the elution solvent. Styrene–divinylbenzene cross-linked gel was used in the column. VPO measurements were made with a Corona 117 instrument in benzene solution.

Registry No. **3**, 102920-04-7; **2**·2Li, 57486-16-5; **2**·2Na, 37244-89-6; **2**·2K, 52219-57-5.

References and Notes

(1) Hirao, A.; Yamaguchi, K.; Takenaka, K.; Suzuki, K.; Nakahama, S.; Yamazaki, N. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 941.
(2) Hirao, A.; Takenaka, K.; Packirisamy, S.; Yamaguchi, K.; Nakahama, S. *Makromol. Chem.* **1985**, *186*, 1157.
(3) Hirao, A.; Takenaka, K.; Yamaguchi, K.; Nakahama, S.; Yamazaki, N. *Polym. Commun.* **1983**, *24*, 341.
(4) Yamaguchi, K.; Hirao, A.; Suzuki, K.; Takenaka, K.; Nakahama, S.; Yamazaki, N. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 395.
(5) Hirao, A.; Kato, H.; Yamaguchi, K.; Nakahama, S. *Macromolecules*, in press.
(6) Kuznetsov, N. A.; Roganova, Z. A.; Smolyanskii, A. L. *Vysokomol. Soedin., Ser. A* **1978**, *20*, 791.
(7) Marvel, C. S.; Overberger, C. G. *J. Am. Chem. Soc.* **1945**, *67*, 2250.
(8) Zak, A. G.; Kuznetsov, N. A.; Lishanskii, I. S.; Smolyanskii, A. L. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1975**, *18*, 951.
(9) Zak, A. G.; Kuznetsov, N. A.; Lishanskii, I. S.; Roganova, Z. A.; Smolyanskii, A. L. *Vysokomol. Soedin., Ser. A* **1974**, *16*, 886.
(10) Osawa, E.; Wang, K.; Kurihara, O. *Makromol. Chem.* **1965**, *83*, 100.
(11) Karapetyan, T. G.; Zhamkochyan, G. A.; Motsoyan, S. G.; Pogosyan, G. M. *Arm. Khim. Zh.* **1975**, *28*, 205.
(12) Yamamoto, T.; Toyoda, M.; Kitano, T.; Ito, K. *Polym. Prepr., Jpn.* **1984**, *33*, 152.
(13) Hirao, A.; Ishino, Y.; Nakahama, S. *Makromol. Chem.* **1986**, *187*, 141.
(14) The $\bar{M}_w/\bar{M}_n$ values were calculated by the method described by Tung (see: Tung, L. H. *J. Appl. Polym. Sci.* **1966**, *10*, 375) with some modifications.
(15) Leebrick, J. R.; Ramsden, H. E. *J. Org. Chem.* **1958**, *23*, 935.
(16) Iwakura, Y.; Uno, K.; Nakabayashi, N.; Kojima, T. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 186.
(17) Meyers, A. I.; Mihelich, E. D.; Nolen, R. L. *J. Org. Chem.* **1974**, *39*, 2783.

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Characterization of Polysilanes by Carbon-13, Silicon-29, and Proton NMR

The recent discovery of soluble polysilanes[1-5] $-(RR'Si)_n-$ (R and R′ = alkyl or phenyl) has stimulated interest in the properties and applications of these materials. Of particular note is their intense UV absorption at 300–380 nm, both in solution[6] and in the solid state.[7] It has been shown[6a] that λ_{max} of the absorption band and the absorptivity per Si–Si bond increase with the length of the silicon backbone, reaching a maximum when the chain is very long. In addition, it is reported that certain polysilanes exhibit abrupt transitions in the UV spectrum at low temperature for dilute solutions[6b] and at the melting point in the case of poly(di-*n*-hexylsilane).[7] These are bathochromic shifts with decreasing temperature and have been attributed to the onset of highly ordered conformations.[6b,c,7]

To better our understanding of the solution and solid-state properties of the polysilanes we have conducted solution-state NMR studies to characterize in detail the microstructure of a number of dialkylsilane homopolymers and copolymers. Previously,[2,4] proton and ^{13}C peak positions have been given for certain polysilanes, but without spectra and mostly without assignments. We report here for the first time ^1H, ^{13}C, and ^{29}Si spectra of four dialkylsilane polymers: poly(methyl-*n*-propylsilane), poly(methyl-*n*-hexylsilane), poly(methyl-*n*-dodecylsilane), and poly(di-*n*-hexylsilane). Peak assignments have been made, in part, with the aid of 2D experiments. Results of studies on the solid state and on copolymers will be reported later.

All polymers were prepared by the sodium metal dechlorination of the corresponding dialkylchlorosilanes and were of relatively low polydispersity (<1.5) and high molecular weight ($M > 10^6$).[8] NMR spectra were obtained with a Varian XL-200 or JEOL GX-500 spectrometer and 1.0–18.5% solutions in benzene-d_6, toluene-d_8, 1,2,4-trichlorobenzene/dioxane-d_8, or methylene-d_2 chloride at 0 to +100 °C. Ten scans were accumulated for ^1H spectra and $(10–20) \times 10^3$ scans for ^{13}C and ^{29}Si spectra. The recorded proton-decoupled ^{29}Si spectra of these polymers contain negative resonances resulting from the nuclear Overhauser enhancement. Because the magnetic moment and the spin of ^{29}Si are antiparallel, the gyromagnetic ratio, γ, is negative. Therefore the maximum enhancement which can result from irradiation of the protons is −1.5. In cases of partial Overhauser enhancement a weak positive or negative signal will be produced. The ^1H COSY and ^{13}C–^1H heterocorrelated spectra were obtained by using data matrices of 256 spectra in 1024 points, with zero filling to 512 by 1024 points. The two-dimensional data were multiplied by a combination of trapezoidal and exponential functions. The COSY spectrum was recorded with 2000 Hz in each frequency dimension, while the heterocorrelated spectrum provided a sweep width of 2000 and 7000 Hz for the proton and carbon frequency dimensions, respectively. (See figure captions for further details.) The sharp resonances labeled with an "×" in Figures 1 and 3 represent as yet unidentified sample impurities. Since the impurities do not produce resonances in the silicon-29 NMR spectra we attribute them to nonpolymeric species unrelated to our polysilane materials.

In Figure 1 the 500-MHz ^1H spectra of these polymers are shown. As expected, the C-1′ protons, being bonded to carbons directly attached to silicon, are strongly shielded; the C-1 protons are less so. Both move downfield as the side chain is lengthened. With the exception of poly(di-*n*-hexylsilane), these polymers contain pseudoasymmetric silicon atoms and must be viewed in terms of triad (or higher "odd-ad") configurational sequences. These sequences are reflected in the C-1′ proton resonances, which show splittings even though there can be no observable *J* coupling. The broadening of the C-1 and C-2 proton resonances in spectra a and b also arises mainly from this cause. The C-4, C-5, and C-6 proton resonances in hexyl side chains show increasingly resolved multiplet structure as they experience decreasing stereochemical influences. However, the proton resonances of poly(methyl-*n*-dodecylsilane) (spectrum c) show no resolved multiplet structure with the exception of the terminal methyl, C-12. It is probable that in this case homogeneous broadening from short spin–spin relaxation times is beginning to play a dominant role, all motions being impeded by the very long side chains.

The assignments of the methylene resonances in the *n*-hexyl and *n*-dodecyl groups are not self-evident from the one-dimensional spectra. In order to establish these assignments, a two-dimensional *J*-correlated (2D COSY) experiment was performed on the poly(methyl-*n*-hexylsilane). The results are shown in Figure 2. Protons on neighboring carbons, which are coupled through three

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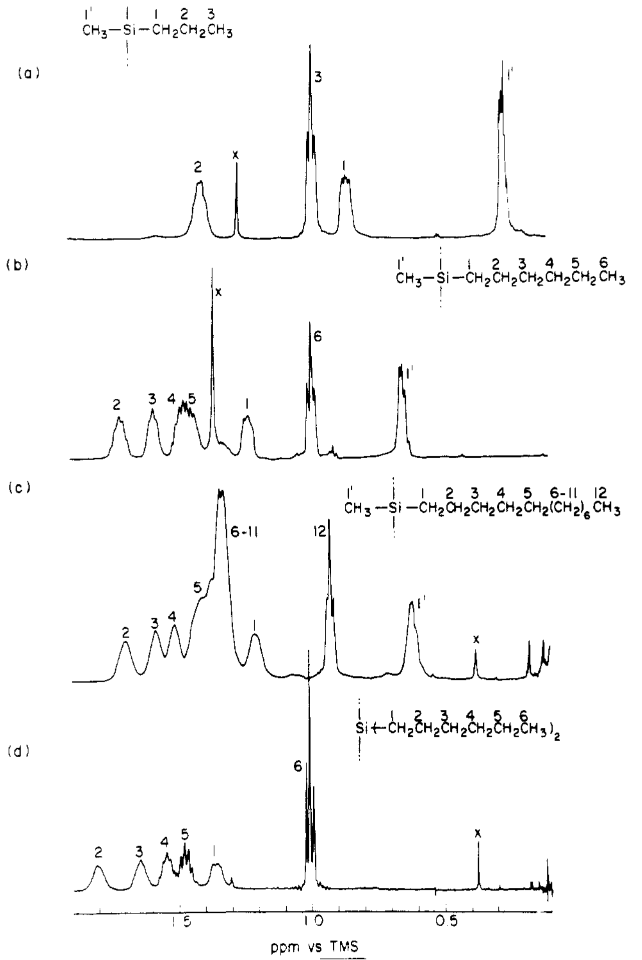


Figure 1. 500-MHz ^{1}H NMR spectra of (a) poly(methyl-*n*-propylsilane) in methylene-d_2 chloride at 23 °C, (b) poly(methyl-*n*-hexylsilane) in benzene-d_6 at 50 °C, (c) poly(methyl-*n*-dodecylsilane) in toluene-d_8 at 60 °C, and (d) poly(di-*n*-hexylsilane) in toluene-d_8 at 60 °C.

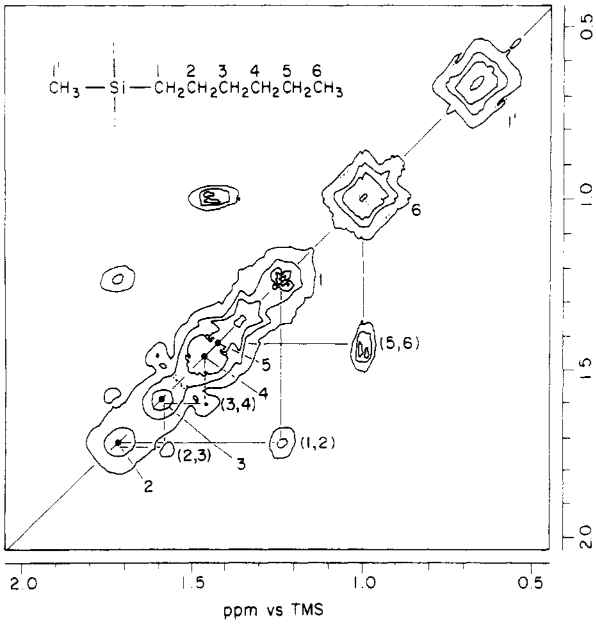


Figure 2. 500-MHz ^{1}H NMR 2D-COSY spectrum of poly(methyl-*n*-hexylsilane) recorded at 22 °C in benzene-d_6.

bonds, are correlated by off-diagonal resonances (cross peaks) connecting their resonances on the diagonal. As expected, the methyl-1′ resonance at 0.65 ppm shows no cross peaks, which serves to confirm its assignment. By following the connections of cross peaks, the assignments of the resonances are unequivocally established. These assignments can be extended without ambiguity to the poly(di-*n*-hexylsilane) and poly(methyl-*n*-dodecylsilane) spectra; in the latter, the peaks for the protons of methylenes 6 through 11 are not resolved.

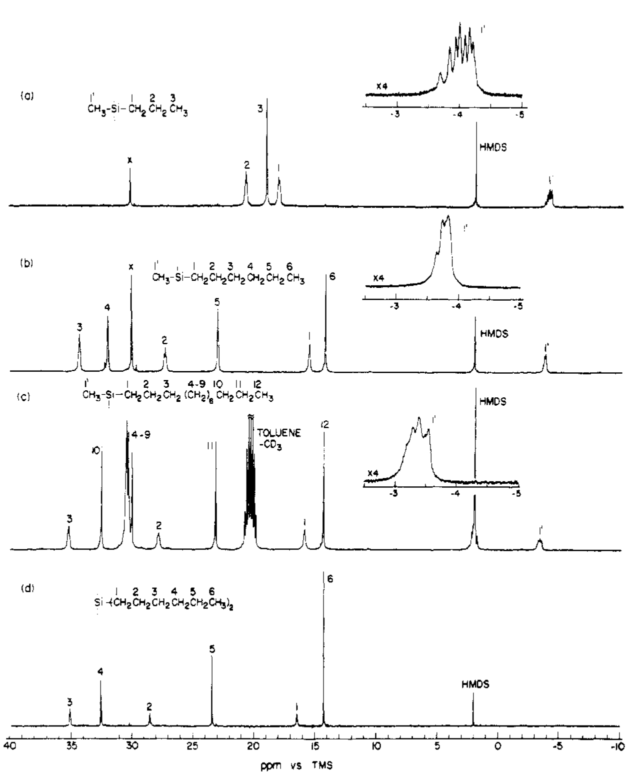


Figure 3. 125.7-MHz ^{13}C NMR spectra of (a) poly(methyl-*n*-propylsilane) and (b) poly(methyl-*n*-hexylsilane) in 1,2,4-trichlorobenzene/dioxane-d_8 solution at 40 and 60 °C, respectively, (c) 125.7-MHz ^{13}C NMR spectrum of poly(methyl-*n*-dodecylsilane) in toluene-d_8 at 23 °C, and (d) 50.3-MHz ^{13}C NMR spectrum of poly(di-*n*-hexylsilane) in toluene-d_8 at 100 °C.

The ^{13}C spectra of these polysilanes are shown in Figure 3. In these spectra, ^{1}H-^{13}C couplings have been removed by broad-band proton decoupling, and therefore line widths are determined by spin–spin relaxation or by tacticity or both. In spectrum d the latter cannot contribute; we observe a regular increase in line width as we progress inward along the hexyl side chain, reflecting increasing restriction of the C–H vectors. This is observed also in the ^{13}C T_1 values at 24 °C: C-6, 1.67 s; C-5, 0.80 s; C-4, 0.43 s; C-3, 0.19 s; C-2, 0.11 s; C-1, 0.10 s.

Assignments of the ^{13}C resonances in the poly(methyl-*n*-hexylsilane) spectrum are made from knowledge of proton assignments and a two-dimensional heterocorrelated experiment in which a correlation is established via the one-bond *J* coupling between each carbon and its attached protons. The result of this is the 2D spectrum in Figure 4 in which each cross peak (vertically elongated because the ^{1}H frequency scale is ca. 5-fold expanded over the ^{13}C scale) connects the associated carbon and proton chemical shift positions.

In Figure 3a–c the C-1′ methyl carbons are the most sensitive to stereochemical configuration. Their resonances are shown expanded 5-fold as insets in each spectrum. The C-1′ resonance in poly(methyl-*n*-propylsilane) (spectrum a) is particularly striking, exhibiting at least seven subpeaks, corresponding to pentad configurational sequences.

The ^{29}Si spectra, shown in Figure 5, exhibit multiplicity very similar to that of the C-1′ carbons. It is clear that this too arises from sensitivity to tacticity[9] since the

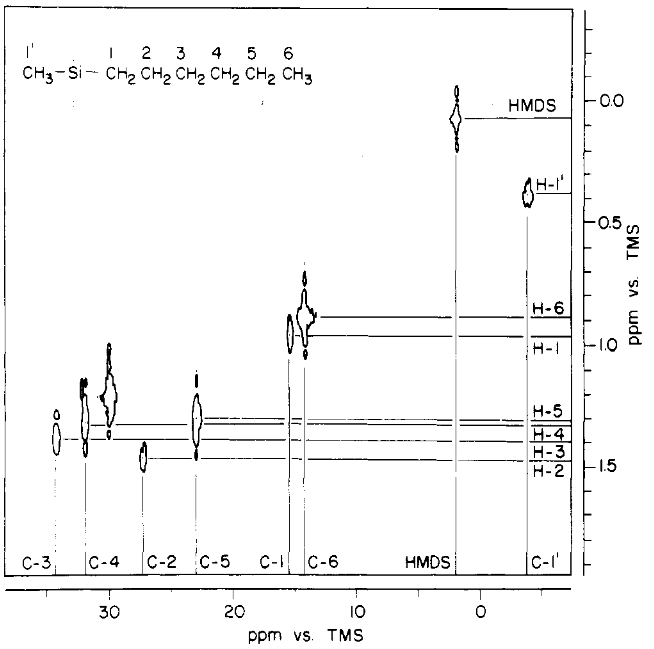
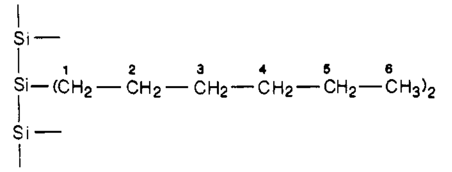


Figure 4. 500-MHz ^{1}H and 125.7-MHz ^{13}C NMR 2D-heterocorrelated spectrum of poly(methyl-*n*-hexylsilane) in 1,2,4-trichlorobenzene/dioxane-d_8 at 50 °C.

Table I
125-MHz Carbon-13 NMR Chemical Shifts (ppm) of Poly(di-*n*-hexylsilane) Observed in Toluene-d_8



$$-\mathrm{Si}(\overset{1}{\mathrm{C}}\mathrm{H_2}-\overset{2}{\mathrm{C}}\mathrm{H_2}-\overset{3}{\mathrm{C}}\mathrm{H_2}-\overset{4}{\mathrm{C}}\mathrm{H_2}-\overset{5}{\mathrm{C}}\mathrm{H_2}-\overset{6}{\mathrm{C}}\mathrm{H_3})_2-$$

temp, °C	C-6	C-5	C-4	C-3	C-2	C-1
100	14.26	23.43	32.54	35.10	28.51	16.45
24	14.45	23.49	32.55	35.19	28.41	15.92
0	14.52	23.52	32.60	35.26	28.41	15.86

spectrum of poly(di-*n*-hexylsilane) (spectrum d) is a narrow singlet. The ^{29}Si multiplet of poly(methyl-*n*-hexylsilane) (spectrum b) can be fitted to Bernoullian propagation statistics with a P_m of approximately 0.5; spectrum a is similar.[10] It is possible that the asymmetric ^{29}Si resonance of poly(methyl-*n*-dodecylsilane) (spectrum c) corresponds to a more biased model, but as we cannot make individual resonance assignments at this time we cannot be sure. At present there is no evidence for "runs" of either meso or racemic placements in the dechlorination reaction.

In an attempt to correlate changes in molecular conformation with the observed shift to longer wavelengths in the UV spectrum as the solution temperature is lowered, we followed the carbon-13 shift data of poly(di-*n*-hexylsilane) as a function of temperature. The results are shown in Table I. As expected, the chemical shifts of most of the carbon nuclei in the side chain change little with temperature since the side-chain trans:gauche ratio increases only slightly as the temperature is decreased over this range. However, methylene-1 shows a downfield shift of 0.6 ppm over the 100 °C range. This probably reflects a significant change in backbone conformation. Damewood[11] has recently reported empirical force field calculations which indicate that polysilanes with bulky substituents will adopt the trans conformation in the ground state. Therefore, as the temperature is lowered, the probability of the trans conformation increases. This will result in the methylene-1 carbon having a greater probability of being gauche to a silicon atom three bonds removed. On the basis of preliminary studies of carbon–silicon shift effects, we expect the gauche interaction with a silicon atom to be more shielding than the gauche interaction with a carbon atom. Therefore, the chemical shift of the methylene-1 carbon can be used to monitor backbone conformation. This preliminary result is consistent with the hypothesis that the shift in UV absorption to longer wavelength is the result of a higher population of trans conformations along the silicon backbone. Studies are in progress to follow the carbon chemical shift changes to lower temperatures and also to measure the change in the silicon-29 chemical shifts with temperature in both solution and the solid state.

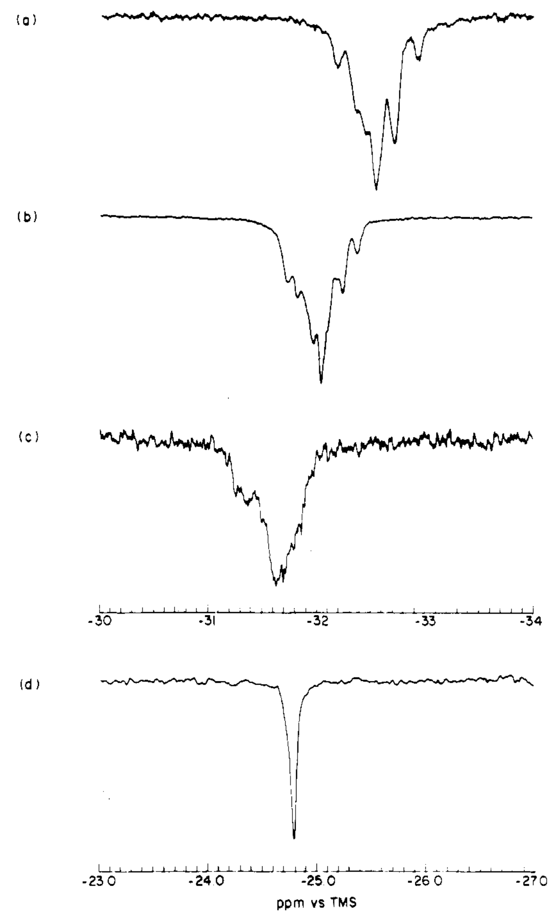


Figure 5. 99.25-MHz ^{29}Si NMR spectra of (a) poly(methyl-*n*-propylsilane) and (b) poly(methyl-*n*-hexylsilane) in 1,2,4-trichlorobenzene/dioxane-d_8 at 40 and 60 °C, respectively, (c) 99.25-MHz ^{29}Si NMR spectrum of poly(methyl-*n*-dodecylsilane) in toluene-d_8 at 60 °C, and (d) 39.7-MHz ^{29}Si NMR spectrum of poly(di-*n*-hexylsilane) in toluene-d_8 at 30 °C. Note change in chemical shift scale for (d).

Registry No. Poly(methylpropylsilane), 88003-13-8; poly(methylhexylsilane), 88003-15-0; poly(methyldodecylsilane), 88018-84-2; poly(dihexylsilane), 94904-85-5; poly(dichloromethylpropylsilane), 88002-81-7; poly(dichlorohexylmethylsilane), 88002-83-9; poly(dichlorododecylmethylsilane), 88002-84-0; poly(dichlorodihexylsilane), 97036-67-4.

References and Notes

(1) Wesson, J. P.; Williams, T. C. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 959.
(2) Trujillo, R. E. *J. Organomet. Chem.* **1980**, *198*, C27.
(3) West, R.; David, L. D.; Djurovich, P. I.; Stearly, K. L.; Srinivasan, K. S. V.; Yu, H. *J. Am. Chem. Soc.* **1981**, *103*, 7352.
(4) Trefonas, P., III; Djurovich, P. I.; Zhang, X. M.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 819.
(5) Zeigler, J. M.; Harrah, L. A.; Johnson, A. W. *SPIE Adv. Resist Technol.* **1985**, *539*, 166.

(6) (a) Trefonas, P., III; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 823. (b) Harrah, L. A.; Zeigler, J. M. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 209. (c) Trefonas, P., III; Damewood, J. R., Jr.; West, R.; Miller, R. D. *Organometallics* **1985**, *4*, 1318.

(7) Miller, R. D.; Hofer, D.; Rabolt, J.; Fickes, G. N. *J. Am. Chem. Soc.* **1985**, *107*, 2172.

(8) Zeigler, J. M. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1986**, *27*(1), 109.

(9) We have recorded the ^{29}Si NMR spectra of the poly(methyl-*n*-hexylsilane) with and without the nuclear Overhauser enhancement (NOE). We do not observe any change in the relative signal intensities, indicating uniform enhancement for the different stereosequences. The observed NOE of −0.91 suggests a small increase in S/N would be obtained by suppressing the NOE during signal accumulation. Carbon-13 measurements on poly(methylcyclohexylsilane) have also shown uniform NOE's for the different stereosequences.

(10) In order to fit the spectrum we assume the following order of pentad resonances of uniform line width, where the number in parentheses is the relative pentad intensity for Bernoullian statistics of $P_m = 0.5$ and the brackets indicate the sequences assigned to each of the seven resonances starting at either the high-field or low-field side of the multiplet: [*mmmm*(1)], [*mmmr*(2)], [*rmmr*(1) + *mmrm*(2)], [*mmrr*(2) + *mrmr*(2)], [*rrmr*(2) + *mrrm*(1)], [*rrrm*(2)], [*rrrr*(1)]. The simulated spectrum resulting from this procedure agrees well with the observed spectrum of Figure 5b.

(11) Damewood, J. R. Jr. *Macromolecules* **1985**, *18*, 1793.

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