Communication: The dynamics of poly(dimethylsiloxane) in its inclusion compound with \( \gamma \)-cyclodextrin are elucidated using modern fast-MAS solid-state NMR techniques. Measurements of methyl \( ^1H-^1H \) and \( ^1H-^{13}C \) dipolar coupling constants indicate that the polymer undergoes a uniform motion, rendering all methyl groups equivalent. The dynamics of the Si–C bond is characterized by either a dynamic order parameter of \( S = 0.72 \), or, assuming a stably rotating helical structure, an inclination angle of \( 73^\circ \) relative to the rotation axis.

An Investigation of Poly(dimethylsiloxane) Chain Dynamics and Order in Its Inclusion Compound with \( \gamma \)-Cyclodextrin by Fast-MAS Solid-State NMR Spectroscopy

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Introduction

Inclusion complexes of different polymers with low-molecular-weight organic compounds, such as urea, perhydrotriphenylene, or cyclodextrin, represent an interesting class of materials in which the individual polymer chains exhibit a perfect, crystal-induced unidirectional ordering. This can be used to advantage in the preparation of, e.g., novel chain-extended crystal morphologies by coalescence of the chains upon dissolution of the host.\(^{[1]}\) Another interesting aspect is the possibility to study local dynamics of the isolated polymer chain without the complications arising from cooperative motions,\(^{[1,2]}\) which would usually dominate the relaxation properties of the chains in bulk.\(^{[10]}\) As the picture of the dynamic behavior of polymers in inclusion compounds has not been clarified yet satisfactorily,\(^{[2,4,5]}\) and NMR investigations of guest dynamics in inclusion compounds are generally rare,\(^{[2,4–7]}\) we present the first quantitative solid-state NMR investigations of local segmental fluctuations and order in such a system. Our methods of choice are novel multiple-quantum magic-angle spinning (MAS) techniques,\(^{[8,9]}\) which do not require isotopic labeling, and are well-suited to study local polymer dynamics very selectively.\(^{[10,11]}\)

The propensity of an organic compound to include an extended polymer chain rests on its ability to form stable crystalline modifications of channel-like cavities with the right size and polarity. Cyclodextrins (CD) meet this requirement; the individual molecules have an apolar cavity, and are capable of forming stabilizing intermolecular hydrogen bonds. Inclusion compounds of CD with low-molecular-weight compounds are known to exist in three different structural varieties: herringbone cage-, brick cage-, and channel-type structures.\(^{[12]}\) The channel-type structure is, of course, realized in inclusion compounds with polymers. \( \gamma \)-CD \(( n = 8 \) in Scheme 1 in Figure 1a) readily forms inclusion compounds with a variety of polymers,\(^{[2,4,13–16]}\) of which we focus on the inclusion compound with poly(dimethylsiloxane) (PDMS).\(^{[15,16]}\)

Since in well-resolved MAS spectra, the separation of signals from the host and the polymer is straightforward, it is possible to measure residual homonuclear \(( ^1H-^1H \) \) and heteronuclear \(( ^1H-^{13}C \) \) dipolar couplings associated with the polymer. We concentrate on the influence of
segmental motions on the averaging of couplings within the individual methyl groups of PDMS. Methyl groups are well suited local dynamic probes on account of the possibility of approximating the description of experimental data from experiments performed under MAS in terms of the dominating intra-methyl interactions only.\(^\text{[17]}\) On account of the fast three-site jump motion of methyl protons,\(^\text{[10]}\) the \(^1\text{H}\)-\(^1\text{H}\) and \(^1\text{H}\)-\(^13\text{C}\) dipolar coupling tensors are preaveraged and symmetric with respect to the symmetry axis of the jump process, which coincides with the Si—C bond vector. The results reported in the following thus describe the motion of the Si—C bond.

**Experimental Part**

**Sample Preparation**

The anionically synthesized PDMS sample was kindly donated by J. Naim and Th. Wagner, Max-Planck-Institute for Polymer Research, Mainz, Germany. The molecular weight as determined by means of GPC was \(M_\text{n} = 2640\) g/mol (about 35 siloxane units) with a polydispersity index of 1.36. The inclusion compound was prepared following the procedure published by Harada and coworkers.\(^\text{[16]}\) \(^1\text{H}\) NMR analysis of the precipitated and washed product indicated a significant contamination with surface-absorbed, likely cyclic PDMS. The major part of the impurity could be removed by washing in cyclohexane. As a result of this treatment, a small amount of cyclohexane became included into the CD (vide infra).

**NMR Experiments and Data Analysis**

All experiments were carried out on a Bruker Avance 500 solid-state NMR spectrometer running at Larmor frequencies of 500.2 MHz and 125.8 MHz for protons and carbons, respectively. The measurements were performed using a 2.5 mm MAS probe with typical \(\omega_0/2\pi\) frequencies of 125 kHz for \(^1\text{C}\) and \(^1\text{H}\) pulses, and 125 kHz for TPPM (two-pulse phase modulation) decoupling.\(^\text{[8]}\) The heteronuclear recoupling sequence used to probe \(^1\text{H}\)-\(^13\text{C}\) dipolar couplings was REPT-HDOR;\(^\text{[9]}\) \(^1\text{H}\) double-quantum experiments were performed using the compensated BaBa pulse sequence.\(^\text{[8]}\)

The two quantitative NMR techniques used in this paper are heteronuclear and homonuclear recoupling techniques operating at high MAS frequencies. They are based on essentially the same principles, and can both be used to extract residual (motionally averaged) dipolar coupling constants \((D_{\text{res}})\) that characterize the extent of local order of a polymer chain as a result of anisotropic dynamics.\(^\text{[10, 11, 20]}\) The order can be described in terms of a dynamic order parameter

\[
S = D_{\text{res}}/D_{\text{stat}} = \frac{1}{2} \left( \frac{3}{2} \cos^2 \theta(t) - 1 \right) \tag{1}
\]

which depends on the time-averaged instantaneous azimuthal angle \(\theta(t)\) and is calculated by comparison with the coupling constant in the static limit \((D_{\text{stat}})\). By virtue of MAS, the multi-spin coupling topology of a system of many dipolar-coupled proton spins breaks up into a sum of pair couplings,\(^\text{[17]}\) which allows the determination of localized individual order parameters associated with specific pair coupling vectors.\(^\text{[10]}\) However, the methyl groups of PDMS cannot be analyzed in terms of the common spin-pair approximation.\(^\text{[21]}\) The theoretical description of the behavior of a methyl group in the \(^1\text{C}\)-detected heteronuclear experiment (REPT-HDOR) can be found in the literature.\(^\text{[8]}\) An analogous treatment for the homonuclear DQ experiment, BaBa,\(^\text{[8]}\) is still missing. Double-quantum excitation in methyl groups was investigated previously for different pulse sequences,\(^\text{[22, 23]}\) but not for BaBa used here. The derivation of the theoretical formula for BaBa is the subject of a separate publication.\(^\text{[24]}\) The result is:

\[
I_{\text{dall}}(N, t_1) = \frac{2}{3} \left( \sin \left( 2\sqrt{3}N, \Phi^{\text{HH}}(0, \tau_\text{e}/2) \right) \right) \times \sin \left( 2\sqrt{3}N, \Phi^{\text{HH}}(t_1, t_1 + \tau_\text{e}/2) \right) \times \cos \left( 3 \Phi^{\text{HH}}(0, t_1) \right) \tag{2}
\]

Angular brackets denote the powder average. \(N\) is the excitation time in multiples of the rotor period, \(\tau_\text{e}\), and is a parameter under the experimentalist’s control. \(\Phi^{\text{HH}}(t_1, t_0)\) are phase factors associated with the excitation and reconversion periods of the DQ coherence, which depend on the dipolar tensor orientation and are proportional to the coupling constant between individual protons over the spinning frequency \((D_{\text{HH}}/\omega_0)\). The indirect time domain variable, \(t_1\), is relevant only for 2D DQ correlation or sideband spectra.

Both the hetero- and homonuclear experiments can be analyzed in the same way: given a proper spectral separation of the signals associated with individual functional groups, the associated dipolar coupling constants can be extracted either by fitting the intensity build-up behavior (varying \(N\)) or by analyzing the sideband pattern in a full 2D spectrum for fixed \(N\).\(^\text{[8]}\) A special case of the latter is the homonuclear 2D SO/DQ shift correlation spectrum used below to probe approximate spatial proximities between spectrally resolved protons\(^\text{[22]}\) in which case the \(t_1\)-increment equals \(1 \tau_\text{e}\), and no sidebands are observed.

**Results and Discussion**

**Characterization of the Inclusion Compound**

\(^1\text{C}\) CP MAS spectroscopy represents a convenient method with which to prove the formation of the actual inclusion compound.\(^\text{[15, 16]}\) As demonstrated in Figure 1, \(\gamma\)-CD adopts an asymmetric, non-circular ring conformation in the crystalline state, resulting in multiple \(^1\text{C}\) signals. In the channel structure, the CD ring is more symmetric, and as a consequence, the signals corresponding to like carbon atoms in different glucopyranosyl rings have much closer chemical shifts.

A simple \(^1\text{H}\) spectrum provides preliminary insight into the dynamic states of host and guest in the inclusion com-
pound (Figure 2a, bottom slice). Even at 30 kHz MAS and a 1H larmor frequency of 500 MHz, the resonances of the individual protons in the glucopyranose rings are not resolved and form a broad resonance extending from 1 to 8 ppm. This line broadening indicates an essentially rigid 1H dipolar coupling environment for these signals. In contrast, signals from the OH/H2O hydrogen bonding region and the guest molecules are much sharper as a result of dynamics faster than hundreds of kHz, by which 1H dipolar couplings are partly averaged.

This reasoning is confirmed by comparison of 1D double-quantum filtered experiments with increasing recoupling times (Figure 2a, upper slices). The spectral intensities in such spectra are solely derived from nuclei which have a dipolar-coupled partner. The shorter the recoupling time needed to see a signal, the stronger is the coupling of the corresponding nucleus. The spectrum taken with the shortest possible recoupling time of 1 rotor period is dominated by the signal from the CD host matrix. Signals of such strongly coupled protons are subject to an ensuing decay at longer recoupling times due to the perturbing influence of further protons and the excitation of higher spin modes. This is what is observed upon going to a recoupling time of $4 \tau_R$, where signals from the OH/H2O and guest protons become the main contributors.

The persistence of these signals at $8 \tau_R$ supports the assumption of a much weaker coupling. In all spectra, the cyclohexane (ch) impurity can easily be identified. Since its signal intensity follows the trend of the PDMS signal, it also seems to be included in the CD. However, the presence of this impurity is not expected to have a negative effect on any of the investigations and conclusions to be drawn in this paper.

Although being composed of signals from pairwise coupled protons, the 1D DQ-filtered spectra do not contain any information on the chemical identity of the coupling partner of the proton corresponding to the observed signal. Possible coupling partners are protons of the same kind (auto peaks from, e.g., intra-CH2 or intra-CH3), or protons in adjacent functional groups (cross peaks). A 2D SQ/DQ correlation spectrum serves to identify the nature of the dipolar coupled pair, since the coupling partner of the directly detected spin can be identified in the indirect dimension, where the chemical shift is the sum of the shifts of the two involved protons. Auto peaks are located on the DQ diagonal, which has a slope of $2 \Delta \omega_{SQ}$. Figure 2b exhibits such auto peaks for the CD, ch, and PDMS-CH3 resonances, respectively. More interesting, however, are the intense and well resolved cross peaks between CD and PDMS (the cross peak detected at the CD signal position is much weaker as a result of dephasing due to strong intra-CD couplings). The dipolar coupling constant between the guest and the host must therefore be on the order of or exceed a few hundred Hz, proving that whatever fast motion the polymer chain performs, it must be a local one. Chain motion along the tube on a timescale of 100 μs (the approximate timescale of the experiment) or faster per translation on the lengthscale of one CD unit (about 7 Å), corresponding to an estimated diffusion constant of $5 \times 10^{-15} \text{ m}^2/\text{s}$, can be excluded.
Dynamics of the Included PDMS Chain

Having identified the dynamic states of the different molecular species in the inclusion compound qualitatively, we now turn to a quantitative analysis of the PDMS chain dynamics. We restrict our attention to characterizing the degree of anisotropy exhibited by the methyl groups moving together with the chain at about 40 °C (slight heating due to rotor friction). This motion is in the fast motion limit with respect to the magnitude of the rigid-limit dipolar coupling constants, which is confirmed by the fact that the experimental results described in the following are not a function of temperature, as is apparent from the data in Figure 4a. The knowledge of the dipolar coupling constant, averaged over the motional process, allows us to compare the result with a plausible motional model.

When dipolar coupling constants involving protons are to be determined, particular care has to be devoted to the consideration of remote couplings in the abundant proton spin bath. These remote couplings typically increase the experimental result relative to the ideal one, which would be measurable only in isolated moieties. The methods used here are known to be only weakly influenced by such effects,\textsuperscript{[9,21,25]} mainly due to the effect of fast MAS.\textsuperscript{[17]} Since the homo- and heteronuclear dipolar coupling tensors within a single methyl group have the same orientational dependence as a result of the fast rotation of methyl groups, the determination of the associated coupling constants yields the same type of information, and a comparison of the results serves as a consistency check. A second check is provided by the option of extracting the coupling constants in two different ways for each of the methods: build-up and sideband patterns are sensitive to remote couplings in different ways.

Figure 3 shows the results of intensity build-up and sideband analyses for the heteronuclear intra-CH\textsubscript{3} coupling. Data generated by the theoretical formula\textsuperscript{[9]} are seen to fit the experimental data satisfactorily. A known influence of secondary couplings on REPT-HDOR patterns are the slightly increased first-order sidebands in the experimental spectra, which are apparent in Figure 3a.\textsuperscript{[9]} By exclusion of the first-order sidebands from the fit, an accurate result can nevertheless be obtained. The influence of remote couplings on the intensity build-up is less straightforward. The fact that the characteristic oscillations of the signal at longer recoupling times can be observed is a very strong indication that not only are the secondary couplings weak, but moreover that the data can be described by a single dipolar coupling constant. Considering that an extended polymer chain most likely forms a helix, it is not self-evident \textit{a priori} that there is only one type of methyl group with one well-defined inclination angle \(a\) between the Si–C bond and the helical axis. A mixture of different local conformations with different angles \(a\) would lead to different observable coupling constants. This scenario would lead to a smearing of the oscillations, which is not observed. Furthermore, the chemical shift of the CH\textsubscript{3} group of PDMS (2 ppm) is very close to the corresponding shift in bulk crystalline PDMS (3 ppm), which can be taken as an indication for a regular, helical structure.\textsuperscript{[26]}

In conclusion, PDMS seems to exist in a highly symmetric conformation with all methyl groups experiencing the same local environment and the same kind of motion. Of course, it is also possible that all methyl groups behave the same as a result of fast conformational fluctuations. We will analyze the data in terms of both models.

Before turning to a quantitative analysis, we shall also consider the measurement of the homonuclear coupling constants among the protons of the methyl groups, which, as explained above, are influenced by the motional process in the same way as the heteronuclear couplings. Figure 4 shows experimental homonuclear DQ sideband spectra along with numerical results. The homonuclear \(^1H\) data is much more susceptible to the influence of remote couplings.\textsuperscript{[21,23,25]} Therefore, a simple fit using Equation (2) does not give a unique result. By comparison of various numerical 6-spin simulations including couplings to the remote methyl protons within the same monomeric unit, it was possible to extract an estimated coupling constant of 3.6 kHz. It should be emphasized that this coupling constant is still more likely to be overestimated than the \(^1H–^13C\) data as a result of further couplings to remote protons. We note, however, that the number and approximate intensity distribution of the outer sidebands is already reproduced in the result calculated from Equation (2), as can be seen in Figure 4b. The effect of remote protons again seems to be predominant.

Figure 3. Quantitative determination of the \(^1H–^13C\) dipolar coupling constant for the methyl groups of the PDMS chain in the inclusion compound using the REPT-HDOR experiment at 30 kHz MAS. (a): Spinning sideband pattern (\(\tau_p = 24\,\tau_s\)), and (b): 1D intensity build-up as a function of the recoupling time. The dashed lines represent fits to the experimental data using the theoretical formula from the literature\textsuperscript{[5]} with \(D_{\text{cis}}/2\pi = 2.65\) and 2.13 kHz for (a) and (b), respectively, from which the angle \(a\) can be derived (see text). In (b), an empirical exponential damping function with a decay constant of 0.48 ms was included in the fit.
Figure 4. Quantitative determination of the $^1$H–$^1$H dipolar coupling constant for the methyl groups of the PDMS chains in the inclusion compound using spinning sidebands as measured using the BaBa pulse sequence at 30 kHz MAS and a recoupling time of 8 $\tau_p$. In (a), experimental spectra are shown for two different temperatures, which are corrected for the frictional heating in fast-MAS probes. (b) shows the analytical result calculated from Equation (2) (bottom trace) and a result of a numerical simulation considering the complete 6-proton system of a single PDMS monomer unit (top trace), both calculated using an intra-CH$_3$ dipolar coupling constant of 3.55 kHz.

in the first-order sidebands, in analogy to the heteronuclear experiment.

The experimental data can be analyzed in the following way: assuming a well-defined and uniform rotation of a helix, the angle $\theta$ is related to the experimental dipolar coupling constant by way of the second Legendre polynomial, in equivalence to Equation (1):

$$P_2(\cos \theta) = D_{\text{exp}}/D_{\text{stat}} = \frac{1}{2} (3 \cos^2 \theta - 1)$$

(3)

Since the sign of $D_{\text{HH}}$ cannot be determined with our methods, two solutions for $\theta$ are possible. Values for $\theta$ smaller than the magic angle (54.7$^\circ$) are, however, unlikely from steric considerations, so we will report only the larger value. If an assumption on the average chain structure exists, and the experimental value of $D_{\text{exp}}$ differs from the one predicted by the above relationship, fast conformational fluctuations instead of a rotation may be assumed to reduce the coupling. One can then redefine the order parameter in Equation (1):

$$S_0 = \frac{D_{\text{exp}}}{D_{\text{stat}}} \frac{1}{P_2(\cos \theta)}$$

(4)

$S_0$ now describes the chain order in terms of the projection of the internuclear coupling vector onto the local polymer backbone direction.$^{[10, 11]}$ For our analysis, we assume $\theta = 90^\circ$, which represents a likely average orientation of the Si–C bond in view of the fact that the vector between two oxygen atoms in the SiO$_2$(CH$_3$)$_2$ tetrahedron should be on average parallel to the chain axis.

Using $D_{\text{CH,stat}}/2\pi = 6.9$ kHz$^{[9]}$ and $D_{\text{HH,stat}}/2\pi = 8.9$ kHz$^{[31]}$ as the rigid-limit values for methyl groups (which are rotating themselves), the average $D_{\text{exp}}/D_{\text{stat}}$ over all three measurements is calculated to be $0.36 \pm 0.05$. The order parameter $S_0$ is thus $0.72 \pm 0.1$. Alternatively, assuming that the chain is in a stable helical conformation and performs a well-defined rotation, we obtain $\theta = 73 \pm 3^\circ$. The error margins are based on the deviations of the three different experiments and thus represent the systematic error introduced by the different effects of remote couplings on the various experiments. The influence of centrifugal forces in fast-MAS rotors on these results is still an open question; we assume that such effects are weak. Scheme 2 in Figure 1b shows a sketch of our model of PDMS chain motion in the inclusion compound.

We note that local angular conformational excursions of the chain with amplitudes large enough to explain the observed reduction of the dipolar coupling seem rather unlikely considering the small diameter of the cavity in $\gamma$-CD (about 8 Å). Additional measurements (not shown) on an inclusion compound with a PDMS of $M_n = 1000$ g/mol (about 13 siloxane units) yielded equivalent results, indicating a negligible influence of finite-chain effects. Further investigations on inclusion compounds of PDMS chains within smaller cavities of $\beta$-CD are underway to prove this assumption. Results from neutron scattering experiments indicate that the helices formed by PDMS are surprisingly stable even in the melt.$^{[28]}$ Therefore, we favor the model of a rotating helix and believe that our result is significant in that it may provide valuable information about the helix structure, which is still a matter of debate even in crystalline PDMS.$^{[29]}$ The possible analogy is corroborated by the narrow PDMS signal and its chemical shift, as mentioned above.

**Conclusions**

Our results prove that PDMS chains in $\gamma$-CD most likely perform rotational motions about the polymer backbone or segmental fluctuations in the MHz regime. All methyl groups exist in the same motional state, which is characterized by a tilt angle of about 73$^\circ$ between the Si–C bond and the rotation axis or, more generally, by a dynamic order parameter of $S_0 = 0.72$. The presented NMR data alone does not allow a definite validation of the rotational model; the real situation may also be a combination of rotation and bond librations. The situation is reminiscent of inclusion compounds of alkanes in various host matrices$^{[7]}$ or discotic liquid crystals$^{[30]}$ where the all-trans chains or mesogens, respectively, feature similarly well-defined rotational motions. It was further possible to identify weak through-space dipolar contacts between the rotating PDMS chain and the rigid host. Therefore, chain motion along the channels with a diffu-
sion constant much larger than $5 \times 10^{-15}$ m$^2$/s can be excluded.

This work represents the first step towards using the particularly sensitive homonuclear $^1$H DQ approach to measure chain order also in PDMS melts or samples with very small volume fraction of polymer, as for instance absorbed to a surface, without the need for isotopic labeling. First results for a PDMS melt indicate that even though the order parameter in an entangled melt is almost two orders of magnitude smaller than in inclusion compounds, the system is still well behaved in that the order parameter can be estimated to a good approximation by analysis of spinning sideband patterns or DQ intensity buildup (not shown here) within the single-methyl group approximation, Equation (2).[24] This is an important advantage because in earlier work on order and dynamics in mobile polymers,[10, 11, 20] the DQ experiments had to be limited in highly mobile PDMS systems.

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