (p, 1H), 1.58 (m, 2H), 0.88 (m, 4H). $^{13}$C NMR (C$_6$D$_6$, ppm): 136.2, 135.4, 129.9, 128.6, 20.7, 16.65, 16.61. $^{29}$Si NMR (C$_6$D$_6$, ppm): −10.49, −10.56, −10.62.

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MA961534G