Silicon-29 and Carbon-13 Nuclear Magnetic Resonance Identification of Intermediates Developed During the Formation of a Hybrid Based on Tetraethoxysilane (TEOS) and 4-[(5-dichloromethyl)(silyl)pentyloxy]cyanobenzene (DCN)

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ABSTRACT: During the formation of organic–inorganic hybrid materials by the sol–gel process, the observation of multiphase systems at different stages of the reaction is not uncommon. An assessment of the chemical species formed before and after gelation is not an easy task because complex mixtures are generally found in these systems. In this study, the identification of intermediates developed during the formation of a hybrid obtained from tetraethoxysilane (TEOS) and 4-[(5-dichloromethylsilyl)pentyloxy]cyanobenzene monomer has been undertaken. Solution and solid-state ^{29}Si- and ^{13}C-NMR spectra, recorded at different degrees of conversion, allow the elucidation of the mechanism of hybrid formation. 4-[(5-dichloromethylsilyl)pentyloxy]cyanobenzene, (DCN), DCN–TEOS cyclosiloxanes and low-molecular-weight linear copolysiloxanes are formed in the early stages of the process and before gelation occur. Before the gel is formed, cyclic species undergo an acid-catalyzed ring-opening copolymerization with silica to produce a random copolymer. Other intermediates of the Q_{ij} type (where Q indicates a four-functional silicon, the first subscript indicates the number of siloxane bridges connected to the silicon site, and the second subscript indicates the number of silanol groups) that develop before the gel is formed have also been identified. Spectral peak patterns of the final hybrid, observed in solid-state ^{29}Si and ^{13}C-NMR spectra, are also discussed. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 520–531, 2006

Key words: copolymerization; NMR; nonlinear polymers; polysiloxanes

INTRODUCTION

The sol–gel process has found widespread use in material science because it represents a convenient route for the fabrication of different devices used mainly as photonic materials. Different physical appearances, such as monoliths, coatings, fibers, and films, can be conveniently produced by this method. The final products can be properly manipulated to produce porous materials.[1,2] Semiconductor quantum dots and ormosils prepared by means of the sol–gel process allow the production of glasses with enhanced nonlinear properties with applications in optics.[3–7]

Many organic–inorganic hybrid materials are prepared by the introduction of polymeric components into silica with the sol–gel process. In some cases, a copolymer due to the reaction between an initial monomer species and silica is formed.[2,8–14] Chemical reactions observed during the sol–gel process involve hydrolysis to form oxide particles in a liquid phase, followed by polycondensation and crosslinking reactions. The properties of hybrids, such as the film thickness, shrinkage, porosity, and optical quality, strongly depend on the reaction conditions and the type of catalyst used in the preparation of the initial solution from which hybrids are produced.[15]
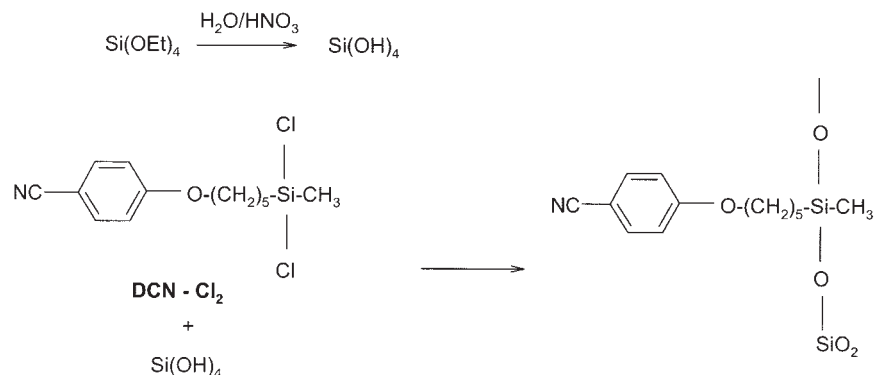
In the formation of hybrids, the hydrolysis of silicon alkoxides by water proceeds at low reaction rates. However, acid or base catalysts can increase reaction

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$$Si(OEt)_4 \xrightarrow{\text{H}_2\text{O/HNO}_3} Si(OH)_4$$

Scheme 1   Reaction pathway for the synthesis of hybrid glasses.

rates. In fact, the gelation time of tetraethoxysilane (TEOS) dissolved in ethanol can be reduced from 1000 to only 92 h when 0.05M HCl is used as a catalyst.[16]

We have recently reported the synthesis of hybrids based on a diorganodichlorosilane, 4-[(5-dichloromethylsilyl)pentyloxy]cyanobenzene (DCN-Cl$_2$)] and TEOS.[17] The nature of the starting solution is complex because it includes three solvents [water, tetrahydrofuran (THF), and toluene], two solutes (DCN-Cl$_2$ and TEOS), and a strong acid (HNO$_3$). A proper manipulation of this complex physicochemical system must be exercised to produce good-quality glasses. Final hybrids consist of a random copolymer immersed in a silica environment. They show elastomeric properties and different degrees of transparency, depending on the weight percentages of the DCN-Cl$_2$ monomer, water, and acid used in the feed. The final product can be conveniently handled to produce different forms and shapes.

Even though there are many references in the literature related to the formation of hybrid materials, few efforts have been made to understand the mechanism involved during different stages of the reaction. In this work, the chemical species formed before and after the gelation of hybrids, based on the DCN-Cl$_2$ monomer and TEOS, have been studied by ^{13}C and ^{29}Si-NMR. The formation of cyclosiloxanes and oligomeric linear copolysiloxanes derived from DCN and TEOS occur in the early stages of the reaction. Later, cyclosiloxanes and linear oligomers undergo copolymerization with hydrolyzed TEOS to form a random copolymer.

EXPERIMENTAL

Synthesis of organic–inorganic glass hybrids

5-Bromo-1-pentene and 4-cyanophenol were used to obtain 4-[(pentenyl)oxy]cyanobenzene, as described elsewhere.[17,18] After purification, the olefin was reacted with dichloromethylsilane in the presence of hexachloroplatinic acid, under a nitrogen atmosphere, to obtain DCN-Cl$_2$. The solution was concentrated up to 20 wt % DCN under a nitrogen flow. The product

was kept in toluene to prevent decomposition by air and in this form was used for the synthesis of hybrids.

TEOS was dissolved in THF, and nitric acid was added dropwise. Then, distilled water was slowly added (50 μL/min) under continuous stirring. The DCN-Cl$_2$ monomer solution (20 wt % in toluene) was slowly added (ca. 50 μL/min) to the mixture with a hypodermic syringe. The reaction mixture was heated under a nitrogen atmosphere for 18 h at 23°C. Hybrids were dried at room temperature for several days and isolated as glassy monoliths. The molar ratios used in the reaction mixture were TEOS/THF/H$_2$O/DCN/HNO$_3$ = 1/3/0.3/x/y (x = 0.7 or 7 vol % and y = 0.3 or 3 vol %; see Scheme 1).

Procedures

Solution ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra were recorded at room temperature on a Varian Gemini 200 and a Varian Unity Plus 300 (Palo Alto, CA), with chloroform-d (CDCl$_3$) as the solvent. The Insensitive Nuclei Enhancement by Polarization Transfer (INEPT) technique was used to obtain ^{29}Si-NMR in solution. In all spectra, the internal reference was tetramethylsilane (TMS). Solid-state ^{13}C- and ^{29}Si-NMR spectra were recorded under proton decoupling on a Varian Unity Plus 300 NMR spectrometer. Approximately 150 mg of the solid was packed into a 7-mm-diameter zirconium rotor with Kel-F packs. The spectra were
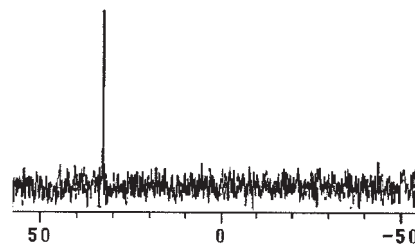
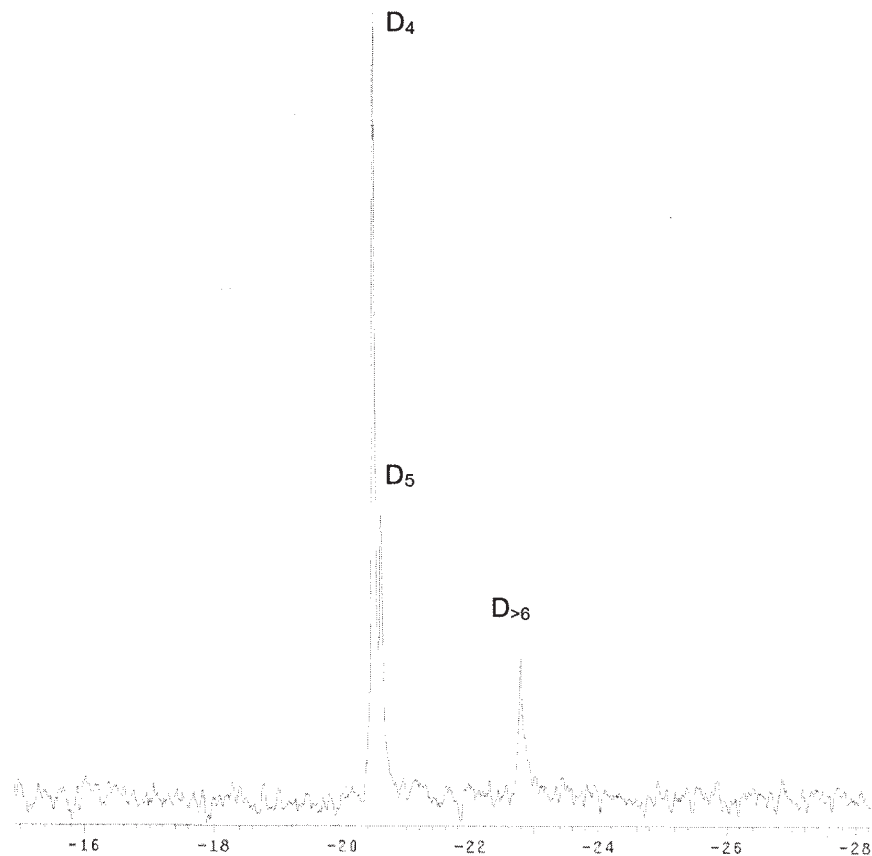Figure 1   Solution ^{29}Si-NMR spectrum of the DCN-Cl$_2$ monomer.

Figure 2   Solution ^{29}Si-NMR spectrum of the DCN oligomers.

obtained under Hartmann–Hann matching conditions and at a spinning rate higher than 4 kHz. For cross-polarization/magic-angle spinning (CP–MAS) spectra, a contact time of 2.5 ms and a repetition time of 8 s were used for ^{13}C and ^{29}Si. For magic-angle spinning (MAS) spectra, a repetition time of 30 s was used. The measurements were made with a spin–lock power in radio frequency units of 60 KHz, and typically 10,000
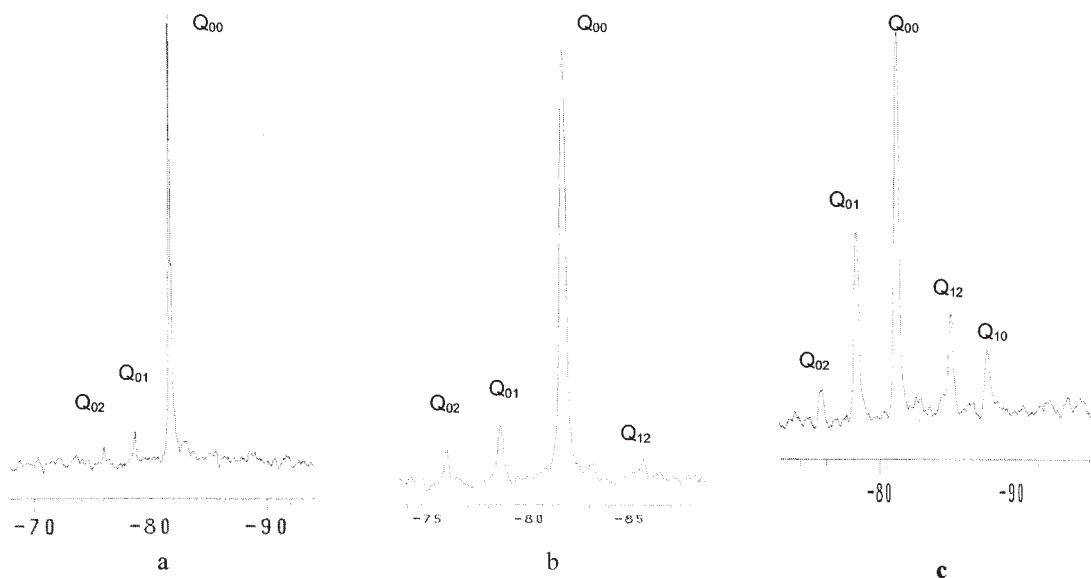

Figure 3   Solution ^{29}Si-NMR spectra of TEOS: (a) before hydrolysis, (b) after 40 min of hydrolysis, and (c) after 55 min of hydrolysis.
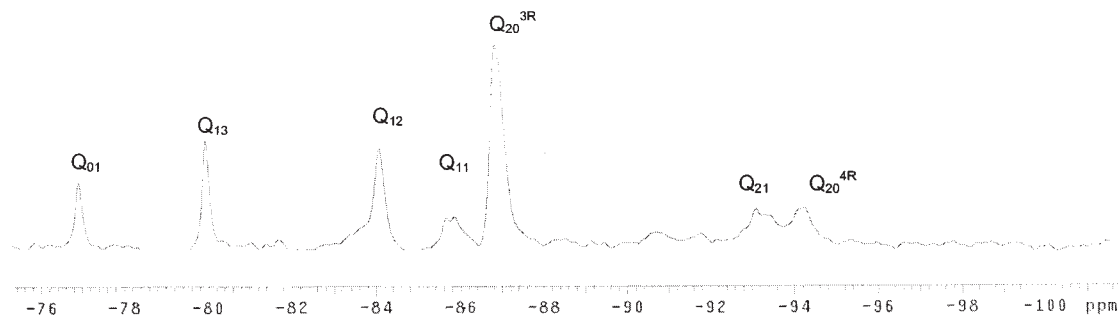
Figure 4 Solution ^{29}Si-NMR spectrum of TEOS after 75 min of hydrolysis.

transients were recorded. In some spectra, the elimination of spinning sidebands was accomplished by the total supression of spinning side bands (TOSS) sequence. Chemical shifts were referenced for ^{13}C to the upfield peak of adamantane at 29.5 ppm and for Si^{29} to the talc peak at -90 ppm (both with respect to TMS), as determined on separate samples.

RESULTS AND DISCUSSION

Polycondensation of DCN-Cl$_2$

In the ^{29}Si-NMR spectrum of DCN-Cl$_2$ in CDCl$_3$, one peak at 32.6 ppm can be observed (see Fig. 1). The

observed chemical shift agrees well with those reported for other similar dichlorosilanes, such as SiC$_2$H$_6$Cl$_2$ (31.8 ppm) and SiC$_9$H$_{12}$Cl$_2$ (31.6 ppm).[19]

When DCN-Cl$_2$ was reacted in the presence of distilled water, a DCN oligomer was obtained. The hydrolysis of DCN-Cl$_2$ occurs very rapidly because of the high reactivity of the monomer. In the early stages of reaction, a peak at -12 ppm due to silanol end groups can be seen. This signal quickly disappears, and signals in the range of -20 to -40 ppm, corresponding to D units, can be observed. The final ^{29}Si-NMR spectrum shows three peaks at -20.4, -20.6, and -22.7 ppm (see Fig. 2).
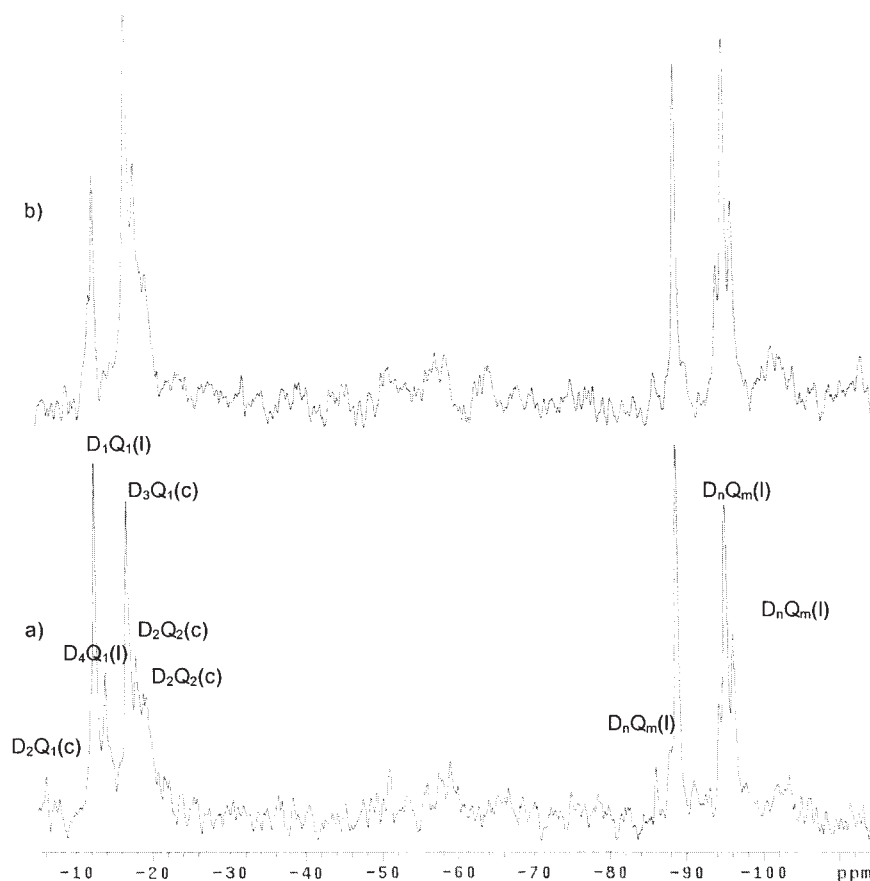

Figure 5 Solution ^{29}Si-NMR spectra of a TEOS and DCN mixture hydrolyzed with low water and acid contents at (a) 90 min and (b) 20 h after DCN addition.

TABLE I
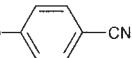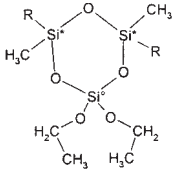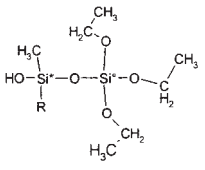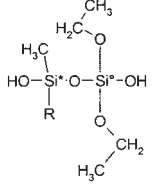**Observed ^{29}Si-NMR Chemical Shifts (ppm) and Assignments Before the Gelling of the DCN–TEOS System**
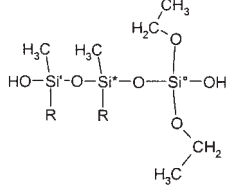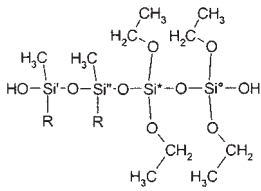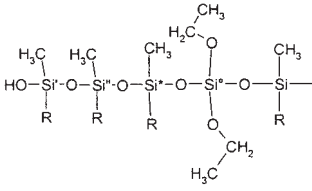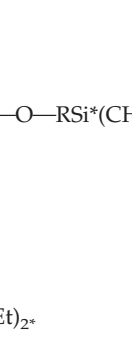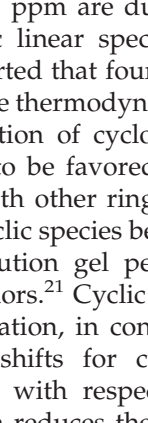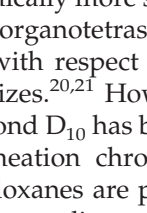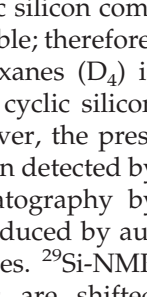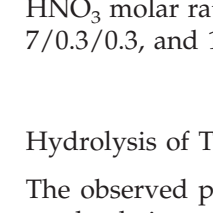
$R = —(CH_2)_5—O—\langle\text{ring}\rangle—CN$	Si*, Si°, Si′, Si″ observed in ^{29}Si-NMR

$D_2Q_1(c)$

  −6.121 ppm (Si*)

  −96.2 ppm (Si°)

  —O—(CH$_3$)Si°R—O—Si°(OEt)$_2$—O—Si*R(CH$_3$)—

$D_1Q_1(l)$

  −12.54 ppm (Si*)

  −88.7 ppm (Si°)

  HO—RSi*(CH$_3$)—O—Si°(OEt)$_3$

$D_1Q_1(l)$

  −12.0 ppm (Si*)

  −86.80 ppm (Si°)

  HO—RSi*(CH$_3$)—O—Si°(OEt)$_2$—OH

$D_2Q_1(l)$

  −13.9 ppm (Si′)

  −18.9 ppm (Si*)

  −86.8 ppm (Si°)

  HO—RSi′(CH$_3$)—O—RSi*(CH$_3$)—O—Si°(OEt)$_2$-OH

$D_2Q_2(l)$

  −13.9 ppm (Si′)

  −18.9 ppm (Si″)

  −95.1 ppm (Si°)

  −96.2 ppm (Si*)
  HO—RSi′(CH$_3$)—O—RSi″(CH$_3$)—O—Si*(OEt)$_2$—O—Si°(OEt)$_2$-OH

$D_4Q_4(l)$

  −13.9 ppm (Si′)

  −18.9 ppm (Si″)

  −19.3 ppm (Si*)

  −96.2 ppm (Si°)
  HO—RSi′(CH$_3$)—O—RSi″(CH$_3$)—O—RSi*(CH$_3$—O—Si°(OEt)$_2$—O—

TABLE I
(Continued)

R = —(CH$_2$)$\overline{_5}$—O—⟨benzene ring⟩—CN

Si*, Si°, Si', Si" observed in ^{29}Si-NMR

D$_2$Q$_2$(l)

−19.33 ppm (Si*)

−86.8 ppm (Si')

−95.1 ppm (Si°)

HO—RSi(CH$_3$)—O—Si°(OEt)$_2$—O—RSi*(CH$_3$)—O—Si'(OEt)$_3$

D$_3$Q$_1$(c)

−16.8 ppm (Si*)

−96.2 ppm (Si°)

—O—(RSi*(CH$_3$))$_3$—O—Si°(OEt)$_{2*}$

D$_2$Q$_2$(c)

−17.9 ppm (Si*)

−96.2 ppm (Si°)

—O—(RSi*(CH$_3$))2—(O—Si°(OEt)$_2$)$_{2*}$

D$_2$Q$_2$(c)

−19.33 ppm (Si*)

−96.2 ppm (Si°)

—O—RSi*(CH$_3$)—O—Si°(OEt)$_2$—O—RSi*(CH$_3$)—O—Si°(OEt)$_2$-

The peak observed at −20.4 ppm corresponds to a cyclic tetramer species (D$_4$), whereas peaks at −20.6 and −22.7 ppm are due to pentamer cyclic (D$_5$) and oligomeric linear species (D$_{>6}$), respectively. It has been reported that four-membered cyclic silicon compounds are thermodynamically more stable; therefore, the formation of cyclodiorganotetrasiloxanes (D$_4$) is expected to be favored with respect to cyclic silicon species with other ring sizes.[20,21] However, the presence of cyclic species beyond D$_{10}$ has been detected by high-resolution gel permeation chromatography by other authors.[21] Cyclic siloxanes are produced by autocondensation, in contrast to linear ones. ^{29}Si-NMR chemical shifts for cyclic compounds are shifted downfield with respect to the linear ones because cyclization reduces the —O—Si—O— valence angles and, as a result, the density of the positive charge on the silicon atom decreases.[14] However, some deviation from this behavior has been reported, particularly between 20 and −20 ppm.[22]

Copolymerization of DCN-Cl$_2$ and hydrolyzed TEOS

Hybrid formation from DCN and TEOS was studied with solution ^{29}Si-NMR under three different reaction conditions. The following TEOS/THF/H$_2$O/DCN/HNO$_3$ molar ratios were used: 1/3/0.7/0.3/0.3, 1/3/7/0.3/0.3, and 1/3/7/0.3/3.

Hydrolysis of TEOS

The observed peaks in the ^{29}SiNMR spectra are well resolved since the beginning of the reaction. This allows us to monitor the evolution of the silicon sites on three-membered (Q$_{2j}^{3R}$) and four-membered (Q$_{2j}^{4R}$) rings as well as those for the monomers (Q$_{0j}$), end groups (Q$_{1j}$), and middle-size groups (Q$_{2j}$). The site nomenclature follows the precedent of Engelhardt;[23,24] Q indicates a four-functional silicon, the first subscript indicates the number of siloxane bridges

connected to the silicon site, and the second subscript (j) indicates the number of silanol groups, which is distinguishable in NMR up to 40% conversion. Assignments for the different species formed during hydrolysis were made with substituent additivity rules and data from the literature.[19,23,25–27] Before the hydrolysis starts, one peak for TEOS can be observed at −82.1 ppm in the ^{29}Si-NMR spectrum. Progressive hydrolysis of TEOS occurs after the addition of both nitric acid and water when a TEOS/H_2O/HNO_3 molar ratio of 1/3/0.7/0.3 is used. A peak at −78.7 ppm (Q_{01}) appears just after the reaction starts because of the formation of a silanol Si—OH bond from the hydrolysis of the Si—OEt functionality; a second peak, corresponding to species Q_{02} at −75.9 ppm, can be observed after 40 min of reaction. At 55 min, two peaks due to the formation of Si—O—Si bonds at −85.3 and −88.1 ppm can be observed in the spectrum (Q_{12} and Q_{10} units, respectively; see Fig. 3). After 75 min, the signal for TEOS is no longer present; peaks at −77.1 and −81.0 ppm (assigned to Q_{01} and Q_{13}), −84.3, −85.8.0, and −87.2 ppm (Q_{12}, Q_{11}, and Q_{20}^{3R}, respectively), and −93.9 and −94.5 ppm (Q_{21} and Q_{20}^{4R}) due to the hydrolysis of TEOS can be observed (see Fig. 4). Cyclization can also be observed under the used reaction conditions. TEOS has been reported to form cyclic species at a higher rate than tetramethoxysilane, and this behavior becomes more favorable when the water–silicon ratio and pH are low.[24]

Copolymerization of DCN-Cl₂ and hydrolyzed TEOS in solution

With low water and acid contents When TEOS and DCN-Cl₂ are reacted with low water and acid contents (H_2O/HNO_3 = 0.7 mol %/0.3 vol %), hydrolysis proceeds at low reaction rates. Under these conditions, the gelation point is reached in 2 weeks. A complex mixture of intermediate species is obtained (see Fig. 5). Peak assignments of intermediates have been made with substituent additive rules and data from the literature[11,14,19,22,24,25,26] (see Table I). Copolymerization started when DCN-Cl₂ was added to a solution of TEOS that had been hydrolyzed for 90 min. The reaction was monitored by ^{29}Si-NMR every hour for 20 h, and the monitoring started 120 min after the initiation of hydrolysis. The first and last recorded spectra are shown in Figure 5. A peak pattern due to the copolymerization reaction between DCN and TEOS is present. Peaks in the range of −10 to −30 ppm can be assigned to D units, whereas signals in the range of −80 to −120 are due to Q units. The ^{29}Si-NMR results indicate that only linear chains and small rings are present because no Q_3 species were detected. The peaks observed between −16 and −20 are thought to indicate the presence of mainly siloxanes with four

repeating units. Cyclic species are composed of DCN and partially hydrolyzed TEOS units in different molar ratios. The cyclic species are identified in Table I as $D_nQ_m(i)$, where n and m are the number of DCN and TEOS hydrolyzed units present in the copolymer, respectively (n and m are 1–3), and i indicates if a linear (l) or cyclic (c) species is present. Signals for DCN units with fewer than four repeating units in the linear copolymer backbone appear at lower fields (< -16 ppm). The peak observed at −6.1 ppm can be attributed to a three-membered cyclic siloxane formed from the condensation reaction between two DCN molecules and one TEOS molecule. Signals for TEOS repeating units in the copolymer appear in the range of −94 to −96.5 ppm.

In Figure 6, the evolution of peak intensities against the hydrolysis time is depicted. The rate of DCN-Cl₂ disappearance is very fast and cannot be detected in the first recorded spectrum. As a result, the formation of DCN dimers, trimers, and oligomers occurs in seconds. These species quickly react with hydrolyzed TEOS units, forming copolymer units [species D_1Q_1(c), D_2Q_1(l), and D_2Q_1(c); see Table I]. Linear tetramers are formed from the reaction among these species or with hydrolyzed TEOS units [species D_2Q_2(l) *and* D_4Q_1(l)]. The formation of cyclic siloxanes D_2Q_2(c) and D_3Q_1(c) can also be seen. This means that chain growth may occur only by monomer/end-group or end-group/end-group condensation. Cyclization reactions are expected under these conditions.

It is well known that cyclic trimer cyclosiloxanes are relatively unstable, mainly because of conformational strain. The rapid disappearance of the peak at −6.1 ppm (D_2Q_1(c)) can be explained in terms of the thermodynamically favored ring-opening polymerization of a six-membered cyclosiloxane ring. Peaks that resonate downfield to −16 ppm (due to siloxane dimers) also show a high rate of disappearance. This behavior is associated with the formation of tetramers, which subsequently undergo a cyclization reaction to form thermodynamically stable four-membered ring cyclosiloxanes (peaks between −16 and −19.5 ppm). The hydrolysis of TEOS proceeds at a lower rate than that observed for the formation of the copolymer (see the observed trends in Fig. 6). The Q peak intensities remain relatively stable during the hydrolysis time, whereas the changes in the peak intensity are higher for D peaks.

With high water and low acid contents When the H_2O/HNO_3 ratio is 7 mol %/0.3 vol %, the hydrolysis of TEOS proceeds at a faster rate. Under these conditions, cyclization is favored.[24] The development of the reaction was followed by ^{29}Si{H}-NMR spectra, which were recorded with the normal one-pulse experiment (standard two-pulse sequence; INEPT was not used).
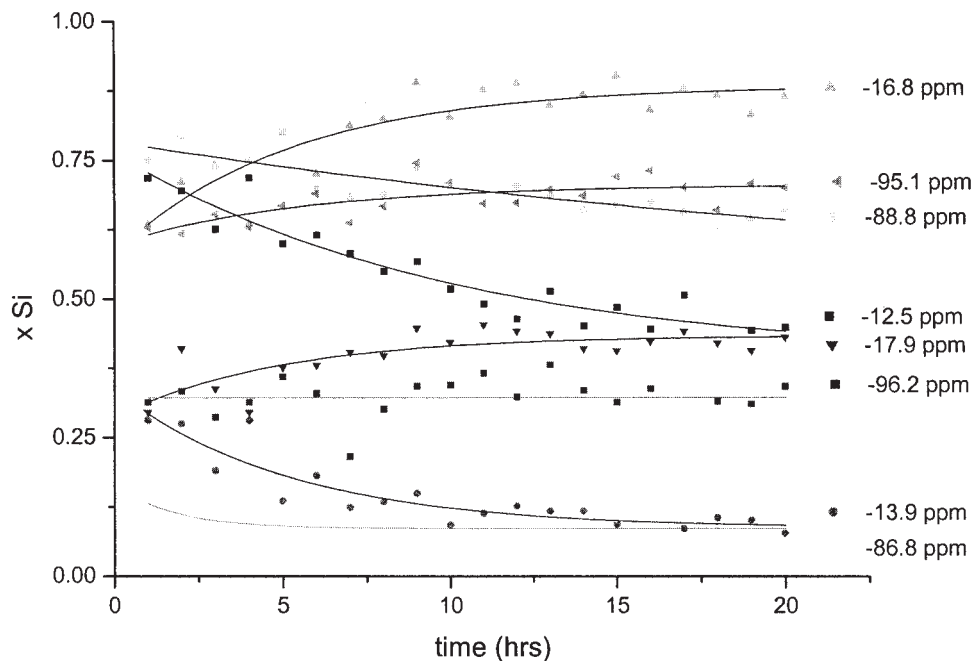
Figure 6 Plot of different peak heights against time for a DCN–TEOS system hydrolyzed with low acid and water contents.
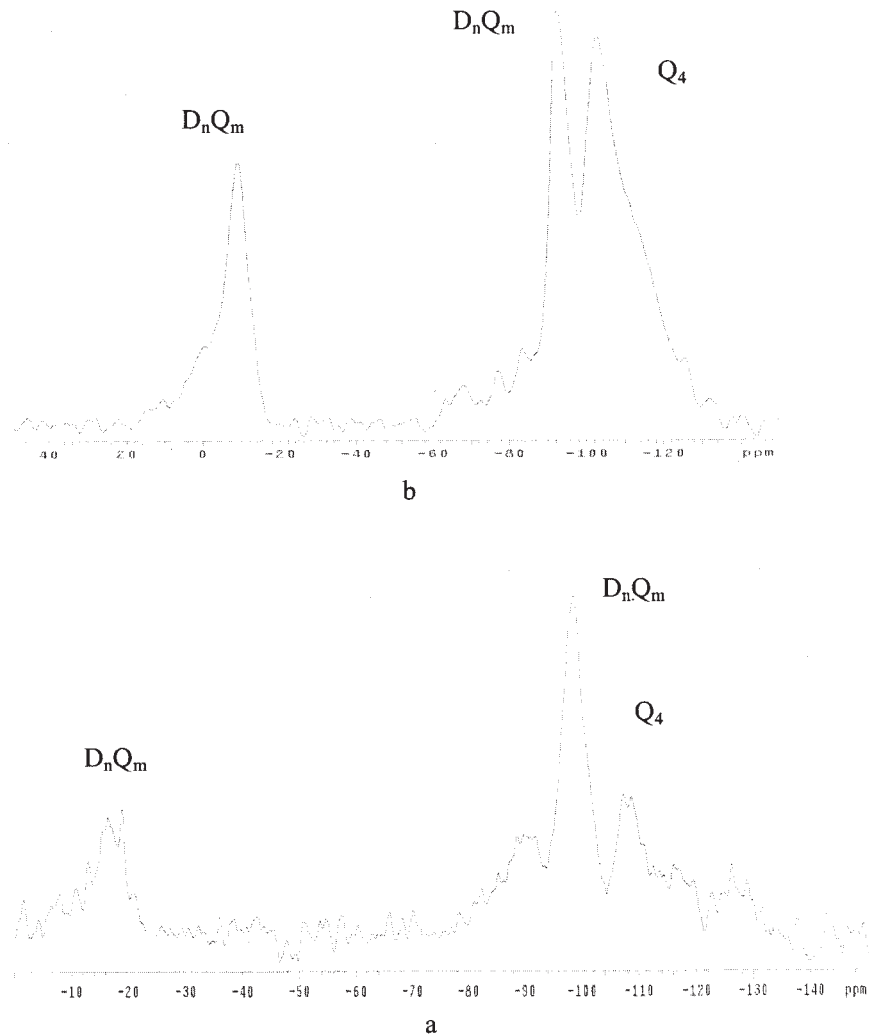

Figure 7 Solution ^{29}Si-NMR spectra of a hydrolyzed TEOS and DCN system with high water and low acid contents at (a) 60 min and (b) 36 h after DCN-Cl$_2$ addition.
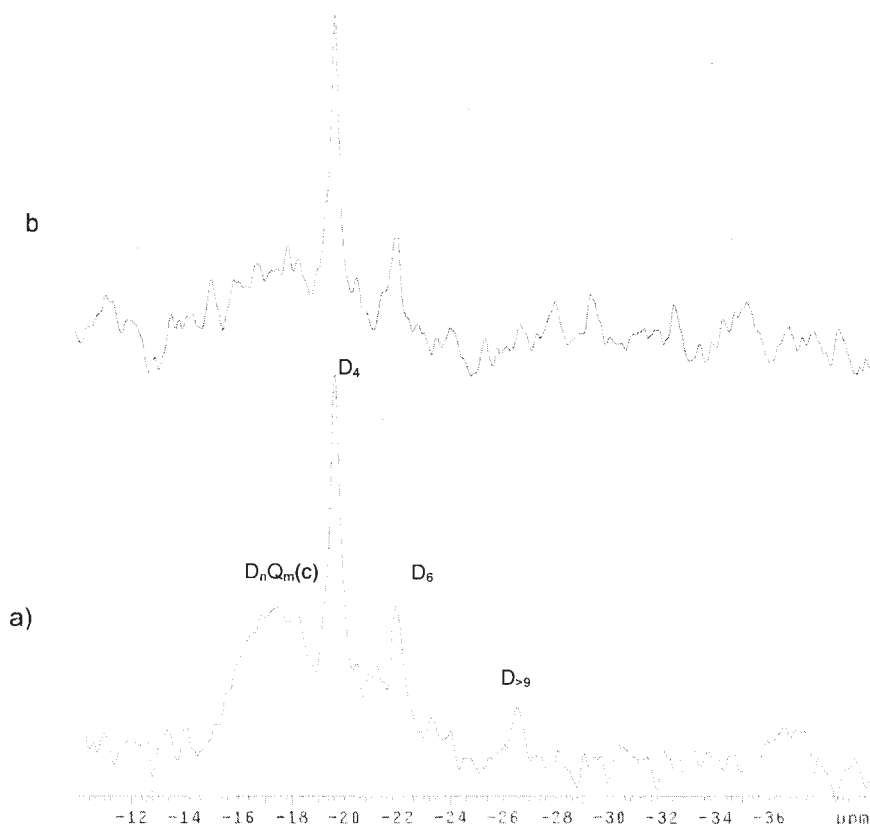
Figure 8 Solution ^{29}Si-NMR spectra of a hydrolyzed TEOS and DCN system with high water and acid contents at (a) 90 min and (b) 20 h after DCN-Cl$_2$ addition.

To be able to see the signals quickly enough to follow the reaction, the use of a relaxation agent was needed. Chromium nitrate [Cr(NO$_3$)$_3 \cdot$ 9H$_2$O; 8 $\times$ 10^{-3} mol/L] was chosen to avoid changes in the pH.[14]

To avoid the observance of a glass signal, a delay time between the 90° pulse and the Free Induction Decay (FID) acquisition was included in the pulse sequence. The delay time was calibrated for the particular tube allowing the ^{29}Si signal due to the glass to decay almost completely. A broadening of signals due to the presence of the relaxation agent was observed, and information on the formed intermediates was limited by the loss of resolution [see Fig. 7(a)]. A similar trend for the main signals was observed as in the previous case. After the gel point was reached, the spectrum depicted in Figure 7(b) was recorded. A DCN–TEOS solution reaches the gelling point at 36 h. This spectrum shows that complete copolymerization is obtained at the gel point. The peak pattern observed in the NMR solution spectrum is very similar to that observed in the solid-state NMR spectrum.

With high water and acid contents When the reaction is carried out with higher acid and water contents (H$_2$O/ HNO$_3$ = 7 mol %/3 vol %), the hydrolysis of TEOS is very fast. Under these conditions, cyclization reactions are effectively suppressed, and the formation of highly

branched high-molecular-weight polymers is favored because biomolecular reactions proceed at high rates.[24] When DCN-Cl$_2$ is added to the reaction mixture, the hydrolysis of TEOS is almost complete, and signals due to TEOS and partially hydrolyzed species derived from TEOS are absent. On the other hand,
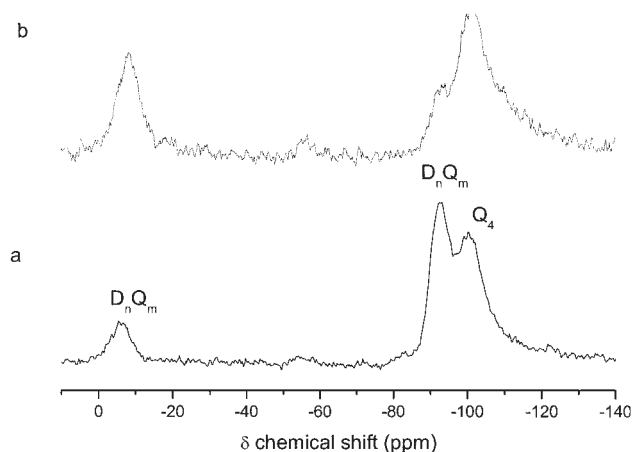

Figure 9 Solid-state MAS ^{29}Si-NMR spectra of hybrids obtained with (a) low water and acid contents and (b) high water and acid contents.
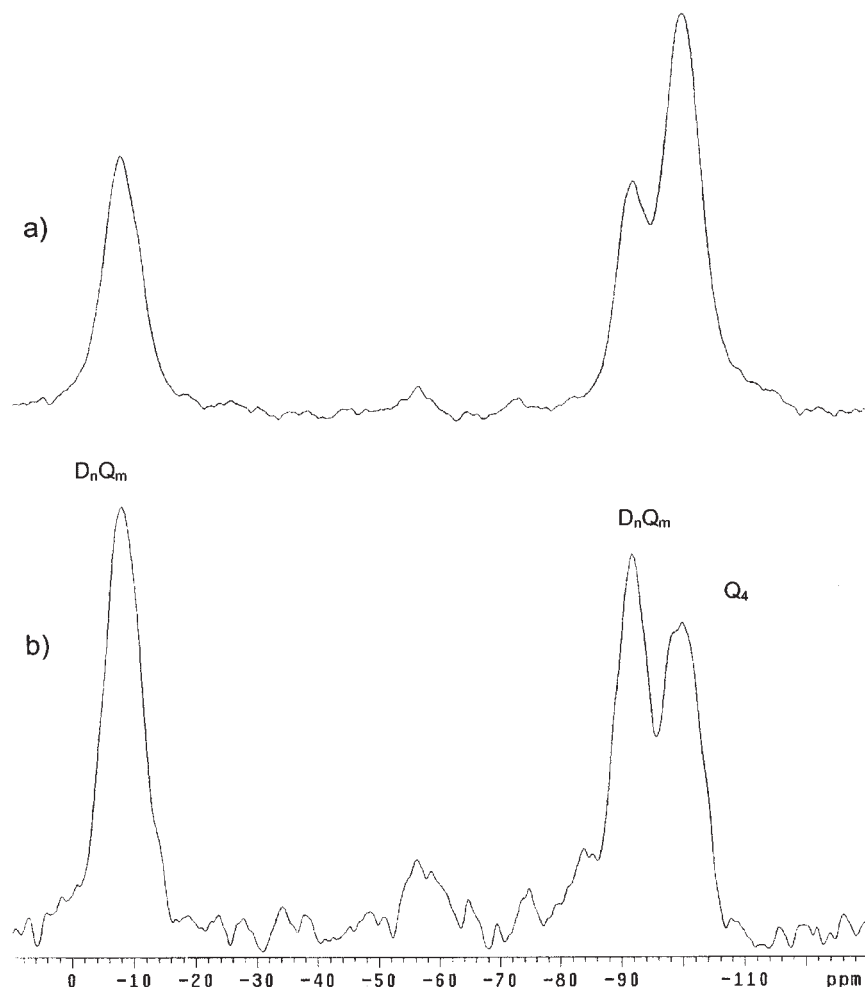
Figure 10 (a) MAS and (b) CP–MAS solid-state ^{29}Si-NMR spectra of hybrids with high water and acid contents.

signals for DCN homopolymers and DCN–TEOS copolymer units appear between -10 and -30 ppm. The reaction was monitored for 20 h, and the first and last spectra recorded are shown in Figure 8. In the first spectrum [see Fig. 8(a)], peaks at -17 ppm [for $D_2Q_2(c)$ and $D_3Q_1(c)$ species] and at -20.1, -22.4, and -26.5 ppm (cyclic homopolymers D_4, D_6, and $D_{>9}$) can be seen. In the last recorded spectrum, signals for cyclic homopolymers D_4 and D_6 are present. Under these conditions, the solution DCN–TEOS system reaches the gelling point at 26 h.

At this stage, it is thought that reactions between hydroxyl groups of Q units and low-molecular-weight linear and cyclic species have occurred, with the formation of a copolymer. Peaks between -16 and -19 ppm cannot be seen, as they are very rigid. Figure 9 shows the solid-state ^{29}Si MAS spectra of the hybrids obtained with low water and low acid conditions and with high water and high acid conditions. The chemical shifts observed for D_nQ_m and Q_4 are similar in both spectra. This means that notwithstanding the conditions used for hydrolysis, the

same peak pattern is obtained in the ^{29}Si-NMR spectrum of hybrids.

It is clear that cyclic units of DCN are present when the system is close to the gel point. The ring-opening polymerization of cyclic species in a strong acidic medium occurs through cationic intermediates.[21] Copolymerization between hydrolyzed TEOS and DCN ought to take place under these conditions, as nitric and chlorohydric acids are present in different proportions at different stages of the reaction (HCl is formed *in situ* from the hydrolysis of DCN-Cl$_2$). Acidic conditions used to produce the hybrids are strong enough to promote copolymerization between DCN oligomers and end units from Q_{2j} and Q_{3j} formed from TEOS and to minimize side reactions and degradation processes. We assume that the copolymerization process occurs through ring opening followed by a reaction with DCN or hydrolyzed TEOS.

The final hybrid physical appearance depends on the reaction conditions.[28] However, the same spectral
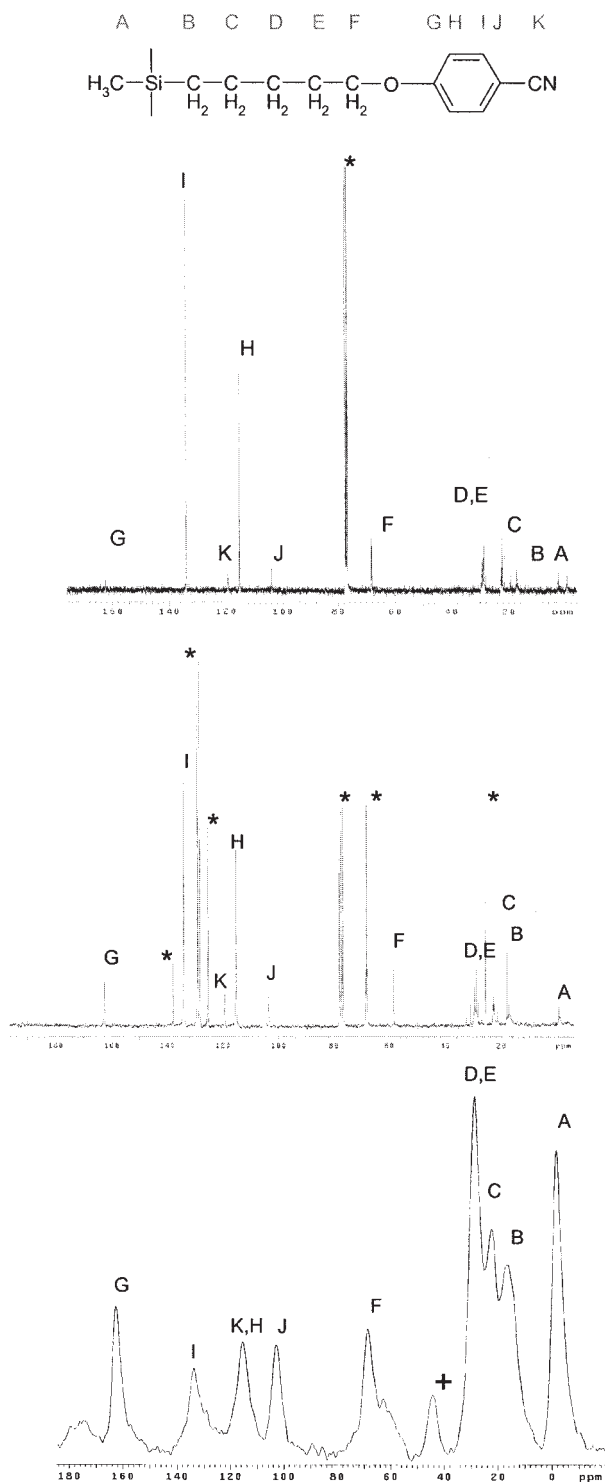
ter and acid contents were used. The peak observed at -9 ppm corresponds to the copolymer and is similar to that observed in the spectrum shown in Figure 7(b). The signal observed at -93.5 ppm is due to $D_n Q_m$ units in the copolymer, and the peak at -100.7 ppm correspond to Q_4 units. The peak pattern observed in the solid-state ^{29}Si-NMR spectrum for hybrids closely resembles that reported in the literature for a hybrid obtained from polydimethylsiloxane and TEOS.[29]

^{13}C-NMR analysis

A solution ^{13}C-NMR spectrum of the DCN-Cl$_2$ monomer, a solution spectrum observed before gelation, and solid-state CP–MAS ^{13}C-NMR spectra of the hybrid are shown in Figure 11. The assignments for the observed chemical shifts are shown in Table II.

In the solution spectrum of DCN–TEOS, broader signals can be observed in comparison with those seen in the DCN-Cl$_2$ monomer spectrum. The peak pattern evidences the formation of oligomers and cyclosiloxanes. The more important difference is that observed for the methyl group [A in Fig. 11(a,b)], as chloride is displaced by the alkoxide during hydrolysis. Upfield shifts can also be observed for B and C methylene signals but to a lesser extent.

In the solid-state ^{13}C-NMR spectrum of the hybrid, broad signals can be observed because the system is mainly amorphous [see Fig. 11(c)]. However, the formation of regions with intermolecular packing order has been detected by means of wide-

Figure 11 (a,b) ^{13}C-NMR spectra of the DCN-Cl$_2$ monomer in solution and DCN–TEOS in solution, respectively, and (c) solid-state CP–MAS ^{13}C-NMR spectrum of a hybrid. Asterisks indicate solvents, and the plus sign indicates a spinning sideband.

peak pattern has been observed in the solid-state spectra for the hybrids for all analyzed cases.

Figure 10 shows the solid-state ^{29}Si CP–MAS and MAS spectra of the hybrid obtained when high wa-

TABLE II
^{13}C-NMR Chemicals Shifts (ppm) and Assignments for DCN-Cl$_2$, DCN–TEOS, and the Corresponding Hybrid

^{13}C–NMR chemical shifts δ (ppm)

Letter	DCN-Cl$_2$ monomer[a]	DCN–TEOS[a]	Hybrid[b]
A	5.2	0.3	−1.0
B	21.4	22.6	14.3
C	22.3	23.0	23
D	28.6	28.9	27
E	28.9	29.5	29.6
F	68.4	68.5	70.4
G	162.3	162.5	164.3
H	115.1	115.3	116.4
I	133.9	134.0	136.8
J	103.8	103.7	103.7
K	119.2	119.3	NR

NR = peaks were not resolved
[a] Solvent = CDCl$_3$.
[b] Solid state.

angle X-ray diffractometry.[17] In comparison with the spectrum of DCN–TEOS in solution, an upfield shift for the methyl A and methylene B carbons can be observed. A more shielded environment exists for these carbons in the solid state. These differences can be attributed to changes in packing conformations that occur when the gel is converted to a solid, glassy material.

CONCLUSIONS

Hybrids from TEOS (hydrolyzed under acidic conditions) and DCN-Cl$_2$ monomer have been successfully obtained by the sol–gel technique. The different chemical species present before and after gel formation have been properly identified by ^{13}C- and ^{29}Si-NMR. In the first stages of the process, intermediates of the copolymer formed by DCN and TEOS units develop. The formation of the copolymer under different reaction conditions can be explained before the gelation point in terms of the acid-catalyzed ring-opening copolymerization of DCN cyclic species with silica. The copolymer shows a random distribution of monomeric units. A similar peak pattern has been observed in the solid-state ^{29}Si- and ^{13}C-NMR spectra of hybrids obtained with different TEOS/DCN/H$_2$O/HNO$_3$ molar ratios.

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