# Solid State NMR Investigation of C1-Deuterated Poly(di-*n*-hexylsilylene)

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**Introduction.** Polysilanes (polysilylenes) are inorganic−organic hybrid polymers exhibiting unusual $\sigma$-delocalization[1,2] that leads to UV absorptions as well as photoconductivity and semiconducting properties[3,4] similar to those of $\pi$-conjugated polymers. Potential applications of polysilylenes include the use as photoinitiators,[5] application for nonlinear optics,[6] microlithography,[7] display fabrication,[8] and data storage.[9]

Poly(di-*n*-alkylsilylene)s with *n*-alkyl side chains longer than ethyl form peculiar mesophases with conformational disorder and hexagonal packing. Diffraction studies have shown that the polymer chains remain packed in virtual cylinders but become conformationally disordered in the mesophase. The resulting abrupt change of the conformation of the backbone chromophores causes thermo- and piezochromism.[10−12] Similar mesomorphic behavior is observed for a number of inorganic/organic hybrid polymers, such as polysiloxanes and polyphosphazenes.[13,14] We are currently investigating polycarbosilanes with *n*-alkyl side chains with respect to the formation of conformationally disordered phases.[15]

The structural prerequisites for the formation of conformationally disordered mesophases for polysilylenes are still a subject of controversial discussions.[16] Whereas in the case of the polysiloxanes and polyphosphazenes amphiphilicity, i.e., molecular incompatibility between backbone and side chains, has been suggested as the underlying structural cause, for poly(di-*n*-alkylsilylene)s other factors must play a role. Although in solution polysilylenes are not rigid macromolecules, showing a characteristic ratio $C_\infty$ of 20 under unperturbed conditions[17] (this is slightly higher than for most carbon-based polymers, which are in the range 10−12), it has been suggested that the dense substitution pattern may lead to stiffening of the backbone as the actual cause of mesophase formation.[18] Therefore, the question may be raised whether the methylene units close to the backbone are mobile or induce local chain stiffness due to the extremely dense substitution pattern.

Poly(di-*n*-hexylsilylene) (PDHS) has been investigated intensely with respect to conformational disordering and related electrooptical changes. $^{13}C$ as well as $^{29}Si$ magic angle spinning (MAS) NMR studies of Schilling[19] and Gobbi[20] have shown the onset of side chain and backbone mobility concurrent with the transition to the mesophase. We have prepared a C1-deuterated sample of poly(di-*n*-hexylsilylene) (PDHS), using the $CD_2$ group in the vicinity of the polymer backbone as a probe for local mobility. Variable temperature solid state nonspinning $^{29}Si$- and $^2H$-NMR spectra have been recorded in order to investigate the onset of backbone mobility

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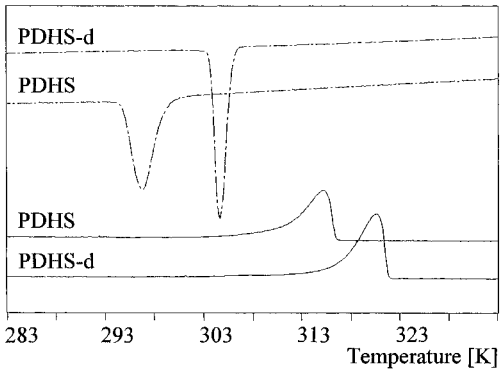
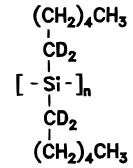



**Figure 1.** Comparison of DSC scans of PDHS and PDHS-d. Cooling (top, - - -) and heating (bottom, —) scans at a rate of 1 K/min are shown.

**Chart 1. Structure of Deuterated PDHS**




in the crystalline and the mesomorphic ($\mu$) phase. Furthermore, the C1-deuterated PDHS (Chart 1) is compared to nondeuterated PDHS with respect to its mesomorphic behavior in general.

**Experimental Section.** The deuterated PDHS sample (PDHS-d) was prepared in a four-step synthesis, starting from hexanoic acid anhydride, which was reduced with $LiAlD_4$. Subsequently, the resulting C1-deuterated hexanol was converted to *n*-hexyl chloride, using $SOCl_2$ and reacted to the respective Grignard compound. The Grignard compound was reacted with $SiCl_4$ to prepare the C1-deuterated di-*n*-hexyldichlorosilane. This monomer was polymerized using the common Wurtz-type coupling reaction[21] in a mixture of toluene/isooctane. Analogously, nondeuterated di-*n*-hexyldichlorosilane was polymerized to prepare a sample of ordinary PDHS. Both polymers were carefully fractionated to ensure the absence of low molecular weight impurities. This is a crucial prerequisite for the $^2H$-NMR studies described in the following. According to gpc, calibrated to narrow polystyrene standards, the polymers possess molecular weights of $M_w = 353\,000$ (PDHS; $M_w/M_n = 1.88$) and $M_w = 198\,000$ (PDHS-d; $M_w/M_n = 2.02$).

NMR experiments were performed with a Bruker CXP 300 spectrometer at resonance frequencies of 46.073 and 59.625 MHz for $^2H$ and $^{29}Si$, respectively. $^2H$ spectra were obtained with the quadrupole echo technique, and $^{29}Si$ spectra, by using cross-polarization and high-power decoupling below 310 K and only high-power decoupling above 310 K.

**Results and Discussion.** For PDHS-d as well as for PDHS, DSC scans have been recorded. Typical traces are depicted in Figure 1. Both materials showed a glass transition ($T_g$) in the range 232−234 K (not shown in Figure 1) as well as a mesomorphic transformation. Although precipitation of both polymers had been carried out in exactly the same manner, PDHS-d possessed a higher crystallinity, which was clearly visible from the smaller increase of the heat capacity observed at $T_g$ in the DSC diagrams ($\Delta C_p = 12.6$ J/(mol K) for PDHS-d vs $\Delta C_p = 71.6$ J/(mol K) for PDHS). Surprisingly, a strong effect of the deuteration on the

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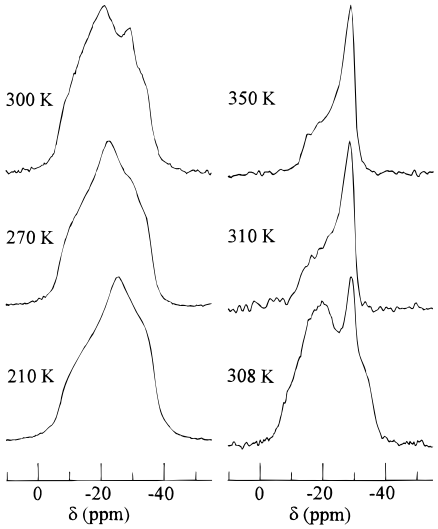


**Figure 2.** $^{29}$Si spectra of PDHS showing the chemical shift anisotropy (CSA) at various temperatures. Relative intensities of rigid and mobile fractions are distorted because of different cross-polarization and relaxation rates. Chemical shifts are referenced to $Q_8M_8$ (Bruker).

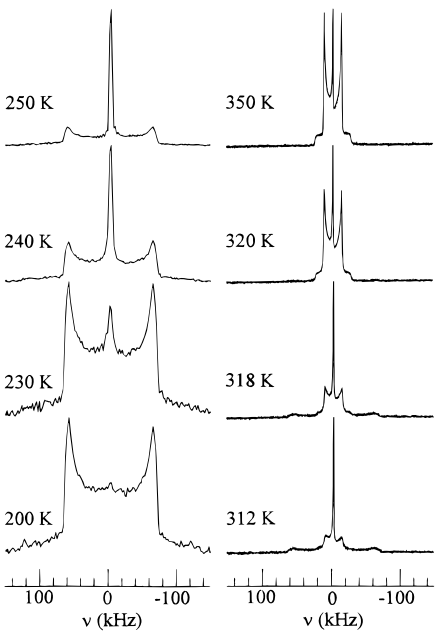


**Figure 3.** Variable temperature $^2$H-NMR spectra. Relative intensities of rigid and mobile fractions are distorted because of different relaxation rates. The vertical scale of the spectra in the right column is enlarged by a factor of 13. The isotropic peak is truncated to display the signals of the mesomosphic and crystalline fractions.

phase transition temperature was observed. PDHS-d showed a phase transition at 320 K in contrast to PDHS, that revealed a phase transition at 315 K. This difference was reproducible and occurred in all DSC scans for polymer samples from different batches. We are not aware of any other example where deuteration has a similarly strong influence on thermotropic phase behavior. The strong deuterium effect observed here may be due to the uniquely dense substitution pattern of polysilylenes.

We employed $^{29}$Si-NMR spectroscopy to study the variation of backbone mobility with temperature, in particular upon the transformation to the conformationally disordered mesophase. Figure 2 shows the variable temperature $^{29}$Si-NMR spectra of PDHS without sample spinning in the temperature range between 210 and 350 K. At 210 K the signal exhibits a line width of over 30 ppm due to chemical shift anisotropy, evidencing rigidity of the polysilylene backbone. While the line width remains relatively unchanged up to the temperature of the mesomorphic transition, the line shape varies slightly, indicating a change of the principal values of the chemical shift tensor. Already at 270 K, well below the temperature where the phase transition is observed by DSC, an additional peak starts growing. This signal may arise from the onset of the phase transition or from the mobile amorphous fraction. The phase transition leads to a pronounced narrowing of the line width to about 20 ppm. The signal of the mesophase exhibits an axially symmetric averaged chemical shift tensor in agreement with rotational mobility about the main-chain axis. The spectrum of the mesophase resembles the chemical shift anisotropy signals observed for polysiloxanes in the conformationally disordered mesophase.[22] $^{29}$Si magic angle spinning spectra recorded by us show a small downfield drift of the isotropic chemical shift with increasing temperature, both in the crystalline phase and in the mesophase. At the phase transition, a discontinuous upfield shift by more than 3 ppm gives evidence of the increasing fraction of gauche conformations.[19,20]

The $CD_2$ group adjacent to the polymer backbone was used as a probe for the mobility of both the alkyl side chain and the Si backbone. Figure 3 shows the variable temperature $^2$H-NMR spectra between 200 and 350 K. The spectrum at 200 K is a typical Pake spectrum with a splitting of 123 kHz. The line shape evidences that the polymer is immobile and rigid at this temperature. At 230 K an isotropic peak is discerned that grows with increasing temperature. The appearance of a mobile, isotropic fraction of the material is related to the $T_g$ observed at 233 K by DSC. Thus, the isotropic peak can be attributed to a small amorphous fraction of the sample that attains mobility above $T_g$, while the main fraction of the polymer is present in the crystalline state. This is not revealed by $^{29}$Si-NMR.

Raising the temperature further to 312 K leads to a slight narrowing of the Pake spectrum to a splitting of only 118 kHz. This finding is consistent with the gradual change of the $^{29}$Si line shapes and points at a slightly increasing mobility of the polymer chains, which may exhibit small-angle librational motions in the crystalline phase already.

The transformation into the conformationally disordered mesophase changes the $^2$H-NMR spectrum drastically. In the temperature interval between 310 and 320 K the intensity of the Pake spectrum decreases gradually and the spectrum evidences the simultaneous presence of three components, the almost rigid crystalline fraction and the mobile mesomorphic and isotropic fractions. Above 320 K a Pake spectrum with a line width of 23 kHz is observed, that reflects axial symmetry of the molecular motions and the highly dynamic nature of side chains in this phase. The axially symmetric line shape of the $\mu$-phase shows clearly that anisotropic motions with an at least 3-fold symmetry axis occur. The small value of the splitting further proves that the Si−C1 bonds reorient by large angles, which is feasible only if the backbone is flexible. The backbone motion can be visualized as polymer segments reptating in cylinders, causing a rapid exchange of backbone conformations. Thus both $^{29}$Si- and $^2$H-NMR give clear evidence of the high mobility of the Si-

catenated backbone as well as adjacent methylene units of PDHS.

**Conclusion.** Solid state $^{29}$Si- and $^{2}$H-NMR spectroscopy have been employed to study the mobility of PDHS in the temperature range between 200 and 350 K. For the $^{2}$H-NMR measurements, a PDHS sample deuterated in the C1 position, which is the most sensitive to backbone motions, was used. The experiments show clearly that the polysilylene backbone is highly mobile in the $\mu$-phase. Thus, the Si backbone is locally flexible despite the dense substitution pattern. It is reasonable to assume that this conclusion is valid for both the deuterated and the nondeuterated PDHS sample, in spite of the morphological differences (i.e., higher crystallinity and slightly different packing of the deuterated sample).

The $^{2}$H-NMR spectra clearly show that an amorphous fraction coexists with the mesophase. We observe furthermore that this isotropic fraction is not transformed into the columnar like mesophase, even after keeping the sample at an elevated temperature (above the phase transition) for prolonged periods. This may be explained by amorphous areas with entangled chains that can neither crystallize nor adopt the order of the $\mu$-phase, in spite of the mobile state.

The considerable shift of the phase transformation temperature caused by the deuteration of the C1 position is not yet fully understood but appears to arise from a small difference in chain conformation or packing. The magnitude of the effect is probably related to the dense substitution of the polysilylene backbone, in analogy to the strong effects observed when a small fraction of chiral comonomer is introduced in poly(di-*n*-pentylsilylene).[23]

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