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Study of Molecular Interactions and Dynamics in Thin Silica Surface Layers by Proton Solid-State NMR Spectroscopy

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We present results from proton double-quantum magic-angle spinning NMR spectroscopy in support of tight molecular contacts of the modifier bis(triethoxysilylpropyl) tetrasulfane with the surface of precipitated, amorphous silica. While chemical bonding cannot be proven directly, its presence is indicated by through-space dipolar contacts between surface-OH groups and all aliphatic protons of the modifier, as well as strongly anisotropic motions of the surface-bound molecules. Silica−modifier contacts are further only found when the samples were heated during preparation. Only small amounts of ethanol were seen to leave the silica surface upon modification. A good part of the ethanol set free upon condensation becomes bound to the silica surface, which is supported by the presence of tight contacts in silica treated with pure ethanol. The anisotropy of molecular motions of the surface-bound molecules is characterized by the estimation of proton dipole−dipole coupling constants from double-quantum sideband patterns and build-up curves. Self-condensed samples of the modifier either exhibit very different dynamic properties or show no indication of contacts between hydroxyl and aliphatic protons.

I. Introduction

Wherever surfaces are exposed to external media, the ever-growing demands for improved properties necessitate their modification with organic or inorganic materials. For instance, modification of polymer surfaces is paramount to the design of biocompatible devices such as artificial arteries or cardiac valves, or for the design of materials with optimized scratch-resistant or low surface energy surfaces.[1] Silanization of glass and silica surfaces ranges among the most common approaches to surface modification. For example, to improve the mechanical properties of polymers, silanized fillers such as glass fibers or inorganic particles are used to ensure good matrix/filler adhesion.[2]

A particular example related to the present study is the modification of silica with silane coupling agents using the condensation reaction of alcohol or halogen functions with the silanol groups of the silica surface.[3−5] Focusing on the particular case of bis(triethoxysilylpropyl) tetrasulfane (TESPT) as one of the most commonly used modifiers in rubber applications,[6] we show how modern solid-state NMR methods can be used to gain rich insight into the surface modification process. The presented approach should be useful for many other investigations focusing on the as yet not fully understood processes involved in silanization.

TESPT is the most commonly used organosilane and is the key to the use of silica for tire tread compounds. Modified silica compounds exhibit improved high- and low-temperature dynamic hysteresis properties as compared to compounds with carbon black. These are key properties for improved tire performance with respect to lower rolling resistance and better wet skid resistance.[6] The coupling between silica and rubber is believed to be achieved by the substitution of the ethoxy groups of TESPT with the silanol groups of silica, and that between the tetrasulfane group and the rubber is achieved during vulcanization with sulfur.

Model studies of the silica-TESPT reaction based on ^{29}Si and ^{13}C chemical shifts measured by rather time-consuming cross-polarization (CP) MAS NMR spectroscopy have provided indirect evidence that a chemical reaction is likely to occur,[7] although many details are still unclear. While the proof of silica-modifier bonding by 2D homo- or heteronuclear NMR spectroscopy involving *J*-couplings among ^{29}Si and ^{13}C or ^{1}H would be the most straightforward approach, it is a notoriously difficult task due to the weak signal of ^{29}Si at the surface.[8] Further, as the modifier in question is a silicon-based material which might also undergo self-condensation reactions, ambiguities must be expected. We here

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present a robust and time-efficient alternative approach providing additional, also indirect evidence of tight surface contacts using ^1H solid-state NMR spectroscopy.

Exhaustive studies of the surface of sol−gel and fumed silica by different high-resolution ^{29}Si, ^{13}C, and ^1H methods are due to Maciel and co-workers.[3,4,9−11] Chemical bonding of chloro- and ethoxysilanes to silica surfaces was inferred from ^{29}Si chemical shifts, and different species of surface water and silanol groups on the untreated silica surface could be identified, assigned, and characterized with respect to their thermal behavior, spatial distribution, and molecular motion.

Recently, ^1H methods employing very fast magic-angle spinning (MAS) became recognized as very robust and efficient tools for the high-resolution characterization of surfaces and interfaces.[12−16] Here, multiple-quantum and, more specifically, double-quantum (DQ) techniques are particularly suited for the determination of intermolecular contacts via dipole−dipole couplings[17,18] and have successfully been applied to surface and thin-film samples.[12,13,15,16,19,20]

In this work, we demonstrate for the first time the use of ^1H DQ MAS methods for the investigation of the extent of formation of tight molecular contacts between silica and organosilane modifiers as well as for a site-resolved characterization of the molecular dynamics in a surface layer. We have employed the robust and easy to setup back-to-back (BaBa) pulse sequence.[21,22] The experiment works well at very fast MAS, but it does not feature the fine intensity build-up time resolution needed for the determination of dipolar couplings, as provided by more advanced experiments such as the C-type sequences.[23] This is, however, compensated by the possibility of performing a spinning sideband analysis in the indirect dimension of two-dimensional DQ correlation spectra.[24−26]

The subjects of our investigations are the precipitated, amorphous silica Ultrasil VN3 and the modifier bis(triethoxysilylpropyl) tetrasulfane (TESPT) as well as pure ethanol. The latter is set free upon condensation of TESPT with the surface or itself. We demonstrate the feasibility of the ^1H DQ MAS approach for the establishment of information on surface bonding, and a qualitative understanding of the dynamics of the surface-bound species. Our findings are compared to results obtained from acid- and base-catalyzed self-condensation products of TESPT. The molecular mobility of the surface-attached molecules is characterized by estimation of the dynamically averaged dipole−dipole coupling constants.

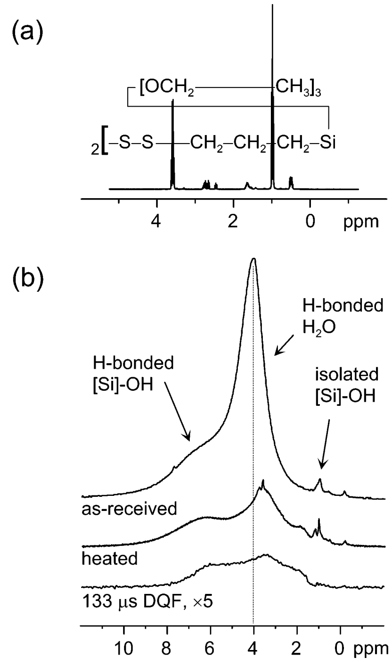

Figure 1. (a) ^1H solution-state NMR spectrum of TESPT and signal assignments. (b) ^1H MAS solid-state one-pulse and DQF NMR spectra of as-received and heated silica VN3 along with assignments according to refs 10 and 11.

II. Experimental Section

A. NMR Spectroscopy. The ^1H solution-state NMR spectrum in Figure 1 was recorded on a Bruker ARX 300 using $CDCl_3$ as solvent. ^1H solid-state NMR experiments were performed on a Bruker Avance 500 solid-state NMR spectrometer operating at a Larmor frequency of 500.2 MHz. All experiments were conducted under magic-angle spinning conditions using a 2.5 mm MAS probe at a spinning frequency of 30 kHz with 90° pulses of 2 μs length, corresponding to a B_1 nutation frequency of 125 kHz. The chemical shift was externally referenced to the ^1H resonance of solid adamantane at 1.63 ppm. The recycle delays for most of the displayed spectra were 500 ms. The T_1 relaxation times of the different components averaged to around a second, and integrations were performed on completely relaxed spectra with a waiting time of 10 s between scans, showing that the relative peak intensities were not substantially different. DQ experiments in this work were conducted using the back-to-back (BaBa) pulse sequence,[21] where the compensated version[22] was used for experiments with excitation times equal to an integer multiple of 4 rotor cycles ($n \times 133\ \mu$s).

^1H double-quantum (DQ) spectroscopy involves the excitation of coherences which comprise two coupled protons by applying a specific, so-called recoupling pulse sequence for a certain excitation time (τ_{exc}), thereby providing a means to estimate the coupling constant between two spins in a site-resolved fashion. DQ coherences are in principle not observable; therefore, their detection is achieved in an indirect

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Table 1. Samples Investigated in This Study

	preparation	appearance	degree of condensation[a]
VN3	dried in vacuo at 105 °C	white powder	
VN3-TESPT1	heated for 24 h at 105 °C	white powder	8%
VN3-TESPT2	heated for 24 h at 165 °C	white powder	7%
VN3-EtOH	heated for 24 h at 105 °C	white powder	
TESPT-c1	condensation with 10% $HCOOH/H_2O$	glassy solid ($T_g \approx 45$ °C)[b]	~75%
TESPT-c2	condensation with 90% $HCOOH/H_2O$	glassy solid ($T_g \approx 30$ °C)[b]	~60%
TESPT-c3	condensation with 99% HCOOH	brittle gel	45%
TESPT-c4	condensation with 25% NH_3 in H_2O	brittle gel	33%

[a] Given in terms of the loss of EtO− as estimated by integration of the EtO-resonances in the ^1H NMR spectra of Figure 3. [b] Very broad transition (±20 °C), determined by DSC.

manner by filtering (using a four-step phase cycle) and then reconverting them to observable magnetization using the same pulse sequence.[27] Note that, by nature of the experiment, multiple-quantum coherences comprising higher even numbers of spins are also excited, but contribute only at longer recoupling times and to a much lesser extent and are therefore negligible.

Dipolar coupling constants depend on the distance between the spins ($D_{HH} \sim 1/r^3$) and on the extent of molecular motion. The mere observation of a dipolar contact between two spins proves their spatial proximity on the order of 2−5 Å in the experiments performed herein. Moreover, fast anisotropic molecular motion as a result of conformational fluctuations, which are expected for surface-immobilized molecules, reduce the strong dipolar coupling between two protons attached to the same carbon in a systematic way. For example, for the common case of fast uniaxial rotation, with the internuclear vector being inclined by θ with respect to the rotation axis, a reduction of the coupling by a factor of $P_2(\cos\theta) = {}^1/_2(3\cos^2\theta - 1)$ is observed. Therefore, the knowledge of intra-CH_2 dipolar coupling constants allows us to draw conclusions on the motional process and its amplitude.

Coupling constants can be estimated by monitoring the intensity of DQ-filtered (DQF) spectra as a function of the incremented excitation and reconversion time. DQF spectra shown in this paper are always obtained by summation of 32 transients, as are the one-pulse NMR spectra. The comparison of DQF spectra with one-pulse spectra allows us to roughly estimate the amount of dipolar-coupled, that is, immobilized molecules, at the surface. In the absence of relaxation and signal loss due to experimental imperfections, a theoretical maximum of about 50% of the spectral intensity of a powdered sample can be filtered through DQ coherences, while in a typical, rigid organic solid under realistic conditions, 20−30% is possible when $\tau_{exc}D_{HH}/2\pi \approx 0.7$.[21] This efficiency is realized for some of the investigated samples, such as water and ethanol bound to silica as well as two of the self-condensed TESPT samples. This number represents an upper estimate, with which our data shall be compared. We will further use DQ build-up curves, that is, the integrated DQF intensities of specific peaks in the spectra, normalized with respect to the intensity after a 90° pulse, for a qualitative comparison of the dipolar couplings associated with different CH_2 groups of surface-bound molecules and an estimation of a distribution of couplings.

It is further possible to introduce an indirect spectroscopic dimension between DQ excitation and reconversion. The resulting DQ correlation spectrum provides a means to identify coupling partners by their double-quantum shift, which is just the sum of the chemical shifts of the two involved nuclei. This approach is the solid-state analogue of the INADEQUATE method known from solution-state NMR.[27] Further, for certain DQ pulse sequences, characteristic spinning sideband patterns appear in the DQ dimension when magic-angle spinning is employed and the indirect time domain is incremented in steps smaller than a single rotor period.[24−26] These sideband patterns are a sensitive function of the internuclear coupling constant and provide an alternative way to extract quantitative information.

B. Materials and Preparations. The subject of the investigations is the precipitated, amorphous silica Ultrasil VN3 manufactured by Degussa. VN3 has a specific BET surface area of 175 m^2/g, contains about 5.5% w/w water, and is slightly acidic (pH = 6.2). Prior to use, VN3 was kept at 105 °C in a membrane vacuum (~20 mbar) for 24 h in all cases so as to obtain a controlled, low amount of surface water. TESPT (trade name Si69) was purchased from Degussa and was used without further purification. NMR spectra of TESPT and VN3 along with chemical structures and signal assignments are shown in Figure 1.

The comparison of ^1H spectra of the as-received and heated VN3 (Figure 1b) unveils the typical dehydration pattern of silica surfaces and permits an estimate of the amount of residual surface water: the H_2O resonance, initially located at 4 ppm due to rapid exchange between the free (4.8 ppm) and the H-bonded (3.5 ppm) state,[11] decreases in intensity upon heating in vacuo and shifts to 3.5 ppm, indicating the sole presence of a monolayer of H-bonded species. From the signal integrals, the amount of protons associated with surface water is seen to be comparable to the amount of silica−OH protons.

As can further be seen by comparison of the one-pulse spectrum of heated VN3 with the corresponding DQF spectrum, all resonances except the small and very sharp ones are associated with dipolar-coupled protons. Sharp signals of isolated protons at around 1 ppm have been assigned by Liu and Maciel,[11] while the weak signal at 0 ppm may well be a mobile impurity. DQ excitation proceeds somewhat slower for the protons associated with H_2O at 3.5 ppm, indicating a higher degree of molecular motion, as was already discussed by Maciel.[10] In all, about 20% of all signal could be converted into DQ, which shows that the majority of all −OH and H_2O species are dipolar coupled and are thus part of a solidlike surface layer.

Surface modification was performed by mixing with 30% w/w TESPT or ethanol, heating and vigorous stirring for 24 h, and subsequent drying in vacuo. The weight loss upon modification with TESPT was found to be 4% (corresponding to a loss of only about 8% of the EtO-units) when the sample was prepared at 105 °C, while in the case of pure ethanol, about 93% was removed again, leaving 7% EtO-units at the surface. The weight loss upon modification with TESPT is in very good agreement with the loss of EtO as estimated from relative integrals in the respective ^1H NMR spectrum (see Table 1 and Figure 3). Note that, as opposed to the semiquantitative nature of integrals in ^{29}Si or ^{13}C CP MAS spectra, ^1H signals comprise all species in the material, even the most mobile ones.

The VN3 samples are compared with self-condensation products of TESPT obtained for reaction times of about 24 h using 30% w/w acid, water, or base, covering a wide range of pH values. The preparation conditions and properties of the selected samples are compiled in Table 1. All samples were quickly transferred into 2.5 mm MAS rotors and measured immediately. The polyimide caps of these rotors turned out not to be completely airtight, such that re-uptake of water in

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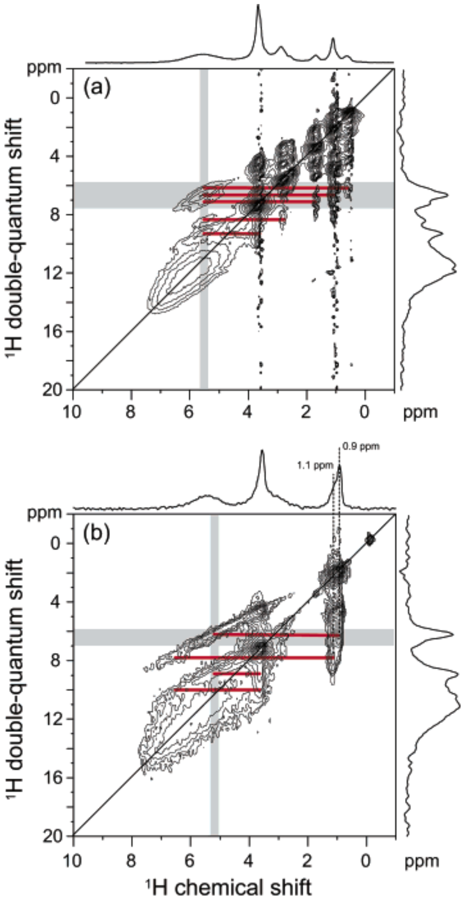

Figure 2. ^{1}H 2D DQ MAS correlation spectra ($\tau_{exc} = 133\ \mu s$) of the surface-modified VN3: (a) VN3-TESPT1 and (b) VN3-EtOH. The gray shaded areas indicate the regions over which the sum projections were taken, and horizontal bars identify dipolar contacts between the surface-attached molecules and the OH protons associated with the silica surface.

the course of several days in the VN3 samples could be observed by an additional broad signal at 3.8 ppm. In this work, we report only measurements from samples lacking this peak.

III. Results and Discussion

A. ^{1}H 2D DQ MAS Correlation Spectra. Immediate proof of a tight contact of a surface-bound molecule with the surface is the identification of dipolar couplings between spins located in the molecule and spins associated with the surface. The DQ correlation spectrum shown in Figure 2a serves this purpose. Apart from numerous correlations among the individual protons of TESPT (see Figure 1a for an assignment), we can clearly identify contacts between these protons and the silica−OH signals centered around 5.5 ppm.

The observation of the cross signals located below the aliphatic signals is somewhat challenged by the signal-proportional "t_1-noise" resulting from the strong overhead of alkyl groups, in particular when such moieties are partially mobile. This phenomenon is well-known to result from imperfect cancellation of these contributions by the phase cycle and does not challenge the assignment via the cross signals in the upper left of the spectrum.[28] The projection shown at the top is composed of all DQ coherences with a DQ shift between 6 and 7.5 ppm and therefore particularly shows the summed cross signals between the silica around 5.5 ppm plus the three TESPT resonances located between 0.5 and 2 ppm.

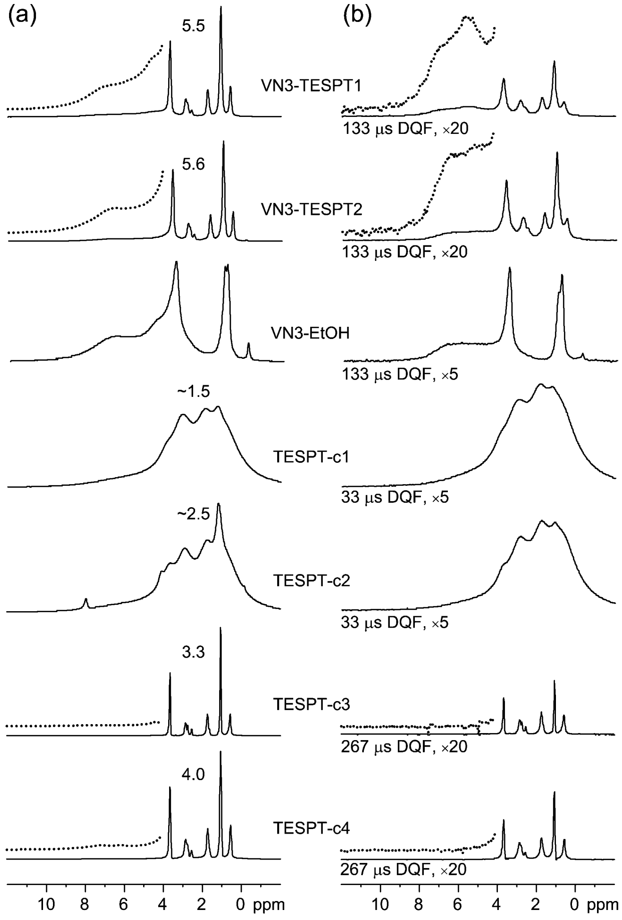

Figure 3. ^{1}H MAS spectra of the compounds listed in Table 1. Spectra in column (a) are one-pulse spectra, while spectra in column (b) are double-quantum filtered spectra, taken with the same number of scans as the one-pulse spectra. DQ excitation times and scaling factors are indicated beneath the DQF spectra. Dotted lines show 10-fold amplifications of the spectral region above 4 ppm, and the numbers in (a) indicate the average number of EtO-units per TESPT moiety as estimated from the peak integrals.

The information thus obtained is, unfortunately, not unique enough to state that the modifier is chemically bound to the surface. In particular, it is not clear whether the observed type of contact is indeed responsible for the reinforcement effect observed in rubber filled with modified silica, where the sulfur atoms of TESPT undergo a vulcanization reaction with C═C double bonds of the rubber. First, the TESPT could just be adsorbed to the surface (resulting in rather labile bonding), and, second, TESPT could also undergo self-condensation reactions, where the observed [Si]−OH groups involved in contacts could be associated with the silicon in the TESPT.[7] In the following, we discuss these issues, supplement the arguments with measurements on different, suitably prepared reference samples, and characterize the dynamic state of the surface-bound species.

Most importantly, no appreciable DQ signal was observed for samples where either TESPT or EtOH was just mixed with VN3 without heating. This means that,

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in such samples, TESPT is isotropically mobile and that surface adsorption effects are weak and easily overcome by thermally activated motion. It would be quite unlikely that adsorption could be enhanced by heat treatment. Rather, heating leads to the formation of either TESPT−TESPT or silica−TESPT bonds, resulting in species which perform only constrained motion and thus exhibit residual dipolar couplings. A strong argument in favor of a thermally activated chemical reaction with the silica surface-OH is that the inhomogeneous shift dispersions of [Si]−OH in contact with either TESPT or ethanol observed in the two 2D spectra in Figure 2a or b, respectively, are very similar, with a maximum around 5.5 ppm (the apparent differences are mainly due to different contour levels). [Si]−OH associated with self-condensation products of TESPT would probably not exhibit this same type of shift dispersion.

However, we are left with the observation that the apparent degree of condensation in VN3-TESPT is rather low. We believe that the actual degree of condensation is substantially bigger than the value given in Table 1, because EtOH set free upon condensation is apparently able to form chemical bonds with the silica itself. This is what is corroborated by the spectrum in Figure 2b, where dipolar contacts are apparent between EtO-resonances and the silica−OH in a VN3 which was simply heat-treated with EtOH instead of TESPT. Modification with ethoxysilanes[4] was previously observed to lead to the appearance of surface-bound ethanol. It was even argued that quantitative retention should indicate a direct reaction of the ethoxysilane with Si−O−Si bonds (instead of Si−OH) in dehydrated silica.[5]

An observation worthy of comment is that there are apparently two species of Et−O−silica which differ in the dynamically averaged conformations of the O−CH_2 and CH_2−CH_3 bonds or their local packing environment, as indicated by two distinct methyl shifts. These species are further different in that one couples to silica−OH around 5.5 ppm (as observed in VN3-TESPT), and the other couples to silica−OH around 6.5 ppm. Further investigations of this phenomenon are beyond the scope of this paper, but we would like to emphasize that this effect might open up the way to a deeper understanding of structure and dynamics associated with the broad shift distribution of hydrogen-bonded surface-OH. From the data discussed in this paper, in particular from the data describing the dynamic state of the surface-bound molecules (vide infra), we are not able to draw any further conclusions, as both species exhibit similar responses within the error limit of our methods.

B. ^{1}H One-Pulse and DQ-Filtered Spectra. To address the possibility of self-condensation of TESPT, where Si−OH generated by this process could mimic the observations discussed so far, we prepared four TESPT samples that were self-condensed under different conditions (see Table 1). Under neutral or acidic conditions and in the presence of sufficient amounts of water, glassy and amorphous solids were obtained (TESPT-c1/2). Approximate glass transition temperatures were determined by differential scanning calorimetry (DSC) and are listed in Table 1. The pronounced loss of EtO-units indicates high cross-link densities, whereby the glass transition temperature of the resulting polymer network is apparently shifted to above room temperature. Reactions using almost pure formic acid (containing only traces of water), as well as strongly basic conditions, lead to a weak condensation, and the products are elastic but brittle gels, with correspondingly low cross-link densities and a lower glass transition range.

The spectra of these compounds, along with corresponding spectra of VN3-TESPT1/2 and VN3-EtOH, are displayed in Figure 3. Signals of TESPT bound to VN3 exhibit a good spectral resolution, indicating substantial fast-limit averaging of dipolar couplings by molecular motion. A maximum of about 5% of all signals can be converted into DQ coherences after a τ_{exc} as short as 133 μs, as is shown by the DQF spectra on the right. This should be compared to the 20−30% conversion possible in rigid solids. Therefore, at least 20% of the TESPT undergoes anisotropic motions and can be assumed to be bound. The mere presence of these solidlike segments is in stark contrast to spectra of TESPT just being mixed with VN3, where the resolution is even better, but motions are completely liquidlike and no DQ intensity is observable. The preparation of modified VN3 samples at 165 °C (VN3-TESPT2) leads to a slight increase of the DQ intensity, and to some changes in the signal from the silica−OH region around 5 ppm, indicating an increase in surface binding or condensation, and a higher degree of dehydration, respectively.

In the next section, we will refine our estimate of the 20% bound TESPT and show that probably the whole TESPT fraction is composed of molecular segments exhibiting a wide range of motional anisotropy from the rather tightly bound to the liquidlike state.

The spectrum of VN3-EtOH appears less well resolved. This is, however, not due to a stronger surface binding and stronger dipolar couplings (vide infra). First, the broad signals from the silica are much stronger, as the EtO-content is rather small. Second, as shown in the preceding section, the shift dispersion is heterogeneous and probably due to packing effects at the surface. Note that the DQF spectra of VN3-TESPT1/2 also exhibit broader signals as compared to the one-pulse spectra, indicating the presence of similar packing effects. From the 20% conversion of EtO-signals into DQ coherences after 133 μs, we see that most of the ethanol left in this sample is strongly bound.

Turning to the self-condensed samples TESPT-c1−4, we immediately see that the two samples with a high degree of condensation exhibit the spectral features of rigid solids. All peaks are 1−2 ppm broad, and the DQF intensity reaches its maximum of about 25% of the initial intensity already at the shortest possible DQ excitation time of 33 μs (1 rotor period). Except for the CH_3 group, which exhibits fast motion around the C_3 axis even in crystalline solids and an improved resolution, all other moieties are presumably almost rigid on the experimental time scale (which is expected at temperatures in the vicinity of the glass transition). These samples do exhibit a featureless shoulder in the OH region around 6 ppm. We do not, however, believe that such a signal can be made responsible for the pronounced cross signals in the VN3-TESPT samples. On one hand, 2D DQ correlation spectra of these compounds (not shown) are basically featureless blobs with not much similarity to the spectrum in Figure 2a, and, on the other hand, a much higher fraction of solidlike self-condensed TESPT would have to be present in the VN3 samples to yield enough signal in the OH region. As is seen in the one-pulse spectra of VN3-TESPT, no appreciable amount of glassy TESPT is present in this sample.

The two samples with lower degrees of condensation feature spectra that are very similar to the signal from TESPT on VN3. The DQF intensity reaches a similar magnitude, but after a considerably longer τ_{exc} beyond 267 μs. DQF intensities are still appreciable at much longer times, indicating a wide distribution of rather small coupling constants (vide infra). Such a behavior is very typical for polymeric networks with a large distribution of network chain lengths or a large degree of heterogeneity.[29] Importantly, neither in the one-pulse nor in the DQF spectra do we observe any appreciable signal in the OH region. Therefore, even though the dynamic state of TESPT in these two samples is similar to the case when TESPT is bound to silica, the surface contacts observed in the preceding section are with good confidence not due to potential [Si]−OH in weakly self-condensed TESPT. Ultimately, the above arguments rely, of course, on the (realistic) asssumption that self-condensation of TESPT close to a silica surface does not yield a much higher amount of hydroxy groups than that in free solution.

C. Molecular Dynamics from ^{1}H DQ Sideband Spectra and Buildup. As shown above, almost all EtO-units in VN3-EtOH are involved in strongly anisotropic motion. We have therefore attempted to obtain a more detailed picture of the dynamics from the measurement of the dipolar coupling constants within this moiety. We compare these results with measurements on VN3-TESPT and draw some conclusions on the dynamics of this more complicated, heterogeneous system. We focus our attention to intra-CH_2 couplings, as this group features a strongly coupled proton spin pair with a static coupling of about 21 kHz,[30] while secondary couplings to other protons in the molecule are at least 4 times smaller. The following considerations will highlight the potential as well as the limitations of DQ sideband and build-up analysis when applied to complicated, distributed systems.

In Figure 4a, sideband patterns for the OCH_2 group in VN3-EtOH obtained for two different τ_{exc} values are compared with best-fit calculations described below. The patterns are not compatible with patterns generated by single, well-defined coupling constants. In particular, the first-order sidebands appear much too high. From slices through the OCH_2 peak region of the corresponding 2D spectra (analogous to the top slice of Figure 2b), it can be inferred that about 10% of the sideband intensity is due to the underlying broad signal associated with bound water. Previous work has further shown that, in certain cases, increased first-order sidebands can be due to couplings to remote spins.[31] Because such effects were never observed to exceed a 30% increase over the outer sidebands (which are only apparent at longer τ_{exc} values), we conclude that the observation can only be explained in terms of a distribution of differently coupled species.

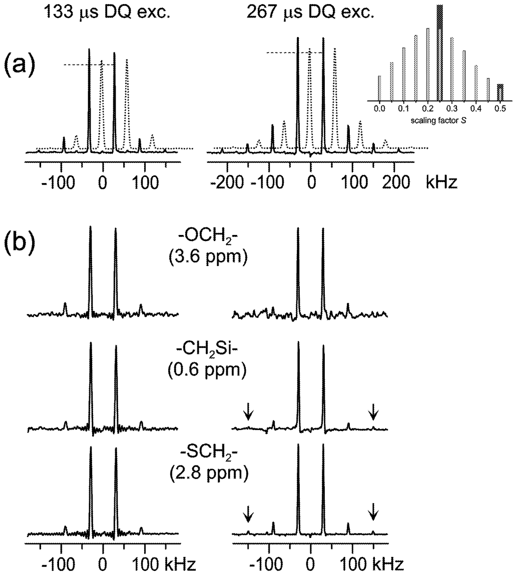

Figure 4. ^{1}H DQ MAS sideband spectra of (a) VN3-EtOH (OCH_2 signal) and (b) VN3-TESPT1, using the excitation times shown above the spectra. The dashed lines in (a) indicate the contribution from the underlying water signal, and the dotted lines correspond to best-fit simulations. The 267 μs-pattern could be fitted using the assumption of an internally rotating Si−OEt group and different distributions of a scaling factor (see inset), which parametrizes the mobility of the Si−O bond (see also Figure 5).

Distribution effects on BaBa sideband patterns have been investigated in a very recent publication.[32] In this work, deviations of such patterns from ideal ones were explained in terms of distributions of pair couplings. As we are dealing with $-CH_2-CH_3$ groups, which, in addition, exhibit couplings to surface-OH groups (see Figure 2b), we have resorted to spin dynamics simulations of a likely scenario of surface-bound ethanol. The simulations were performed with a home-written spin dynamics code based on a stepwise integration of the Liouville-von-Neumann equation, with the density matrix represented in terms of product space operator matrices. The program is in many respects similar to the publicly available SIMPSON program[33] and has been tested and applied in a number of previous publications. The simulation takes account of experimental limitations such as timings and finite pulses, which were earlier shown to have only a minor influence on the sideband patterns.[34]

The motional model is depicted in Figure 5. We assume uniaxial, fast-limit dynamics around all bonds and include one surface-bound proton which does not participate in the dynamics (calculations with more than 6 spins are hardly feasible). CH_3 rotation merely scales its perturbing influence on the CH_2 pattern somewhat,

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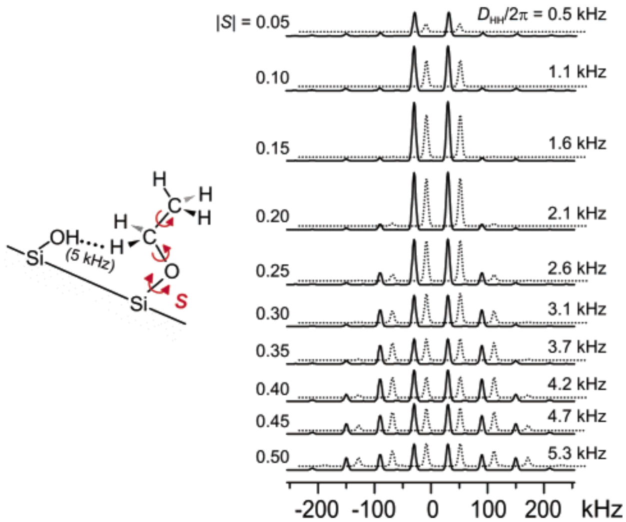

Figure 5. Simulated ^{1}H DQ MAS sideband spectra of a CH_2 group of surface-attached EtOH, subject to dipolar couplings to four remote spins and dynamic processes as indicated. Conformational freedom around the Si−O bond is taken into account in terms of a factor S, which scales all intra-CH_2−CH_3 couplings. The dotted lines are from calculations of the isolated CH_2 spin pair, with effective coupling constants indicated.

while rotation around the O−CH_2 bond scales its intraproton coupling by a factor of 2. The motion around the Si−O bond is considered in terms of a scaling factor. Full rotation around this bond, assuming an Si−O−C angle of 115°, would lead to $|S| = |P_2(\cos 115°)| = 0.25$. Lower factors correspond to additional librational motion, and higher values indicate restrictions of the rotation around this bond by, for example, surface topology.

Sideband patterns for different values of S can be inspected in Figure 5. The comparison with the spin-pair simulations shown as dotted lines confirms earlier findings of slightly increased first-order sidebands for $S > 0.3$. For lower scaling factors (lower intra-CH_2 couplings) first-order sidebands always dominate. For very low intra-CH_2 couplings, the remote couplings lead to an increased overall intensity, as well as very weak higher-order sidebands. The changes upon inclusion of remote spins are thus seen to be overall weak, and qualitatively similar conclusions would result when spin-pair patterns were used for the estimation of the distribution presented below. It is further not expected that the inclusion of even more spins would change our (semiquantitative) interpretation.

We have used the series of simulated sideband patterns for a fit of the four meaningful sideband intensities measured at $\tau_{exc} = 267$ μs. A Gaussian distribution centered at around $|S| = 0.22$ with a half-width of $\Delta S = 0.15$ as well as a bimodal scenario with $|S| = 0.5$ and $|S| = 0.25$ provide an equally good fit, which is shown in Figure 4a. The latter finding might be explained with a restricted and a freely rotating population of surface-OEt. Notably, the pattern acquired at $\tau_{exc} = 133$ μs is only compatible with an equal relative weight of the two contributions. This is expected, because transverse relaxation under the pulse sequence is different for the populations with different couplings, and highlights a general limitation of the technique when distributions are to be quantified. The actual population of more strongly coupled units might therefore be somewhat larger than 50%.

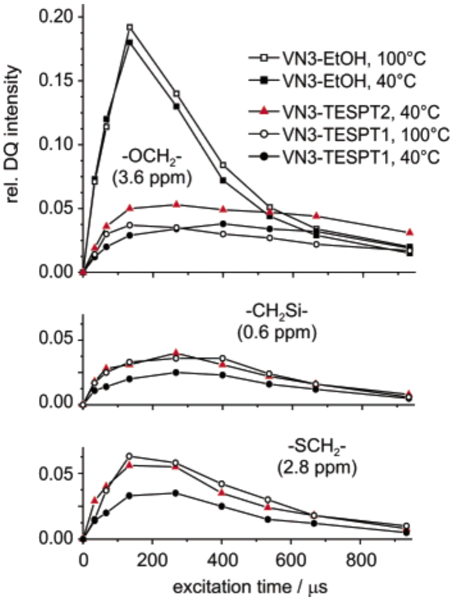

Figure 6. ^{1}H DQ MAS build-up curves for the modified VN3 samples. The intensities were obtained by integration of the signals in the individual DQF spectra and are plotted relative to the signal in the one-pulse spectra taken with the same number of scans. Sample temperatures during measurement are also indicated.

The interpretation should therefore be taken with a grain of salt, also considering the ambiguity of a fit to only four intensities. The minimum statement that can be made with very good confidence is, however, that the majority of −OEt groups visible in a one-pulse spectrum is quite strongly coupled (i.e., contributes fully to the DQF spectra at rather low τ_{exc} values) and thus performs rather constrained motions. In particular, by simple inspection of the highest-order sidebands, we can clearly exclude the presence of a substantial amount of methylene groups with couplings in large excess of 5 kHz ($S = 0.5$). These constraints are compatible with what would be expected for a surface-bound species.

Turning to TESPT bound to the silica (Figure 4b), we observe similar behavior for all types of methylene groups (as is also the case for the CCH_2C group not shown in the figure). Third- and, at $\tau_{exc} = 267$ μs, even fifth-order sideband intensities are apparent above the noise level for all moieties. Note that data for the OCH_2 group are particularly challenged by t_1-noise. From a theoretical point of view, at $\tau_{exc} = 133$ and 267 μs, third- and fifth-order sidebands, respectively, reach appreciable intensity only when the coupling exceeds 3 kHz (see Figure 5). The extent of motional anisotropy for the most strongly coupled segments is therefore similar to silica-OEt. Yet, the first-order sidebands are much increased. Therefore, a good part of the signal must be associated with more weakly coupled segments.

Complementary supporting evidence for the existence of more weakly coupled species can be inferred from the DQ build-up curves plotted in Figure 6. Because of the limited time resolution of BaBa, the initial slopes, from which quantitative information on the strongest coupling constants in the system could in principle be obtained, are not accessible. Yet, the difference in width of the dipolar coupling distributions for the two systems is apparent in these data.

For the OCH_2 in VN3-EtOH, no dependence on the sample temperature during measurement is observed, indicating that fast-limit averaging of motions is complete and that effects of intermediate motions are negligible.[29] Further, the DQ intensity goes through a pronounced maximum at $\tau_{exc} = 133\ \mu s$. The ensuing decay is mainly due to relaxation effects under the pulse sequence and depends on the magnitude of the involved couplings. The time scale of the buildup is consistent with an average coupling on the order of 4 kHz, for which the maximum intensity would be expected at around $\tau_{exc} = 200\ \mu s$.

A precise determination of coupling constants from build-up curves from first principles is no less difficult than sideband analysis, in particular when the system is heterogeneous and the components have different relaxation times.[20,29,35] Under MAS conditions, experimental imperfections (timing problems and finite pulses) on the intensities are more serious, and the sideband method, despite its limitations highlighted above, is better suited to yield an estimate of a distribution. The curve under consideration supports only the essential feature of restricted CH_2 rotation derived from the sideband spectra, with hardly any evidence for a distribution. Better quantitative agreement of sideband analysis and intensity buildup is only found in better-defined cases such as anisotropic host dynamics in inclusion compounds.[36]

For the resonances of VN3-TESPT1/2, the most significant observation is that all build-up curves exhibit much shallower maxima. Even though the maxima are also reached within 133 μs in most cases, the signal persists for much longer times. This means that, while strongly coupled segments relax away, more weakly coupled segments reach their respective intensity maxima. From this, we deduce that more than the previously estimated 20% of the TESPT on VN3 is, although weakly, coupled. If there were only a 20% contribution of strongly coupled and otherwise liquidlike TESPT, a more pronounced maximum and ensuing decay would be expected. Further, when the whole TESPT were only weakly coupled, the maximum intensity would be expected to shift to a longer τ_{exc}, and outer sidebands would also not be observable in Figure 4b, as is the case for self-condensed TESPT-c3/4 (data not shown).

Yet, the fact that the build-up curves of both VN3-TESPT and TESPT-c3/4 exhibit significant intensity at a long τ_{exc} suggests that inter-TESPT cross-linking plays a role, leading to a mobility gradient away from the silica surface. This interpretation is supported by the results of static ^1H DQ NMR investigations of the mobility of non-cross-linked polymer chains grafted to a silica surface,[20] where the mobility difference between coupled chains close to the surface and nonattached chains farther away from it was even more pronounced, leading to two distinct maxima in DQ build-up curves.

The $-SCH_2-$ moieties are seen to appear somewhat more strongly coupled, as their DQ intensities are roughly 50% larger than the ones for the other methylene groups. This could reflect either an additional adsorption of the S_4 moiety to the surface or a more restricted conformational space as a result of the bulkiness of the sulfur atoms.

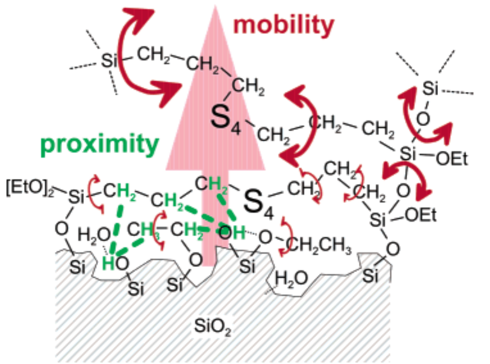

Figure 7. Model for structure and dynamics on a TESPT-modified silica surface, showing features derived from NMR data: (i) surface bonding evidenced by dipolar contacts (thick dashed lines), (ii) EtO− at the surface, (iii) motional heterogeneity (conformational fluctuations of varying amplitude, as indicated by double arrows of increasing size), and (iv) self-condensation.

Finally, the ambient-temperature response (at 40 °C due to frictional heating in the rotor) for all functional groups of VN3-TESPT2 is about 50% higher than that for VN3-TESPT1, indicating that the higher preparation temperature leads to a more efficient condensation (which is not detectable from the loss of EtOH!). A somewhat counterintuitive finding is the increase of the DQ signal on increasing the measurement temperature (open vs closed symbols). At higher temperature, motions are expected to speed up and maybe increase their amplitude, leading to weaker couplings. That this is not the case indicates that the fluctuations apparently probe all available conformational space at the lower temperature. The apparent increase in the coupling must be due to the speeding-up of motions. At 40 °C, the dynamics is probably not in the fast limit for a part of the moieties, and, in the intermediate regime, motions lead to a loss of signal during recoupling.[37] This is yet another argument in favor of much of the TESPT being (dipolar) coupled.

IV. Conclusion

In Figure 7, we have depicted the proposed model for structure and dynamics of TESPT on a silica surface. In summary, we have shown that (i) TESPT is very likely to undergo a chemical reaction with the surface. This was previously inferred from small changes in the ^{29}Si chemical shift distributions observed in CP MAS spectra,[7] and more support has been presented here through surface contacts being detectable only in DQ spectra of heated samples. (ii) Ethanol is found to be able to condense on to the silica surface under the conditions applied for modification with TESPT. We therefore suggest that the rather low loss of EtO− groups from the TESPT is indicative of surface binding of EtOH set free upon condensation, rather than a very low overall degree of condensation.

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As far as the molecular dynamics of the surface-bound molecules are concerned, we have seen that (iii) much of the TESPT is condensed and therefore performs anisotropic conformational fluctuations, leading to measurable intra-CH_2 dipolar couplings. A significant fraction of all TESPT resides close to the surface and exhibits a motional anisotropy similar to that of EtO− which is directly bound to the surface. The latter was also shown to exhibit a notable distribution of freely rotating and hindered species. Last (iv), the residual H_2O at the silica surface most probably promotes some self-condensation of the TESPT farther away from the surface, explaining the large amount of material which appears relatively weakly coupled.

Reinforcement of rubber is usually performed by blending it with silica and TESPT in a one-pot reaction. From our findings, we might expect that a pretreatment of the silica with TESPT involving curing at elevated temperature enhances strong interactions of TESPT with the surface and therefore leads to an improved reinforcement effect (see ref 6, and references therein). Finally, a caveat is on the order concerning the determination of the degree of condensation by measuring the amount of EtOH liberated upon processing. Such a procedure might lead to substantially underestimated results.

In summary, we have shown that robust and time-efficient ^{1}H DQ MAS techniques based on the BaBa sequence can readily be applied for a site-resolved and semiquantitative elucidation of surface contacts and dynamics in thin molecular layers. Estimates of distributions of dipolar couplings as perceived from the shape of sideband patterns or DQ build-up curves will prove useful for thorough characterizations of surface-modified silica. More advanced DQ MAS recoupling experiments providing a finer build-up time resolution, such as the C-type sequences,[23] along with a better understanding of relaxation effects, might allow for more quantitative assessments of distributions, but require considerably more experience with respect to the tune-up of the spectrometer. For BaBa, only 90° pulse lengths have to be determined.

While we have here merely provided a proof of principle, more quantitative studies involving model compounds and systematic variations of reactants and preparation conditions are envisioned to resolve open questions concerning the general understanding of silanization reactions on surfaces. One example is the mode of modifier polymerization, for which different mechanisms, such as a horizontal (cross-linking among surface-bound silanes) and a vertical one (cross-linking of free and surface-bound silanes) have been proposed,[4] but could not be differentiated using ^{29}Si chemical shift information alone.

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