isolobal relationship between the organometallic Mn_3Pb compound **3** and *exo*-methylene cyclopropane: d^6-ML_5 fragments are isolobal with methylene, CH_2.[10]

Whereas the linear Mn_2Pb complex **1** reacts with diazomethane under extrusion of elemental lead and formation of $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2(\pi\text{-}C_2H_4)$, the trigonal-planar Mn_3Pb species **3** polymerizes diazomethane rapidly, but otherwise remains completely unchanged. Further reactivity studies of this class of organometallic "heterocumulenes" are in progress.

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(10) Hoffmann, R. *Angew. Chem.* **1982**, *96*, 725; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

Poly(di-*n*-pentylsilane): The Spectral Consequences of a Helical Conformation in the Solid State

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Polysilane derivatives,[1] which contain only silicon in the backbone, constitute a new class of polymers of scientific interest for which many applications have become apparent.[2-6] Considerable theoretical[7-10] and experimental[11-14] attention has been focused on understanding the nature of the strong electronic transition of the σ-bonded backbone. Recently, however, it was found[15-17] that films of certain polysilane derivatives which are symmetrically substituted with long-chain alkyl substituents [e.g., poly(di-*n*-hexylsilane) (PDHS)] show a remarkable red shift to 370–380 nm. This spectral shift was attributed to the locking of the backbone into a planar zigzag conformation initiated by the crystallization of the hydrocarbon side chains.[15-17] Structural evidence is now presented for poly(di-*n*-pentylsilane) (PDPS) which demonstrates for the first time that deviations of the polymer backbone from a planar zigzag conformation, even in a regular structure, result in a strong blue shift in the electronic absorption spectrum.

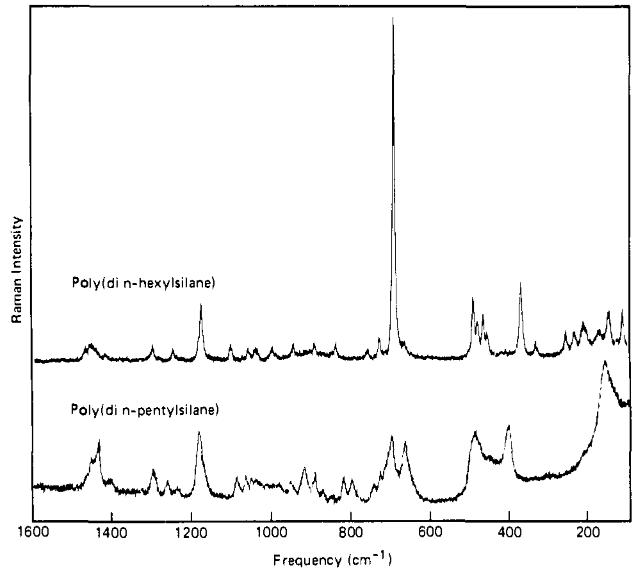

Figure 1. Raman spectra of PDHS (upper) and PDPS (lower). The strong band at 689 cm^{-1} for PDHS has previously been assigned as a carbon–silicon vibration of the planar zigzag backbone conformation based on ^{13}C isotopic labeling studies.

The polymerization of di-*n*-pentyldichlorosilane was performed as previously described.[18] The high molecular weight fraction ($\bar{M}_w \sim 1 \times 10^6$) was isolated by slow precipitation from hexane using isopropyl alcohol. This sample was used in the subsequent spectroscopic studies.

The λ_{max} of a thin film of PDPS at room temperature occurred at 313 nm and appeared similar to the absorption spectra of other amorphous polysilane derivatives *except* that the band was symmetrical and much sharper ($\omega_{1/2} \sim 22$ vs. 50 nm). Upon cooling the film from room temperature to −110 °C, there was little change in band shape or position except for the appearance of a small, broad shoulder around 355 nm. However, when the film was heated above 80 °C, the absorption band broadened significantly ($\omega_{1/2} \sim 58$ nm) although the λ_{max} remained unchanged. This behavior was reversible upon cooling. Thermal analysis of PDPS showed a reversible, endothermic transition around 74 °C ($\Delta H = 0.45$ kcal/mol) which was strikingly different from that observed for PDHS (41 °C, $\Delta H = 5.0$ kcal/mol). Since the transition in the latter case has been attributed to a combination of side-chain melting and the subsequent disordering of a planar zigzag backbone,[15-17] the thermal and UV data for PDPS suggest a regular but nonplanar backbone conformation at ambient temperatures.

Raman studies (Figure 1) demonstrate that the polymer structure of PDPS is significantly different from that of PDHS. Particularly obvious was the absence of a very intense band around 689 cm^{-1} which had previously been assigned[17] as a silicon–carbon vibration in the planar zigzag conformation of PDHS. There are also significant differences in the silicon–silicon stretch region (350–450 cm^{-1}) which indicate that the backbone of PDPS is no longer planar.

The molecular structure of PDPS was further probed by variable-temperature ^{29}Si CPMAS NMR and compared with similar studies on PDHS. The differences in the spectra are striking. Measured at −33 °C, the ^{29}Si resonance of PDPS is significantly upfield from that of PDHS (−29.2 vs. −23.0 ppm, relative to Me_4Si). The observation of a single, relative narrow ^{29}Si resonance ($\omega_{1/2} = 73$ Hz) for PDPS upfield from PDHS further confirms

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(1) For a recent review of polysilane high polymers, see: West, R. *J. Organomet. Chem.* **1986**, *300*, 327.

(2) Yajima, S.; Hasegawa, Y.; Hayashi, J.; Iimura, M. *J. Mat. Sci.* **1978**, *13*, 2569.

(3) West, R. In *Ultrastructure Processing of Ceramics, Glasses and Composites*; Hench, C. O., Ulrich, D. R., Eds.; Wiley: New York, 1984; Chapter 19.

(4) Miller, R. D.; Hofer, D.; McKean, D. R.; Willson, C. D.; West, R.; Trefonas, P. T. in *Materials for Microlithography*; Thompson, L., Willson, C. G., Frêchet, J. M. J., Eds.; ACS Symposium Series 266, American Chemical Society: Washington, DC, 1984; p 293.

(5) Hofer, D.; Miller, R. D.; Willson, C. G. *Proc. SPIE* **1984**, *469*, 19.

(6) West, R.; Wolff, A. R.; Peterson, D. J. *J. Radiat. Curing* **1986**, *13*, 35.

(7) Pitt, C. G. In *Homoatomic Rings, Chains and Macromolecules of the Main Group Elements*; Rheingold, A. L., Ed.; Elsevier: New York, 1977 and references cited therein.

(8) Bigelow, R. W.; McGrane, K. *J. Polymn. Sci., Polym. Phys. Ed.* **1986**, *24*, 1233.

(9) Halevi, E. A.; Winkelhofper, G.; Meisl, M.; Janoschek, R. *J. Organomet. Chem.* **1985**, *294*, 151.

(10) Klingensmith, K. A.; Downing, J. W.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 7438.

(11) Kumada, M.; Tamas, K. *Adv. Organomet. Chem.* **1968**, *6*, 80.

(12) Boberski, W. G.; Allred, N. C. *J. Organomet. Chem.* **1968**, *6*, 80.

(13) Trefonas, P. T.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 823.

(14) Zeigler, J. M.; Harrah, L. A.; Johnson, A. W. *Proc. SPIE* **1985**, *539*, 166.

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

(16) Rabolt, J. F.; Hofer, D.; Miller, R. D.; Fickes, G. N. *Macromolecules* **1986**, *19*, 611.

(17) Kuzmany, H.; Rabolt, J. F.; Farmer, B. L.; Miller, R. D. *J. Chem. Phys.* **1986**, *85*, 7413.

(18) Trefonas, P. T.; Djurovich, P. L.; Zhang, X. H.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *26*, 819.

(19) Gobbi, G. C.; Fleming, W. W.; Sooriyakumaran, R.; Miller, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 5624.

0002-7863/87/1509-2509$01.50/0

2510 *J. Am. Chem. Soc.* **1987**, *109*, 2510–2512

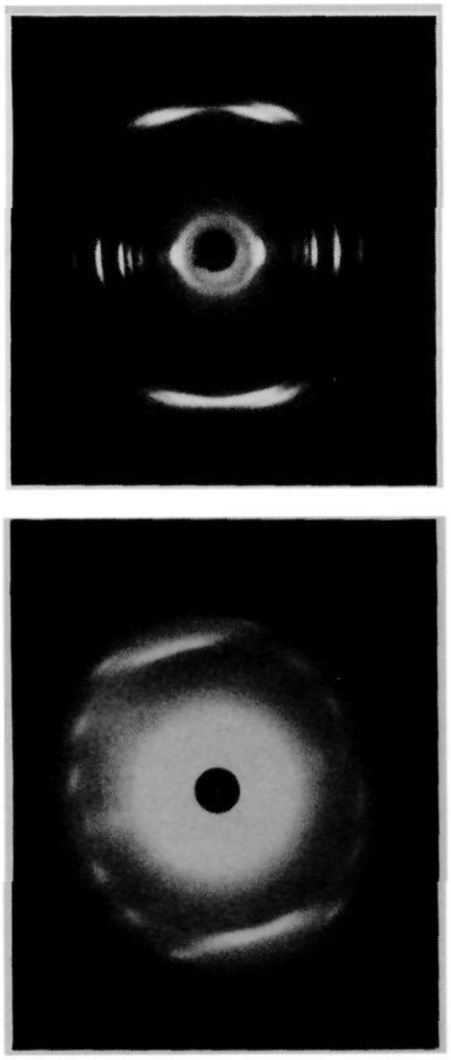

Figure 2. Room temperature, wide-angle X-ray diffraction (WAXD) pictures of stretch-oriented samples of PDHS (upper) and PDPS (lower).

that the molecular structure of the two polymers is different. Since the backbone conformation of PDHS below its transition temperature (~41 °C) is predominantly planar zigzag, the narrow line width and upfield position of the PDPS signal at comparable temperatures suggest a regular, *albeit* nonplanar, backbone conformation. At 87 °C, which is above the respective phase transition temperature of both polymers, the silicon signal of each sample becomes a narrow, time-averaged resonance around −23.5 ppm.

Fiber diffraction patterns for a stretch-oriented sample of PDPS (lower photograph, Figure 2) show sharp reflections out to ~4 Å. Similar studies on samples of PDHS (upper photograph, Figure 2) revealed defined reflections to ~1.5 Å which were consistent with side-chain crystallization.[20] For PDPS, instead of a layer line spacing indicative of a planar zigzag backbone conformation (4.07 Å) as observed for PDHS, the layer line spacing was found to be 13.8 Å, clearly representative of a helical conformation of the polymer. Strong near-meridional reflections occurred on the third-layer line. Both these reflections and the *c*-axis repeat were found to be consistent with a 7/3 helical conformation of the polymer backbone. In addition, a meridional reflection in diffraction patterns from a tilted fiber sample was observed on the seventh-layer line at 1.9–2.0 Å. The strongest reflection, which appeared on the zero-layer line, was about 11.8 Å and corresponds to the interchain backbone spacing. Interestingly, fiber patterns of PDPS taken above the transition temperature are comparable to those recorded for PDHS at 50 °C. In this regard, the strongest reflection for each remained sharply defined on the zero-layer line. This and other spectral information suggest that all molecular order is not lost above the respective transition temperatures.

In summary, spectroscopic evidence indicates that PDPS exists in the solid state at room temperature in a regular 7/3 helical conformation. This is in contrast to PDHS which has been demonstrated to prefer a planar zigzag conformation below 41 °C. A stable helical conformation is also in accord with recent calculations.[21] Our studies imply that PDHS and higher homologues adopt a trans planar backbone conformation in the solid state primarily due to the side-chain crystallization. Comparison of the UV and WAXD data for PDPS and PDHS shows conclusively for the first time that significant deviation from the trans backbone geometry, even for regular structures, results in a large blue shift (~60 nm) in the UV absorption spectrum.

Registry No. PDPS (SRU), 96228-24-9; PDPS (homopolymer), 97036-66-3.

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[20] Jones, A. T. *Makromol. Chem.* **1964**, *71*, 1.

[21] Farmer, B. L.; Rabolt, J.; Miller, R. D. *Macromolecules*, in press.

Interactions of a Diarylmagnesium Compound with Cryptands and Crown Ethers: Formation of Ar_3Mg^-, $ArMg(cryptand)^+$, and Threaded Ar_2Mg(crown ether)

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Three new species result from treating Tol_2Mg (Tol = *p*-methylphenyl) with cryptands and crown ethers. We believe that the ^1H NMR spectrum in Figure 1 of a solution prepared by stirring benzene with a 2:1 mixture of solid Tol_2Mg (itself insoluble in benzene) and 2,2,1-cryptand is of $TolMg(2,2,1\text{-cryptand})^+$ and Tol_3Mg^-.[1] The spectrum shows two kinds of tolyl groups in a 3:1 ratio and one cryptand for four tolyl groups. The three multiplets (each representing two H's) in the δ 1.1–1.5 region, though remarkably upfield, are due to cryptand H's.[2] Spectra of solutions prepared by using initial Tol_2Mg to cryptand ratios less than about 2 are similar except for the presence of additional absorptions identical with those exhibited by the cryptand alone.[3]

Arylmagnesium ions such as Ar_3Mg^- and $ArMg^+$ have not previously been observed.[4] The disproportionation (eq 1) that

$$2(Tol)_2Mg + \text{cryptand} \rightarrow TolMg(\text{cryptand})^+ + Tol_3Mg^- \quad (1)$$

forms these ions is analogous, however, to that recently observed for dialkylmagnesium compounds (R_2Mg). Structures of solid $NpMg(2,1,1\text{-cryptand})^+\,Np_3Mg^-$ (Np = neopentyl) and $[EtMg(2,2,1\text{-cryptand})^+]_2\,Et_6Mg_2^{2-}$ were determined,[5] and ^1H NMR spectra of solutions prepared from several R_2Mg's and cryptands show absorptions attributed to similar species.[5,6] R_2Mg's form $RMg(\text{crown})^+$ ions with 15-crown-5, though disproportionation never is as complete as in eq 1.

Tol_2Mg and crown ethers lead to organomagnesium species of composition Tol_2Mg(crown) that we think have "threaded" structures (**1**), in which the crown ether surrounds the Mg in an equatorial fashion and the aryl groups occupy apical positions.

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[1] The anion could instead be $Tol_6Mg_2^{2-}$ if its tolyl groups become equivalent on the NMR time scale.

[2] When the δ 2.5 region was irradiated in a coupling experiment, the δ 1.13 and 1.50 doublets collapsed to singlets.

[3] As initial Tol_2Mg to 2,2,1-cryptand ratios are increased much above 3, absorptions due to cryptand residues and tolyl groups are progressively weaker, indicating that little material has dissolved. Cryptand and tolyl absorptions also are weak in benzene solutions prepared from combinations of Tol_2Mg and 2,1,1- or 2,2,2-cryptand.

[4] A solid of composition Ph_3MgLi has been prepared from Ph_2Mg and PhLi (Wittig, G.; Meyer, F. J.; Lange, G. *Justus Liebigs Ann. Chem.* **1951**, *571*, 167), and ^1H NMR studies of diethyl ether solutions have been interpreted to indicate the presence of species of composition Ph_3MgLi and Ph_4MgLi_2 (Seitz, L. M.; Brown, T. L. *J. Am. Chem. Soc.* **1967**, *89*, 1602). It is likely that even in solution, however, the Li's are involved significantly in C–Li covalent bonds, as found in the crystal structure of $Ph_6Mg_2Li_2$(tetramethylethylenediamine)$_2$ (Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3726), so that there are not the "free" magnesiate ions that must be present when the cation is $TolMg(\text{cryptand})^+$.

[5] Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 432.

[6] Kushlan, D. M., Pajerski, A. D. The Pennsylvania State University, unpublished observations.