

## Silica–Dimethylsiloxane Hybrids—Non-Hydrolytic Sol–Gel Synthesis and Characterization by NMR Spectroscopy

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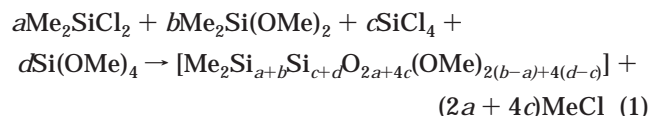
The non-hydrolytic sol–gel process provides a facile route to silica–dimethylsiloxane (DMS) hybrids starting from silicon(IV) chloride, tetraethoxysilane (TEOS), and hexamethylcyclotrisiloxane, D<sub>3</sub>. Both the non-hydrolytic sol–gel silica synthesis and ring-opening polymerization of the D<sub>3</sub> are initiated simultaneously by the presence of an iron(III) chloride catalyst. Evidence for the structures of these hybrids is presented from the results of solid-state 2D NMR correlation spectroscopy. The siloxane component consists of short D units, which show good compatibility with the silica on a molecular level, probably as a result of copolymerization between Q and D units.

### Introduction

The non-hydrolytic sol–gel route has been shown to be a versatile method of producing inorganic oxides and mixed oxides in a facile process,<sup>1–10</sup> which can be carried out in the absence of any solvent. We have demonstrated recently that the method can be extended to the synthesis of organically modified silicas,<sup>11</sup> which can be further converted to microporous silicas on calcination.<sup>12</sup> Analogous silsesquioxane products have been reported by Bourget et al. using different oxygen donors in the non-hydrolytic sol–gel process.<sup>13</sup> In the case of the hydrolytic sol–gel process, a wide range of organic polymers have been successfully combined with silica

to form hybrids, but this is not true of the non-hydrolytic process. A hybrid which has been studied extensively using hydrolytic sol–gel chemistry is the silica–poly(dimethylsiloxane) (PDMS) system,<sup>14–21</sup> which can be varied from a hard, glassy solid to a rubbery product depending on the ratio of PDMS to silica.<sup>17–21</sup> Such materials are of interest for a number of applications, including their potential use in insulating applications in microelectronics.

Non-hydrolytic sol–gel chemistry has been used to synthesize alkoxy-functionalized, liquid polysiloxane D/Q resins using Lewis acid catalysis<sup>22</sup> (eq 1). Redistribution reactions occur, leading to polymers where the Si–OMe and Si–O–Si bonds are randomly distributed around D and Q units.



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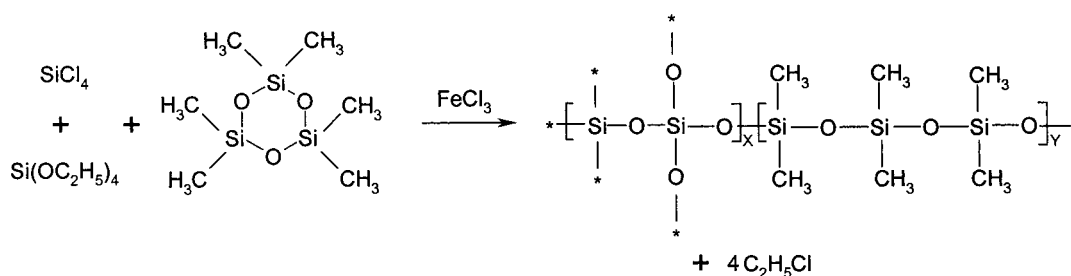
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### Scheme 1. Formation of Silica–DMS Hybrid via Non-Hydrolytic Sol–Gel Synthesis



The authors also report one example of the use of D<sub>4</sub> (octamethylcyclotetrasiloxane) in place of Me<sub>2</sub>SiCl<sub>2</sub>, with zirconium(IV) chloride as the catalyst, resulting in formation of similar liquid resins. We report here, efforts to synthesize silica–dimethylsiloxane (DMS) hybrids by non-hydrolytic sol–gel synthesis, starting from the cyclic siloxane D<sub>3</sub>, but with stoichiometries chosen to lead to formation of a predominant silica network. A detailed study of the structure of the hybrids using solid-state NMR correlation spectroscopy is also presented.

### Experimental Section

**Chemicals.** Reagents used were standard laboratory or AR grades, which were used as received unless stated otherwise. Hexamethylcyclotrisiloxane, D<sub>3</sub>, was mixed with calcium hydride and sublimed at 60 °C, and the purified D<sub>3</sub> was stored under nitrogen until use.

**Instrumentation.** Thermogravimetric analysis was undertaken using a Perkin-Elmer TGA-7 interfaced with a Perkin-Elmer 7700 computer over a temperature range of 40–900 °C. A heating rate of 10 K min<sup>-1</sup> was applied under a nitrogen atmosphere with a flow rate of 50 mL min<sup>-1</sup>.

Differential scanning calorimetry (DSC) measurements were made on samples of ca. 5 mg in sealed aluminum pans, using a TA Instruments MDSC 2920 calorimeter or a DuPont 9900 machine at a heating rate of 10 K min<sup>-1</sup> under a nitrogen atmosphere with a flow rate of 40 cm<sup>3</sup> min<sup>-1</sup>.

A Philips PW1830 X-ray diffractometer was used to determine sample crystallinity. Samples were ground into fine powders before being scanned with Cu K $\alpha$  radiation at 40 kV and 40 mA from 15 to 90° 2 $\theta$ , with a step size of 0.02° and a count time per step of 7 s.

Elemental analyses were carried out on a CE 440 Elemental Analyzer, Leeman Laboratories Inc.

IR spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrophotometer interfaced with a Perkin-Elmer computer. Samples were ground and prepared for diffuse reflectance IR Fourier transform spectroscopy (DRIFTS). The following are the abbreviations used to describe peaks: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, b = broad, sp = sharp, and sh = shoulder.

Solid-state <sup>29</sup>Si and <sup>13</sup>C cross polarized (CP) and directly polarized (DP) nuclear magnetic resonance (NMR) spectroscopy was undertaken at the University of Durham, at ambient temperature on a Varian UNITYplus spectrometer operating at 300 MHz for <sup>1</sup>H. Spectra were recorded against an external TMS standard with magic angle spinning (MAS) at a spinning rate of 4300–5000 Hz. The <sup>13</sup>C CP spectra were obtained as single contact experiments with a contact time of 0.6 ms and a recycle delay of 2.0 s (700 repetitions). The <sup>29</sup>Si DP spectra were obtained using a 90° pulse and a 120 s recycle delay (the number of repetitions varied from 26 to 500). T<sub>1</sub>(H) was obtained by observing the <sup>29</sup>Si signal in an inversion–recovery CP experiment and T<sub>1 $\rho$</sub> (H) was obtained through a delayed contact CP experiment. A WISE heteronuclear correlation experiment was carried out with a 0.1 s recycle delay and 0.5 ms contact time, and 2000 repetitions were accumulated for each of 100 t<sub>1</sub> increments. The spin-rate was 7 kHz.

**Table 1. Composition of Systems Studied**

mass % of D <sub>3</sub> monomer	mass % of combined (TEOS + SiCl <sub>4</sub> )	nominal mol % of D <sub>3</sub> units incorporated in final hybrid <sup>a</sup>
1	99	0.84
10	90	7.8
30	70	20
50	50	30

<sup>a</sup> Assuming complete conversion of (TEOS + SiCl<sub>4</sub>) to silica.

**Hybrid Synthesis.** Hybrids were synthesized with initial mass % (based on total TEOS + SiCl<sub>4</sub>) of D<sub>3</sub> ranging from 1 to 50. Table 1 shows the systems studied and the corresponding nominal mol % of D<sub>3</sub> units in the final hybrid, assuming complete conversion to silica. In a typical experiment, the silica–DMS hybrid was formed by reacting D<sub>3</sub> (5.35 g; 30 mass %), TEOS (9.82 g; 10.50 cm<sup>3</sup>; 0.047 mol), and SiCl<sub>4</sub> (8.00 g; 5.40 cm<sup>3</sup>; 0.047 mol) in the presence of iron(III) chloride catalyst (0.143 g; 0.80 mass %) at 60 °C under nitrogen. The mixture gelled within 80 min. The resulting solid (containing some colorless liquid) was subjected to Soxhlet extraction using methanol for 5 days, followed by drying at 80 °C for 48 h. An aerated, shiny yellow, transparent solid resulted (11.00 g; 100% yield, based on complete conversion of precursors to silica).

### Results and Discussion

The non-hydrolytic sol–gel synthesis of silica from silicon(IV) chloride and TEOS has been described previously.<sup>5,23</sup> PDMS can be synthesized by either the anionic or cationic ring-opening polymerization of the cyclic siloxane, D<sub>3</sub>,<sup>24</sup> and so it was reasoned that it might be possible to synthesize the silica and the PDMS in situ using iron(III) chloride as the catalyst for both the cationic ring-opening polymerization and the sol–gel reaction. Prior to this, there was only one literature report of a related reaction using D<sub>4</sub> to produce *liquid* polysiloxane D/Q resins.<sup>22</sup> It was shown that ring-opening polymerization of D<sub>3</sub> was indeed catalyzed by the presence of iron(III) chloride. Solid hybrids were synthesized successfully using an initial concentration of D<sub>3</sub> ranging from 1 to 50 mass %, based on the total mass of TEOS and SiCl<sub>4</sub>. This corresponds to a nominal D<sub>3</sub> content in the final hybrid of 0.8 to 30 mol %. These products are type IV hybrids according to Novak's classification<sup>25</sup> or type II hybrids according to the classification of Sanchez.<sup>26</sup> The "idealized" reaction is shown in Scheme 1, but as will be seen later, this should not be taken to imply that the hybrid contains D<sub>3y</sub>

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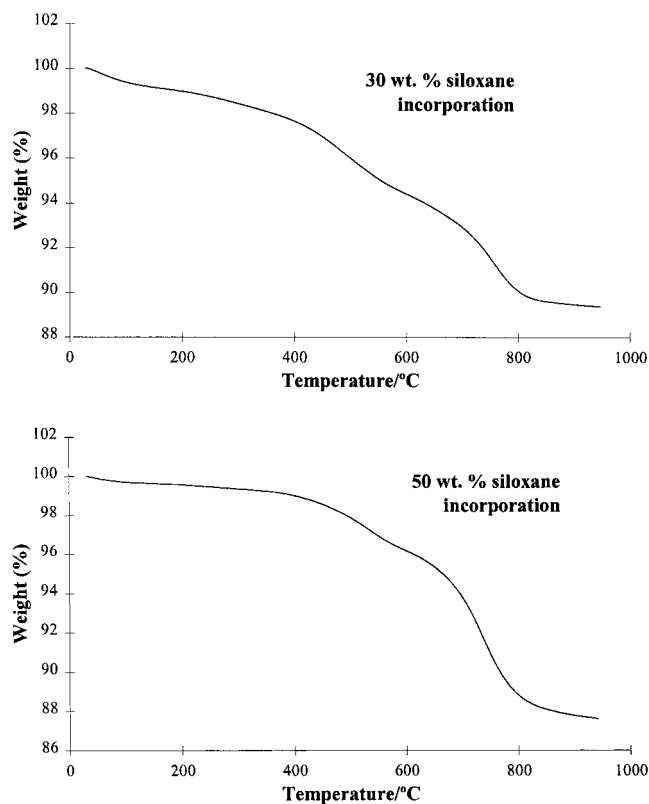
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chains. The  $\text{Fe}^{3+}$  ion acts as both the catalyst for the sol-gel reaction and the initiator of the ring-opening polymerization.

The hybrid products were subjected to Soxhlet extraction with methanol to remove any unreacted material and low molar mass products. This would also convert any accessible, residual Si-Cl groups to Si-OMe, exchange some of the residual ethoxy groups, and perhaps increase the degree of network condensation. Under our experimental conditions, any ether formed by alkoxy group condensation during the reaction<sup>22</sup> would have been swept out of the apparatus and not isolated. Product yields were high (98%+) in all cases, assuming complete conversion to the expected silica hybrid. In practice, complete condensation is never achieved (vide infra). Optical transparency in the products suggested that any phase separation was on a submicron and probably nanoscopic level, if separate domains were present at all. Interestingly, the products showed no evidence of the expected elasticity, even at 50 mass % incorporation of  $\text{D}_3$ . DSC analysis would be expected to show a glass transition ( $T_g$ ) at subambient temperatures if significant PDMS chains were present. In fact, only the 10 mass % product showed any sign of a subambient transition (at ca.  $-38^\circ\text{C}$ ), but this was not sufficiently obvious to be assigned unequivocally as a  $T_g$ . All samples, apart from the 50 mass % one, showed a very broad endotherm centered around  $100\text{--}150^\circ\text{C}$ , with the corresponding enthalpy change decreasing significantly as the proportion of  $\text{D}_3$  increases. This is consistent with further condensation of the silica network on heating, since the degree of initial condensation is likely to increase with increasing D content, which reduces the overall cross-link density of the network. This is also supported by NMR evidence (see below). The 50 mass % hybrid shows no such endotherm but a very sharp  $T_g$  at  $73^\circ\text{C}$ . A second DSC run on the 10% system, following initial heating to  $200^\circ\text{C}$ , shows no endotherm but a  $T_g$  at  $72^\circ\text{C}$ . The breadth of the masking endotherm makes it impossible to know whether this  $T_g$  is present initially in every case. The identical position of this  $T_g$  in the different hybrids is striking. It may be due to sterically constrained D units (which are thus not able to demonstrate the elastomeric behavior of PDMS), but this is simply conjecture and much more work would be needed to clarify this.

Thermogravimetric analysis of the products was carried out in nitrogen to assess their thermal stability (as opposed to thermo-oxidative stability). The results showed mass losses of 12 to 19% over the temperature range  $25\text{--}900^\circ\text{C}$ . Typical thermograms are shown in Figure 1 for both 30 and 50 mass % siloxane incorporation. In the 50 mass % hybrid, decomposition was insignificant below  $400^\circ\text{C}$ . The low mass losses compared to the siloxane content indicate that the siloxane backbone is not lost on heating. The mass lost presumably results mainly from decomposition of the methyl groups and residual groups from the silica precursors. Char yields of close to 90% were obtained up to  $900^\circ\text{C}$ . For the 50 mass % siloxane hybrid, the observed mass loss of 12% is well below that calculated for the organic (CH) content (23%) and that measured by elemental analysis (22%). This may be due to formation of silicon



**Figure 1.** Thermogravimetric analysis of silica-DMS hybrids containing 30% (top) and 50% (bottom) siloxane.

oxycarbide species via exchange reactions, as reported by others.<sup>13,27</sup>

X-ray diffraction showed a broad peak at the low-angle end of the spectrum, indicating an amorphous material. The peaks were too broad and diffuse to allow the extraction of any information about the structure.<sup>28</sup> IR spectroscopy was unable to distinguish clearly between the silica and siloxane components of the hybrids but did show the presence of Si-O-Si and Si-CH<sub>3</sub> functionalities, with characteristic absorptions at 1280, 1180, and  $820\text{ cm}^{-1}$ <sup>29-33</sup> and 1260, 885, and  $805\text{ cm}^{-1}$ ,<sup>33</sup> respectively. All the hybrids show absorption bands in the region  $3300\text{--}3620\text{ cm}^{-1}$ , which are attributable to hydroxyl groups (probably silanols). Although in principle, the chemistry of this non-hydrolytic route (Scheme 1) is ideally suited to forming hybrids of low, or even zero, silanol content,<sup>34</sup> residual alkoxy or Si-Cl groups can react further, and no specific measures were taken to exclude moisture during workup. If low silanol content is desired in practice, efforts must be made to further react these reactive sites to prevent hydrolysis.

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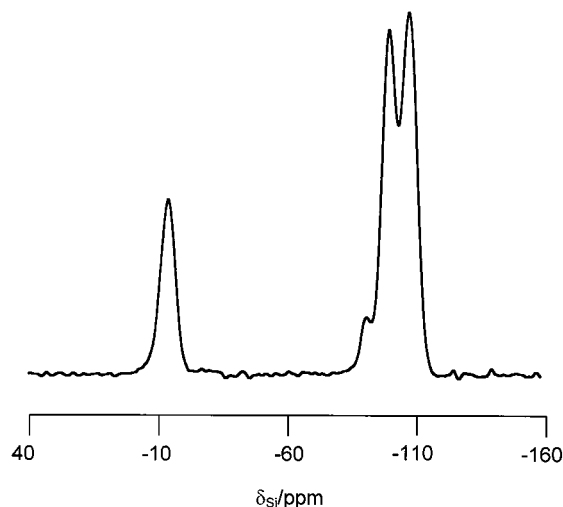
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**Table 2. Solid-State NMR Data on Silica–DMS Hybrids**

nominal mol % D <sub>3</sub> in hybrid	mol % D <sub>3</sub> in hybrid from NMR <sup>a</sup>	DMS D <sup>2</sup> resonance (ppm)	SiO <sub>2</sub> Q <sup>1</sup> propn in hybrid (%)	SiO <sub>2</sub> Q <sup>2</sup> propn in hybrid (%)	SiO <sub>2</sub> Q <sup>3</sup> propn in hybrid (%)	SiO <sub>2</sub> Q <sup>4</sup> propn in hybrid (%)
0.84	1.0	-11.8	0	7	42	51
7.8	7.7	-14.5	0	5	42	53
20	17	-16.9	0	3	27	70
30	30	-18.7	0	0	20	80

<sup>a</sup> Calculated from the percentage of the total silicon signal assigned to D species.



**Figure 2.** Solid-state <sup>29</sup>Si DP NMR spectrum of 10% DMS–silica hybrid.

It is of note that the hydroxyl bands shift to higher frequency and become much weaker as the siloxane content in the hybrid increases. This is consistent with the fact that condensation becomes more complete as the siloxane content increases (vide infra) leading to fewer residual hydrolyzable groups, and any silanol groups formed will be farther apart and less likely to form internal hydrogen bonds.

**Characterization by Solid-State NMR Spectroscopy.** Detailed solid-state NMR spectroscopic studies were carried out to learn more about the molecular level structure of the hybrids. The actual proportion of D<sub>3</sub> units present in the hybrid could be calculated from the percentage of the total silicon NMR signal assigned to the D species. For mass % values of 1, 10, 30, and 50, the measured D signal comprises of 3, 20, 38, and 56%, respectively, of the total silicon signal. The calculated values for the corresponding percentage of D<sub>3</sub> in the hybrid are included in Table 2. The remarkable similarity of the nominal and experimental values suggests that both components remain present in the same proportions following the reaction, with no preferential extraction of either component by Soxhlet extraction.

Figure 2 shows a typical <sup>29</sup>Si DP NMR spectrum for the 10% DMS–silica hybrid. This shows resonances corresponding to Q<sup>2</sup> (–92.7 ppm; 5%), Q<sup>3</sup> (–101.2 ppm; 42%), and Q<sup>4</sup> (–108.7 ppm; 53%) units as well as resonances from D species centered on –14.5 ppm.<sup>35</sup> No Q<sup>1</sup> species are observed. The data strongly support the formation of the hybrid, since residual D<sub>3</sub> cyclic siloxane would lead to a sharp resonance at about –9 to –10

ppm.<sup>36</sup> Long PDMS chains are expected to show a resonance close to –22 ppm, but Babonneau proposed that the formation of D<sup>2</sup> units in a constrained environment, spatially close to Q units, through co-condensation reactions could result in high-frequency shifts and broadened peaks.<sup>37</sup> The position of the D<sup>2</sup> resonance in the hybrids varies significantly according to the proportion of siloxane present (Table 2). The chemical shift becomes increasingly more negative as the siloxane content increases, ranging from –11.8 ppm at 1 mass % siloxane incorporation to –18.7 ppm at 50 mass % siloxane. The peak remains symmetrical and gets slightly narrower. While it might be expected that as the amount of siloxane present increases, the siloxane chain length between silica “cross-links” would increase (assuming covalent bonding between the components), previous studies<sup>27,38,39</sup> suggest that the actual structure is likely to be a copolymer of Q and D species, arising from exchange reactions. The observed physical properties of the hybrids are also consistent with formation of, at most, short siloxane segments, since formation of PDMS chains would be expected to lead to elastomeric behavior in the hybrids above a certain minimum siloxane content and certainly in the 50 mass % siloxane hybrid. The DSC studies also confirmed the absence of elastomeric units.

The positions of the silicon resonances are interesting, since they occur at higher frequencies than are commonly observed for D<sup>2</sup> resonances, whose chemical shift has been reported to lie between –15 and –21.5 ppm<sup>22</sup>. The signals observed are quite broad and are presumably averages of all the D species formed. It is possible to envisage the formation of Me<sub>2</sub>Si(OR)(O–) D<sup>1</sup> groups [R = Et, Me, or H] during the reaction, with a concomitant shift of the <sup>29</sup>Si resonance to higher frequency than –15 ppm. Such D<sup>1</sup> species exhibit silicon resonances between –8 and –12.5 ppm.<sup>38–40</sup> Average values of –11.8 (1 mass % D<sub>3</sub>) and –14.5 ppm (10 mass % D<sub>3</sub>) are therefore not unreasonable and may reflect the increased likelihood of this reaction occurring in systems where the TEOS is in excess over the D<sub>3</sub>. The presence of longer siloxane chains cannot be totally excluded in the hybrids of higher siloxane content, since the peak envelope covers the region of the spectrum where the signals would appear, but these longer chains are unlikely to be present in significant amounts since the symmetry of the peak remains intact.

The incomplete condensation to Q<sup>4</sup> silica is typical of both the hydrolytic and non-hydrolytic sol–gel processes

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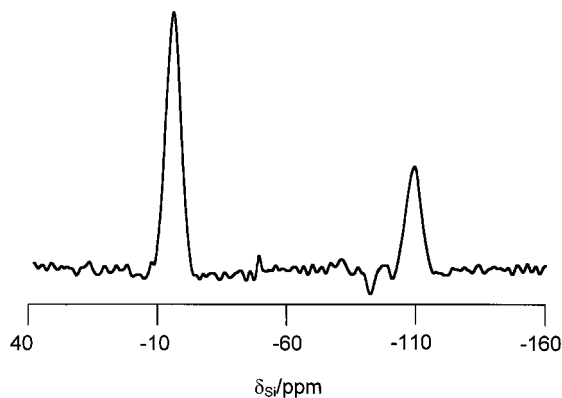
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**Table 3. Solid-State NMR Relaxation Data on Silica–DMS Hybrids**

% D <sub>3</sub> incorporated	$T_1$ (H) (ms)				$T_{1\rho}$ (H) (ms)		
	DMS	SiO <sub>2</sub> Q <sup>2</sup>	SiO <sub>2</sub> Q <sup>3</sup>	SiO <sub>2</sub> Q <sup>4</sup>	DMS	SiO <sub>2</sub> Q <sup>3</sup>	SiO <sub>2</sub> Q <sup>4</sup>
0		3.5	4.3	<i>a</i>		1.0	
1	2.2		1.6		1.4	0.8	
10	8.5	7.6	7.6	8.6	4.0	2.7	4.1
30	55		54	53	30	29	35
50	400		380	370	99		96

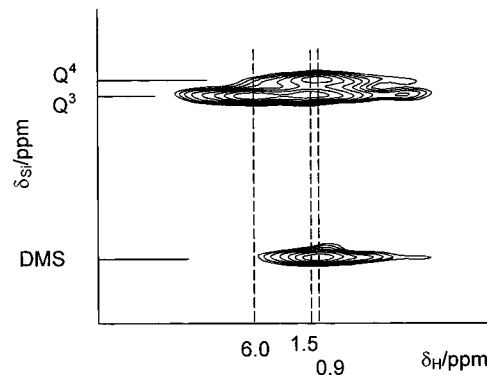
<sup>a</sup> Not determined because of unresolved signal, but band shape around null point suggests that Q<sup>4</sup>  $T_1$  is slightly longer than that for Q<sup>3</sup>.



**Figure 3.** Solid-state <sup>29</sup>Si CP NMR spectrum of 10% DMS–silica hybrid incorporating an inversion pulse followed by a 3.3 ms delay before cross-polarization.

and arises from steric trapping of functional groups in the evolving 3D network. The <sup>13</sup>C CP NMR spectrum further supports formation of an incompletely condensed silica–DMS hybrid. A strong DMS Si–CH<sub>3</sub> resonance was seen at 0.5 ppm, together with resonances at 17.5 and 59.6 ppm due to residual ethoxy groups, and at 50.6 ppm assigned to a Si–OCH<sub>3</sub> carbon, arising from reaction of residual Si–Cl groups and/or exchange of Si–OEt groups with methanol used for the Soxhlet extraction. The methoxy and ethoxy signals, in combination, are less than 5% of the total carbon signal. It can be seen from Table 2 that the degree of condensation of the silica network increases as the proportion of siloxane present increases, consistent with previous studies.<sup>41</sup> At 50% siloxane, Q<sup>2</sup> species are no longer present and the proportion of fully condensed Q<sup>4</sup> species has increased from 51% at 1% siloxane to 80%. This is consistent with the silica network being made flexible by the more flexible siloxane component, lending more mobility to the condensing network and hence a higher degree of condensation.

In view of the chemistry involved, it seems likely that the silica and dimethylsiloxane moieties are covalently linked at a molecular level. To provide further information about this, relaxation and 2D <sup>29</sup>Si–<sup>1</sup>H heteronuclear correlation measurements were undertaken. It might be expected that any Fe<sup>3+</sup> present could have some effect on the relaxation behavior; however, if it is a dominant cause of relaxation, all the samples would be expected to behave in a similar way and this is not observed.  $T_1$ (H) and  $T_{1\rho}$ (H) values were determined indirectly through the <sup>29</sup>Si spectrum for the samples containing siloxane as well as for material containing



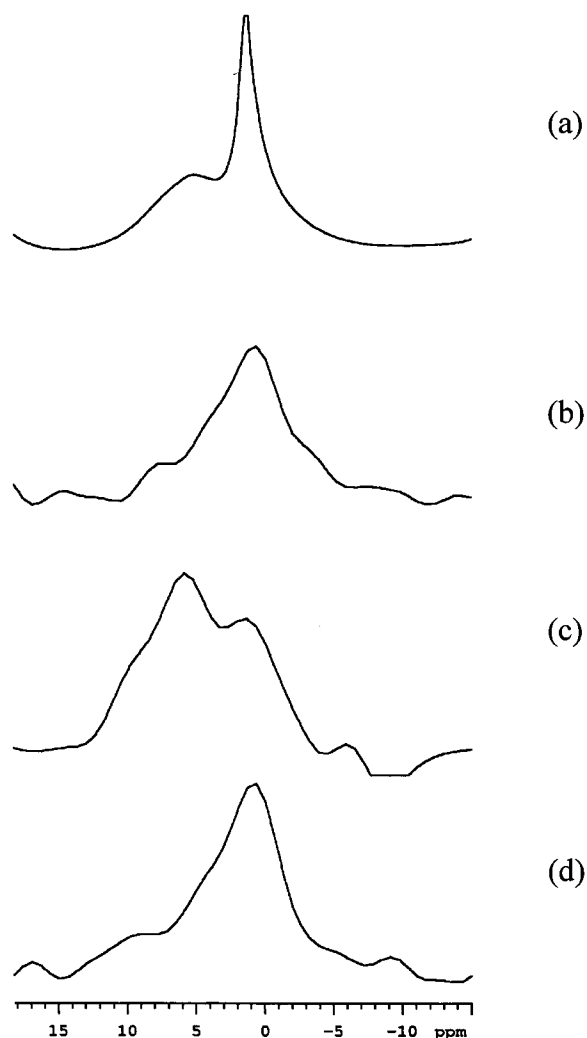
**Figure 4.** Solid-state WISE <sup>29</sup>Si–<sup>1</sup>H heteronuclear correlation spectrum of 10% DMS–silica hybrid.

no siloxane. The results are given in Table 3. At high siloxane content, the hydrogen associated with the DMS and Q<sup>n</sup> signals behaves with common  $T_1$ (H) and  $T_{1\rho}$ (H) values. Furthermore, these values are significantly different from those of the siloxane-free material. For the samples containing 1 and 10% siloxane, there is evidence of some difference in the  $T_1$ (H) and  $T_{1\rho}$ (H) values for the different signals in the silicon spectrum. However, for the 10% sample (where values were obtained for all the signals) the Q<sup>4</sup> and DMS signals still appear to have a common behavior. This can be demonstrated by carrying out an editing experiment in which the signal with the shorter  $T_1$ (H) value is nulled. The resulting spectrum, Figure 3, shows only signals from the DMS and Q<sup>4</sup> species. All the relaxation data suggest that there is a high degree of homogeneity in the hybrid systems—the siloxane segments do not form separate domains from the silica but are uniformly distributed throughout the silica network. In a physical mixture of silica and oligodimethylsiloxane (ODMS), it would be expected that the  $T_1$  values would be quite different because of the different physical natures of the silica and ODMS components. The different behavior of the silicon signals in the low siloxane content hybrids (particularly noticeable in the 10% siloxane system) suggests that the Q<sup>4</sup> signal is at least partly derived from “pseudo” Q<sup>4</sup> species, i.e., (SiO)<sub>3</sub>Si–O–Si(CH<sub>3</sub>)<sub>2</sub>–. This is indicative of direct covalent bonding between the silica and the DMS.

Further evidence for the homogeneity of the materials was obtained from heteronuclear correlation spectra. The result of a WISE (Wideline SEparation) type correlation experiment<sup>42</sup> on the sample containing 10% siloxane is shown in Figure 4. The results are also plotted as 1D spectra in Figure 5. The DMS and Q<sup>4</sup>

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**Figure 5.** The 10% DMS-silica hybrid: (a) one-dimensional  $^1\text{H}$  NMR spectrum and slices parallel to the  $^1\text{H}$  axis in the WISE spectrum in Figure 4 taken at a  $^{29}\text{Si}$  shift of (b)  $-14$  ppm, (c) at a shift of  $-101$  ppm, and (d) at  $-110$  ppm.

silicon signals appear to correlate only with the same  $^1\text{H}$  signal at  $0.9$  ppm. The  $\text{Q}^3$  signal correlates with a

slightly higher frequency  $^1\text{H}$  signal at  $1.5$  ppm and a signal at  $6$  ppm, probably arising from residual ethoxy groups. The absence of a correlation between the  $\text{Q}^3$  silicon atoms and the DMS proton signal suggests that pseudo  $\text{Q}^3$  species (cf. pseudo  $\text{Q}^4$  species above) do not exist. This is not unreasonable since the less sterically crowded environment around silicon atoms attached to the D units will facilitate full condensation around these atoms. The correlation between the DMS silicon signal and the  $0.9$  ppm  $^1\text{H}$  shift indicates that this  $^1\text{H}$  signal is due to  $\text{Si}-\text{CH}_3$ . Fyfe<sup>43</sup> gives this shift as  $0.45$  ppm. The  $^1\text{H}$  signal at  $6$  ppm is likely to be due to the  $\text{SiO}-\text{CH}_2$  protons from residual ethoxy groups but could also have a contribution from strongly hydrogen-bonded OH. Attempts to increase the resolution in the  $^1\text{H}$  dimension by using a high-resolution correlation experiment<sup>44</sup> were unsuccessful. The necessarily short contact time and resulting poor signal-to-noise ratio proved too restrictive. Nevertheless, the results obtained are consistent with the relaxation measurements and with materials with a high degree of homogeneity. The products thus consist of siloxane components of short D units linked to silica on a molecular level, resulting from copolymerization between Q and D units.

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