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Polycondensation of Aminosilanes in Methanol

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Polycondensation of (3-aminopropyl)trimethoxysilane and ((trimethoxysilyl)propyl)diethylenetriamine in methanol was studied using ^{29}Si NMR spectroscopy, small-angle X-ray scattering, and viscosity measurements. Calculations based on ^{29}Si NMR data show a cluster–cluster growth mechanism is present. Differences in reactivity and in the structures obtained will be discussed.

Introduction

Hybrid organic–inorganic materials such as ORMOSILs (organically modified silicates)[1,2] can be described as a silicate matrix onto which are grafted organofunctional groups (e.g., alkyl, alkene, aminopropyl). The organic groups can be a polymerizable ligand such as an epoxide or vinyl species which allow cross-linking between organic moieties to take place to improve the mechanical properties of the material. Regardless of this last example where both organic and inorganic polymerization has occurred, the mechanical properties are usually provided solely by the silica matrix while other properties such as hydrophobicity and thermoplasticity can be tailored by choosing suitable types of organosubstituents.[3]

Ravaine et al. proposed a new class of anhydrous protonic conductors[4] using the idea of modified silicate networks. The structure can be represented by a silicate network supporting amino functions (e.g., aminopropyl). When doped by an acid such as CF_3SO_3H, they exhibit good electrochemical properties.[5] A stability window of 1.3 V at 100 °C and conductivities at room temperature in the order of 10^{-5} S cm^{-1} can be obtained for this class of material. Considering other properties like transparency and the possibility to readily obtain the material in the form of thin films, they are seen as good candidates for electrochemical devices such as smart windows.

The synthesis of these materials is via a sol–gel route. It can be depicted by the following scheme:

$$R'Si(OR)_3 + 1.5H_2O \rightarrow 3ROH + R'SiO_{3/2} \qquad (I)$$

where R′ is an alkylamine chain and R is an alkyl group. The silicium atom is bound to three oxygens shared with neighboring silicium atoms bearing similarly alkylamine chains R′.

At a functional group level three reactions are involved in the sol–gel process: The hydrolysis reaction replaces an alkoxy group with an hydroxyl group:

$$\equiv Si{-}OR + H_2O \rightarrow \equiv Si{-}OH + ROH \qquad (II)$$

Alcohol condensation involves the loss of an alkoxy group and a hydroxyl group leading to the production of alcohol and formation of a siloxane bond $\equiv Si{-}O{-}Si\equiv$:

$$\equiv Si{-}OR + HO{-}Si\equiv \rightarrow \equiv Si{-}O{-}Si\equiv + ROH \qquad (III)$$

The water condensation involves two silanol groups whose condensation leads to the formation of a siloxane bond Si–O–Si and water:

$$\equiv Si{-}OH + HO{-}Si\equiv \rightarrow \equiv Si{-}O{-}Si\equiv + H_2O \qquad (IV)$$

These three reactions are reversible and the reverse processes are called esterification, alcoholysis, and hydrolysis respectively.

Numerous studies have been devoted to the reactivity of silicon alkoxides toward hydrolysis and condensation reactions. They include TEOS (tetraethoxysilane), TMOS (tetramethoxysilane), and also some organically modified alkoxysilanes such as (γ-(methacryloxy)propyl)trimethoxysilane.[6] All the reactions involved are under kinetic control. Their kinetic constants depend on a large number of parameters especially the pH of the solution, the initial water (silicon alkoxide bond ratio: the number of water molecules used to hydrolyze one Si–OEt bond; in our case $0.5H_2O$), the nature of the solvent and the concentration of monomer. Depending on the initial conditions and then on the reaction kinetic constants, various polymeric structures can be obtained in the sol. At the onset of gelation the particles formed initially determine the subsequent structure of the gel. Consequently a better knowledge of the AMINOSILs

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structure would be obtained by characterizing the oligomers composing the sol and by following the kinetics of hydrolysis and condensation reactions.

Our attention was focused on two families of electrolytes obtained by polycondensation of the (3-aminopropyl)trimethoxysilane ($(CH_3O)_3Si(CH_2)_3NH_2$) and of the ((trimethoxysilyl)propyl)diethylenetriamine ($(CH_3O)_3Si(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2$). The initial conditions are the same as those taken for the synthesis of these polymer electrolytes which use a high concentration of monomer and a low concentration of water with methanol as a solvent.[4b] Some results are reported in the literature concerning the hydrolysis of (3-aminopropyl)triethoxysilane. Ishida and Suzuki[7] studied the polycondensation of (3-aminopropyl)triethoxysilane in very dilute aqueous media. Kang[8] compared the rates of hydrolysis of the (3-aminopropyl)trimethoxysilane and of the (3-aminopropyl)triethoxysilane in an acetone−water mixture; however, information concerning the condensation process was not reported. First results showing the behavior of the (3-aminopropyl)triethoxysilane toward condensation was given recently by Hoebbel et al.[9] using ^{29}Si and ^{14}N NMR spectroscopic investigations. The (3-aminopropyl)triethoxysilane was hydrolyzed in an acidic solution in the presence of silicic acid.

However, differences in the solvent, the alkoxy group, and the initial conditions of hydrolysis (acidity of the medium, water concentration) from those we used means we cannot use these results to understand the polycondensation processes of the monomers used in this study. We will report here some results of the hydrolysis and the condensation processes of these monomers in an alcoholic solution. Results were obtained using ^{29}Si NMR spectroscopy, small-angle X-ray scattering and viscosity measurements. Growth processes and the structure of the oligomers obtained will be discussed in detail as well as the influence of the organic substituent.

Experimental and Instrumental Section

Synthesis. The solution was stirred at 25 °C with methanol as solvent. Other alcohols such as ethanol would probably slow down the reaction and might lead to transesterification reactions which would complicate the kinetic study. The concentration of the monomer in methanol is important (1:9.6 in a molar ratio) and the ratio of water:alkoxide is 0.5 which is the stoichiometric quantity required for a full condensation of the aminosilane. Thus, the ratio of water:methanol:monomer was 1.5:9.6:1. The water was added to half of the methanol and the monomer added to the other half to get two homogeneous solutions. The polycondensation reaction was then started by mixing the two solutions. The monomers were purchased from Petrarch Systems and used without further purification.

^{29}Si NMR Spectroscopy. (*a*) *Advantages of the method*: ^{29}Si NMR spectroscopy has been extensively used in the past decade to study the structure of sols obtained by polycondensation of alkoxysilanes[10,11] including more recently some organo-substituted alkoxysilanes.[6,12] This technique gives precise information concerning the first neighbors of silicon atoms (−OR, −OH, −OSi≡) for which in the case of a trifunctional silicon, 10 different species are possible. Considering the second neighbors, 98 different Si are possible, all of which could not be experimentally observed.

Interpretation of the results is based on the reading of the chemical shift of the silicon atoms which is mainly influenced by the nature of the first neighbors. The nature of the organic substituent appreciably affects the value of the chemical shift (e.g., $(MeO)_4Si$ and $(MeO)_3SiCH_3$). The values of the angle between two bridging silicons and the length of the silicon−oxygen bond also have a great influence on the Si chemical shift. Thus Si atoms contained in a closed small ring structure, e.g., $(\equiv Si{-}O)_3$ will have a chemical shift 10 ppm down field of Si atoms in a linear chain.

(*b*) *Notation*: For the assignment of the different peaks we used the terminology employed by Noll.[13] Each silicon atom is noted T_x^y with $0 < x + y < 3$, x and y being an integer and positive. T refers to the trifunctional monomer, while x is the number of bridging oxygens and y is the number of hydroxides on the silicon center. To simplify the terminology, the (3-aminopropyl)trimethoxysilane monomer and its solution will be referred to as AMO and the ((trimethoxysilyl)propyl)diethylenetriamine as TRIAMO.

(*c*) *Measurement*: Addition of chromium(III) acetylacetonate was necessary to shorten the spin−lattice relaxation time T_1 of the ^{29}Si nuclei from 30 to 1 s. Measurements with or without the paramagnetic substance do not exhibit differences in chemical shift or in intensity. The magnetic field is locked on the resonance of the deuterated methanol which was a part of the solvent. Spectra were recorded at 59.6 MHz on a Brucker AM300 spectrometer with inverse gate decoupling. The acquisition time is 3 s; the pulse delay time is 5 s; 200 scans were used for each spectrum. As shown in previous studies[14,15] these precursors are reacting rapidly compared with the NMR time scale. To stop the reactions at the desired time, the NMR tubes were frozen in liquid nitrogen. The samples were kept frozen till measurement. Furthermore they were scanned at low temperature (208 K for AMO and 238 K for TRIAMO), a noticeable change in viscosity of the solution being observable at 243 K for AMO. We used 10 mm quartz tubes purchased from Aldrich.

Small-Angle X-ray Scattering. In many systems and especially for silica, small-angle X-ray scattering has been employed to investigate the growth and topology of particles prior to gelation. At low scattering angles (Guinier region) information is obtained concerning the polymer mass or radius. For AMO and TRIAMO the average particle size was determined in solutions which had been aged for 2 days. By this time the solutions should be in a quasi-stable state as indicated by the kinetic information provided by ^{29}Si NMR spectroscopy. Measurements were performed on a compact Kraktky camera equipped with a Braun detector. Cu Kα rays were used and filtered by Nickel foils. Solutions were placed in a quartz capillary (diameter 1 mm, wall 0.01 mm).

Viscosity Measurements. We recorded the dynamic viscosity of the solution as a function of the time in order to detect eventual structural changes occurring during the reaction and differences of behavior of the two precursors. The viscosity was determined by measuring the rate of fall of a sphere in the reaction solution at 25 °C.

Results

^{29}Si NMR Spectroscopy. As illustrated in Figure 1 for AMO and Figure 2 for TRIAMO changes occur

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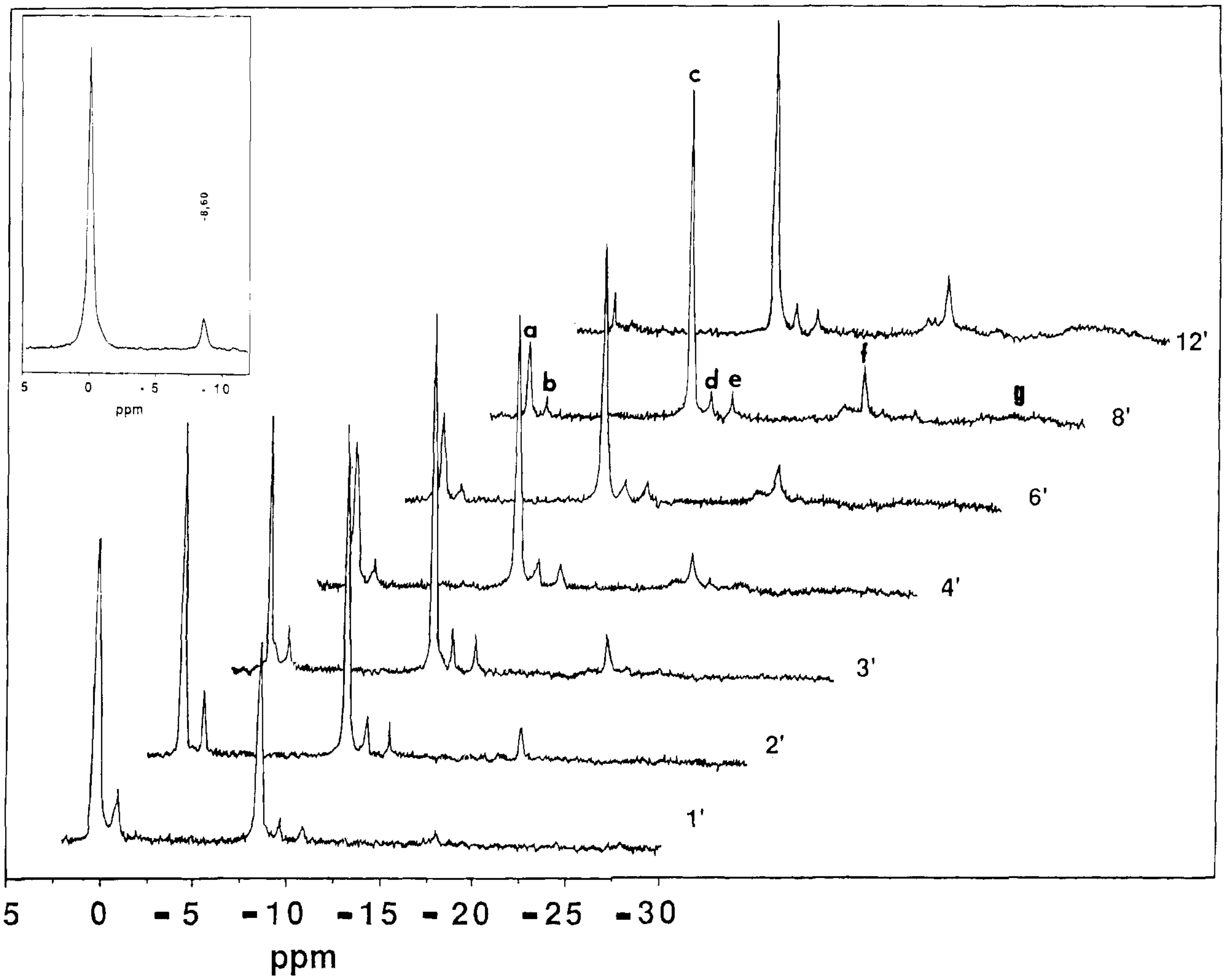

Figure 1. Series of ^{29}Si NMR spectra for the hydrolysis of the (3-aminopropyl)trimethoxysilane (AMO) as a function of the time (T = 208 K). Initial molar ratios AMO/H_2O/CH_3OH are 1/1.5/9.6. Insert: spectrum of the starting AMO. The small peak at −8.6 ppm (−52.8 ppm compared to TMS), is determined versus that of AMO taken as reference (−44.2 ppm compared to TMS). Chemical shift variations of the ^{29}Si NMR resonance peaks recorded during the precursor AMO polycondensation (b, $T_0{}^1$; c, $T_1{}^0$; d, $T_1{}^2$; e, $T_1{}^1$; f, $T_2{}^0$).

rapidly in the first minutes of the reaction. Chemical shifts are expressed in relation to the chemical shift of TMS, the abscissa scale is graduated by respect to the monomer's chemical shift, arbitrarily given as 0. Although the ^{29}Si NMR spectroscopy was used in numerous studies to follow the hydrolysis and condensation kinetics of TMOS or TEOS,[16−18] few similar works have been devoted to organically modified alkoxysilanes.[12,19] The only reported spectra obtained for an alkylaminosilane has been published by Hoebbel et al.[9] where no kinetic study per se nor structural determinations were done. Therefore the first part of this publication will discuss the assignment of the different resonance peaks observed.

(*a*) *Peaks assignment*: The spectrum of the starting AMO solution is shown in Figure 1. It has two resonance peaks, the bigger one having a chemical shift of −44.2 ppm compared to TMS (tetramethylsilane). This chemical shift is comparable with those usually observed for other trifunctional alkoxysilanes (−41.4 ppm for the methyltrimethoxysilane and −41.8 for the acrylpropyltrimethoxysilane) we assign this peak to the monomer or $T_0{}^0$. The second peak at −8.6 ppm (−52.8 ppm/TMS) is attributed to the dimer considering the intensity changes during the reaction and the difference in chemical shift usually observed between species n condensated and $n + 1$ condensated (n = 0, 1, 2).

On the spectrum recorded after 8 min of reaction, shown in Figure 1, peaks are labeled a−g. Peaks a and c have been already assigned to $T_0{}^0$ and to $T_1{}^0$ species. We focused our attention on peaks b, d, and e, whose position seems at first unusual. On one hand, the chemical shift of b is too low to correspond to an hydrolyzed species of type T_1 (silicon center involved in one condensation reaction); on the other hand −OH groups are more electronegative than $-OCH_3$ groups and would cause hydrolyzed monomeric species to be shifted to fields lower than that of the monomer.[20,21] The position of this peak can in fact be explained by the acidic character of the silanols which are interacting with the amines on the alkylamine chains.[15] Indeed

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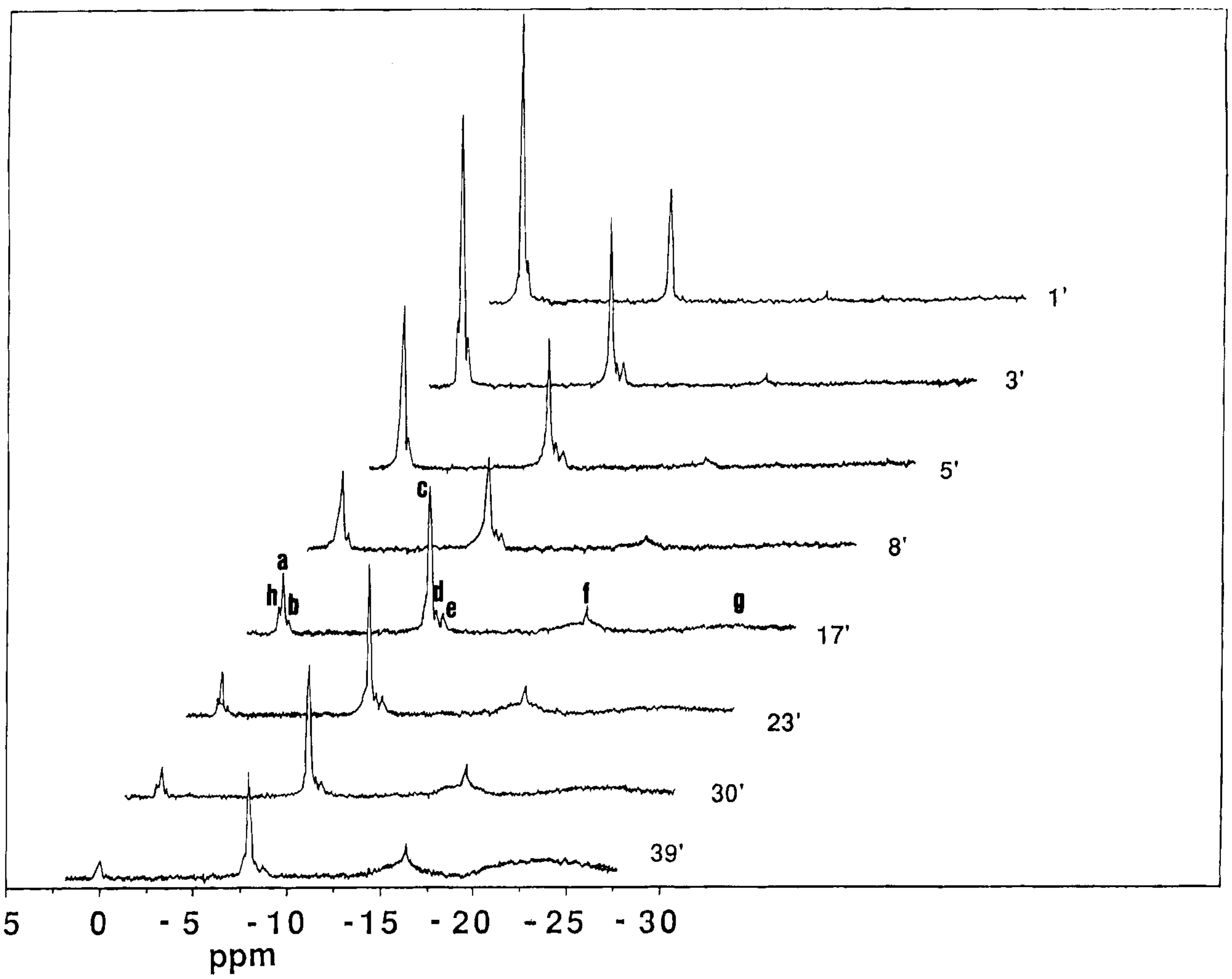

Figure 2. Series of ^{29}Si NMR spectra for the hydrolysis of the ((trimethoxysilyl)propyl)diethylenetriamine (TRIAMO) as a function of the time. Initial molar ratios TRIAMO/H_2O/CH_3OH are 1/1.5/9.6 (T = 243 K). After 17 min, the small peaks resolved on the $T_0{}^0$ are labeled h, a, b, on the $T_1{}^0$ c, d, e, and f for T_2.

Table 1. Precursors AMO and TRIAMO Chemical Shifts Observed on ^{29}Si NMR Spectra Drawn in Figures 1 and 2 and Expressed by Respect to $T_0{}^0$

	AMO	remarks	TRIAMO	remarks
$T_0{}^1$	−0.98, −1.01		−0.24	overload with $T^0{}_0$
$T_0{}^2$		not observed	−0.26, −0.33[a]	
$T_1{}^0$	−8.68	−8.67 dimer		
		−8.77 end chain	−8.61	
$T_1{}^1$	−10.91, −10.93		−9.30, −9.35	
$T_1{}^2$	−9.71, −9.75		−8.91, −8.99	
$T_2{}^0$	−16, −22	−17.98 at midchain	−16, −20	−17.74 at midchain
$T_3{}^0$	−23, −29		−23, −29	

[a] This peak position is dependent on the silanol dissociation rate.

such an interaction should lead to a weakening of the SiO−H and thus to a decrease of the positive partial charge on the silicon atom, whose position will be shifted to higher fields. Conductivity measurements carried out on these systems[15] show the existence in solution of an equilibrium between silanoate ions and silanol groups:

$$\equiv SiO{-}H \rightarrow \equiv SiO^- + H^+ \qquad (V)$$

This equilibrium is fast compared with the NMR time scale. Consequently the spectrum obtained does not show two distinct resonance peaks for the silicons corresponding to ≡SiO−H and to ≡SiO$^-$ but an intermediate signal whose position depends on the dissociation degree of the silanol bond.[22] As shown in Figure 1b and Table 1 the maximum chemical shift observed for the peaks b, d, and e as a function of the reaction time corresponds to the maximum in acidity of the solution whereas the position of the peaks c and f is not a function of the time of reaction. Consequently peaks b, d, and e are assigned to silicons of type $T_0{}^1$, $T_1{}^1$, and $T_1{}^2$. The peak f corresponds to $T_2{}^0$ silicon atoms. The appearance of peak g between −67.2 and −73.2 ppm corresponds to the formation of fully condensated silicon atoms $T_3{}^0$.

The assignment of the peaks in the TRIAMO solution can be done following the same procedure. A spectrum of the solution after reacting for 17 min (Figure 2) exhibits similar features to the AMO solution. However, shifting of the hydrolyzed species toward lower fields was noted. The observation of a peak h around 0.3 ppm

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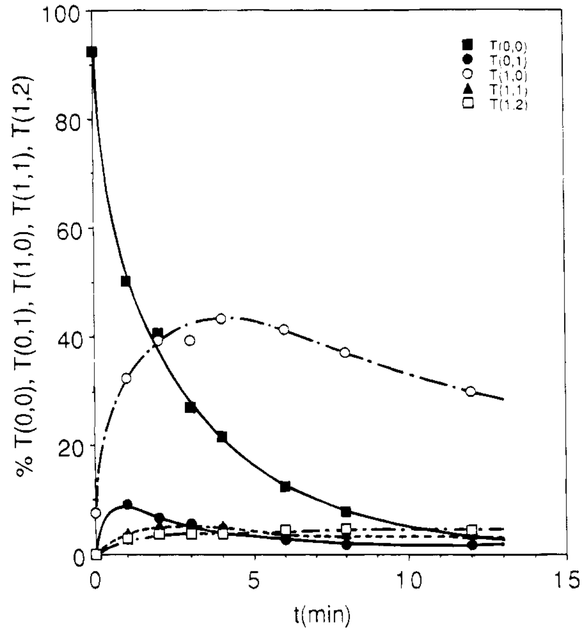

Figure 3. Intensity variations for AMO of T_0^0, T_0^1, T_1^0, T_1^1, and T_1^2 as a function of the time (data obtained from the ^{29}Si NMR recorded at 208 K).

compared to T_0^0 and whose position depends on the reaction time was assigned to T_0^2.

(*b*) *Distribution and intensity variations of the species*: Concentrations are expressed as a percentage of the silicon atoms present initially in solution. Variations in the concentration of T_0^0, T_0^1, T_1^0, T_1^1, and T_1^2 for the AMO solution are represented in Figure 3. The disappearance of the monomer and the appearance of the T_1^y species occur at a very low silanol concentrations confirming the high reactivity of the silanol bond toward condensation.[23] The silanol concentration within several percent stays almost constant during the reaction. The calculation of percentages was not possible for the TRIAMO solution due to the overlapping of the T_x^0 peaks and T_x^y peaks ($y \geq 1$). However, the silanol concentration seems to remain low during the polycondensation process.

Variations of the T_0, T_1, T_2, and T_3 are represented for AMO in Figure 4 and for TRIAMO in Figure 5 where T_x means the sum of the intensities of the peaks corresponding to the species of type T_x^y. Both sets of curves show similar characteristics regardless of the time scale. We observe a rapid disappearance of the monomeric species which occurs with production of T_1 type silicons. T_2 species (T_3) are observable after a sufficient proportion of T_1 (T_2) is present. T_2 (T_3) appears after consumption of roughly 40% (70%) of the initial T_0 (T_1).

It is possible to calculate an average number of Si−OH (noted [Si−OH]) and Si−OSi (noted [Si−OSi]) bond per silicon atom using these data. For example [Si−OSi] can be expressed as $\%T_1 + 2\ \%T_2 + 3\ \%T_3$ where $\%T_x$ is the percentage of silicon of type T_x. The values found were in accordance with those measured previously by a combination of FT-IR and Karl Fischer measurements[14,15] confirming the validity of the NMR peaks assignment.

After several hours of reaction, spectra of the precursor AMO were recorded every hour. Three examples

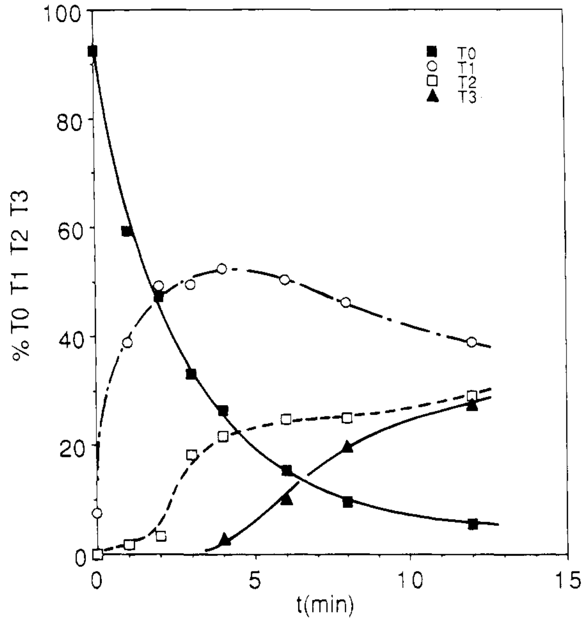

Figure 4. Intensity variations for AMO of T_0, T_1, T_2, and T_3 as a function of time (data obtained from the ^{29}Si NMR (T = 208 K).

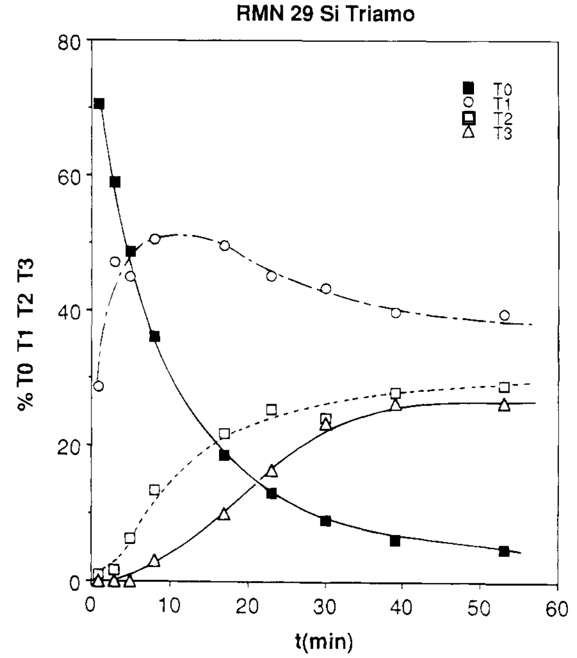

Figure 5. Intensity variations for TRIAMO of T_0, T_1, T_2, and T_3 as a function of the time (data obtained from the ^{29}Si NMR; T = 243 K).

are shown in Figures 6−8. They correspond respectively to 1, 5, and 30 h of reaction. The product obtained is still liquid, the solution being stable toward gelation or precipitation even after several months. After reacting for 1 h, the solution is composed essentially of silicons of type T_2 and T_3 and to a smaller extent of some T_1. After 5 h there is no T_1 left in solution, rather only T_3 type silicons and some T_2 whose concentration is slowly diminishing are present. The solution does not give a gel but however is progressing toward a state in which every atom of silicon is bridged with three others. A more accurate observation of the T_3 massif (between −23 and −30 ppm/AMO or −67.2 and −74.2 ppm/TMS) reveals the existence of a large number of sharp peaks having a constant chemical shift. We can assume that these peaks belong to rigid structures. Englehardt *et*

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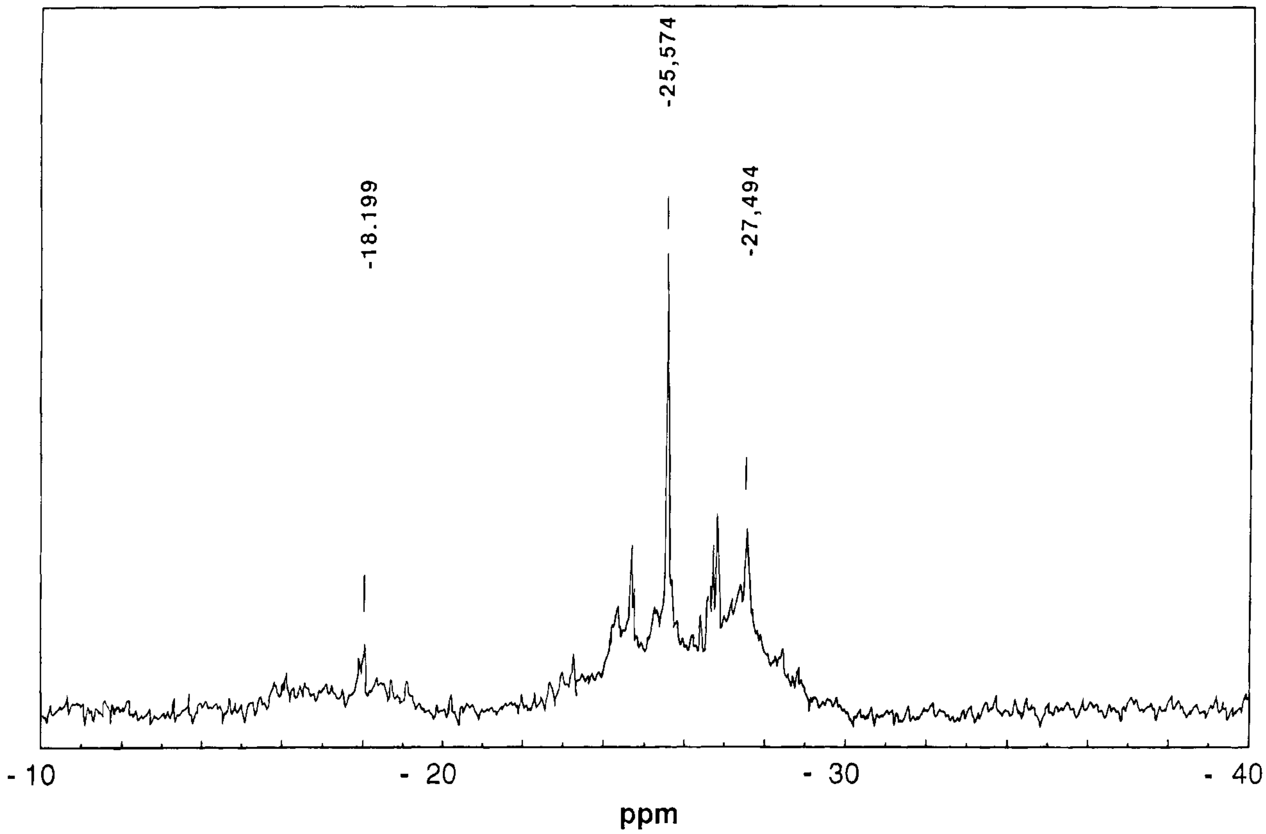

Figure 6. ^{29}Si NMR spectrum of AMO after 1 h. Chemical shifts noted on the figure are expressed compared to T_0^0. They are respectively −62.4, −69.774, and −71.694 ppm compared to TMS.

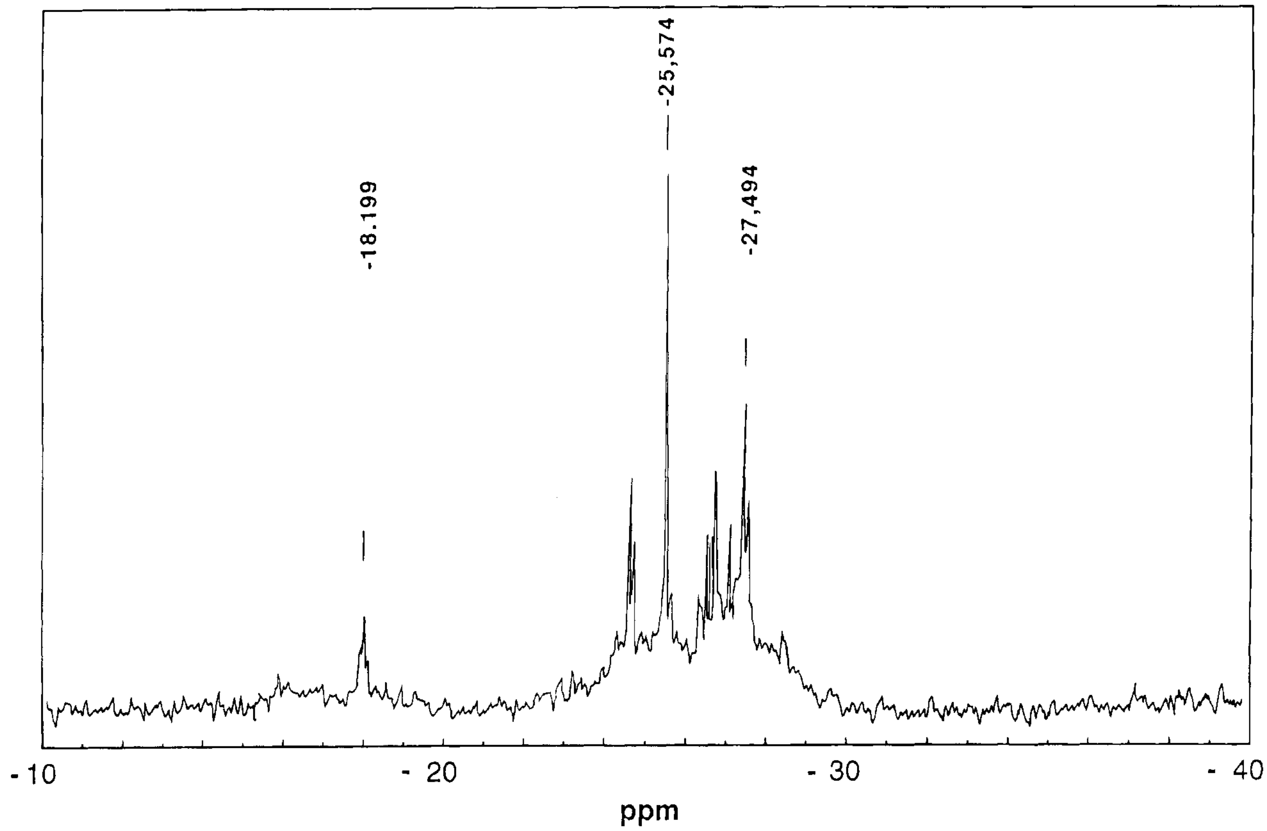

Figure 7. ^{29}Si NMR spectrum of AMO after five hours. They are respectively −62.4, −69.774, and −71.694 ppm compared to TMS.

al.[23] note that a difference of 1° of the Si-OSi angle leads in the ^{29}Si NMR spectra to a chemical shift change of 0.6 ppm. Consequently we can suppose that less rigid structures would probably give much broader peaks. According to the literature[24] we can assume that the peak at −27.494 ppm (−71.694 ppm/TMS) corresponds to silicon centers within cubic octamers.

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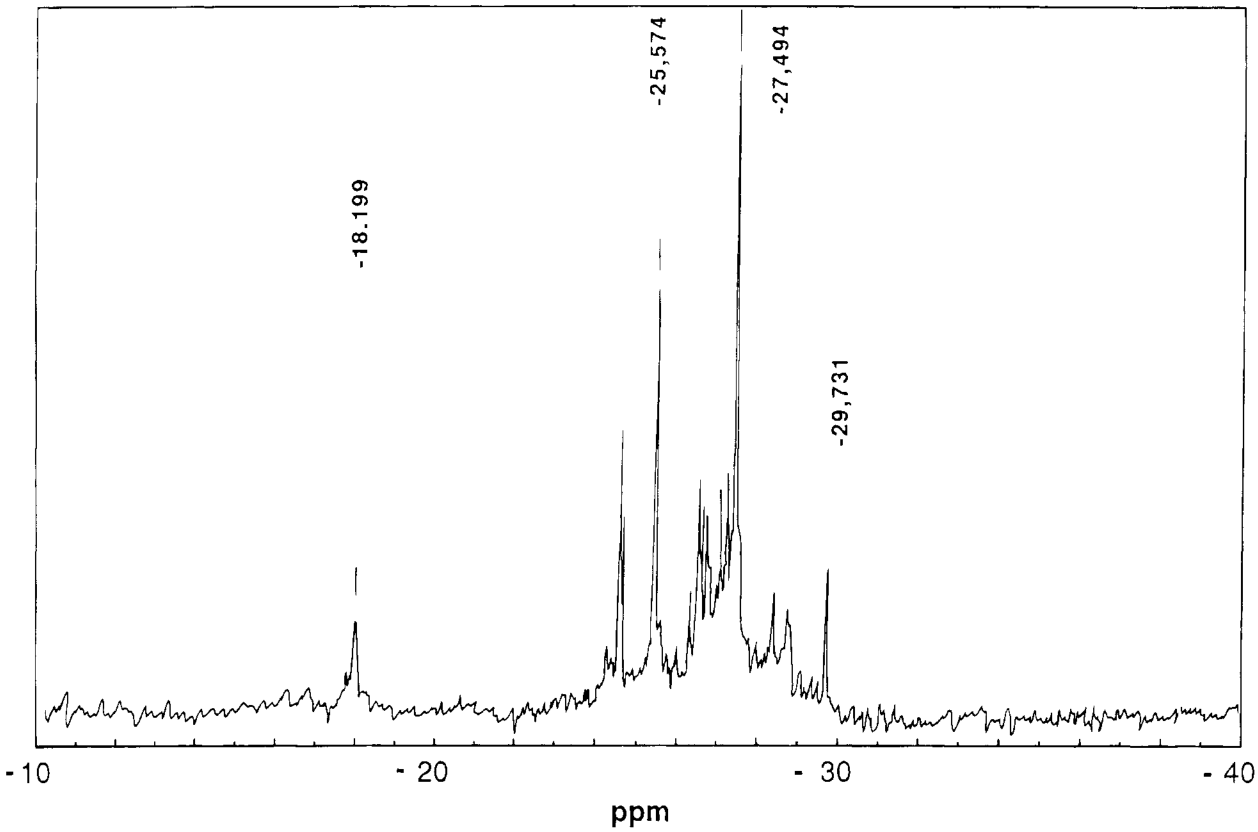

Figure 8. ^{29}Si NMR spectrum of AMO after 30 h. They are respectively −62.4, −69.774, −71.694, and −73.94 ppm compared to TMS.

Comparing the distribution of the different T_x after reaching a quasi equilibrium state (few hours of reaction) shows that the degree of condensation of the solution is higher for AMO than for TRIAMO. Furthermore one can notice than the condensation reaction occurs for both precursors at low silanol concentrations which indicates that condensation proceeds by methanol evolution (III) rather than by formation of water (IV).

(*c*) *Calculation of an average number of silicon atoms per particle*: Considering an oligomer *j* resulting of the polycondensation of trialkoxysilanes which contains *n* silicon atoms, if n_i^j is the number of silicon atom of type T_i we can write

$$n_1^j + n_2^j + n_3^j = n \tag{1}$$

Supposing no ring within the oligomer, the number of Si−OSi bonds per particle $n_{\mathrm{Si-OSi}}$ can be expressed by

$$n_{\mathrm{Si-OSi}} = n_1^j + 2n_2^j + 3n_3^j = 2(n - 1) \tag{2}$$

From (1) and (2) comes

$$n_1^j - n_3^j = 2 \tag{3}$$

Considering systems such as AMO or TRIAMO for which no rings have been observed during the first minutes of the reaction (see NMR spectra), we can apply eq 3. *p* is the number of oligomers present in solution; therefore

$$\sum_{j=1}^{p}(n_1^j - n_3^j) = 2p \tag{4}$$

which can be expressed as

$$p = {}^1/_2(\sum_{j=1}^{p} n_1^j - \sum_{j=1}^{p} n_3^j) \tag{5}$$

If N_{Si} the number of silicon atoms per particle is defined by the ratio of silicon atoms present in solution to the total number of particles (sum of monomeric and oligomeric species), we have

$$N_{\mathrm{Si}} = (N_0 + N_1 + N_2 + N_3)/(N_0 + {}^1/_2(N_1 - N_3)) \tag{6}$$

with N_i being the number of silicon atoms of type T_i. Using the percentage of silicon atoms of type T_i (written $\%T_i$) which is given by the ^{29}Si NMR results, we can write

$$N_{\mathrm{Si}} = 100/\{\%T_0 + {}^1/_2(\%T_1 - \%T_3)\} \tag{7}$$

These calculations have been done for AMO and TRIAMO as a function of the reaction time. The results are shown in Figure 9. The curves obtained for both monomers present similar features, the particle growth being for AMO faster. In the first minutes of the reaction the particle size is growing slowly until roughly 85% of the monomer has been consumed. Then the number of silicon atoms per oligomer is increasing much faster (from approximatively 3 to 9) while concentrations of monomeric species decrease slowly. The observed phenomenon excludes a growth mechanism for which the particle size would increase by progressive addition of monomeric species to bigger particles. These observations indicate that the first step is the formation of small units which in a second step condense together, leading to formation of bigger particles. Considering the

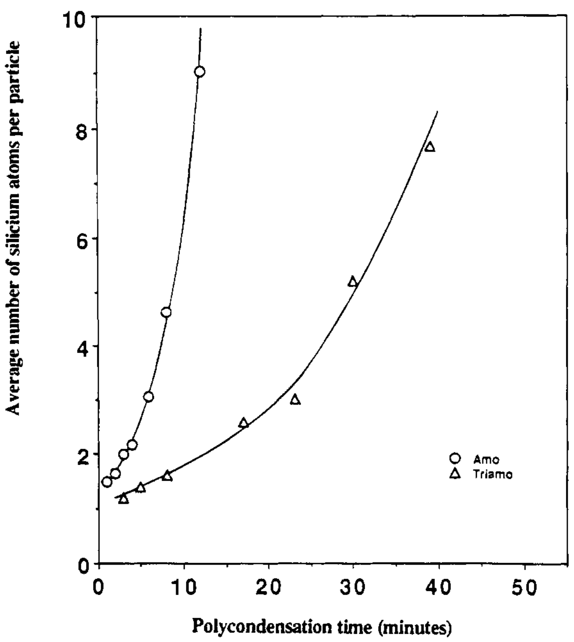

Figure 9. Average number of silicon atoms per particle calculated from ^{29}Si NMR data as a function of the time for AMO and TRIAMO.

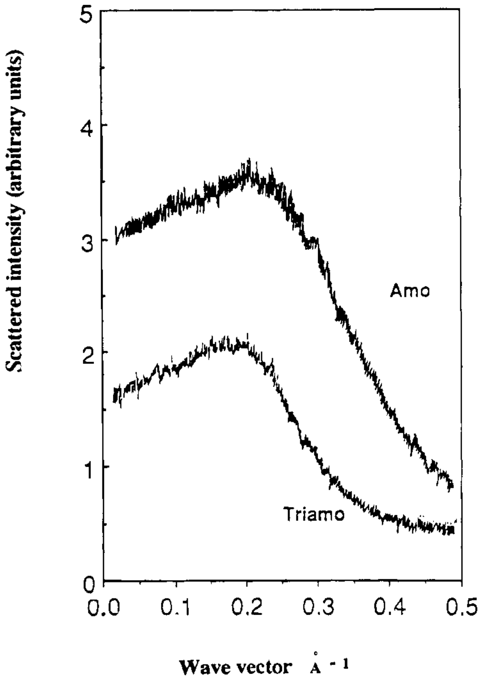

Figure 10.

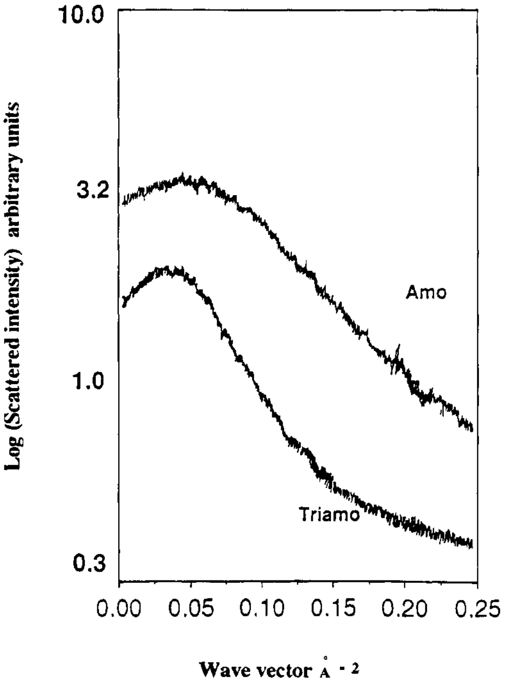

Figure 11. Guinier plot after 48 h for AMO and TRIAMO.

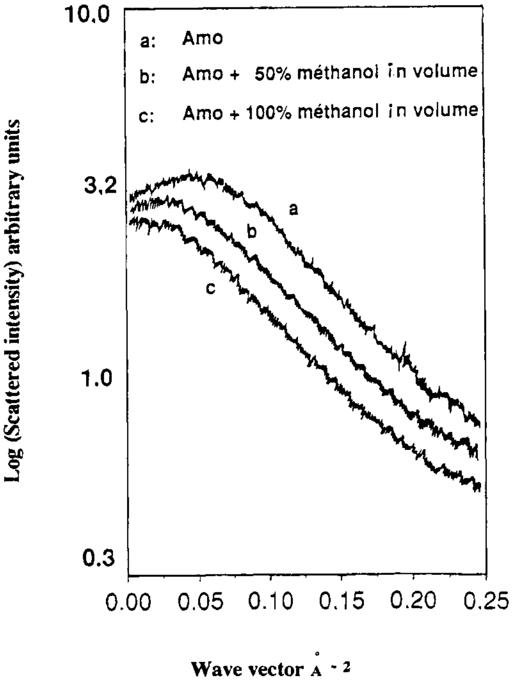

Figure 12. Guinier plot after 48 h for AMO and AMO solutions diluted in methanol.

monomeric species as particles might induce some distortions in the calculation. Considering units containing at least two silicon atoms as particles gives curves having the same kind of shape as those observed and consequently leads us to the same conclusions.

Small-Angle X-ray Scattering. Figure 10 shows the scattered X-ray intensity I as a function of the scattering vector $\mathbf{q}$ for the two solutions AMO and TRIAMO after 48 h of reaction. The spectra were obtained after subtracting the spectrum of the solvent alone from the spectrum of the solution. The presence of an interference peak shows the presence of particles in the solution. At small angles, the Guinier plot log $I(q)$ (see Figure 11) exhibits a linear part for both AMO and TRIAMO solutions. The slope of the linear part is $-R_g^{2/3}$, where R_g is the electronic radius of gyration of the particles.[25] Dilution of the solution with methanol does not affect this value as shown in Figure 12, which indicates that the particles are not aggregated. We can qualitatively observe in Figure 14 that the slope obtained for the TRIAMO solution is bigger than for the AMO one. Considering the differences of electronic density between the silicon and the other atoms present in solution, the measurement gives only the radius of gyration of the inorganic part of the particles. This means that differences observed between AMO and TRIAMO solutions are due to differences in the structure of the silica network. Thus monomers bearing a longer alkylamine substituent seem to give particles

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(25) Guinier, G.; Fournet, C.; Walker, C. B.; Yudavitch, K. L. *Small Angle Scattering of X-Rays*; Freeman: New York, 1955.

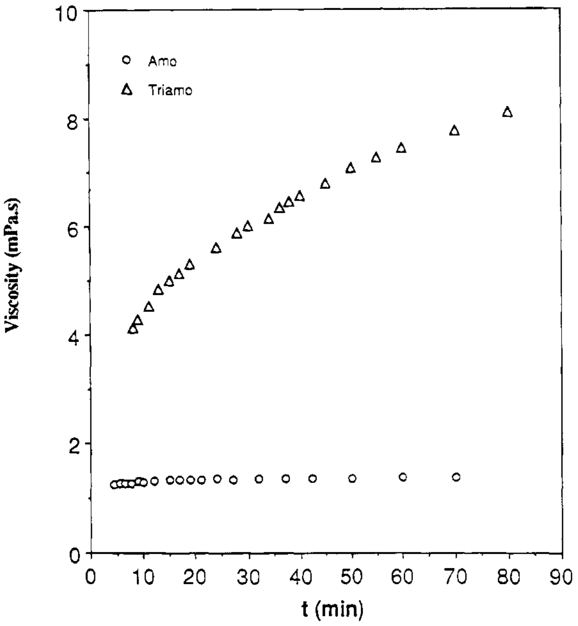

Figure 13. Viscosity of the solutions AMO and TRIAMO as a function of the time.

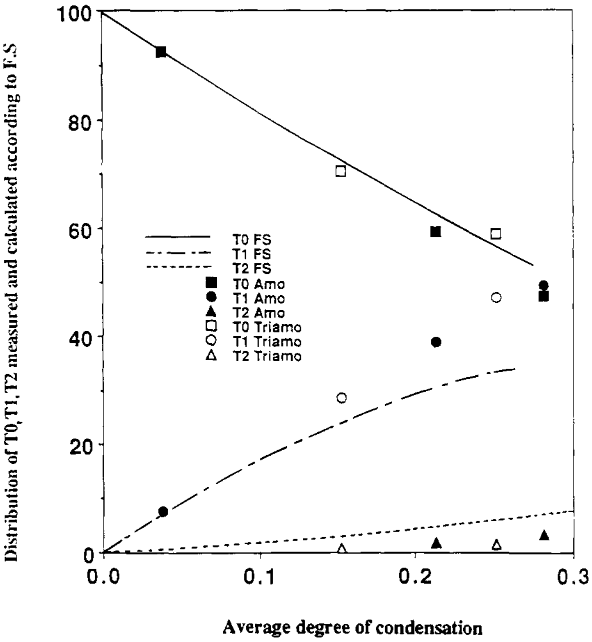

Figure 14. Comparison of T_0, T_1, and T_2 calculated from the Flory–Stockmayer theory with values found by ^{29}Si NMR.

having a broader silica network. Moreover the Guinier region (linear part of the curve log $I(q)$ as a function of q^2) is reduced for the TRIAMO solution, indicating a diminishing of the homogeneity of the solution. Supposing a spherical shape of the particles the radius of gyration R_g is related to the geometrical radius R_s by $R_s = (5/3)^{1/2}R_g$. Applying this relation gives diameters of the inorganic part of the particles in the order of 1.5 nm.

Viscosity Measurements. Curves of viscosity versus time of reaction are given for the two precursors AMO and TRIAMO in Figure 13. While the reaction seems to occur at almost constant viscosity for the AMO solution, the TRIAMO solution exhibits an increase in viscosity. However, the curvature observed for both solutions is different from that observed at the same times with precursors such as tetraalkoxysilanes in conditions leading to gelation of the system. This kind of curve may indicate formation of stable sols. We do not observe the gelation step before condensation in these studies.

Discussion

Engelhardt et al.[26] have studied the polymerization of silicates in aqueous media. In acidic solution the polycondensation reaction proceeds following different steps leading to the formation of dimers, linear trimers, cyclic trimers, and cyclic tetramers. At low pH the polycondensation of TMOS in methanol and of TEOS in ethanol gives a broad distribution of products,[27] monomeric species disappearing before gelation of the solution.[16] On the other hand, monomeric species are present in the gel structure when the polymerization occurred at a basic pH. This behavior was explained by the existence of depolymerization reactions which readily occur in an aqueous medium.[28] These depolymerization reactions give an oligomer distribution broader than those obtained in acidic solutions.[29] The polymerization of trifunctional monomers such as methyltrimethoxysilane leads in aqueous solution to the formation of a gel, the gelation time decreasing appreciably with an increasing concentration of base.[30] This confirms our own experiments carried out on the propyltrimethoxysilane in methanol for which we observed a similar behavior.[31]

The facts mentioned above seem to contradict some of the results found for AMO and TRIAMO whose polycondensation reaction occurs in a basic medium as shown in a previous work.[15] Monomeric species are totally consumed; the average degree of condensation is high without gelation of the solution where the initial concentration of monomer is nevertheless important; finally we obtained a narrow distribution of the oligomers. However the conditions of the synthesis are quite different from those used in the works mentioned above. They depend on the nature of the monomer employed (trifunctional, high basicity) and on the conditions of the synthesis (solvent methanol, high concentration of monomer). Therefore one has to compare carefully the results obtained for AMO and TRIAMO with data obtained from the literature where the conditions mentioned above are only partially present.

In the first part we will discuss the growth model of the particles, in the second part the stability in time of the sol obtained, and in the third one the effect of the organic substituent on the growth process and on the structure of the particles.

(a) Growth Model. *(a.1) Statistical approach of the polymerization*: It can be done applying the theory of Flory–Stockmayer. Flory[32] takes the two following hypothesis: all reactive sites have the same probability to react regardless of the structure and the size of the

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(27) Kelts, L. W.; Amstrong, N. J. *Better Ceramics through Chemistry III*; *Mater Res. Soc. Symp. Proc.* **1988**, *121*, 519.

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(32) Flory, P. J. *Principles of polymer chemistry*, Cornell University Press: Ithaca, NY, 1953.

oligomers they belong to; the polymerization proceeds only by intramolecular reaction. This means that no rings are built. This hypothesis is particularly justified with solution having high concentration of monomer, the probability of intramolecular reaction increasing with the dilution of the solution.

Applying the theory of Flory–Stockmayer to a trifunctional alkoxysilane, one gets a size distribution given by:

$$\%\mathrm{Si}(n) = 300\,(2n)!(2r/3)^{n-1}([3-2r]/3)^{n+2}(n+2)!^{-1}(n-1)!^{-1} \qquad (8)$$

where $\%\mathrm{Si}(n)$ is the percentage of silicon atoms belonging to an oligomer containing n silicon atoms and r is the average degree of condensation of the system which can be obtained from the ^{29}Si NMR data. The size distribution $\%\mathrm{Si}(n)$ cannot be obtained experimentally by this method. However we can calculate the theoretical size distribution of the silicon of type T_0, T_1, and T_2. It was obtained considering only linear oligomers containing less than five silicon atoms and for average degrees of condensation of the solution ranging between 0 and 0.25. This calculation is valid only for the first minutes of the reaction where no rings and no T_3 type silicons atoms are present as shown by ^{29}Si NMR measurements. Furthermore, for $r = 0.25$, $\sum_{n=1}^{4}\%\mathrm{S}_i(n)$ is bigger than 98% which justifies to consider only oligomeric units of this size.

The theoretical distribution and the experimental distribution of the T_0, T_1, and T_2 are compared in Figure 14. While the concentration of monomeric species follows the theoretical concentration, some distortions are observed for silicons of type T_1 whose concentration is more important than predicted by the model. Consequently, T_2 type silicons are found in a smaller concentration. Differences observed between the model and the experiment can be probably explained by a smaller reactivity of the dimeric species and oligomers of bigger size compared with monomeric species.

(*a.2*) *Growth model*: Calculations based on ^{29}Si NMR results show that the growth mechanism is not of the monomer–cluster type since the size of the particles is increasing exponentially after the monomer has been totally consumed. A growth mechanism of type cluster–cluster gives usually open structures which have not been observed in the final state of the sol.

The concentration variations of T_0 and T_1 (T_2 and T_3, as a function of the average condensation degree of the silicon centers which can be expressed by $r = 1/2\,(\%T_1 + 2\,\%T_2 + 3\,\%T_3)$ are shown in Figure 15 for AMO and in Figure 16 for TRIAMO. The observed variations are exactly the same for both precursors which means that oligomers obtained by polycondensation of AMO or TRIAMO have a similar distribution of T_0, T_1, T_2, and T_3 for the same degree of condensation. Consequently, particles of the solutions AMO and TRIAMO have probably similar structures for the same degree of condensation. However as can be seen on the plots, the two precursors do not reach the same limiting degree of condensation. The average degree of condensation for AMO is roughly $r = 1.4$ while the value obtained for TRIAMO is 1.1. This last result might appear to contradict the SAXS measurements which show that the TRIAMO solution gave slightly bigger particles. This can be explained by considering the possible existence of ring formation when the system reaches a sufficient degree of condensation. In the case of AMO an increase of concentration of T_3 silicons after $r = 1.2$ may indicate the existence of more intramolecular condensation reactions which tend to densify the oligomers and consequently tend to reduce their size. Objects formed by condensation of the precursor TRIAMO do not reach a degree of condensation sufficient to create large quantity of intramolecular condensation reactions. Therefore shrinkage of the particles formed is more important for AMO than that existing in the case of TRIAMO.

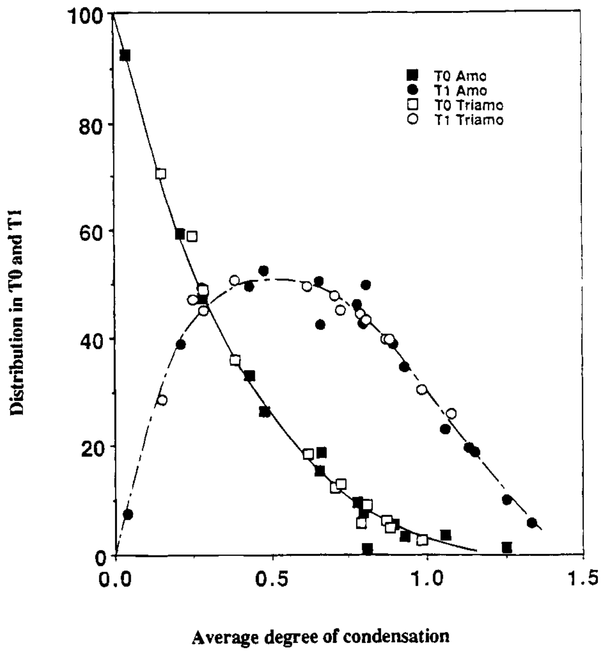

Figure 15. Intensity variations for AMO and TRIAMO of T_0 and T_1 as a function of the average degree of condensation (obtained from the ^{29}Si NMR).

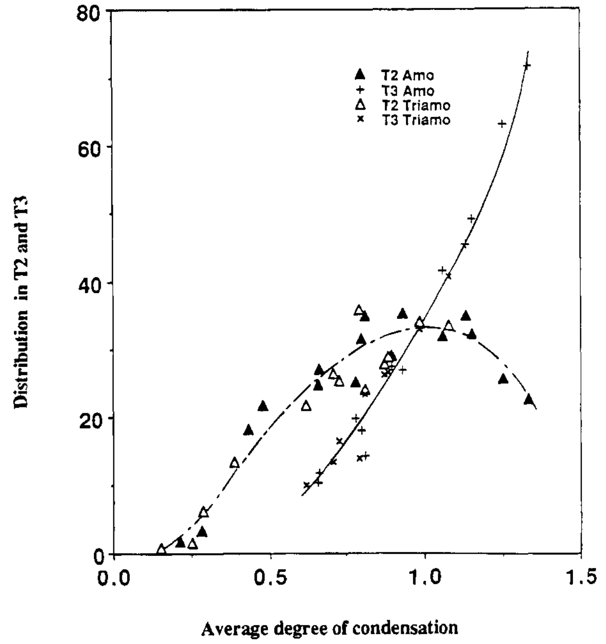

Figure 16. Intensity variations for AMO and TRIAMO of T_2 and T_3 as a function of the average degree of condensation (obtained from the ^{29}Si NMR).

Although TRIAMO particles have a smaller condensation degree, they have a bigger size corresponding to a more branched structure. A statistical study done by

Zarzycki[33] shows that the growth process of the polymer chains is limited by their overlapping, which leads to intramolecular condensation reactions. According to West et al.[34] the formation of chains is favored when the number of silicon atoms of the chain is small. This was experimentally proved by Klemperer and Ramamurthi[28] and also by Orcel and Hench,[35] who found the chains formation growth model was more consistent with the structure of the oligomer before gelation than the rings formation growth model. Hench and West[36] report calculations done by Davis. They compare formation enthalpies of chains and rings which have the same number of silicon atoms. Formation of rings is favored when the number of silicons is greater than 4. Brinker and Scherer[37] underline that rings containing two or three silicon tetrahedra are not major species of the polymerization when operated in normal synthesis conditions ($H_2O/Si > 2$ for a tetrafunctional precursor and $pH < 12$). However rings containing four silica tetrahedra are present in a large concentration in numerous synthesis because of their quasi-stability. Our ^{29}Si NMR measurements show that rings containing three silica tetrahedra are not present during the polycondensation of AMO and TRIAMO. Presence of rings of four silica tetrahedra were observed; they belong to cubic octamers whose concentration appears not to be negligible considering the intensity of the corresponding resonance peak. However we were not able to use ^{29}Si NMR measurements to determine whether or not rings of four silica tetrahedra alone are present during the polycondensation. Raman spectroscopy experiments might give more information concerning this point.[45]

(a.3) Stability of the sol: At high pH values the base-catalyzed solutions lead to the formation of monodisperse spherical particles[38] whose diameter ranges up to several mm. SAXS measurements show that their structure is compact.[37] According to Bogush and Zukoski[39] small homogeneous particles appear in the solution acting as nucleation centers. Though these particles bear a negative charge, they are unstable and lead to formation of aggregates due to their small size (smaller than 10 nm). Our results show that small particles produced by polycondensation of AMO or TRIAMO are stable against gelation.

The stability of a sol can be considered as the ability of the particles to approach each other close enough to form permanent associations. This problem refers usually to the DLVO (Derjaguin, Landau, Verwey, and Overbeek).[40,41] Only van der Waals interactions and electrostatic repulsions created by charges borne on the particles are taken into account to explain whether the particles aggregate or not during their collisions. Repulsive forces depend on the two kinds of ions belonging to the double layer which for one kind give this charge to the particle and for the second kind act as counterions surrounding the particle. For a silicon oxide particle in an aqueous medium, the charge borne by the particle depends on the pH of the solution. Work done by Rousseau shows the existence of the following equlibrium which occurs during the synthesis of AMO and TRIAMO particles:

$$-CH_2NH_2 + H{-}OSi{\equiv} \rightarrow -CH_2\,NH_3^+ + {}^-OSi{\equiv} \qquad (VI)$$

Particles of AMO or TRIAMO can be seen as a group of silicon tetrahedra with organic substituents being directed toward the outside because of their steric hindrance and because of the small size of the particle. This creates an organic envelope around the particle which can prevent particles from aggregating. It is believed to be due to a steric barrier and to an electrostatic barrier created by the partial protonation of the amines.[15] Furthermore, molecules of solvent (water, methanol) probably surround the particles due to hydrogen bonding with the amines. Aggregation is thermodynamically unfavored. The approach of the particles lead to an overlapping of the organic substituents reducing the freedom of motion of chains and consequently the entropy of the system. Considering enthalpic factors, the approach of two particles would lead to the desorption of solvent molecules which costs energy. Isolation of the particles lead to intramolecular condensation reactions. Transformation of the T_3 region of the ^{29}Si NMR spectra can be interpreted as resulting from the condensation reaction of residual T_2 silicon atoms whose condensation leads to changes in the distribution of length and angles of the Si−O−Si bond.

(b) Influence of the Organic Substituent. AMO and TRIAMO precursors polymerise following the same polycondensation path. However, as seen by ^{29}Si NMR spectroscopy measurements the polycondensation kinetics of these two monomers are quite different. AMO polymerizes much faster giving a more compact structure than TRIAMO. These different behaviors can be discussed in term of reactivity of the silanols, steric factors, and hydrogen bonding.

As shown by ^{29}Si NMR spectroscopy data observed of Figure 1a,b and listed in Table 1, silanol groups borne by AMO are shifted toward higher fields than those belonging to TRIAMO. On the basis of this observation, one can conclude that silanols borne by AMO have a more acidic character than silanols borne by TRIAMO. This higher acidic character probably leads to a higher concentration of silanoates which are an intermediate species involved in the condensation reaction. Therefore one can expect higher rate of condensation.

Bulkier organic substituents slow down the condensation reaction as found by Voronkov.[20] Using a bulkier substituent as in TRIAMO can result in interfering with the approach of silanoate groups and consequently the condensation reaction. Inductive effects can be considered negligible considering the similar nature of substituents borne by AMO and TRIAMO. Calculations based on the partial charge model[42] show almost identi-

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cal values of the positive charge borne by the silicon atom for both precursors.[15]

The existence of strong interactions of silanols and amines belonging to the organic substituent was illustrated for these systems by potential and conductivity measurements.[15] Furthermore we can suppose the existence of hydrogen bonding between amines borne by the organic substituent with water, methanol, or themselves. All these interactions should lead to higher dynamic viscosity values of the solution of TRIAMO compared to the solution based on the precursor AMO as was observed. Differences in viscosity lead to differences in diffusion coefficients of the species present in solution and consequently to different reaction rates. Furthermore interactions of amines with silanols as postulated by Plueddemann[43,44] could result in hindering silanols in their condensation reactions with other silicon centers.

Conclusion

^{29}Si NMR spectroscopy experiments have given useful information concerning the polycondensation pathway of two aminosilanes: (3-aminopropyl)trimethoxysilane and ((trimethoxysilyl)propyl)diethylenetriamine. Hydrolysis in methanol of these trimethoxysilanes is followed by a complete depletion of the monomer concentration within the first steps of the polycondensation. Condensation occurs from the beginning simultaneously to hydrolysis. In the first moments of the reaction, a rapid condensation and a low silanol concentration in the presence of a majority of methoxy groups indicate a condensation reaction proceeding by methanol elimination rather than by water release. Distribution of the T_0, T_1, T_2, and T_3 as a function of the average condensation degree complemented with measurements of the particles size (small-angle X-ray scattering) and calculation of the average number of silicon atoms per particle as a function of the time leads us to think the following growth mechanism is suitable.

Small oligomers are formed which are less reactive toward condensation than the monomeric species. Following a condensation mechanism of type cluster–cluster, these small oligomers condense further leading to larger oligomers with a branched structure. Due to electrostatic repulsion forces and to a protective organic layer formed by the organic substituent and the solvent, these particles become stable against gelation. Therefore there is a decrease of the intermolecular condensation reactions favoring intramolecular condensation reactions whose existence contribute to a densification of the oligomers.

Differences in reaction kinetics and differences in the structures obtained are observed for both precursors. They can be explained in term of steric factors, acidity of the silanols formed, and existence of different types of hydrogen bonding between amines, silanols, and solvent.

Acknowledgment. The authors are indebted to T. Heinrich for the SAXS measurements and fruitful discussions and acknowledge Procope Program and Prof. H. Schmidt, director of ISC (Würzburg, Germany) for financial support.

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