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INVESTIGATION OF HYDROLYSIS AND CONDENSATION IN ORGANICALLY MODIFIED SOL-GEL SYSTEMS: ^{29}SI NMR AND THE INEPT SEQUENCE[†]

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ABSTRACT

The spectral editing properties of the ^{29}Si NMR INEPT heteronuclear transfer experiment have been utilized for the identification and characterization of hydrolysis and initial condensation products in methyltrimethoxysilane (MTMS) sol-gel materials. ^{29}Si NMR assignments in MTMS are complicated by a small spectral dispersion (~0.5 ppm) and two different ^{29}Si-^{1}H J couplings. By using analytical expressions for the INEPT signal response with multiple heteronuclear J couplings, unambiguous spectral assignments can be made. For this organomethoxysilane the rate of hydrolysis was found to be very rapid and significantly faster than either the water or alcohol producing condensation reactions. The hydrolysis species of both the MTMS monomer and its initial T^1 condensation products follow statistical distributions that can be directly related to the extent of the hydrolysis reactions. The role of the statistical distribution of hydrolysis products on the production and synthetic control of organically modified sol-gels is discussed.

INTRODUCTION

Development of new highly crosslinked materials from organically modified alkoxysilanes continues to be an area of active research. A basic understanding of the kinetics and chemistry of the hydrolysis and condensation reactions responsible for the polymerization will allow the rational design of new and improved materials. Since hydrolysis produces the reactive silanolic species essential in subsequent condensation reactions, the relative concentrations and rate of formation of the hydrolyzed components should play an important role in the final structure of the sol-gel material. Hydrolysis and condensation chemistry in various sol-gel systems has been investigated using high resolution ^{29}Si NMR, with the majority of these investigations concentrating on tetraalkoxysilanes. The effect of organic modifications on the hydrolysis and condensation reactions is still unclear, due to the limited number of studies on organically modified alkoxysilanes[1-6].

Two difficulties encountered in these ^{29}Si NMR investigations are the *identification* and *quantification* of the different silicon environments as the reaction progresses. This is especially true in some organically modified alkoxysilanes such as MTMS where the small spectral dispersion makes even the assignment of the monomer hydrolysis products difficult. The large downfield changes in chemical shift with increasing number of hydroxyls observed in tetraalkoxysilanes, is altered in organically modified alkoxysilanes resulting in smaller changes in chemical shifts or even upfield variations with increasing number of hydroxyls [7]. This can lead to chemical shift changes being different from the expected downfield progression with hydrolysis.

It is important that experimental techniques that allow for the correct assignment of ^{29}Si NMR resonances be developed. In this note the spectral editing powers of the standard INEPT

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sequence are used to investigate the distribution of hydrolysis species in the monomer (T^0) and initial condensation (T^1) products in methyltrimethoxysilane (MTMS).

EXPERIMENTAL

A stock solution of 2.24 M MTMS in MeOH was prepared and analyzed for hydrolysis and condensation contaminants prior to use by ^{29}Si NMR. Different H_2O/Si molar ratios (R_w) were investigated by adding chilled H_2O (273K) to the stock solution. Solutions were acidified with 1 N HCl such that the final acid concentrations were 1.58 mM, giving a nominal pH of 2.8. To reduce the ^{29}Si spin-lattice relaxation times in kinetic investigations chromium acetylacetonate ($Cr(acac)_3$) was added for a final concentration of 15.7 mM. For the INEPT experiments, no $Cr(acac)_3$ was added, as this severely degrades the performance of the pulse sequence. All ^{29}Si NMR spectra were obtained at 79.49 MHz on a Bruker AMX400 spectrometer. Kinetic investigations of the different silicon species were performed using the 10 mm broadband probe and standard inverse gate pulse sequences to reduce NOE effects. Spectra were obtained using 2-8 scan averages, an 18 s relaxation delay, and a 20 μs $\pi/2$ ^{29}Si pulse. The INEPT experiments for resonance assignments were obtained using a 5 mm probe, 8 - 16 scans, a 2 s recycle delay. For the INEPT sequence the interpulse delay τ was 60.2 ms, while the refocussing delay Δ was varied as described in the text.

RESULTS AND DISCUSSION

The inverse gated ^{29}Si NMR spectra of the stock MTMS solution at 233 K, pH = 2.8 with 1.5 molar equivalents of water as a function of time is shown in Figure 1. At this reduced temperature only the monomer T^0, the initial condensation T^1 and associated hydrolysis products are present. The uncondensed silicon T^0 species resonate between δ = - 37 and -39 ppm, while the singly condensed T^1 species were observed between δ = -46 and -47.5 ppm. The hydrolysis products of both the monomer and condensed species show a very narrow chemical shift dispersion making resonance assignments challenging.

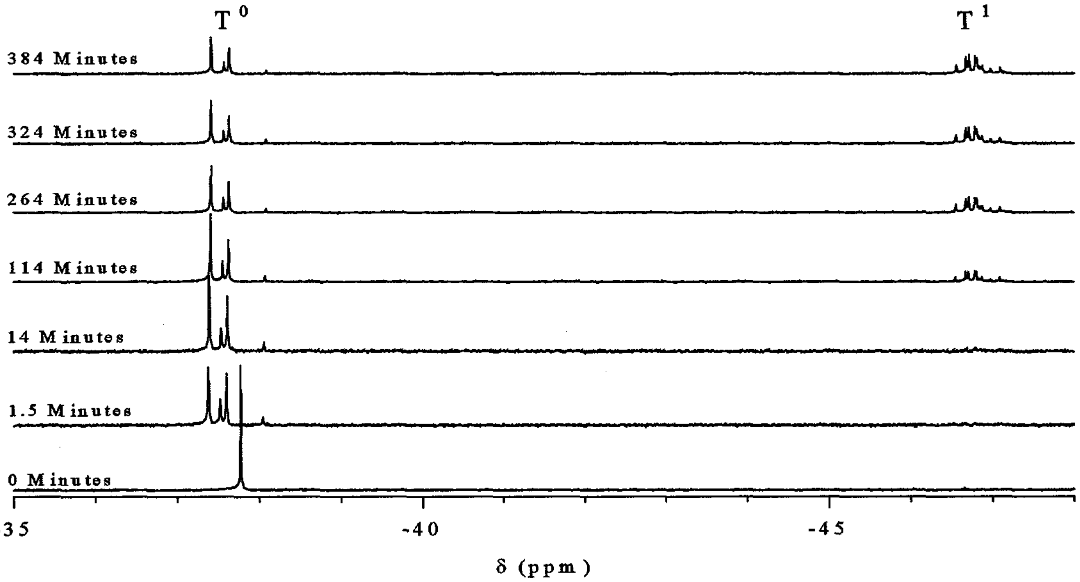

Figure 1. ^{29}Si NMR spectra of 2.24 M MTMS solution in MeOH, 233 K, pH = 2.8, with a molar water ratio of R_w = 1.5 as a function of hydrolysis time.

The response of the INEPT pulse sequence is complicated by the presence of different J(Si,H) couplings in MTMS. In order to identify the hydrolysis products of MTMS, the coupling between the methyl protons and the silicon, J(Si, H) = 8.3 Hz, is significantly different than the scalar coupling between the methoxy protons and the silicon, J(Si, H) = 3.9 Hz. The influence of heteronuclear and homonuclear couplings on the response of the INEPT pulse sequence has previously been investigated [8]. If proton-proton homonuclear couplings are zero or negligible, the intensity of the silicon signal following the INEPT pulse sequence is [7,8]

$$E_{\mathrm{INEPT,dec}}(\tau,\Delta) = \frac{\gamma_S}{\gamma_I} \sum_{p} \sin[\pi\tau J(I,S^p)] \sin[\pi\Delta J(I,S^p)] \prod_{q,q\neq p} \cos[\pi\Delta J(I,S^q)] \qquad (1)$$

where the summations p and q run over all abundant nuclei (i.e. ^{1}H) J coupled to the insensitive nuclei (i.e. ^{29}Si). The variation of the INEPT sequence as function of the refocusing delay Δ for MTMS is shown in Figure 2 for both the hydrolyzed monomer T^0 species and the hydrolyzed condensed T^1 species. The signal response as a function of Δ is complex, allowing the identification and assignment of the different hydrolyzed species. For example, Figure 3 shows an expansion of the T^0 NMR spectra for different refocusing delays. In 3a (Δ = 20 ms) all the hydrolyzed species show a positive signal intensity as expected from Figure 2a. Figure 3b (Δ = 220 ms) and 3c (Δ = 90 ms) quickly allow the assignment of the fully hydrolyzed T_3^0 and singly hydrolyzed T_1^0 species. Assignment of the unhydrolyzed T_0^0 and doubly hydrolyzed T_2^0 were originally based on experiments with variation in water content [7], but are confirmed in 3d (Δ = 350 ms) where only T_2^0 and T_3^0 are expected to have positive signal intensity. Note that if the peak assignments had been based on arguments of downfield chemical shift with increasing numbers of attached hydroxyls, the assignments for the monomer MTMS hydrolyzed species would be incorrect.

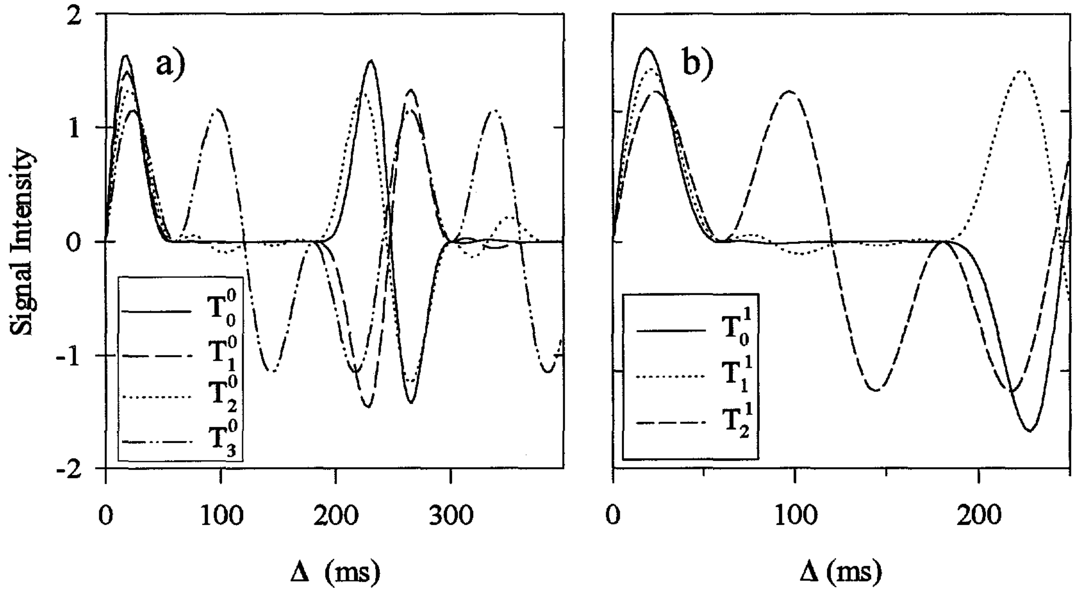

Figure 2. Theoretical signal intensity for the refocussed, proton decoupled INEPT pulse sequence as a function of the final refocusing delay Δ, for a) the monomer T^0 and b) the singly condensed T^1 hydrolyzed species. Intensities were obtained using Eqn. (1) assuming two different couplings for MTMS, J(Si,H) = 8.3 Hz for the methyl protons, and J(Si,H) = 3.9 Hz for the methoxy protons. The interpulse delay τ of 60.2 ms was optimized for the methyl coupling, $\tau_{\mathrm{opt}} = 1/2J$(Si,H), since all species in MTMS contain this coupling.

In Figure 4 the NMR spectra of the T^1 region is shown at three different refocusing delays Δ. Spectra obtained using an inverse gate pulse sequence (not shown) allowed pairs of resonances that had the same signal intensity, plus identical variation with increasing water content to be assigned to T^1 silicons environments in the same dimer molecule. Using this information, plus the predicted signal intensity variation (Figure 2b) for the condensed species all of the hydrolyzed condensed species were assigned. These assignments are given in Table 1. It is interesting to note that the T_1^1 environment gives rise to two distinct resonances due to the two possible diastereoisomers occurring for the chiral residues in the $T_1^1 - T_1^1$ dimer, denoted as D and D'. Differentation of diasterioisomers have been observed in polymethylhydrosiloxanes [9].

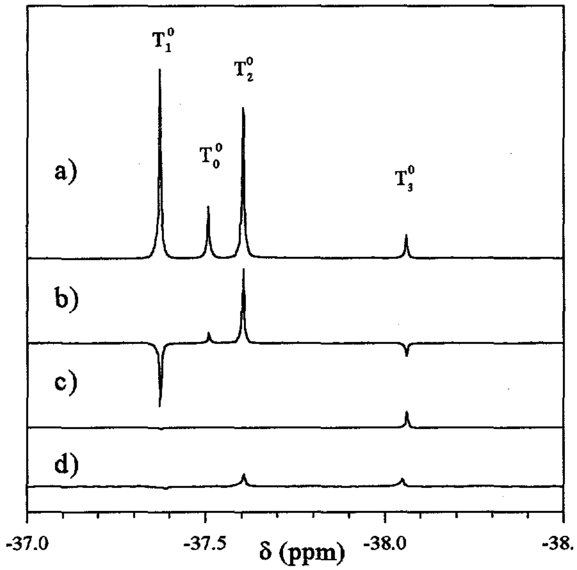

Figure 3. ^{29}Si INEPT spectra for a 2.24 M MTMS, 233 K, pH = 2.8, R_w = 1.5 solution at different refocusing delays Δ: a) 20 ms, b) 220 ms, c) 90 ms, d) 350 ms. Comparison of the observed signal intensity to Figure 2 allows for the unambiguous assignment of the hydrolyzed species.

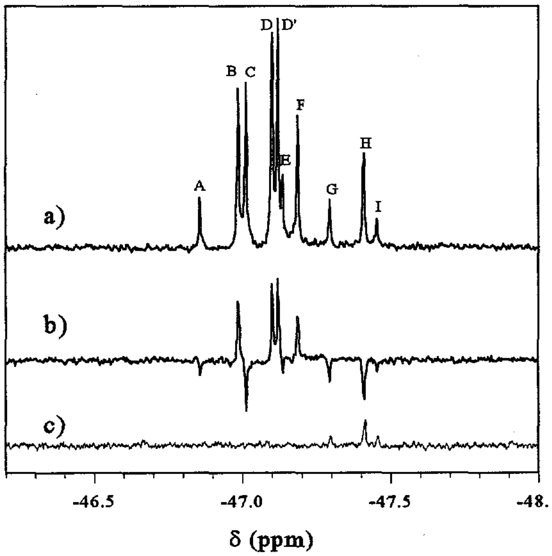

Figure 4. ^{29}Si INEPT spectra of the T^1 region for the same MTMS in Figure 3. Spectra for different refocusing delays are shown: a) Δ = 20 ms, b) Δ = 220 ms and c) Δ = 90 ms. Inspection of Figure 2 allows the identification of the hydrolyzed T^1 as detailed in Table 1.

Table 1. ^{29}Si NMR resonance assignments for T^1 hydrolysis species. Italicized correspond to the observed resonance.

	$-[T_0^1]$	$-[T_1^1]$	$-[T_2^1]$
$-[\mathrm{T}_0^1]$	A	C	G
$-[\mathrm{T}_1^1]$	B	D D'	H
$-[\mathrm{T}_2^1]$	E	F	I

Inspection of Figure 1 shows that acid-catalyzed hydrolysis of the monomer MTMS species is very rapid at 233 K and is significantly faster than the condensation rate. Since the hydrolysis reaction is essentially complete within the first few minutes, monitoring the appearance of the various hydrolyzed species by NMR overtime is not possible, but allows the lower limit for the hydrolysis rate to be estimated at 0.01 M^{-1} s^{-1}. However, the ability to assign the individual ^{29}Si NMR resonances for both the monomer and singly condensed species does allow the population distributions to be evaluated. These populations distributions have been shown to be very sensitive to the rates of hydrolysis, allowing information about the hydrolysis kinetics to be determined .

It has been shown that for hydrolysis in alkoxysilanes, both *reversible* or *irreversible* models predict relative populations of hydrolyzed species that follow a binomial distribution, if the relative ratio of the hydrolysis rates for subsequent reactions are governed purely by statistical processes [6]. This implies that the rates for hydrolysis or esterification (reverse hydrolysis) are directly proportional to the number of reactive groups within a molecule. For example, the rate for the first hydrolysis reaction (MTMS to singly hydrolyzed) will be 1.5 and 3 times faster than the subsequent 2nd and 3rd hydrolysis reactions for the MTMS monomer. A similar trend is observed for the esterfication reaction.

If the observed number of SiOH bonds surrounding a silicon is governed entirely by statistics (not influenced by the chemical identity) then the concentration of the various hydrolysis products can be defined by a binomial distribution. For hydroxyl groups distributed randomly over n Si-O bonds the population or probability of silicons having ν hydroxyl groups, $P(\nu,n)$ is given by [6]

$$P(\nu,n) = C_{\nu}^{n} p^{\nu} q^{n-\nu} \tag{2}$$

where p gives the probability of hydrolysis for a single bond, $q = 1 - p$ defines the probability for an alkoxy SiOR bonds, and C_{ν}^{n} is the binomial coefficient. The probability p is equivalent to the extent of reaction for hydrolysis (ε), and defines the probability of a Si-O bond delonging to a hydroxyl. For the monomeric T^0 hydrolysis products in MTMS, the extent of reaction is given by

$$\varepsilon = \frac{[\mathrm{SiOH}]}{[\mathrm{Si-O}]} = \frac{[\mathrm{Si-OH}]}{[\mathrm{Si-OCH_3}]_0} = \frac{[\mathrm{T}_1^0]+2[\mathrm{T}_2^0]+3[\mathrm{T}_3^0]}{3[\mathrm{T}_0^0]_0} \tag{3}$$

where $[\mathrm{T}_1^0], [\mathrm{T}_2^0]$, and $[\mathrm{T}_3^0]$ are the observed concentrations of the various hydrolysis species and $[\mathrm{T}_0^0]_0$ is the initial concentration of the unhydrolyzed monomer. For MTMS there are three possible sites for hydrolysis ($n = 3$). With Eqn. 2 the distribution for each of the hydrolyzed monomer species can be easily evaluated. The extent of reaction for the T^1 condensed species is defined as

$$\varepsilon = \frac{[\mathrm{T}_1^1]+2[\mathrm{T}_2^1]}{2\sum\limits_{i=0,2}[\mathrm{T}_i^1]} \tag{4}$$

where $[\mathrm{T}_0^1]$, $[\mathrm{T}_1^1]$ and $[\mathrm{T}_2^1]$ are the observed concentrations of the hydrolyzed singly condensed species, allows Eqn. 2 to predict the distribution in the T^1 hydrolyzed species.

Figure 5 shows the distribution of the hydrolyzed species from MTMS and its singly condensed dimeric derivatives for different extents of reaction. The hydrolyzed T^0 species are well described by a simple binomial distribution for the entire range of extent of reaction ε. The condensed T^1 species also follow the binomial distribution for the range of ε observed. The ε for the T^0 and T^1 species were nearly identical regardless of the water concentrations studied.

Conclusions

Hydrolysis of MTMS is extremely rapid (< 0.01 M^{-1} s^{-1}), and is over a hundred times more rapid than either water or alcohol producing condensations. From the analysis of the concentration profiles, information about the relative hydrolysis rates in the MTMS monomer and single condensed dimer species can be determined. It has been shown that the hydrolysis reaction is reversible in MTMS [6]. The observation of binomial distributions for both the T^0 and T^1 hydrolyzed products suggest that the ratio of rates for consecutive hydrolysis reactions and consecutive esterfication reactions are governed by simple statistical arguments. The similarity of ε between T^0 and T^1 species suggest equilibrium partitioning of H_2O between monomer and condensed species.

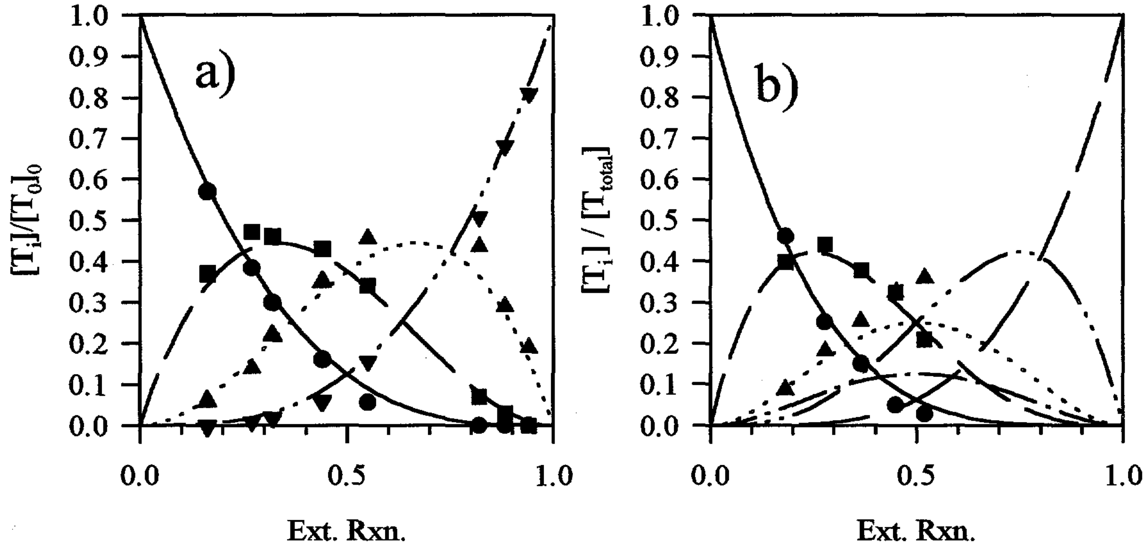

Figure 5. Experimental and theoretical concentration ratios for a 2.24 M MTMS (pH = 2.8) for different extents of reactions. Theoretical lines were obtained assuming a binomial distribution. a) Concentration ratios for the hydrolyzed monomer $[T_i^0]/[T_0^0]_0$, theoretical (——) $i = 0$, (— —) $i = 1$, (••••) $i = 2$, (— •• —) $i = 3$, experimental (●) $i = 0$, (■) $i = 1$, (▲) $i = 2$, (▼) $i = 3$. b) Concentration ratios for selected species in the hydrolyzed dimer $[T_i^1 - T_j^1]/[T^1 - T^1]_{total}$, theoretical (——) $i = j = 0$, (— — —) $i = 0, j = 1$, (••••) $i = j = 1$, (—•• —) $i = 0, j = 2$, (—••—) $j = 2$, $j = 1$, (— —) $i = j = 2$, experimental (●) $i = j = 0$, (■) $i = 0, j = 1$, (▲) $i = j = 1$.

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