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First Direct Observation by ^{17}O Liquid NMR of Co-condensation Reactions between Methyl-Substituted Silicon Alkoxides

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Sol−gel synthesis based on hydrolysis and condensation reactions of alkoxysilanes, $X_xSi(OR)_{4-x}$ ($x = 0, 1, 2$) is now widely used for the preparation of siloxane-based organic−inorganic materials.[1,2] X is an organic group attached to the Si atom through a nonhydrolyzable Si−C bond. These precursors permit us to build an entirely new family of materials in which the silica network is functionalized by organic groups. The properties of the final materials will strongly depend on the respective arrangement of the organic and inorganic components within the hybrid network. One of the main advantage claimed for such synthetic approach is that homogeneity could be achieved at a molecular level in solution. One way to try to prevent possible phase separation is to favor co-condensation rather than self-condensation reactions between the various silicon alkoxides:

self-condensation:

$$-Si_A-OH + -Si_A-OX \rightarrow -Si_A-O-Si_A + XOH \quad (X = H \text{ or } R)$$

co-condensation:

$$-Si_A-OH + -Si_B-OX \rightarrow -Si_A-O-Si_B + XOH \quad (X = H \text{ or } R)$$

Very few in situ studies have been performed so far, most using ^{29}Si NMR.[3-5] ^{17}O solution NMR can be a unique technique to follow co-condensation reactions, but its low natural abundance ($3.7 \times 10^{-2}\%$) and its quadrupole moment renders its detectability difficult.[3] The use of enriched water in sol−gel syntheses will be of great advantage: it will lead to a specific labeling of the M−*O*H and M−*O*−M′ groups and thus greatly enhances their detectability compared to ROH or M−*O*R groups.

The various chemicals (dimethyldiethoxysilane, DMDES, methyltriethoxysilane, MTES and tetraethoxysilane, TEOS) were used as received. ^{17}O NMR experiments were conducted on a AM250 (33.9 MHz) Bruker spectrometer using 10 at. % enriched H_2O (Euriso-Top, France). The sample was held in an 8 mm tube which was in turn placed in a 10 mm tube with C_6D_6 in the annulus as lock solvent. A 12 μs (90°) pulse width was used; 500−2000 transients were accumulated with 200 ms recycle delays. Quadrupolar relaxation mechanism is dominant in ^{17}O NMR of siloxanes leading to short relaxation times.[6] Si sites will be labeled with the conventional notation: D refers to difunctional Me_2SiO_2 units, T to trifunctional $MeSiO_3$ units, and Q to tetrafunctional SiO_4 units.

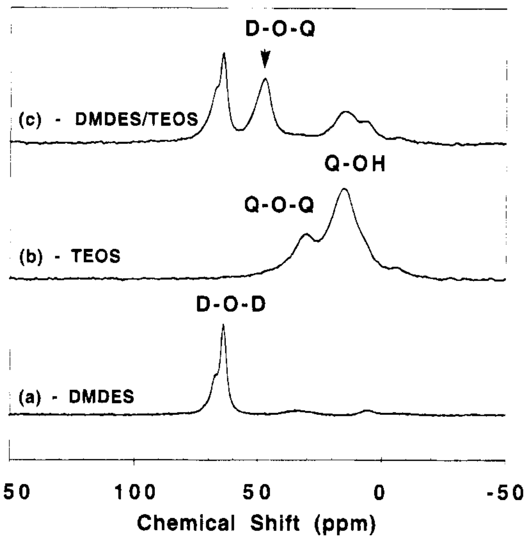
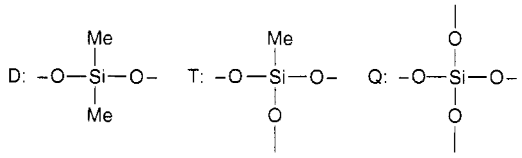


Figure 1. ^{17}O NMR spectra of hydrolyzed solutions of (a) DMDES, (b) TEOS, and (c) a mixture of DMDES and TEOS in a 1/1 ratio (aging time 2 days).



D: $-O-Si(Me)_2-O-$ T: $-O-Si(Me)(O-)-O-$ Q: $-O-Si(O-)_2-O-$

The subscript, *n*, will designate the number of oxo bridges. The spectra were simulated with WINFIT program[7] to get accurate chemical shift values (±0.1 ppm).

Dimethyldiethoxysilane (DMDES), methyltriethoxysilane (MTES), and tetraethoxysilane (TEOS) have been chosen as model compounds for difunctional, trifunctional, and tetrafunctional silicon alkoxides. Three solutions of pure DMDES, MTES and TEOS in ethanol (EtOH/Si = 4) have been hydrolyzed with acidic enriched water (H_2O/OEt = 0.1; pH = 2). The low hydrolysis ratio was chosen to prevent extensive condensation reactions and favor the formation of small oligomeric species such as dimers or trimers. Minor signals around −5 and 6 ppm in all spectra will be due respectively to residual water and ethanol.

After 2 days, the spectrum of the hydrolyzed DMDES solution (Figure 1a) shows two main peaks at 64.0 and 67.5 ppm (84%) due to D−*O*−D bridges.[8]

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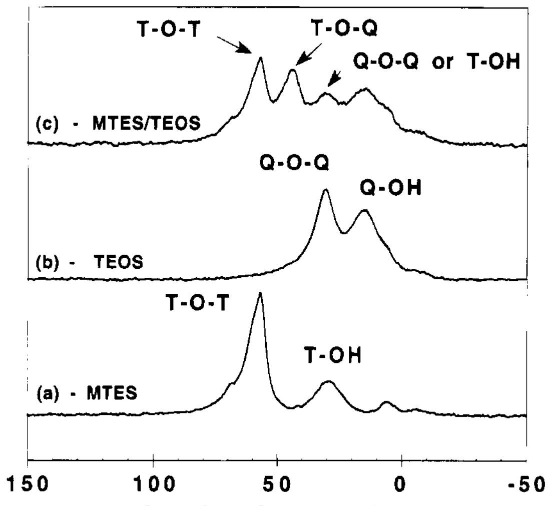
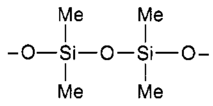


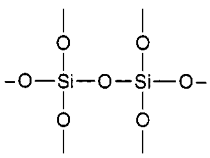
Figure 2. ^{17}O NMR spectra of hydrolyzed solutions of (a) MTES, (b) TEOS, and (c) a mixture of MTES and TEOS in a 1/1 ratio (aging time 19 days).

D-O-D:


$$-\mathrm{O}-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O}-$$

The major peak at 64 ppm can be assigned to oxo bridges in dimers, $\mathrm{D}_1-O-\mathrm{D}_1$, while the peak at 67.5 ppm can be due to oxo bridges in trimers or larger oligomers $\mathrm{D}_1-O-\mathrm{D}_2$. These assignments are in perfect agreement with the ^{29}Si NMR spectrum which shows a majority of dimers among the condensed species. The minor peak at 33.7 ppm (9%) is due to D−*O*H groups: it indicates that most of the condensation reactions are terminated after 2 days aging for this system.

After the same aging time, the behavior of the hydrolyzed TEOS solution (Figure 1b) is totally different: the main peak at 15.3 ppm (66%) is due to Q−*O*H groups and the peak at 31.0 ppm (28%) is due to Q−*O*−Q bridges.

Q-O-Q:


$$-\mathrm{O}-\underset{\mathrm{O}}{\overset{\mathrm{O}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{O}}{\overset{\mathrm{O}}{\mathrm{Si}}}-\mathrm{O}-$$

So after 2 days, condensation reactions are still under progress. After 19 days (Figure 2b), the peak due to Q−O−Q species represents 50% of the total intensity and the peak due to Q−OH groups still 44%.

The behavior of the MTES system is intermediate between the previous ones. After 2 days (Figure 3b), two peaks of similar intensity are present at 56.9 ppm (42%) due to T−*O*−T bridges and at 29.7 ppm (49%) due to T−*O*H groups. After 19 days, the relative intensities of these two peaks are respectively 68% and 26% (Figure 2a).

The evolution of the peak due to hydroxyl groups in the various solutions confirm that the reactivities toward hydrolysis of the various alkoxides are in the order[9]

$$\mathrm{TEOS} < \mathrm{MTES} < \mathrm{DMDES}$$

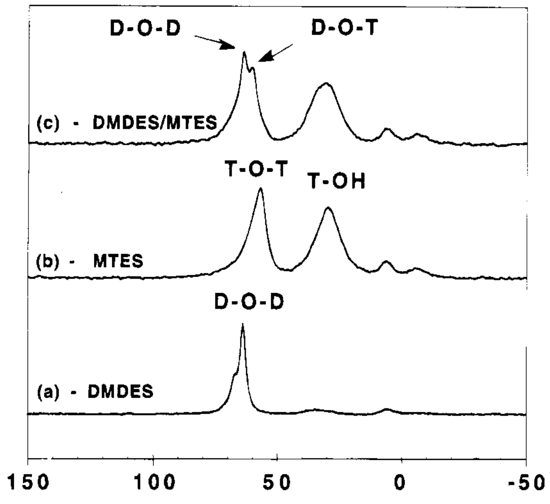
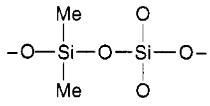


Figure 3. ^{17}O NMR spectra of hydrolyzed solutions of (a) DMDES, (b) MTES, and (c) a mixture of DMDES and MTES in a 1/1 ratio (aging time 2 days).

Table 1. ^{17}O NMR Results Obtained on Hydrolyzed Solutions of Methyl-Substituted Silicon Alkoxides (H_2O/OEt = 0.1, pH = 2, EtOH/Si = 4)

sample	chemical shift (ppm)	assignment
DMDES	33.7	D−OH
	63.9, 67.5	D−O−D
MTES	29.7	T−OH
	56.9	T−O−T
TEOS	15.3	Q−OH
	31.0	Q−O−Q
DMDES/TEOS	15.0	Q−OH
	47.5	D−O−Q
	64.0, 67.5	D−O−D
DMDES/MTES	31.7	D−OH or T−OH
	60.4	D−O−T
	64.1	D−O−D
MTES/TEOS	15.4	Q−OH
	30.3	T−OH or Q−O−Q
	44.7	T−O−Q
	57.1	T−O−T

Solutions of DMDES/TEOS, MTES/TEOS, and DMDES/MTES in a 1/1 ratio have been hydrolyzed in the same conditions as those previously described. The spectrum of the DMDES/TEOS hydrolyzed solution (Figure 1c) after 2 days aging, shows a peak at 64.0 ppm due to D−*O*−D bonds, as well as a peak at 15.0 ppm due to Q−*O*H groups. No peak due to Q−*O*−Q bonds (31 ppm) is clearly detected, but a new peak is now present at 47.5 ppm due to D−*O*−Q bridges.

D-O-Q:


$$-\mathrm{O}-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{O}}{\overset{\mathrm{O}}{\mathrm{Si}}}-\mathrm{O}-$$

A similar peak was already found in a solution of DMDES and TEOS, but hydrolyzed with nonenriched water and thus was difficult to detect.[3]

The spectrum of the MTES/TEOS hydrolyzed solution (Figure 2c) after 19 days aging also shows an extra peak at 44.7 ppm assigned to T−*O*−Q bridges. T−*O*−T bridges are also present with a peak at 57.1 ppm. Evidence for Q−O−Q bridges (31 ppm) is not so clear, because of a possible overlap with the peak due to T−OH bridges (29.7 ppm). Q−OH groups are characterized by the peak at 15.4 ppm. These results are in

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[9] Schmidt, H.; Scholze, H.; Kaiser, A. *J. Non-Cryst. Solids* **1984**, *63*, 1.

perfect agreement with recent ^{29}Si NMR results obtained on similar systems.[5]

Evidence for co-condensation reactions between D and T units is not as easily seen as for the previous cases, because of smaller differences between chemical shift values of D−*O*−D (64 ppm) and T−*O*−T (57 ppm) bridges. However the spectrum of the DMDES/MTES hydrolyzed solution presents a new peak at 60.4 ppm that can be assigned to D−*O*−T bridges (Figure 3c).

In the three systems, it was thus possible to detect co-condensation reactions between different units via the formation of oxo bridges. The results are summarized in Table 1. The relative intensities of the various peaks are in total agreement with the known reactivities of these alkoxides under acidic conditions:

$$\text{TEOS} < \text{MTES} < \text{DMDES}$$

Hydrolysis of the most reactive alkoxide is favored and thus it self condenses or co-condenses with the other alkoxide. Self condensation of the alkoxide with the lower reactivity is largely prevented under these experimental conditions (low hydrolysis ratio). This behavior is clearly illustrated with the DMDES/TEOS system in which only D−O−D and D−O−Q bridges are detected. Investigations are now under progress with higher hydrolysis ratios, typical of those used in sol−gel preparations.

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