Organically Modified $SiO_2-B_2O_3$ Gels Displaying a High Content of Borosiloxane (=B−O−Si≡) Bonds

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Hybrid $SiO_2-B_2O_3$ gels have been synthesized from cohydrolysis of modified silicon alkoxides ($R-Si(OE)_3$ R = Me, Vi, Et) and triethylborate, $B(OEt)_3$. The structure of these gels was investigated by Fourier-transformed infrared (FT-IR) spectroscopy, ^{29}Si and ^{11}B solid-state nuclear magnetic resonance (NMR), X-ray diffraction (XRD), and chemical analysis. The results show, for the first time, the possibility of obtaining a $SiO_2-B_2O_3$ gel in which trigonal boron atoms are homogeneously dispersed in the siloxane network via B−O−Si bonds. The identification of such bonds was mainly based on the FT-IR and ^{11}B MAS NMR results. The formation of the borosiloxane bonds is favored by increasing the pH of hydrolysis water and by the use of Et− or $Vi-Si(OR)_3$ rather than $Me-Si(OEt)_3$. Some hypotheses to rationalize the experimental results are also presented.

Introduction

The sol−gel method based on hydrolysis and condensation reactions of metal alkoxides is widely studied as an alternative, low-temperature approach for the preparation of glasses or ceramics. For binary metal oxide systems, it is generally assumed that a high level of homogeneity can be achieved in the final gel with the formation of M−O−M′ bonds, where M and M′ are two different metals, via cocondensation reactions of the starting alkoxides. However, it is now well-recognized that real systems are often far from this ideal situation and the resulting gels can have a heterogeneous structure. This fact is due either to the different reaction rates of the molecular precursors that lead to the formation of M−O−M and M′−O−M′ bonds or to the low stability of the mixed M−O−M′ oxo-bridges formed in the early stages of the process that finally leads to a phase separation.[1]

$SiO_2-B_2O_3$ gels, obtained from tetrafunctional silicon alkoxides such as $Si(OCH_3)_4$ or $Si(OCH_2CH_3)_4$ and trialkylborates or boric acid have been extensively studied as precursors for borosilicates[2−7] or oxynitride glasses.[8−11] Irwin et al.[12,13] reported a detailed liquid as well as solid-state NMR study of the structural evolution of this system during the entire sol−gel process and clearly demonstrated that no B−O−Si bonds exist in the final gels.

Modified silicon alkoxide such as R'_x-$Si(OR)_{4-x}$, x = 1, 2, 3, where R′ is an organic group, are currently used for the sol−gel synthesis of hybrid organic/inorganic networks.[14−15] These materials find applications in a variety of fields, including precursors for silicon oxynitride[16−18] or oxycarbide[19−23] glasses obtained after pyrolysis in respective reactive (NH_3) or inert (Ar, He) atmospheres.

In the present study we focus on the sol−gel synthesis and characterization of hybrid gels obtained from cohydrolysis of $R'-Si(OR)_3$ (R = Me, Et, Vi) and $B(OEt)_3$.

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Our interest for these materials is primarily related to the preparation of borosilicate gels as precursors for multicomponent silicon oxycarbide glasses in the SiBOC system.[24−25] A preliminary study showed that, when compared with a nonmodified silicon alkoxide such as tetraethoxysilane, $Si(OEt)_4$, some borosiloxane bonds were retained in the hybrid $SiO_2-B_2O_3$ gels obtained from methyltriethoxysilane, $MeSi(OEt)_3$. These promising observations prompted us to investigate the role of the organic substituent in the formation of homogeneous borosilicate gels containing B−O−Si bonds, as well as the possible influence of some synthesis parameters including pH of the hydrolysis water and boron load. In this study, the structure of the hybrid $SiO_2-B_2O_3$ gels is investigated using infrared spectroscopy, X-ray diffraction, and ^{29}Si and ^{11}B solid-state NMR spectroscopy. For comparison purposes and to facilitate the interpretation of the results, some data obtained on gels synthesized from tetrafunctional silicon alkoxides and on hybrid gels heat treated in air will also be presented.

Experimental Section

Synthesis of the Gels. Modified silicon alkoxides, i.e., methyltriethoxysilane (MTES), ethyltriethoxysilane (ETES), and vinyltriethoxysilane (VTES), have been purchased from ABCR (Karlsruhe, Germany). Tetraethoxysilane (TEOS) and triethylborate (TEB) have been obtained from Aldrich (Milwaukee, WI). All the chemicals were used as received without any purification. Water acidified with HCl, having a pH ranging from 1 to 2.5, was used for hydrolysis. To minimize the residual amount of water after hydrolysis and thus to increase the stability of B−O−Si bonds in the resulting gels, a H_2O:Si molar ratio of 1.5 has been used for all the preparations. The gels were prepared according to the following procedure: the silicon alkoxide and the proper amount of water were poured into a beaker and magnetically stirred. Initially, the two liquids are immiscible, but the solution becomes clear after a given hydrolysis time, t_h, due to the consumption of part of the H_2O at the alkoxide/water interface and formation of EtOH. At this point, the proper amount of TEB was added without any further water addition. The solution was stirred for 15 additional minutes and finally poured into test tubes that were left open for gelation. The gels were then dried at room temperature for several weeks and at 60 °C for 10 days.

All the studied gel compositions with their respective hydrolysis and gelation times, t_h and t_g, are summarized in Table 1. In this paper the samples will be designated as follows: identification of the silicon alkoxide (Me for MTES, Et for ETES, Vi for VTES, and Q for TEOS), followed by the nominal B/Si atomic ratio and the pH of the hydrolysis water. For example, ViB0.5/2.5 refers to the gel prepared from VTES with a B/Si ratio of 0.5 and hydrolyzed with H_2O at pH = 2.5.

Table 1. Chemical Parameters, Hydrolysis, Gelation Times, and Appearance of the Studied Gels

sample	B/Si (atomic ratio)	pH	hydrolysis time, t_h (min)	gelation time, t_g (days)	appearance of the gels
Me/1	0	1	5	≈8	transparent
Me/2	0	2	25	≈30	transparent
MeB0.2/1	0.2	1	5	≈10	cloudy, opaque
MeB0.2/1.5	0.2	1.5	15	≈10	cloudy, opaque
MeB0.2/2	0.2	2	25	≈20	transparent
MeB0.2/2.5	0.2	2.5	45	≈20	transparent
MeB0.5/1	0.5	1	5	≈15	cloudy, opaque
MeB0.5/2	0.5	2	25	≈20	transparent
MeB0.5/2.5	0.5	2.5	45	≈22	transparent
MeB0.7/1	0.7	1	5	≈18	cloudy, opaque
MeB1/1	1	1	5	≈20	cloudy, opaque
Et/1	0	1	30	[a]	transparent
EtB0.2/1	0.2	1	30	≈50	cloudy, opaque
EtB0.2/2.5	0.2	2.5	240	≈70	transparent
EtB0.5/1	0.5	1	30	≈115	cloudy, opaque
EtB0.5/2.5	0.5	2.5	240	≈115	transparent
Vi/1	0	1	20	20	transparent
Vi/2.5	0	2.5	150	≈150	transparent
ViB0.2/1	0.2	1	20	≈25	cloudy, opaque
ViB0.2/2.5	0.2	2.5	150	≈40	transparent
ViB0.5/1	0.2	1	20	≈120	cloudy, opaque
ViB0.5/2.5	0.5	2.5	150	≈120	transparent
Q/1	0	1	90	<7	transparent
QB0.2/1	0.2	1	90	<7	cloudy, opaque
QB0.5/1	0.5	1	90	<7	cloudy, opaque

[a] The Et/1 composition leads to a stable, highly viscous liquid that does not gel even after several months.

Characterization Techniques. *FT-IR Spectroscopy*. FT-IR spectra were collected by the KBr disk method in transmission mode; 64 scans were always accumulated with a Nicolet FT-IR 5DXC equipment operating with 2 cm^{-1} resolution.

X-ray Diffraction (XRD). XRD spectra were collected on a Rigaku D/Max-B diffractometer operating at 40 KV and 30 mA, using a Bragg−Brentano configuration with Cu Kα radiation and a monochromator in the diffracted beam. Typically experimental spectra were collected between 10° and 80° (2θ) with a scan speed of 2°/min.

Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) Spectroscopy. ^{29}Si MAS NMR spectra and most of the ^{11}B MAS NMR spectra were recorded at 79.50 and 128.28 MHz using a MSL400 Bruker spectrometer. The ^{29}Si NMR spectra were recorded using a CP-MAS Bruker probe equipped with 7 mm ZrO_2 rotors, spinning at 4 kHz. The following acquisition parameters were used: spectral width of 20 kHz;, 4K data points, pulse width of 1.5 μs ($\theta \approx 30°$), and recycle delay of 30 s; 50 Hz exponential broadening was applied before Fourier transform. Spectra were referenced externally to TMS at 0 ppm. The ^{11}B NMR spectra were recorded using a CP-MAS Doty probe equipped with 5 mm Si_3N_4 rotors, spinning at 9−10 kHz. The following acquisition parameters were used: spectral width of 125 kHz, 4K data points, pulse width of 1 μs, and recycle delay of 1 s; 50 Hz exponential broadening was applied before Fourier transform. Spectra were referenced externally to $(OEt)_2 \cdot BF_3$ at 0 ppm. One ^{11}B NMR spectrum was recorded at 11.7 T on a Bruker ASX500 spectrometer. The experimental spectra were simulated to get a quantitative estimation of the various silicon and boron sites using the WinFit software developed by Massiot et al.[26] The ^{11}B MQ-MAS NMR experiment was recorded using a Bruker MSL300 spectrometer with a 4 mm MAS probehead operating at 96.216 MHz. A two-pulse hypercomplex sequence[27] with triple quantum excitation and conversion pulses of 8 and 3 μs was used, with 20 μs increment for both t_1 and t_2 dimensions and 128 × 128 hypercomplex $t_1 \times t_2$ points. The FIDs were recorded with a recycle delay of 4 s, and 800 scans were accumulated. The spectra were then processed according to a procedure very similar to that described for DAS.[28]

Heat Treatments. Heat treatments of the gels were performed on powders in air, using a muffle furnace with a heating rate of 5 °C/min at various temperatures between 300 and 700 °C. When the selected maximum temperature was reached, the samples were immediately withdrawn and quenched in air.

Elemental Analysis. Selected dried gel samples were analyzed for silicon, boron, carbon, and hydrogen by the Service Central d'Analyse du CNRS, Vernaison, France.

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Table 2. Elemental Analysis of the Studied Gels

sample	composition (wt %)				empirical formula[a]	theoretical composition
	Si	B	C	H		
MeB0.2/1	38.1 ± 0.15	1.35 ± 0.02	16.9 ± 0.1	4.33 ± 0.02	$SiB_{0.09}C_{1.04}H_{3.16}O_{1.82}$	$SiB_{0.2}C_1H_3O_{1.8}$
MeB0.5/1	35.6 ± 0.15	2.41 ± 0.02	16.4 ± 0.1	4.45 ± 0.02	$SiB_{0.18}C_{1.07}H_{3.5}O_{2.02}$	$SiB_{0.5}C_1H_3O_{2.25}$
MeB0.2/2.5	36.8 ± 0.15	2.08 ± 0.02	16.7 ± 0.1	4.71 ± 0.02	$SiB_{0.15}C_{1.05}H_{3.58}O_{1.88}$	$SiB_{0.2}C_1H_3O_{1.8}$
ViB0.2/2.5	31.4 ± 0.15	1.92 ± 0.02	26.7 ± 0.1	4.15 ± 0.02	$SiB_{0.16}C_{2.04}H_{3.70}O_{1.96}$	$SiB_{0.2}C_2H_3O_{1.8}$
EtB0.2/2.5	31.4 ± 0.15	1.99 ± 0.02	27.2 ± 0.1	6.41 ± 0.02	$SiB_{0.16}C_{2.02}H_{5.73}O_{1.84}$	$SiB_{0.2}C_2H_5O_{1.8}$

[a] O was not analyzed and its amount was estimated by difference.

Results

Chemical Analysis. Chemical analysis were performed on selected borosilicate gels, and the results are reported in Table 2. The empirical formula is compared with the theoretical composition obtained considering the formation of a fully condensed gel without any residual OEt or OH groups. It can be observed that the amount of carbon present in the gel is very close to the theoretical value, suggesting the complete retention, in the hybrid siloxane network, of the organic moieties bonded to the silicon atoms. On the other hand, the boron level is very low, compared with the nominal composition. This behavior is well-known in the synthesis of borosilicate gels and is ascribed to the evaporation of boron alkoxides during gelling and drying.[3,12]

The chemical analysis of MeB0.2/1 and MeB0.2/2.5 gels indicates that, for similar nominal boron loads (B/Si = 0.2), more boron is retained in the gel synthesized using water at pH = 2.5 (B/Si = 0.15) than using water at pH = 1 (B/Si = 0.09). This result can be related, as it will be shown later on, to the higher fraction of boron atoms bonded to the siloxane network via B−O−Si bonds in the MeB0.2/2.5 gel compared to the MeB0.2/1 sample. Finally, the experimental hydrogen and oxygen contents are not too far from the expected values (cf. the empirical formula and the theoretical composition), thus suggesting that terminal OH or OEt groups are not abundant in these gels.

FT-IR Study. Since it is not possible to present all the spectra in this paper, only the most representative examples will be reported and discussed.

A comparison between the FT-IR spectra recorded on two borosilicate gels synthesized from TEOS (QB0.5/1) and MTES (MeB0.5/1) is shown in Figure 1.

The spectrum of TEOS-derived silica gel (QB0.5/1) is characterized by the typical bands associated with the Si−O bonds at 1120−1020 cm^{-1} (ν Si−O), 840−790 cm^{-1} (ρ Si−O−Si), and 460−400 cm^{-1} (δ Si−O−Si).[29] Absorptions at 920−950 cm^{-1} (ν Si−OH) and at 1620 cm^{-1} (δ H−O−H) suggest the presence of terminal hydroxyl groups as well as absorbed water. The presence of boron gives rise to peaks at 1500−1300 cm^{-1} (ν B−O) and at 1195 cm^{-1} (δ B−OH).[30] No bands due to borosiloxane bridges at 930−915 cm^{-1} (ν B−O−Si) and at 675 cm^{-1} (δ B−O−Si)[3,10] are present in this spectrum.

In the MeB0.5/1 spectrum, besides the bands due to the Si−O, B−O, and B−OH bonds, the Si−Me moieties lead to peaks at 1275 cm^{-1} (δ CH_3−Si), 800 cm^{-1} (ν Si−C), and 780 cm^{-1} (ρ CH_3−Si).[31] Moreover, two new peaks at 890 cm^{-1} and at 675 cm^{-1} are now visible. The latter one can be assigned, according to the literature,[3,8] to the bending of B−O−Si bridges, whereas the wavenumber of the other band at 890 cm^{-1} is lower than the one currently reported for the stretching of B−O−Si bridges (930−915 cm^{-1}). However, as will be shown later in the Discussion section, we tentatively assign the peak at 890 cm^{-1} to the stretching vibration of the borosiloxane bridges in which the silicon atoms bear three Si−O bonds and one terminal Si−R (R = Me, Et, Vi) group.

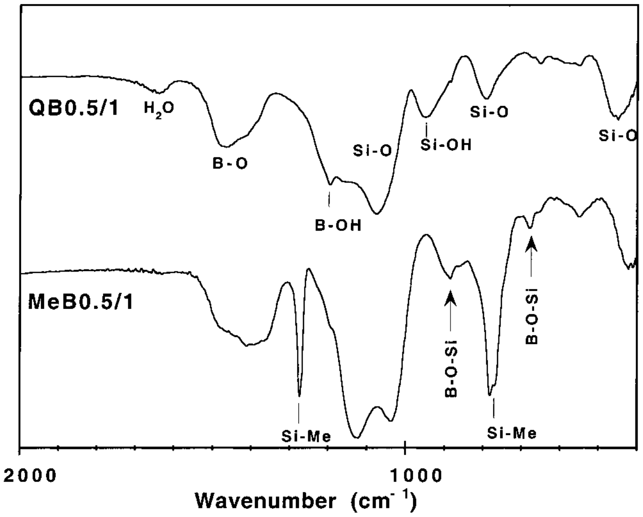

Figure 1. Comparison between the FT-IR spectra of the TEOS- and MTEETS-derived borosilicate gels: (a) QB0.5/1 and (b) MeB0.5/1.

These FT-IR results suggest, in agreement with the literature,[5,13] that in the TEOS-derived SiO_2−B_2O_3 gels, no B−O−Si bridges are present, so the network contains only Si−O−Si and B−O−B bonds with possibly terminal Si−OH and B−OH groups. On the other hand, the FT-IR spectrum of the MTES-derived sample shows for the first time the possibility of producing a SiO_2−B_2O_3 gel in which the boron is partially incorporated in the silica network via B−O−Si bridges. This promising result prompted us to investigate the role of different organic substituents (Me, Et, and Vi) and the influence of some synthesis parameters (pH of the hydrolysis water and boron load) on the incorporation of boron into the silica network. The ultimate aim will be the production of highly homogeneous SiO_2−B_2O_3 gels.

The Role of the B/Si Atomic Ratio. To illustrate the effect of the boron load, spectra recorded on MTES-derived gels are shown in Figure 2 for $0 < x = B/Si < 1$. In the MeB0.2/1 gel, the bands associated with the presence of the B−O−Si bridges at 980 and 675 cm^{-1} are hardly visible, while for the sample with B/Si = 0.5, the two peaks become distinct, suggesting the presence, in this sample, of borosiloxane bridges. In the gels with

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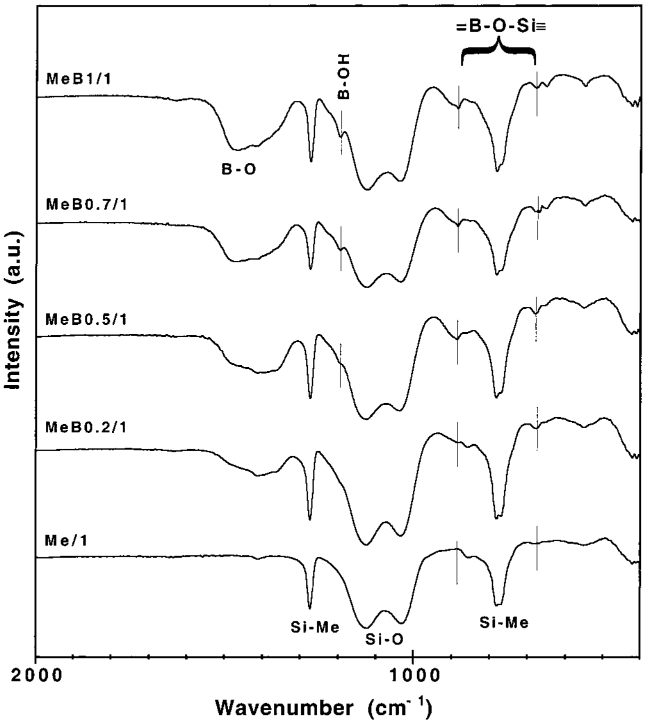

Figure 2. FT-IR spectra collected on MTES-derived borosilicate gels obtained at pH = 1 with different boron loads.

higher B content, the bands at 980 and 675 cm^{-1} are still present, but their intensity does not increase significantly compared to the MeB0.5/1 sample. On the other hand, by increasing the boron content from B/Si = 0.2 to B/Si = 1, the intensity of the peaks related to the B−O−B and B−OH bonds increases (see bands at 1500−1300 cm^{-1} and at 1195 cm^{-1}), suggesting an increase of the total boron load in the sample. Similar FT-IR spectra have been collected on the samples prepared from the other alkoxides as a function of the boron load. These results suggest that the number of borosiloxane bridges initially increases with the boron load up to a certain level, when a plateau is reached. Any further boron addition does not increase the amount of boron incorporated in the silica network but forms preferentially B−OH and B−O−B bonds.

The Role of the pH of the Hydrolysis Water. To illustrate this point, FT-IR spectra recorded on two EtB0.2/x samples (x = 1 and 2.5) are reported in Figure 3. For comparison purposes, the spectrum of the corresponding boron-free sample is also reported.

The FT-IR spectrum of the Et/1 sample is characterized by the bands associated with the presence of the Si−Et groups at 1463 cm^{-1} (δ CH_3-C); 1410 cm^{-1} (δ CH_2-Si), 1255 cm^{-1} (δ CH_2-Si), and 960 cm^{-1} due to the vibrations of the $Si-C_2H_5$ units; and 760 cm^{-1} (ν Si−C) and 697 cm^{-1} (ρ CH_2-Si).[31] Finally, the band at 560 cm^{-1} could be tentatively assigned to the presence, in the siloxane networks, of cage or cyclic structures.[32] In the EtB0.2/1 gel, the presence of boron leads to the formation of B−O bonds (1300−1500 cm^{-1}) and B−O−Si bridges (880 cm^{-1}). The peak at 680 cm^{-1}, also associated to the B−O−Si bridges, is hidden under the strong absorption band of the Si-Et groups at 697 cm^{-1}.

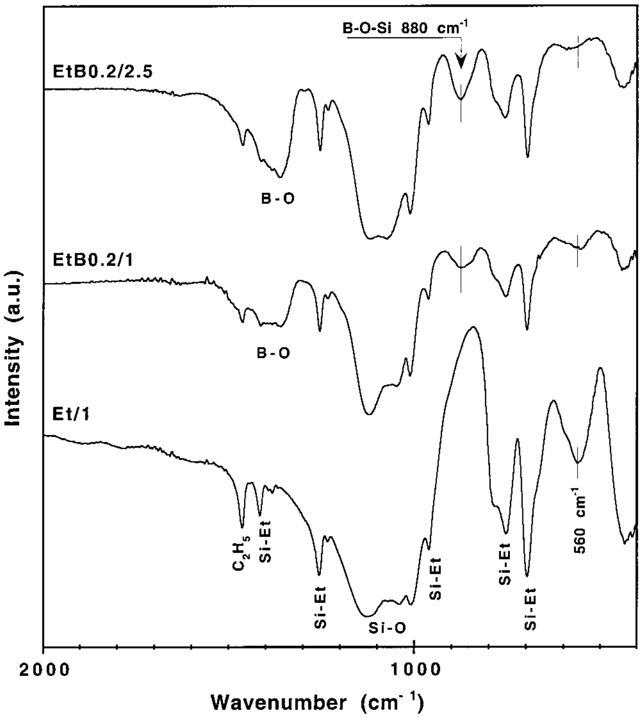

Figure 3. Evolution of the FT-IR spectra collected on ETES-derived borosilicate gels (B/Si = 0.2) as a function of the pH of the hydrolysis water.

Increasing the pH from 1 to 2.5 (cf. FT-IR spectrum of the EtB0.2/2.5 gel) clearly leads to an increase of the intensity of the band at 880 cm^{-1}, suggesting an increase of the fraction of BO_3 units incorporated into the siloxane network via B−O−Si bond formation. It is also worth noticing that boron addition to the ETES-derived gels leads to a rapid reduction of the peak at 560 cm^{-1}, associated with the cages or cyclic siloxane structures. This last result indicates a strong modification of the siloxane network compared with the pure ethyl-containing sample, certainly associated with the formation of the borosiloxane bridges.

The Role of the Organic Substituent of the Silicon Alkoxide. The nature of the organic substituent, R, of the modified $R-Si(OEt)_3$ alkoxides influences the formation of borosiloxane bridges in the hybrid borosilicate gels, as shown by the series of FT-IR spectra reported in Figure 4. The three samples, MTES-, VTES- and ETES-derived gels, have been obtained with a B/Si ratio of 0.2 and water at pH 2.5. The spectra of the MeB0.2/2.5 and EtB0.2/2.5 gels have been already discussed. In the FT-IR spectrum of the vinyl-derived sample, the $Si-CH=CH_2$ groups lead to the peaks at 1600, 1410, 1275, 970, and 770 cm^{-1}.[31] The extra peak at 890 cm^{-1} can be assigned to the stretching of the B−O−Si bridges. For the ETES- and VTES-derived gels, the absorption at 3200 cm^{-1}, related to the BO−H stretching (not shown in the figure), is very weak, suggesting that in these samples the boron atoms are mainly incorporated in the silica network with few terminal B−OH units.

The intensity of the band associated with the borosiloxane bridges at 880−890 cm^{-1} increases from MeB0.2/2.5 to ViB0.2/2.5 and to EtB0.2/2.5. Moreover, in the FT-IR spectra of the ETES- and VTES-derived gels, the bands at 560 and 590 cm^{-1} (the latter one observed in

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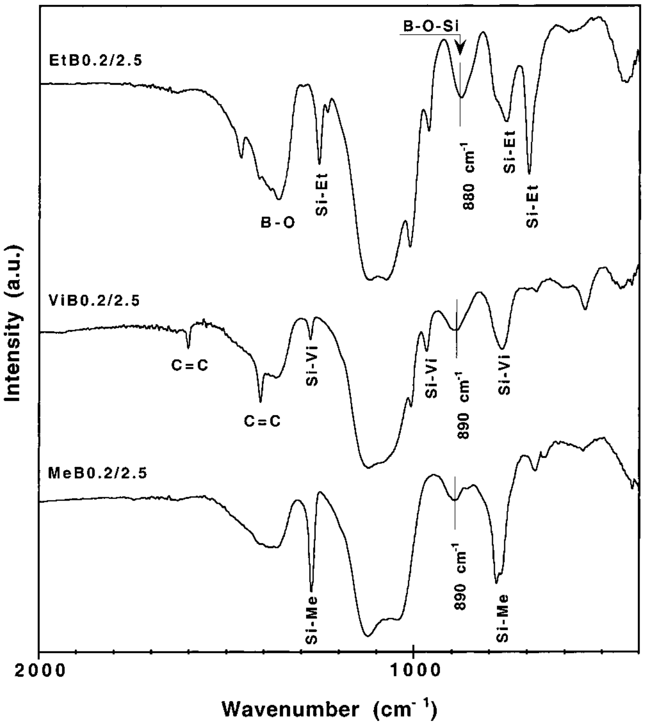

Figure 4. FT-IR spectra of the MTES-, ETES-, and VTES-derived gels with B/Si = 0.2 and water at pH = 2.5.

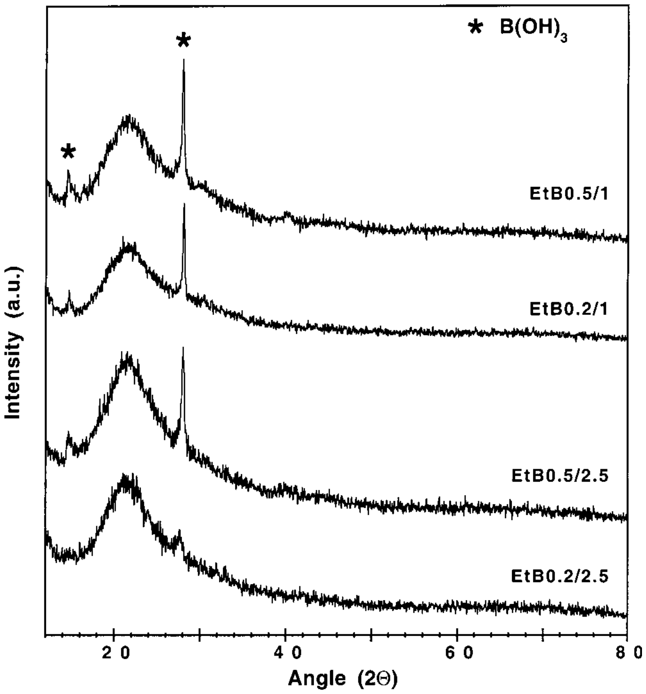

Figure 5. XRD spectra collected on selected ETES-derived gels with two B/Si ratios (B/Si = 0.2 and 0.5) and water at pH = 1 and 2.5.

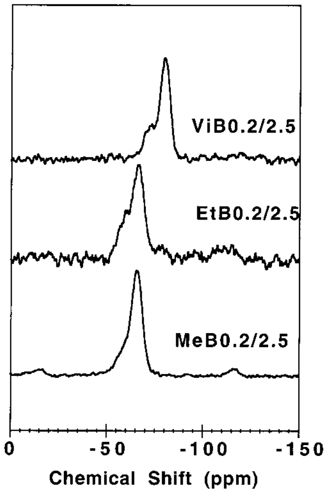

Figure 6. ^{29}Si MAS NMR spectra of the MTES-, ETES-, and VTES-derived gels with B/Si = 0.2 and water at pH = 2.5.

the spectrum of the pure Vi/2 gel not shown here) associated with cyclic or cage species are not present, indicating that boron addition strongly modifies the development of the siloxane network via the formation of B−O−Si bonds.

These results suggest that, all other synthesis parameters being constant, the number of borosiloxane bridges is related to the nature of the organic substituent, R, of the R−Si(OEt)$_3$ alkoxide, and seems to increase according to the following scale: ethyl > vinyl > methyl.

XRD Study. XRD spectra collected on selected ETES-derived borosilicate gels obtained with two B/Si ratios (B/Si = 0.2 and 0.5) and with water at two different pH values (pH = 1 and 2.5) are reported in Figure 5. The spectra show a broad reflection at $2\theta \sim 22°$ due to amorphous silica and two sharp peaks at $2\theta = 28°$ and 15° assigned to the presence of crystalline B(OH)$_3$.[33] Such a pattern is typical of most of the hybrid SiO$_2$−B$_2$O$_3$ gels synthesized in this study. However, in few cases, such as the MeB0.2/2.5 and ViB0.2/2.5 samples (not shown here) and the EtB0.2/2.5 gel, the peaks related to the boric acid phase are hardly visible. Indeed, as already suggested by the FT-IR analysis, the boron atoms in the EtB0.2/2.5 sample are mainly engaged in the formation of borosiloxane bridges, and the crystallization of B(OH)$_3$ is strongly hindered. When the B/Si ratio is increased from 0.2 to 0.5, the formation of crystalline B(OH)$_3$ phase is favored (cf. EtB0.2/2.5 and EtB0.5/2.5 spectra). Moreover, the influence of the pH of the hydrolysis water can be evaluated by comparing the XRD spectra of the EtB0.2/2.5 and EtB0.2/1 gels: decreasing the pH of the hydrolysis water leads to the crystallization of B(OH)$_3$. These results are in agreement with the trend already pointed out by the FT-IR study: the formation of a secondary boric acid rich phase is favored by increasing the boron load and decreasing the pH.

MAS NMR Study. ^{29}Si and ^{11}B MAS NMR spectra have been collected on selected gels that, according to the previously discussed FT-IR and XRD results, should have the maximum amount of borosiloxane bridges and the minimum amount of B(OH)$_3$, like the ones obtained using water at pH 2.5 with a ratio of B/Si = 0.2 (MeB0.2/2.5, EtB0.2/2.5, ViB0.2/2.5).

The ^{29}Si MAS NMR spectra (see Figure 6) show, for the three samples, the presence of one main peak at −64.8, −79.7, and −65.6 ppm, respectively, due to Me−*Si*O$_{3/2}$ Vi−*Si*O$_{3/2}$, and Et−*Si*O$_{3/2}$ silicon units. An upfield shoulder, due to some terminal ≡Si−OEt and/or ≡Si−OH groups is also present in all the investigated gels. The experimental spectra have been simulated with two

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Table 3. ^{26}Si MAS NMR Characterization of the Gels

	$R{-}SiO_{3/2}$			$R{-}SiO_{2/2}OX$ X = Et, H, OSi≡		
sample	δ (ppm)	fwhm[a] (ppm)	%	δ (ppm)	fwhm[a] (ppm)	%
MeB0.2/2.5	−64.9	6.9	81.4	−56.9	6.9	18.6
ViB0.2/2.5	−79.7	6.1	73.9	−71.5	6.1	26.1
EtB0.2/2.5	−65.6	7.0	71.1	−58.0	7.0	28.9

[a] fwhm = full width half maximum.

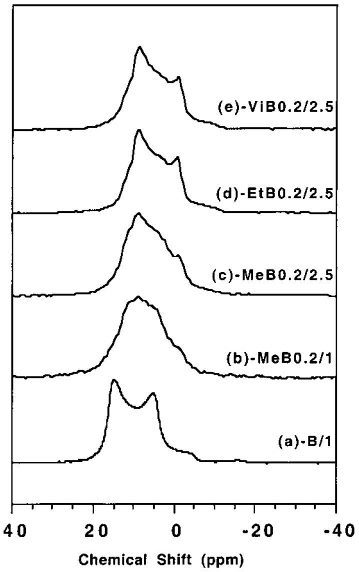

Figure 7. Experimental and simulated ^{11}B MAS NMR spectra recorded at 9.4 T of (a) hydrolysis product of TEB, (b) MeB0.2/1, (c) MeB0.2/2.5, (d) EtB0.2/2.5, and (e) ViB0.2/2.5. Spectra a and b were recorded with ^{1}H decoupling during acquisition.

components, and the percentage of the $R{-}SiO_{2/2}OX$ with X = Et, H sites has been accordingly estimated (See Table 3). It can be seen that the percentage of silicon atoms bearing a terminal unit is ≈19% for the MeB0.2/2.5 sample and goes up to 26−29% for the ViB0.2/2.5 and EtB0.2/2.5 samples. As already reported in the literature,[13,34] there is no chemical shift differences for the Si units to distinguish between $\equiv Si{-}O{-}Si\equiv$ or $\equiv Si{-}O{-}B{=}$ bonds. ^{29}Si NMR is thus not very informative to probe the formation of a borosilicate network.

^{11}B NMR may be more informative: an upfield shift from 19 ppm for boric acid or borate network to 12.5 ppm for borosilicate glasses with low B content is indicative of trigonal boron connected to SiO_4 tetrahedra.[35] ^{11}B MAS NMR spectra recorded at 9.4 T on various samples are reported in Figure 7. ^{1}H decoupling applied during acquisition shows a strong effect on the line shape of spectra a and b and no effect for spectra c−e. The spectrum of the hydrolysis product of TEB prepared at pH = 1 (B/1 sample) is characterized by one single powder pattern whose line shape analysis gives the following parameters: $\delta = 19.2$ ppm; $C_Q = 2.5$ MHz, and $\eta = 0$, in agreement with those found for $B(OH)_3$.[13] Indeed, the XRD pattern of this sample reveals the presence of crystalline boric acid. The signals of the other samples cannot be analyzed with one single component; however, a clear upfield shift is seen when going from B/1 to the Si-containing samples. However a precise identification of the various components is difficult due to the large overlap of the signals. They can however be assigned to trigonal B sites, if one considers the spectrum of EtB0.2/2.5 recorded at 11.7 T (Figure 8a), which shows no signal around 0 ppm, the chemical shift value for tetragonal B sites.

To improve the spectral resolution and to identify the various BO_3 resonances, two techniques have been considered which can be performed with a MAS probe: satellite transition spectroscopy (SATRAS)[36] and two-dimensional triple-quantum MAS (2D MQ MAS) NMR method.[37] SATRAS is based on the observation of the spinning sidebands of the satellite transitions (ST) and takes advantage of the fact that the relative MAS line width of ST transitions $({}^{3}/_{2} \leftrightarrow {}^{1}/_{2}$ or $-{}^{3}/_{2} \leftrightarrow -{}^{1}/_{2})$ is reduced compared to that of the central transition (CT) $({}^{1}/_{2} \leftrightarrow -{}^{1}/_{2})$. The reduction factor is rather large for $I = {}^{5}/_{2}$ (0.29), and indeed, the SATRAS method has been successfully applied to nuclei like ^{27}Al[38,39] and ^{17}O.[40] For $I = {}^{3}/_{2}$, like ^{11}B, the reduction factor is only 0.89, implying no gain in resolution.[35] In that case, to distinguish various signals, one can rely on the shift between the centers of gravity of the CT and ST transitions which depends on $C_Q{}^2/\nu_o{}^2$, C_Q being the quadrupole coupling constant and ν_0 the Larmor frequency: in borosilicate glasses, contributions due to tetragonal BO_4 and trigonal BO_3, which strongly overlap in the CT transition of a spectrum recorded at 7 T, are well-separated in the ST transitions,[35] due to the large difference in C_Q values between BO_3 (2.5−2.6 MHz) and BO_4 (0.5−0.8 MHz) sites. But for different BO_3 sites with similar C_Q values, such as in our case, no significant separation between contributions is expected in the ST transitions.

We thus tried to see whether the use of 2D MQ MAS experiments can bring better resolution in the ^{11}B NMR spectra. This two-dimensional experiment correlates the evolution of the symmetrical $({}^{3}/_{2} \leftrightarrow -{}^{3}/_{2})$ triple quantum transition with the evolution of the CT transition under magic angle spinning to produce highly resolved isotropic NMR spectra.[37] Such an experiment has already been applied to elucidate the structure of vitreous boron oxide (v-B_2O_3).[41] Two different BO_3 sites were identified from the isotropic (ω_1) dimension of the 2D MQ MAS experiment and quantified from the simulation of the one-dimensional (1D) MAS spectra recorded at various fields. The 2D-3Q MAS NMR spectrum of EtB0.2/2.5 is presented in Figure 9. In the ω_1 dimension, the signal is dominated by one main component, which presents a shoulder at lowfield, indicating at least two types of BO_3 sites. As already found in the study on v-B_2O_3,[41] the main factor limiting the resolution in the ω_1 dimension is the distribution of boron sites in this amorphous

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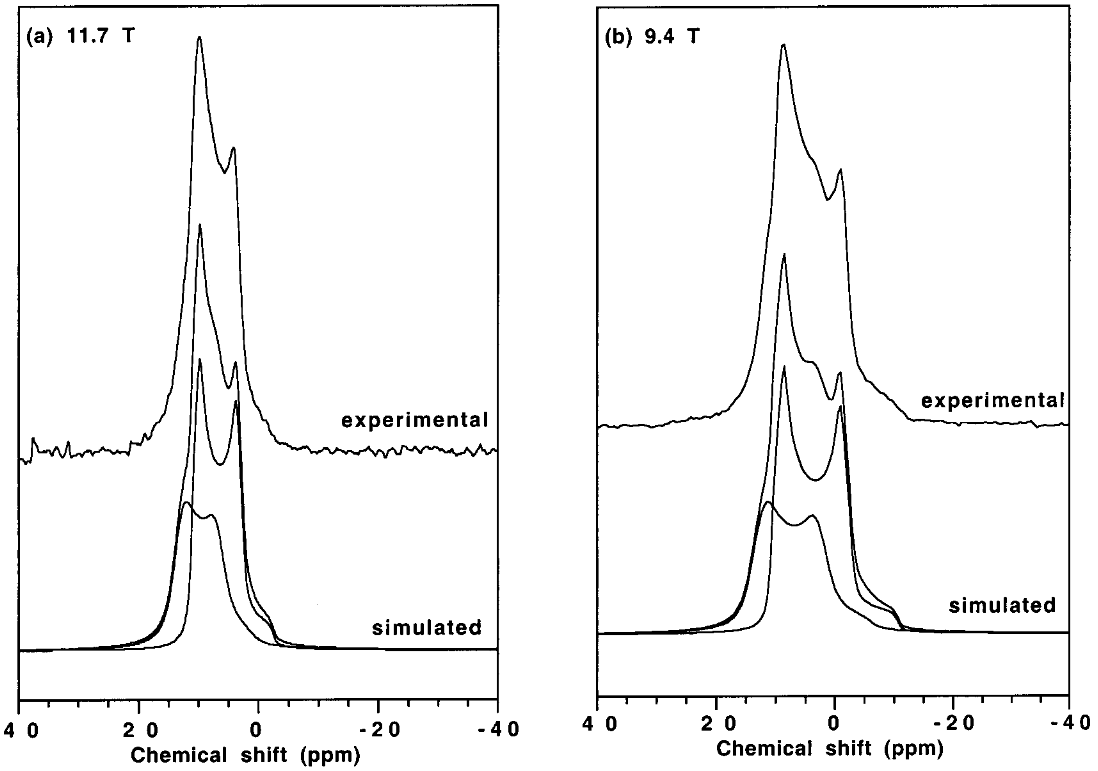

Figure 8. Experimental and simulated ^{11}B MAS NMR spectra of ETES-derived gel (B/Si = 0.2; pH = 2.5) recorded at 9.4 and 11.7 T.

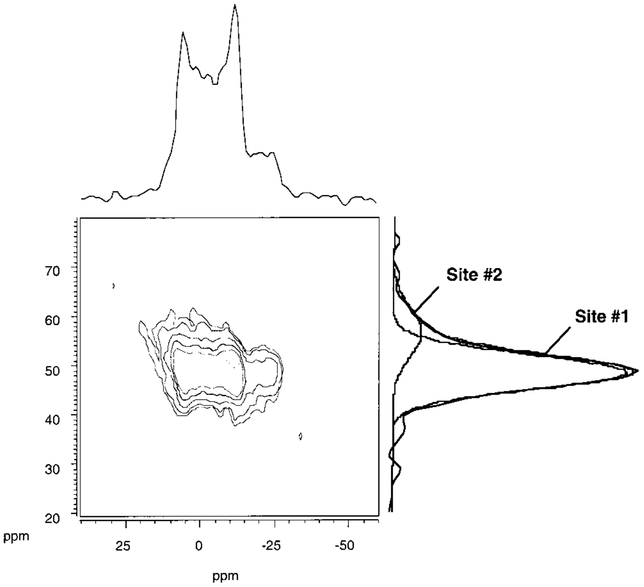

Figure 9. Two-dimensional triple-quantum ^{11}B MAS NMR spectrum of ETES-derived gel (B/Si = 0.2; pH = 2.5) recorded at 7 T.

sample: the spread of the 2D pattern suggests that the distribution results primarily from chemical shifts rather than from quadrupole interactions. From the cross sections at the corresponding peaks for the two sites, NMR parameters for each ^{11}B sites were obtained by line shape fitting and used as starting values to simulate the 1D MAS spectra recorded at 9.4 and 11.7 T (Figure 8). The final results reported in Table 4 give two signals with isotropic chemical shifts of 12.8 ppm (site 1) and 15.6 ppm (site 2) and with an intensity ratio of 60/40. This ratio does not correspond to that extracted from the ω_1 dimension. As already reported,[41] the MQ MAS spectra may exhibit distorted intensities, even if the species are characterized by very close quadrupole interactions. The quadrupole coupling constants of 2.5 MHz (site 1) and 2.4 MHz (site 2), as well as the weak asymmetry parameters (0.15 for site 1 and 0.2 for site 2) are in agreement with values already reported for borosilicate glasses.[13,34,42,43]

Table 4. ^{11}B MAS NMR Characterization of the Gels

sample	chemical shift δ (ppm)	C_Q[a] (MHz)	η[b]	intensity (%)	assignment
B/1	19.2	2.5	0	100	$B(OH)_3$
MeB0.2/1	12.7	2.5	0.15	20	$B(OSi)_3$
	15.8	2.4	0.2	48	B−O−X, X = Si, B
	19.4	2.4	0	32	$B(OH)_3$
MeB0.2/2.5	12.7	2.5	0.15	26	$B(OSi)_3$
	15.8	2.4	0.2	74	B−O−X, X = Si, B
EtB0.2/2.5	12.8	2.5	0.15	60	$B(OSi)_3$
	15.6	2.4	0.2	40	B−O−X, X = Si, B
ViB0.2/2.5	12.8	2.5	0.15	60	$B(OSi)_3$
	16.3	2.4	0.2	40	B−O−X, X = Si, B

[a] C_Q = quadrupolar coupling constant. [b] η = asymmetry parameter.

The results obtained for the EtB0.2/2.5 sample were used to simulate the spectra of the other samples presented in Figure 7. The results are reported in Table 4. Due to the strong overlap of the various signals, they cannot be considered as highly accurate; however, the comparison of the various samples gives a general trend. The component at 19 ppm, sensitive to ^{1}H decoupling

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and assigned to trigonal $B(OH)_3$ sites similar to those present in boric acid, is only present in the MeB0.2/1 sample, in agreement with the previous IR and XRD results. In the other three samples, there is no clear evidence for the presence of $B(OH)_3$ sites; two BO_3 sites are found at $\delta = 12.8 \pm 0.1$ and 16.0 ± 0.4 ppm, and indeed these values are close to those already reported for BO_3 sites in borosilicate glasses[34,42] and more particularly for a Pyrex glass.[43] A precise assignment of the peaks is not straightforward. One should keep in mind that the 2D MQ-MAS experiment has shown a continuous distribution of chemical shifts, suggesting the existence of a distribution of BO_3 sites with increasing number of connected SiO_4 tetrahedra [$B(OB)_{3-x}(OSi)_x$ $0 \leq x \leq 3$). One may suggest that the upfield signal ($\delta = 12.8$ ppm) whose powder pattern presents well-defined discontinuities (Figure 8) could be assigned to a BO_3 site connected with three SiO_4 tetrahedra ($B(O\text{-}Si)_3$). An increase in the intensity of this signal can be seen when going from MeB0.2/1 to MeB0.2/2.5 (Figure 7), suggesting that, by increasing the pH of the hydrolysis water, the formation of a $B(OH)_3$ phase is hindered and the formation of borosiloxane bridges is preferred. Also, the comparison of the three gels obtained from the modified silicon alkoxides in the same synthesis conditions (B/Si = 0.2; pH = 2.5) indicates that borosiloxane bridges form more easily in the Vi- and Et-derived gels compared with the Me-derived one. All these results are consistent with the previous FT-IR and XRD data.

Discussion

Formation of borosiloxane bonds in the gels prepared from modified silicon alkoxides and triethylborate can be identified directly from the FT-IR and ^{11}B MAS NMR results.

Literature data reports the stretching vibration of the borosiloxane bridges at 930–915 cm^{-1}.[3,8] However, in all these studies, the silicon atoms form tetrafunctional SiO_4 sites, whereas in our case the network consists of trifunctional $R-SiO_3$ (R = Me, Et, Vi) silicon units and such a difference could influence the absorption frequency of the B–O–Si bonds. To substantiate this idea, a MTES-derived gel (MeB0.2/2) has been pyrolyzed in air at different temperatures up to 700 °C with the aim of progressively substituting the Si–Me moieties with Si–O bonds.

The evolution of the FT-IR spectra recorded on these samples is reported in Figure 10. The IR spectrum of the starting gel shows the relevant peaks related to the Si–Me group and to the presence of B–O–Si bridges (675 cm^{-1}) and the peak at 887 cm^{-1}, tentatively assigned to B–O–Si stretching. By increasing the pyrolysis temperature, the peaks related to the Si–Me bonds progressively disappear (see, for example, the evolution of the band at 1275 cm^{-1}) due to the oxidation of the organic groups with the formation of new Si–O bonds. At the same time it is very interesting to observe that the band at 887 cm^{-1} shifts toward higher wavenumbers and at 700 °C reaches the value of 915–920 cm^{-1}, reported in the literature for the stretching vibration of the B–O–Si bridges. Indeed, at 700 °C the IR spectrum is very close to the one obtained on a commercial borosilicate (Pyrex) glass. At intermediate temperatures (500 °C), the absorption band is centered at 930–940 cm^{-1}. This high wavenumber is probably due to the superposition of the signal of the Si–OH moieties (at ~950 cm^{-1}) that are abundant at this temperature, as suggested by the presence of bands at 3600–3400 cm^{-1} (not shown in the figure) and 1620 cm^{-1}. A similar behavior has also been observed for the Et- and Vi-modified hybrid gels.

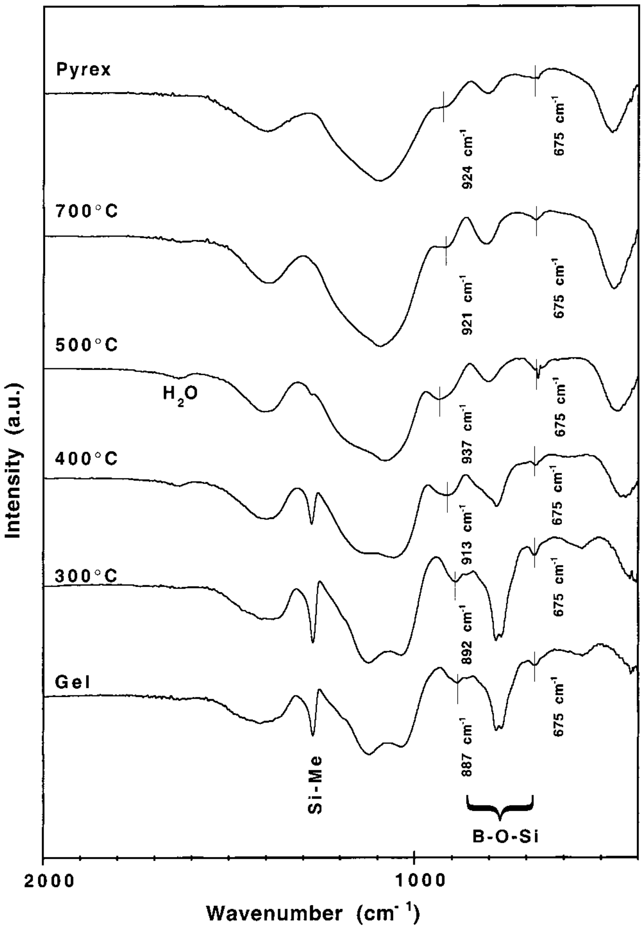


Figure 10. Evolution of the FT-IR spectra recorded on a MeB0.2/2 gel fired in air at different temperatures. For comparison purposes, the FT-IR spectrum of a commercial Pyrex glass is also reported.

According to these experimental results, we propose to assign the band at 880–890 cm^{-1} to the stretching vibration of borosiloxane bridges present in an organically modified silica network built with trifunctional $R-SiO_3$ (R = Me, Et, Vi) silicon units.

Thus, the FT-IR study points out that B–O–Si bonds can exist in hybrid gels obtained by cohydrolysis of $R-Si(OEt)_3$ and $B(OEt)_3$. Particularly, it indicates that the formation of $B(OSi)_3$ units is favored when the hydrolysis is carried out with less acidic water (pH = 2–2.5 rather than pH = 1–1.5) and when the hybrid siloxane network contains ethyl or vinyl groups rather than methyl moieties.

Similar conclusions can be extracted from the ^{11}B MAS NMR study performed on selected samples, which emphasizes the presence of a distribution of BO_3 sites connected to SiO_4 tetrahedra. The ^{11}B resonance signal at $\delta = 12.8$ ppm appears as the fingerprint for the formation of borosiloxane bonds. In the present study, the combination of 1D MAS and 2D MQ MAS experiments proved to be powerful to elucidate the structure of glassy samples.

Moreover, indirect evidence of the incorporation of boron atoms into the siloxane network via B−O−Si bridges can also be obtained from the results of the chemical analysis and the gelation times.

The chemical analysis reveals that, starting from the same nominal boron content (B/Si = 0.2), more boron is retained in the MeB0.2/2.5 gel than in the MeB0.2/1 samples. This result suggests that the formation of B−O−Si bridges can prevent the evaporation of boron-containing compounds, such as $B(OEt)_3$, and thus accounts for the higher B/Si ratio measured in the MeB0.2/2.5 sample.

The analysis of the gelation times points out that the addition of $B(OEt)_3$ to the silicon alkoxide solutions may increase or decrease the t_g (see Table 1). It is believed that, if boron enters the silica structure via $B(OSi)_3$ units, it behaves as a network former with a reduction of the gelation times compared with the corresponding pure silica gels. On the other hand, if the addition of boron preferentially leads to the formation of nonbridging $B(OH)_3$ units, it behaves more as an inert compound that dilutes the solution, decreasing the reaction rates and ultimately leading to longer gelation times. As an example, the gelation time of the pure MTES-derived gel at pH = 2 is ≈30 days. For the sample obtained under the same hydrolysis conditions but with boron addition (MeB0.2/2 sample), t_g is shortened to 20 days, suggesting that it behaves as a network former, in good agreement with the FT-IR and MAS NMR results. On the other hand, for the MTES-derived gels obtained using water at pH = 1, in which fewer B−O−Si bonds have been found, t_g increases from ≈8 days for Me/1 sample to ≈20 days for the MeB1/1 gel. Even more evident is the evolution of t_g for the ETES-based gels. The Et/1 composition leads to a stable highly viscous liquid that does not gel even after several months. The addition of boron, which in this system forms the highest amount of B−O−Si bridges, dramatically decreases the gelation time to ≈50 days.

It is also worth noting that the samples in which the boron is present mainly as $B(OSi)_3$ units (gels obtained with water at pH = 2−2.5 and B/Si ≤ 0.5) are clear, transparent gels, whereas cloudy, opaque samples are produced at pH < 2 and B/Si > 0.5, where boron addition leads to the precipitation of a crystalline $B(OH)_3$ phase.

So far, the formation of hybrid $SiO_2-B_2O_3$ gels in which trigonal boron atoms are homogeneously dispersed in the silica network via B−O−Si bridges has been inferred from many different analytical and structural techniques. On the other hand, the explanation for such a different behavior of $R-Si(OEt)_3$ alkoxides compared with tetrafunctional ones, $Si(OMe)_4$ or $Si(OEt)_4$, is still a matter of speculation.

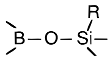
It is known from the work of Irwin et al.[12,13] that during the sol−gel process to obtain $SiO_2-B_2O_3$ glasses from $Si(OR)_4$, R = Me, Et, borosiloxane bridges are initially formed in solution through the reaction

$$\equiv Si-OH + HO-B= \rightarrow \equiv Si-O-B= + H_2O \quad (1)$$

Then, the condensation reactions lead to an increase of the water concentration that can hydrolyze back the borosiloxane bonds so no B−O−Si bonds are found in the final gel.

According to this model, the observed presence of B−O−Si bridges in our final hybrid gels could be ascribed to either (1) a greater amount of borosiloxane bridges formed in solution that are not completely hydrolyzed during the final stages of the sol−gel process or (2) a higher stability of the B−O−Si bridges, initially formed, toward hydrolysis.

Our experimental data refers only to the structure of the final gels and therefore do not allow us to comment on the first hypothesis, which will be the subject of a future detailed study through solution NMR. As for the second assumption, it is worth of noting that the introduction of organic groups leads to a more hydrophobic siloxane network favoring the removal of water. Moreover, the presence of organic groups close to borosiloxane bridges, i.e.,



could act as an in situ protection of the borosiloxane bonds from the water attack. Accordingly, the protection given from the ethyl and vinyl moieties should be higher compared to that provided by the methyl groups, due to their higher steric hindrance. Moreover, by the inductive effect of the organic groups the electron density at the silicon atoms in $R-SiO_3$ units is higher than in SiO_4 units. Thus, the Si−O bond strength is increased.

The effect of the pH of the hydrolysis water is more complicated; indeed, it is well-known that it influences both the hydrolysis and condensation rates of the silicon alkoxides and therefore could be critical in defining the concentration of Si−OH groups available for the formation of B−O−Si bonds through reaction 1, but it could also play a role as catalyst in the reverse hydrolysis reaction of the borosiloxane bridges.

Conclusions

Hybrid $SiO_2-B_2O_3$ gels have been synthesized by cohydrolysis of $R-Si(OEt)_3$, R = Me, Et, Vi, and $B(OEt)_3$. They were characterized by FT-IR, ^{29}Si and ^{11}B MAS NMR spectroscopies, XRD, and chemical analysis. The presence of B−O−Si bridges in the borosilicate gels was deduced from the presence of an absorption peak in the FT-IR spectra at 880−890 cm^{-1} and from a resonance peak at −12.8 ppm in the ^{11}B MAS NMR spectra. Moreover, the XRD, the chemical analysis, and the gelation time studies indirectly suggested the incorporation of boron into the siloxane network instead of the formation of a secondary crystalline $B(OH)_3$ phase.

The number of borosiloxane bridges increases with the pH of the hydrolysis water (from 1 to 2.5) and when the hybrid siloxane network contains ethyl or vinyl groups rather than methyl groups. The explanation for such results is still a matter of discussion. However, it can be suggested that the introduction of Si−R groups that gives an hydrophobic character to the hybrid siloxane network plays an important role by favoring the removal of water and preventing the hydrolytic cleavage of the B−O−Si groups. Moreover, the presence of the organic groups close to the borosiloxane bridges could act as an in situ protection of the borosiloxane bonds from the water attack.

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