

Sol-Gel Formation of Heteropolysiloxanes from Diethylphosphatoethyltriethoxysilane and Tetraethoxysilane

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SYNOPSIS

Transparent monolithic gels were prepared from the cohydrolysis of diethylphosphatoethyltriethoxysilane $(OC_2H_5)_2P(O)CH_2CH_2Si(OC_2H_5)_3$ (SiP) and tetraethoxysilane $Si(OC_2H_5)_4$ (TEOS) in various ratios, under acidic conditions. The hydrolysis and initial polycondensation of SiP were studied by high-resolution ^{29}Si -NMR. Based on signal intensities, signals due to the following oligomers were identified: $R(OH)_2SiOSi(OH)(R)OSi(OH)_2$, $R(OH)_2SiOSi(OH)_2$, $R(OH)(OEt)SiOSi(OH)_2R$, $R(OH)(OEt)SiOSi(OH)_2R$, $R(OH)_2SiOSi(OH)(R)OSi(OH)_2R$ and $[R(OH)SiO^-]_3$. ^{29}Si NMR quantitative analysis was performed on SiP-TEOS mixtures during the hydrolysis-condensation reactions and on the final gels. This provided information on the formation of the gels molecular structure.

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INTRODUCTION

Heteropolysiloxanes receive an increasing interest because these new organic-inorganic hybrid materials offer a wide range of interesting properties; they assemble characteristics of the inorganic glassy network (e.g., mechanical and thermal strength, electrochemical, electrical, or magnetic properties) and properties of the organic species (e.g., hydrophobic/hydrophilic balance, physical or chemical property, chemical, or biochemical reactivity).^{1,2}

The sol-gel process allows to adjust the degree of interpenetration of organic and inorganic networks on an atomic scale. It can be achieved from organoalkoxysilanes $R'_xSi(OR)_{4-x}$ ($R' = \text{alkyl, phenyl}$), which lead to the formation of organic-inorganic hybrid compounds because the Si—C bond can be

conserved upon hydrolysis. In that case, the ligand R acts as a network modifier in the resulting structure.

Many materials of high technology are based on phosphates. They offer electrical and optical properties.³⁻⁶ Here, diethylphosphatoethyltriethoxysilane (SiP) represents an interesting molecular precursor; no cleavage of the Si—C and P—C bonds is observed under hydrolytic, basic, or acidic conditions.^{5,7-9} Moreover, this compound overcomes the instability problem of the P—O—Si bonds upon water when a mixture of phosphorus and silicon alkoxides is hydrolyzed.^{10,11} This organophosphorus compound, which contains a phosphoryl group, may be an efficient extractant for many metal ions.¹² Further applications of this hybrid organic-inorganic material applied to the preparation of facilitated transport membrane are in progress.

This article deals with the sol-gel synthesis of a SiP-tetraethoxysilane (TEOS) mixture. The influence of the molar ratio of the functionalized

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alkoxide, the nature and the concentration of catalyst, and the hydrolysis rate on the gel-time will be discussed. A high resolution ^{29}Si -NMR study of the hydrolysis and initial polycondensation processes of SiP and SiP-TEOS is reported here. Tentative assignments of the different monomers and oligomers that appear during the first steps of SiP hydrolysis and condensation are made. Solid state ^{31}P and ^{29}Si NMR performed on the gels were also investigated.

EXPERIMENTAL

Materials

TEOS (Fluka), SiP (Roth-Sochiel), ethanol (Merck), HF (Fluka), or NaF (Merck) were used as received. HF or NaF were used as catalyst, and deionized water (18 MW) was used for the hydrolysis.

Preparation of Samples

Reactions were studied in silane-ethanol-acidic water systems for both SiP and TEOS. For the preparation of the sols, an aqueous solution of HF was slowly poured into a mixture of precursors and ethanol. The homogeneity of the solution was checked after stirring for a few minutes at room temperature. For testing the gelation, the aging of the solutions was performed in closed glass containers at room temperature. The macroscopic gel time (t_g) was defined by observing the stiffness after tilting the container. Transparent gels were obtained for some compositions. For ^{29}Si NMR studies, the solutions were kept in 10 mm diameter NMR glass tubes and introduced into the spectrometer at various reaction times.

^{29}Si and ^{31}P NMR

Growth kinetics of particles were followed by NMR. For liquid solutions, $^{29}\text{Si}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR measurements were performed on a Bruker AC 250 spectrometer operating at 49.69 and 101.25 MHz. Each sample solution was placed into a 10 mm glass NMR tube, which was rotated at 15 Hz. All the spectra were recorded in nondeuterated solvent with external lock (DMSO-d_6) and obtained with gated decoupling and repetition times of 10 s. The spectra width was 5000 kHz and 32 K of datapoints were

used. Several spectra were obtained at various time intervals.

The molecular structures of the solid gels were determined from 79.49 MHz ^{29}Si and from 161.98 MHz ^{31}P MAS (Magic Angle Spinning) NMR spectra recorded on a Bruker ASX 400 spectrometer. The sample was placed in an alumina rotor, which was rotated at 5 kHz. The spectra were obtained with a pulse width of 7 and 3 μs , respectively, and a repetition time of 60 s (for ^{29}Si) and 10 s (for ^{31}P). The spectra width was 15 kHz and 16 K of datapoints were used.

All the samples were kept at a constant temperature of 21°C throughout the experiment. The chemical shifts are given with reference to tetramethylsilane or phosphoric acid.

The quantitative analysis of line intensities was carried out off line with the program WIN-NMR.¹³ Depending on the signal-to-noise ratio, error margins of the integration were estimated to be $\pm 10\%$.

Classical Q and T notation was used for the different silicate species, depending on the number of carbon and oxygen bridging atoms; i and j indices represent the number of oxo bridges and the number of hydroxo functions, respectively. T^{0i} is used for monomeric species that have one Si—C bond, no siloxane bridge, and i hydroxy side groups attached to the silicon ($i = 0, 1, 2, \text{ or } 3$). T^{1i} is used for monomeric species that have one Si—C bond, one siloxane bridge, and i hydroxy side groups attached to the silicon ($i = 0, 1, \text{ or } 2$). In the same manner, Q^{0i} species have no siloxane bond and i hydroxy side groups. Literature provides information on the average chemical shift ranges of $\text{Q}^0, \text{Q}^1, \text{Q}^2, \text{Q}^3, \text{Q}^4, \text{T}^1, \text{T}^2, \text{ and } \text{T}^3$ species; these are schematized in Figure 1 (in reference to tetramethylsilane TMS). During kinetic studies, two parameters, calculated on the basis of the experimental spectra, will be used: (1) the relative proportion r^i of the T^i species in the solution, $r^i = S^i / \sum S^i$ where $i =$ number of siloxane bridges and $S^i =$ resonance peak area. (2) The condensation ratio t , which enables the quantification

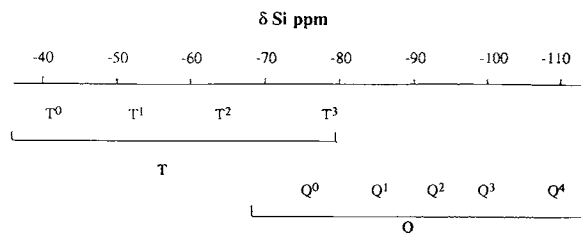


Figure 1 Chemical shift ranges of Q and T species.

of the kinetics of the condensation reactions, $t = \Sigma i \cdot r^i / f$, where f = organoalkoxide functionality.

RESULTS

Nature and Concentration of the Catalyst

Gels from TEOS/ethanol/neutral water were prepared with two different hydrolysis ratios H (i.e., $[\text{H}_2\text{O}]/[\text{alkoxides}]$; $H = 4, 10$) as references of the gel time. These two mixtures gelled in 6 and 8 days, respectively, at room temperature. Because the gelation of the precursors is very slow, HF and NaF were used as catalysts. The influence of the nature and the concentration of the catalyst in the SiP-TEOS mixture was investigated. Figure 2 presents the gel time evolution as a function of the nature and the concentration of the catalyst for the molar ethanol : SiP : TEOS ratio equals to 9.96 : 0.11 : 0.91 with $H = 10$. The gel times of the SiP-TEOS mixtures are higher than those of the references. The gel time decreases as the concentration of the catalyst increases, but the influence of NaF on the gel time is more important than HF. A higher concentration of HF is needed for the same gel time. However, transparent gels are obtained with HF catalyst, whereas the NaF catalyst leads to turbid gels. This turbidity could be explained by the very low solubility of NaF in water. Moreover, hydrolysis reaction reduces the amount of water and increases the amount of ethanol in which NaF is less soluble. Thus, in order to obtain transparent gels with a convenient gel time (≈ 13 h), HF was used with a ratio $[\text{HF}]/[\text{SiP} + \text{TEOS}] = 2.2 \times 10^{-3}$ in further experiments.

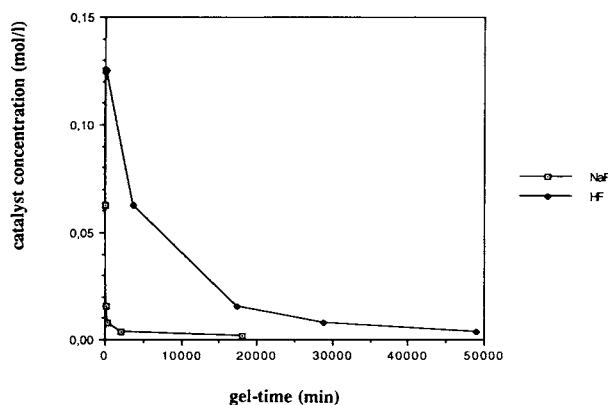


Figure 2 Gel time evolution as a function of nature and concentration of the catalyst for molar EtOH : SiP : TEOS = 9.96 : 0.11 : 0.91 with $H = 10$.

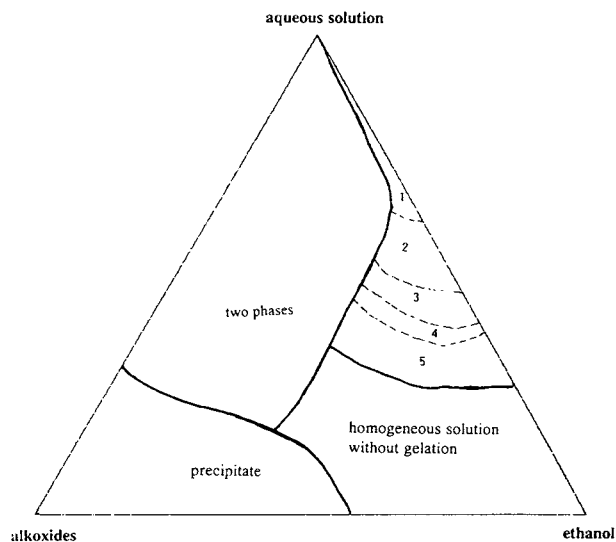


Figure 3 Phase diagram in the SiP : TEOS- H_2O : HF-EtOH ternary system with a SiP : TEOS = 11 : 89 and HF : alkoxides = $2.2 \cdot 10^{-3}$. Gel time: 1: 8 h; 2: 16 h; 3: 32 h; 4: 60 h; 5: 16 days.

Phase Diagram

Figure 3 presents the phase diagram (in molar ratio) of the SiP : TEOS- H_2O : HF-EtOH ternary system with a SiP : TEOS ratio equal to 11 : 89. It presents a large immiscibility area, a precipitate zone for low concentration of acidic water, and an homogeneous solution region without gelification for high concentration of ethanol. However a reasonable region of compositions water/alkoxides/ethanol yields to monolithic transparent or turbid gels. This diagram shows that transparent gels are formed when the $[\text{alkoxides}]/[\text{water}]$ ratio increases. Gel time varies from 7 h to 10 days. It decreases with higher water content

Table I Influence of the Molar Percentage of SiP Precursor on the Gel-Time for a Solution with EtOH/ H_2O : HF/Alkoxides = 35/50/15

% SiP	% TEOS	Gel Time (h)
0	100	3
11	89	10
20	80	13
25	75	14
30	70	24
40	60	no gel

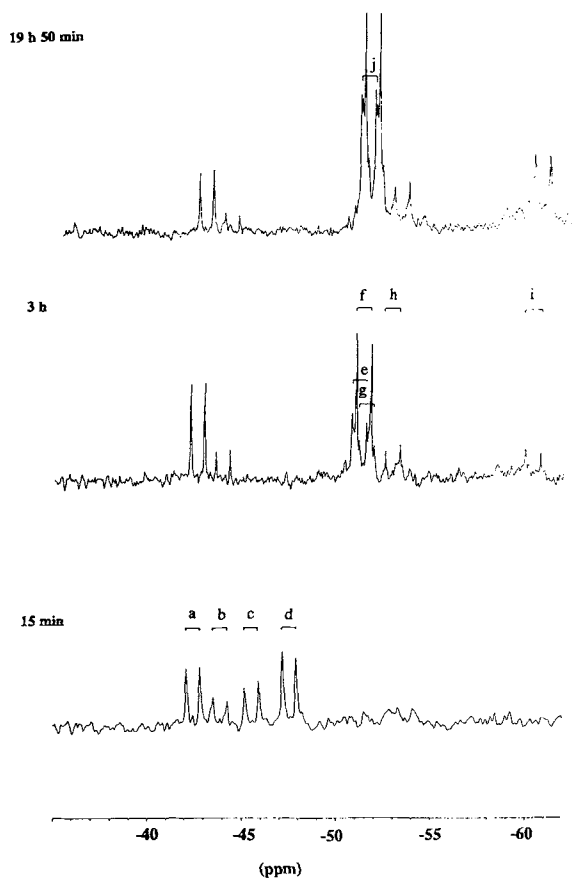


Figure 4 ^{29}Si -NMR spectra of SiP sols hydrolyzed with $H = 5$ after (a) 15 min, (b) 3 h, (c) 19 h 50 min.

and increases with the concentration of alkoxides, at constant [ethanol]/[water] ratio. As the ethanol concentration increases, the gel time increases because of gel dilution and restriction of crosslinking.

The influence of the proportion of SiP has been studied for a specific composition [molar ethanol : water : alkoxides ratio equal to 35 : 50 : 15]. Table I shows that the gel time increases with the proportion of SiP. Over 30% of SiP no gel is observed. The hydrolysis of SiP alone, in the same conditions, always leads to liquid and transparent solutions. The absence of gelation suggests that the presence of a crosslinking agent (e.g., TEOS) is necessary to build a three-dimensional network.

^{29}Si -NMR Kinetics

^{29}Si -NMR spectra of the pure alkoxides contain a single peak at -82.2 ppm and a doublet centered at -47.4 ppm due to the coupling $J_{\text{P-Si}} = 36.5$ Hz for TEOS and SiP, respectively. These spectra do not show any presence of hydrolyzed or modified species, allowing the hydrolysis and condensation of these precursors to be monitored. Solutions of SiP and SiP-TEOS with various H hydrolysis ratios and various amounts of SiP were studied and compared during gelation. Tentative assignments were made for SiP sols. However, in the SiP-TEOS mixture, it was not easy to accurately define the different oligomers because of the overlapping of the chemical shifts and the experimental conditions affecting the signal/noise ratio (concentration of alkoxides, accumulation times, time intervals . . .). Thus, Q^i and T^i species formed during the hydrolysis-condensation reactions were identified and their quantitative evolution calculated.

SiP Sols

Hydrolysis and initial polycondensation of SiP precursor were studied by ^{29}Si -NMR spectroscopy. This

Table II Assignments of Labeled ^{29}Si -NMR Signals for Monomeric and Oligomeric Species Obtained by the Hydrolysis of SiP

^{29}Si -NMR Signal	Structure	Formula	δ ppm
a	T^{03}	$\text{RSi}(\text{OH})_3$	-42.4
b	T^{02}	$\text{RSi}(\text{OH})_2(\text{OEt})$	-43.7
c	T^{01}	$\text{RSi}(\text{OH})(\text{OEt})_2$	-45.4
d	T^{00}	$\text{RSi}(\text{OEt})_3$	-47.4
e	$\text{T}^{12}\text{T}^{21}\text{T}^{12}$	$\text{R}(\text{OH})_2\text{SiOSi}(\text{OH})(\text{R})\text{OSi}(\text{OH})_2\text{R}$	-51.1
f	$\text{T}^{12}\text{T}^{12}$	$\text{R}(\text{OH})_2\text{SiOSi}(\text{OH})_2\text{R}$	-51.3
g	$\text{T}^{11}\text{T}^{12}$	$\text{R}(\text{OH})(\text{OEt})\text{SiOSi}(\text{OH})_2\text{R}$	-51.5
h	$\text{T}^{11}\text{T}^{12}$	$\text{R}(\text{OH})(\text{OEt})\text{SiOSi}(\text{OH})_2\text{R}$	-52.8
i	$\text{T}^{12}\text{T}^{21}\text{T}^{12}$	$\text{R}(\text{OH})_2\text{SiOSi}(\text{OH})(\text{R})\text{OSi}(\text{OH})_2\text{R}$	-60.4
j	cyclic $[\text{T}^{21}]_3$	$[\text{R}(\text{OH})\text{SiO}]_3$	-51.2

For clarity, SiP precursor will be abbreviated to $\text{RSi}(\text{OC}_2\text{H}_5)_3$ with $\text{R} = \text{CH}_2\text{CH}_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$.

organoalkoxide was hydrolyzed with various amounts of water in order to assign the chemical shifts of the species formed during these reactions.

Figure 4 shows the ^{29}Si -NMR spectra of the solution with $\text{SiP} : \text{EtOH} = 1.56 : 6.23$, with $H = 5$ at various times. After 15 min, the spectrum presents four doublets about -42 and -48 ppm (signals a-d). Every signal corresponding to the organophosphorus silicon alkoxide species presents a doublet due to the $J_{\text{P-Si}}$ of 36.5 Hz. Because signal d is due to SiP precursor (T^{00}), the others can be ascribed to hydrolyzed monomers (Table II). These assignments are made according to the literature and show that the substitution of the hydroxy group for the ethoxy group induces the conventional down field shift with a 1–2 ppm increment for each substitution as observed for tetraalkoxysilanes^{14–18} and alkyltri-alkoxysilanes.^{19,20}

Hydrolysis reactions seem to be very fast. After 1 h, signals d and c attributed to T^{00} and T^{01} disappear and a new doublet (signal f) is present centered at -51.3 ppm. According to the literature,^{21,23} this new doublet is the T^1 region, indicating the formation of siloxane bonds. After 3 h, several doublets appear in this region, centered at -51.1 , -51.5 , and -52.8 ppm (signals e, g, and h, respectively) as well as a signal centered at -60.4 ppm (signal i). According to their close chemical shifts, signals e, f, g, and h may belong to the same T^1 family, while signal i corresponds to T^2 species. As silicon species possessing less hydroxy groups are observed at an upper field, signal h may be attributed to T^1 species with less hydroxy groups than signals e, f, and g. So, in the T^1 region, the most downfield subregion is ascribed to a T^{12} environment and the other subregions should be due to T^{11} (middle) and T^{10} (upfield) environments.

These assignments are consistent with the feature of hydrolyzed SiP solutions spectra, obtained for a higher H hydrolysis ratio (Fig. 5). After 120 min, the hydrolysis reactions are completed (signal a alone) and the condensation begins: signals e and i are already present as well as a new doublet centered at -51.2 ppm (signal j) in the range of T^1 area. No peaks are observed into the T^{11} and T^{10} environments and we only see signals into the downfield region (T^{12} species). So downfield subregions become predominant when the hydrolysis ratio increases. This behavior has been noted on other alkoxysilanes.²² When $H = 5$ (Fig. 4), signal j appears after 19 h 50 min, showing that the polycondensation reactions of SiP precursor are low (no T^3 signal) when the hydrolysis ratio is small.

All these different doublets may be assigned on the basis of signal intensities. In fact, it can be noted that

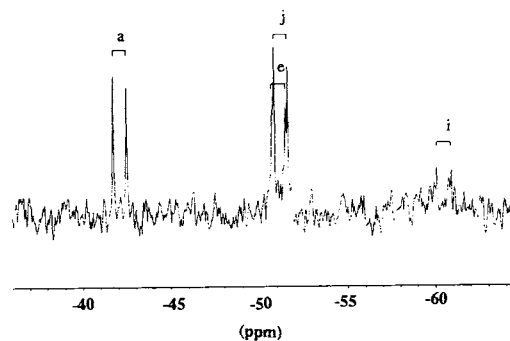
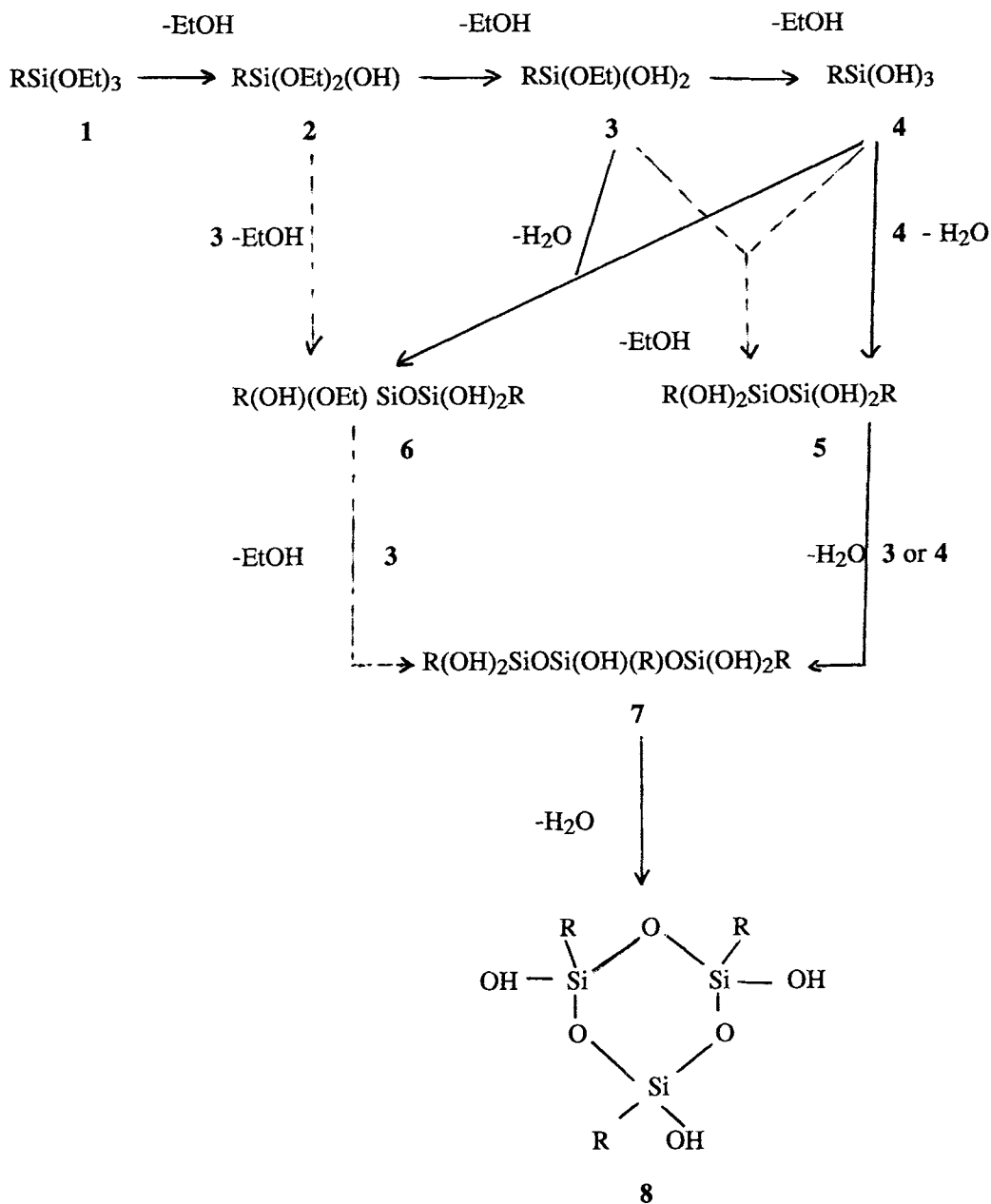


Figure 5 ^{29}Si -NMR spectra of SiP sols hydrolyzed with $H = 50$ after 120 min.

in every spectrum, the intensity relationships between some signals are preserved. The first observed signal in the T^1 region is signal f, which appears when T^{03} is predominant; it seems to have no relationships to the other signals and could be a dimer formed by the same unit. We assign it to the $\text{T}^{12}\text{T}^{12}$ dimer. The (signal g/signal h) and (signal e/signal i) ratios are approximately constant and equal to 1 and 2, respectively. It indicates that they are due to a dimer (T^1T^1) and a trimer ($\text{T}^1\text{T}^2\text{T}^1$), respectively. Because the chemical shifts of signals g and f are very close, signal g may be due to T^{12} unit, whereas signal h in the upper field region may be due to a T^{11} unit. In the same manner, taking into account the subregion assignments, the signals e (T^{12}) and i (T^{21}) yield to the trimer $\text{T}^{12}\text{T}^{21}\text{T}^{12}$. These assignments are made according to previous work²² and are summarized in Table II. Signal j seems to have no intensity relationships with the others. According to the literature,^{22,23} this signal may be described as a cyclic trimer because it is considerably shifted downfield from the usual T^2 region, and because the dominant species in the medium is the trimer $\text{T}^1\text{T}^2\text{T}^1$. Thus, we assign signal j to cyclic $[\text{T}^{21}]_3$. Although further information is needed to discuss these assignments, they could explain why no gels are obtained with SiP alone. This trifunctional alkoxide yields preferentially to cyclic chains as the reactions proceed. Boilot et al.²⁴ explained the absence of gelation in trivalent compounds despite the high degree of condensation, by the formation of small condensed units.

Later, more condensed species are also contained in this solution forming signals in the T^2 and T^3 region at -59 and -60 ppm and -67 and -69 ppm, respectively. These experiments do not enable us to attribute the corresponding condensed species, because of the overlapping shift ranges.

So, the first steps of SiP hydrolysis-condensation under the conditions employed in this study can be summarized in accordance with the following scheme:



It shows the formation of completely hydrolyzed species (4) prior to condensation. The two first hydrolysis reactions are very fast (the compound 1 is consumed very rapidly and the presence of the compound 2 is short-lived). In principle, the condensation reactions preferentially occur between two Si—OH moieties with elimination of water. The fact that the compound 5 is the first dimeric species to be formed implicates the silanetriol 4 as the key intermediate. Nevertheless, the dimer 5 can be obtained from the mixture of the compounds 4 and 3 by condensation between Si—OH and Si—OEt moieties and the loss of ethanol. This reaction is

known to be not favored in water rich-systems.²⁵ However, the condensation of the compounds 4 and 3 with elimination of water is responsible of the formation of the dimer 6; this latter may be also obtained from the condensation of the compounds 2 and 3 by loss of ethanol. As compound 4, responsible of the formation of the dimers 5 and 6, is the major species during the first hour and is not consumed as rapidly as it is generated, the condensation reactions are not very fast. Logical routes to the linear trisiloxane 7 involve the further condensation of the hydroxydisiloxane 5 either with the silanols

3 or 4. Another possible source of the compound **7** is the combination of disiloxane **6** with silanol **3** by loss of ethanol. Then the cyclotrisiloxane **8** is obtained from linear trisiloxane **7** with elimination of water.

SiP-TEOS Sols

The hydrolysis and initial polycondensation of SiP-TEOS mixtures were studied by ^{29}Si -NMR spectroscopy. During the first 30 min, NMR spectra show a doublet at -47.4 ppm assigned to the T^{00} compound (SiP) and five peaks at -72.8 , -74.6 , -76.7 , -79.1 , and -81.9 ppm. They are due to the successive hydrolysis reactions of TEOS and may be attributed to Q^{04} , Q^{03} , Q^{02} , Q^{01} , and Q^{00} compounds, respectively. The position of the Q^{00} species (-81.9 ppm) is slightly shifted when compared with the value obtained for the pure alkoxide (-82.2 ppm). This behavior has been observed previously for other silicon alkoxides.^{26,27} Twenty minutes later, the three SiP hydrolyzed species are present. Figure 6 shows the relative proportions of the Q^{0i} and T^{0i} species as a function of time for the molar ratio ethanol : alkoxides = 6.97 : 1.77 with $H = 5$. Hydrolyzed TEOS species with four hydroxy groups are quickly formed, whereas TEOS slowly disappears. The concentration of Q^{01} and Q^{02} species remains low and these

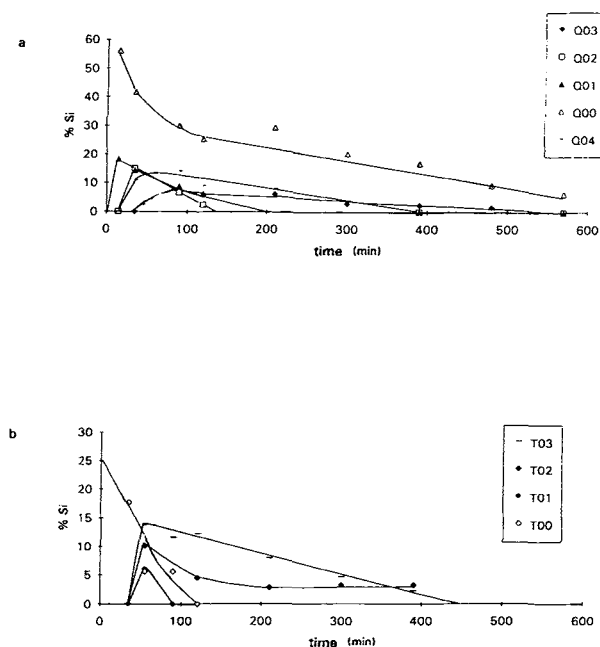


Figure 6 Evolution of the relative proportions of the Q^{0i} (a) and T^{0i} (b) species as a function of time for the molar ethanol : alkoxides ratio = 6.97 : 1.77 with $H = 5$.

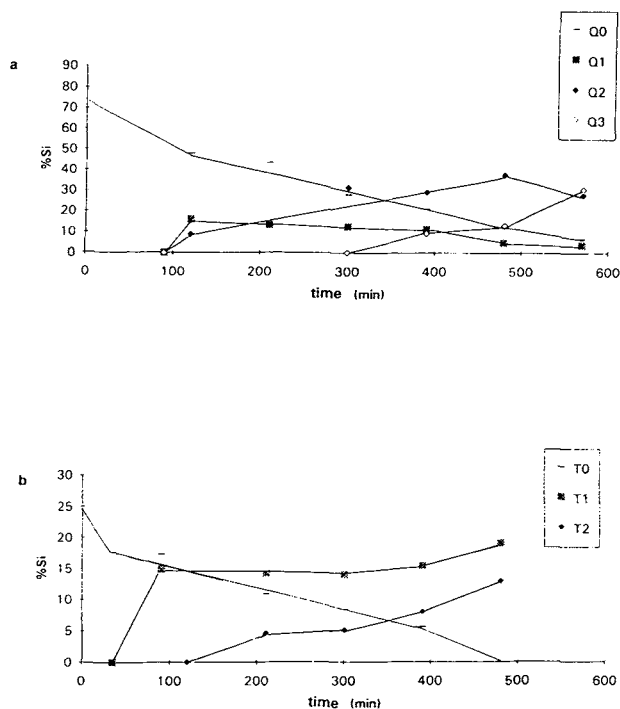


Figure 7 Evolution of the relative proportions of the Q^i (a) and T^i (b) species as a function of time for the molar ethanol : alkoxides ratio = 6.97 : 1.77 with $H = 5$.

monomers quickly disappear. After 120 min, Q^{00} and Q^{04} are the TEOS preponderant species. The hydrolysis of SiP starts a few minutes later than the hydrolysis of TEOS. However, SiP precursor quickly disappears and the presence of T^{01} is fugitive. After 120 min, the only SiP species present in solution are T^{02} (5%) and T^{03} (< 10%). As the Q^{0i} species decrease more slowly than the T^{0i} , the TEOS hydrolysis reactions are slower. After 90 min, the appearance of a new doublet centered at -51.3 ppm reveals that the monomers T^{0i} have condensed. Unfortunately, the attribution of the corresponding condensed species cannot be made in our experimental conditions. However, these spectra could submit accurately to quantitative analysis. Figure 7 displays the evolution of the relative proportion of the monomers and the Q^i and T^i condensed species as a function of time for the molar ethanol : alkoxides ratio = 6.97 : 1.77 with $H = 5$. After 480 min, the hydrolysis of SiP species is completed, whereas Q^0 monomers are still present (15%). The decrease of the relative proportions of the T^0 and Q^0 hydrolyzed species is accompanied with a T^1 dimer increase which stays almost constant at 15% in the range of 90–400 min and a slow increase of the trimers T^2 . The Q^2 and Q^3 species relative proportion grows

rapidly after 90 and 300 min, respectively, whereas the dimers Q^1 are the minor species (<20%) and slowly disappear. After 580 min, there is more than 30% of Q^3 species, whereas the T^3 species are not present. The Q^3 species become predominant and show that the tridimensional network begins to form.

SiP-TEOS Gels

Figure 8 presents the relative proportions of the T^i and Q^i species as a function of SiP molar concentration. One note, that whatever the molar ratio of SiP, for $H = 3.33$, the Q^4 , Q^3 , and T^3 species are, respectively, the three predominant species. This shows that a three-dimensional network is always obtained and, moreover, the absence of the T^1 and Q^1 resonances proves that there is no dangling ends. For $[SiP] = 0.25$ mol/L, there is a little Q^2 resonances, which are responsible of few linear segments in this gel. As the molar concentration of SiP increases, the relative proportion of Q^4 and Q^3 species decrease, whereas T^3 increases progressively. When $[SiP]$ equals 0.56 mol/L, the T^3 species are more numerous than the Q^3 ones. These results show that the SiP connectivity is important and increases with its concentration in the mixture.

Another way to evaluate the network connectivity is to look at the condensation ratio of T and Q spe-

cies. Figure 9 presents the condensation ratio of TEOS and SiP oligomers as a function of the SiP molar concentration. The degree of condensation of the T^i species grows slowly up to 30.6% with the SiP molar concentration, whereas the tQ^i condensation rate decreases. This is further evidence that the SiP connectivity increases with its concentration in the mixture.

The influence of the hydrolysis ratio on the network formation has been also studied. Table III presents the variation of the relative proportions of the different species with the hydrolysis ratio H and the molar ratio of the alkoxides.

These results show that the material has a more or less connected three-dimensional network, depending on the molar ratio of the alkoxides. At low alkoxides concentration and high hydrolysis ratio, the network is less connected (presence of Q^2 and T^2 species, lowest tQ^i and tTi condensation rates). However, the gels are mostly composed of the highest branched species, whatever the composition. The relative proportion of the Q^4 species and the condensation rate of the Q^i species are predominant for $[Si] = 2.26$, whereas the maximum of the T^3 species and the highest condensation rate of the T^i species are obtained for $[Si] = 1.77$. At $[SiP]$ constant, when H increases, the structure of these mixed functional gels yields to a more dense network of T^i species. At $[Si]$ and H constant, the gels have a less condensed

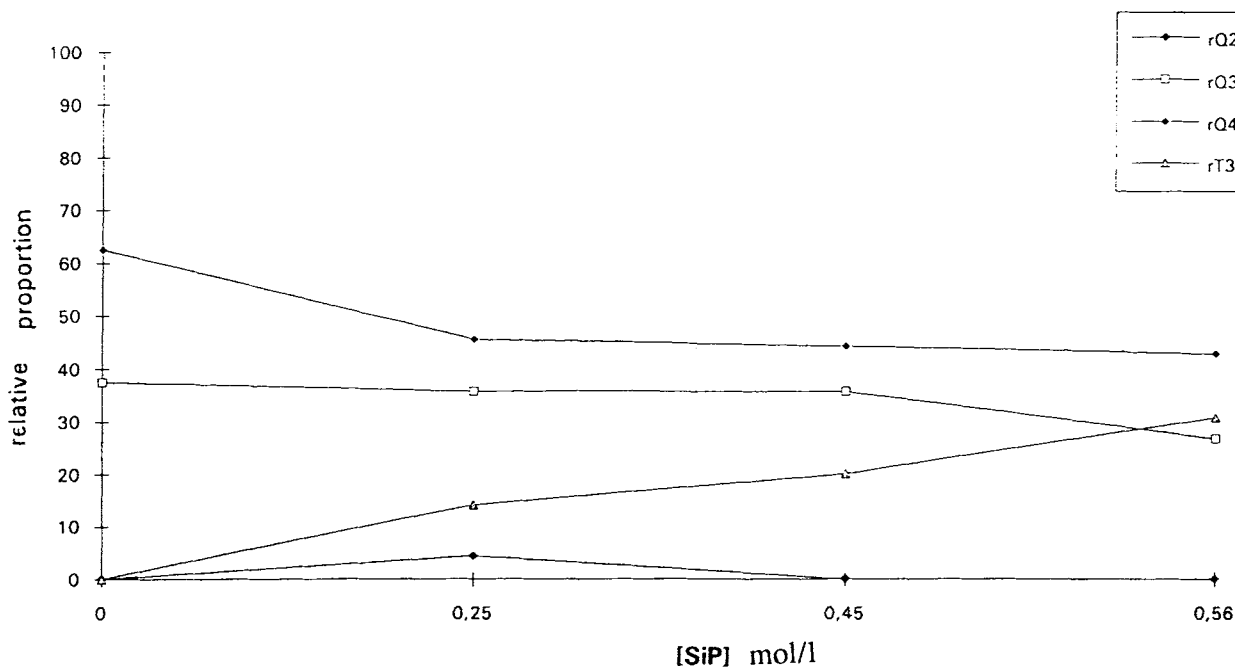


Figure 8 Relative concentrations r^i of the T^i and Q^i species as a function of the SiP molar concentration at $H = 3.33$.

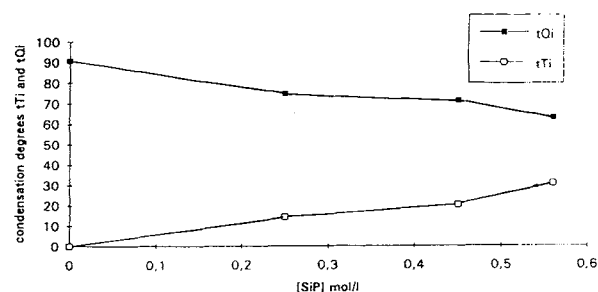


Figure 9 Evolution of the condensation degrees tT^i and tQ^i of the T^i and Q^i species as a function of the SiP molar concentration at $H = 3.33$.

T^i network when the concentration of the functional alkoxide decreases in the mixture.

^{31}P -NMR Study

The ^{31}P -NMR spectrum of the pure SiP alkoxide contains a single peak at 32.9 ppm [Fig. 10(a)] and is consistent with the literature.²⁸ Spectra of SiP-TEOS hydrolyzed solutions in different conditions of hydrolysis ($H = 2$ or 20, with HCl or HF or without catalyst, at different times of hydrolysis) show more or less complex signals between 34 to 36 ppm [Fig. 10(b)]. This suggests the formation of species very close to each other in chemical composition. Two possible exchange reactions on the phosphorus of phosphate compounds are known in acidic hydrolytic conditions:

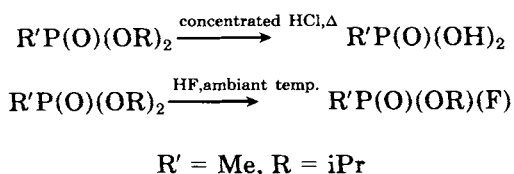


Table III Evolution of the Relative Proportions r^i of the Q^i and T^i Species and Their Condensation Degree t with the Hydrolysis Ratio H and the Concentration of Alkoxides

H	18	5	3.33	3.33
[Si] mol/L	0.87	1.77	2.26	2.27
[SiP] mol/L	0.17	0.44	0.45	0.56
rQ^2	4.1	—	—	—
rQ^3	23.7	26.9	35.7	26.7
rQ^4	36	41.9	44.2	42.7
rT^2	20.7	—	—	—
rT^3	15.4	32	20.1	30.6
tQ^i	55.8	62.1	70.9	62.7
tT^i	29.2	32	20.1	30.6

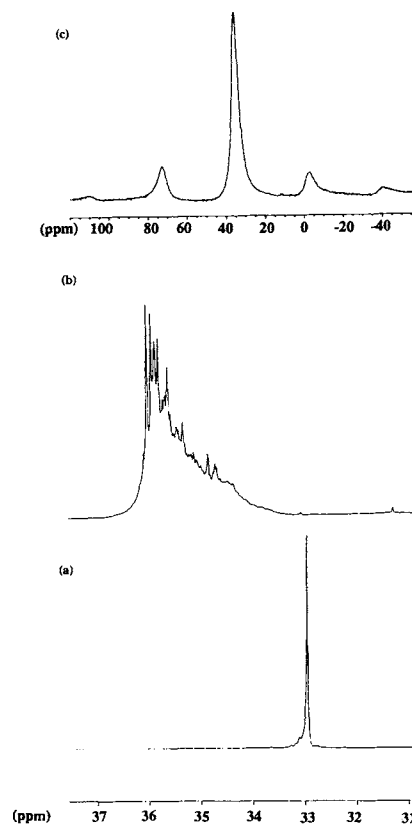


Figure 10 $^{31}\text{P}\{^1\text{H}\}$ spectra of (a) pure SiP alkoxide (b) SiP-TEOS sol, and (c) ^{31}P MAS NMR spectrum of SiP-TEOS gel.

Depending on the nature of R' and R , their chemical shifts may be close to those of the observed signals.²⁹ However, the spectra obtained in the different experimental conditions mentioned above are similar and preclude these exchange reactions. The complex signals we observe are very close to the signal of pure SiP alkoxide, broaden during the hydrolysis-condensation reactions and are due to the changes on the Si environment. This was confirmed by ^{31}P MAS NMR spectra, which show a single peak around 33 ppm with a weak half-line width [Fig. 10(c)]. So, in the gels, there is no change of the phosphorus environment.

CONCLUSION

Heteropolysiloxane materials were prepared from cohydrolysis via sol-gel process of an alkoxy silane (TEOS) and a phosphorus functionalized silicon alkoxide (SiP) with HF as a catalyst.

The first monomers and condensed species of the SiP hydrolysis-condensation were characterized by

^{29}Si -NMR spectroscopy. The formation of small of cyclic units may be responsible for the absence of gelation of this trivalent alkoxide, whatever the experimental conditions. The presence of a crosslinking agent like TEOS is necessary to build a three-dimensional network. The highest SiP concentration that can be introduced in these mixed organic-inorganic systems in order to obtain monolithic and transparent gels is 30% molar. The ^{29}Si -NMR study of the SiP-TEOS sols shows that the hydrolysis of TEOS starts before that of the SiP but is slower. On the other hand, the condensation of the Q^0 monomers starts after those of the T^0 monomers but is faster.

The gels molecular structures were studied by ^{29}Si MAS NMR. This investigation showed that the TEOS connectivity is important in these gels and varies with the composition of the mixture. The structure of the materials varies from a less connected three-dimensional network for $H = 18$, $[\text{Si}] = 0.87$, and $[\text{SiP}] = 0.17$ to a more connected network for $H = 5$, $[\text{SiP}] = 1.77$. A ^{31}P -NMR study showed that the environment of the phosphorus is unchanged in these experimental conditions.

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