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Acetone-induced polymerisation of 3-aminopropyltrimethoxysilane (APTMS) as revealed by NMR spectroscopy

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We followed the reactivity of acetone with 3-aminopropyltrimethoxysilane, a potential organosilane coupling agent, by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. Selective 1D and 2D-edited NMR experiments significantly contributed to simplify the spectral complexity of reaction solution and elucidated molecular structures within progressive reaction phases. The course of the 3-aminopropyltrimethoxysilane reaction with acetone was shown by a progressive decrease of both reactants, and a concomitant appearance of water and methanol, due to formation of imine and hydrolysis of alkoxysilane groups, respectively. The occurrence of multiple siloxane linkages in a progressively larger cross-linked macromolecular structure was revealed by DOSY-NMR experiments and new signals in ^{29}Si-NMR spectra at different reaction times. The NMR approach described here may be applied to investigate the reactivity of other γ-aminopropylalkoxysilanes and contribute to define procedures for the preparation of silica-based materials. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: 3-aminopropyltrimethoxysilane (APTMS); polymerisation; NMR; DOSY; selective excitation; HMQC-TOCSY; DEPT-HMQC; ^{1}H; ^{13}C; ^{29}Si

Introduction

A large attention has been recently devoted to the reactivity of several classes of organosilanes molecules on which research studies and commercial applications were produced, especially in engineering, electronic and photovoltaic domains.[1–3] Organosilanes have become attractive and promising molecules, prevalently in the fast-growing field of advanced materials, because of their activity as adhesion promoters, coupling agents and surface primers.[3,4]

These molecules can be employed to bind specific functional groups on desired substrates, such as polymeric thin films, in order to modify the reactivity/affinity of surfaces and confer to them additional functional properties.[5–7] In particular, γ-aminopropylalkoxysilanes, such as 3-aminopropyltrimethoxysilane (APTMS) and aminopropyltriethoxysilane, show an enhanced reactivity for an efficient use as multifunctional coupling agents.[8–10] Aminoalkoxysilanes may react with ketones to produce a progressive condensation of silane silanols and form siloxanes by Si–O–Si linkages.[9,11,12] The reaction involves the condensation of a ketone with the γ-aminopropylalkoxysilane amino group and formation of an imine intermediate. Water molecules are released during the condensation and promote the hydrolysis of alkoxysilane groups,[12] thereby exposing silane silanols, which condense with each other in siloxane linkages.[8,13,14] Polycondensation of bridged organosilane precursors appears promising for the production of next-generation functional materials.[2,3,15,16]

The objective of this study was to apply 1D and 2D multinuclear and DOSY NMR spectroscopy to elucidate the various phases involved in the hydrolysis and condensation of APTMS induced by acetone in chloroform. In fact, the simplification of spectral complexity and identification of reaction products by two edited hetero-correlated 2D experiments, such as in ^{1}H-^{13}C HMQC-TOCSY and DEPT-HMQC, allowed to enlighten the different steps in the reaction course. Moreover, the NMR approach described here may be applied to investigate the reactivity of other γ-aminopropylalkoxysilanes and contribute to define procedures for the preparation of silica-based materials.

Experimental

Samples preparation

Samples for NMR experiments were prepared by dissolving 2.82 mmol of acetone (Carlo Erba, LC grade, Italy) in 350 μl of deuterated chloroform-*d1* (Eurisotop, 99.8% D, $H_2O < 0.01\%$, France), containing 1% (v/v) of TMS as internal standard. Then, 0.94 mmol of APTMS (Sigma-Aldrich, 97%, Italy) were added to this solution in order to start a reaction on the basis of a 1 : 3 APTMS/acetone stoichiometric relationship. Immediately after dissolution of APTMS, the sample was stirred for 30 s and transferred into a stoppered borosilicate glass 5 mm NMR tube, where the reaction was allowed to occur at 298 ± 1°K and monitored by ^{1}H and ^{13}C NMR spectroscopy for 15 days. The reaction was also followed with ^{29}Si NMR spectroscopy by transferring an analogously prepared reaction mixture into a polytetrafluoroethylene (PTFE liner

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combined with a 5 mm adapter, 8 in., PTFE-5 mm-kit, Wilmad labGlass, USA) NMR tube.

In order to evaluate the rapid initial changes of NMR signals due to silanol condensation, an additional NMR sample was prepared, whereby acetone addition was reduced to reach a 1 : 1 APTMS/acetone ratio and allowed a slower progressive disappearance of precursors and appearance of reaction products. All samples for NMR analyses were prepared in duplicates.

NMR experiments

A 400 MHz Bruker Avance spectrometer (Bruker Biospin, Rheinstetten, Germany), equipped with a 5 mm Bruker broadband inverse probe, working at the ^{29}Si, ^{13}C and ^{1}H frequencies of 79.46, 100.62 and 400.13 MHz, respectively, was employed to conduct all liquid-state NMR measurements at 298 ± 1°K. Acquisition of 22 ^{1}H-NMR spectra was obtained at 0.25, 0.55, 0.78, 1.27, 1.83, 3.07, 7.57, 11.8, 16.03, 20.27, 24.5, 30.75, 36.98, 43.22, 49.45, 66.02, 90.42, 162, 217.42, 231.58, 287.58 and 351.58 h after reaction start. ^{13}C spectra were immediately acquired after completion of each ^{1}H-NMR spectrum. Likewise, a sequence of 22 ^{29}Si NMR spectra was recorded, for the reaction mixture loaded in PTFE NMR tube, at 0.25, 0.73, 1.05, 1.55, 2.32, 3.58, 5.85, 8.12, 12.37, 16.63, 20.90, 27.15, 33.4, 39.65, 46.9, 53.17, 68.42, 140.42, 190.42, 242.42, 260.42 and 334.42 h after reaction start. Acquisition of ^{1}H-NMR spectra comprised 2 s of thermal equilibrium delay, 5.5 μs 45° pulse length, 32 768 time domain points and 50 transients (4 min per acquisition). ^{13}C NMR spectra were acquired by applying a quantitative inverse gated pulse sequence, including 80 μs length Waltz-16 decoupling scheme with about 15.6 dB of power level attenuation, 5 s of initial delay, 8.5 μs 45° pulse length, 32 768 time domain points and 100 transients (20 min per acquisition). ^{29}Si spectra were acquired by a DEPT pulse sequence optimised for a $^{2}J_{SiH}$ of 7 Hz and a proton DEPT pulse of 45° that represents the most efficient condition for ^{29}Si nuclei, which are geminally correlated to 2 protons (−CH_2−Si−).[17] ^{29}Si-NMR spectra were acquired with 2 s of thermal equilibrium delay, 17.5 μs 90° pulse length, 65 538 time domain points and 128 transients (18 min per acquisition). FID were multiplied by an exponential weighting function equivalent to a line broadening of 5, 2 and 0.1 Hz, respectively, for ^{29}Si, ^{13}C and ^{1}H, whereas no zero filling was performed.

^{1}H DOSY NMR experiments were conducted by choosing a stimulated echo pulse sequence with bipolar gradients, combined with two spoil gradients and an eddy current delay. This sequence reduced signal loss due to short spin–spin relaxation times that were significantly enhanced in the case of reaction products. The acquisition was conducted by setting 2100 μs long sine-shaped gradients (δ), which were linearly ranging from 0.674 to 32.030 G cm^{-1} in 32 increments, and selecting a diffusion delay of 0.1 s (Δ) between encoding and decoding gradients.

2D homonuclear and heteronuclear spectra (2048 points in F2 dimension and 256 experiments in F1 domain) allowed characterisation of unknown reaction products. Both ^{1}H−^{1}H COSY and TOCSY were executed with 48 scans, 2 s of thermal equilibrium delay and 16 dummy scans. For TOCSY experiments, a trim pulse of 2500 μs and a mixing time of 0.08 s were applied. ^{1}H−^{13}C HSQC experiments were acquired with a trim pulse of 1 ms, and experimental parameters were optimised for a $^{1}J_{CH}$ short range of 145 Hz, whereas HMBC experiments were optimised for a long-range J_{CH} of 6.5 Hz.

The HMQC-TOCSY is a hybrid inverse experiment consisting in an initial HMQC pulse train followed by a TOCSY mixing sequence. In particular, when the magnetisation is retro-transferred via ^{1}J(CH) from the ^{13}C nucleus to the directly bonded ^{1}H nuclei, such magnetisation is step-wise propagated through the whole coupled homonuclear spin network via J(HH), thus permitting to identify the whole protonic spin system associated to each signal of protonated carbon.[18] Instead, the DEPT-HMQC pulse sequence is designed to discriminate carbons according to the number of protons they are bonded and uses DEPT block to create a heteronuclear double quantum coherence. This is allowed to evolve in the usual manner, with a 180° proton pulse in the centre of a T_1 period, followed by the reconstitution of proton single quantum coherence achieved by a 90° heteropulse, refocusing and detection under heterodecoupling.[19] HMQC-TOCSY and DEPT-HMQC sequences were optimised for a short-range $^{1}J_{CH}$ of 145 Hz and comprised a suppression of ^{1}H−^{12}C artefacts by a Bird scheme, on the basis of an 0.8 s inversion recovery pulse. In DEPT-HMQC experiment, a β flip angle of 180° generated positive CH_2 signals and negative CH and CH_3 signals.[19]

Two selective ^{1}H 1D TOCSY spectra were acquired, with a mixing time of 0.08 s, by exciting selectively the signals at 3.21 or 2.65 ppm, whereas a selective ^{1}H 1D NOESY, including a 0.6 s mixing time, was achieved by exciting selectively the signal at 3.21 ppm. In both selective experiments, a 100 ms Guassian shape pulse was applied.

The spectral widths for ^{29}Si, ^{13}C and ^{1}H nuclei were 250 (19 841 Hz), 300 (30 120 Hz) and 12 ppm (4790 Hz), respectively, and the frequency axes were calibrated, in all cases, by associating TMS signal to 0 ppm. All 1D and 2D spectra were baseline corrected and processed by both Bruker Topspin Software (v.2.1) (Bruker Biospin, Rheinstetten, Germany) and MestReC NMR Processing Software (v. 4.9.9.9) (Cambridgesoft, Cambridge, Massachusetts, USA).

Results and Discussion

The reaction scheme reported in Fig. 1 shows that the first phase consists in the condensation between an acetone molecule and the amine group in APTMS (A) to form an imine intermediate (B).[12] Such nucleophilic addition is believed to produce a hemiaminal −C(OH)(NHR)− intermediate, which is then followed by elimination of a water molecule and formation of an imine Schiff base.[20,21] Then, the water molecules released by the imine formation are assumed to cause the hydrolysis of APTMS methoxyl groups, thus liberating the silane silanols, which may then form a siloxane linkage between two different silane molecules, and release methanol (Fig. 1).[8,13,14] Subsequently, the resulting imine Schiff base may condense, as well as the residual free APTMS, as depicted in Fig. 2 to form a polymeric network.

NMR spectra were acquired during the early stages of reaction between APTMS and acetone, and the changes in NMR signals are shown in Figs. 3 and 4, whereas signal assignments for APTMS are described in the Supporting Information and Figs. S1 and S2. They indicated that acetone took part in the reaction because its signal's intensity progressively decreased (singlet at 2.16 ppm) while new signals appeared. The new signals were already visible in both ^{1}H (Fig. 3) and ^{13}C (Fig. 4) spectra after 0.55 and 0.88 h, respectively, and they should be attributed to the imine product B (Fig. 1). A molecular characterisation for these NMR signals was reached by heteronuclear-edited 2D NMR experiments, such as ^{13}C−^{1}H DEPT-HMQC[19] and HMQC-TOCSY,[22] which allowed recognition of spin patterns and

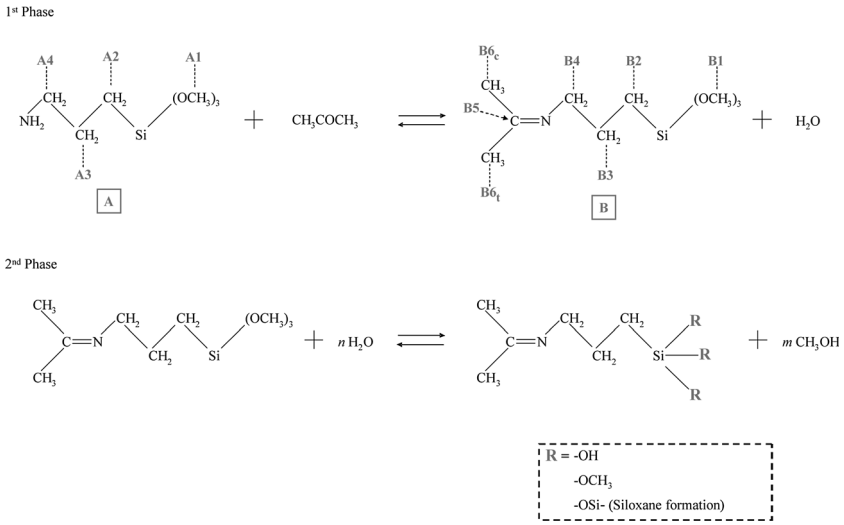

Figure 1. Scheme of reactions induced by addition of acetone to 3-aminopropyltrimethoxysilane (A). The scheme describes the formation of imine Schiff base (B), accompanied by water release (first phase) and followed by the hydrolysis of B methoxyls (second phase). The latter produces silanol groups, which condense with each other to form siloxanes thus enabling the polymerisation.

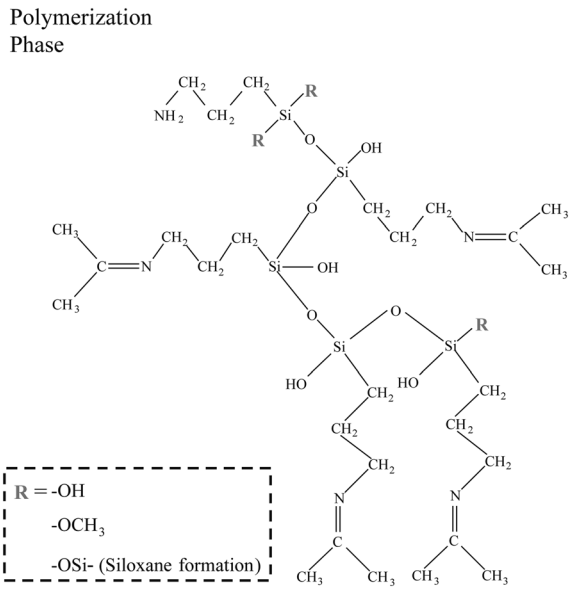

Figure 2. Different types of condensation occurring in the polymerisation phase, which follows the reaction of acetone with 3-aminopropyltrimethoxysilane.

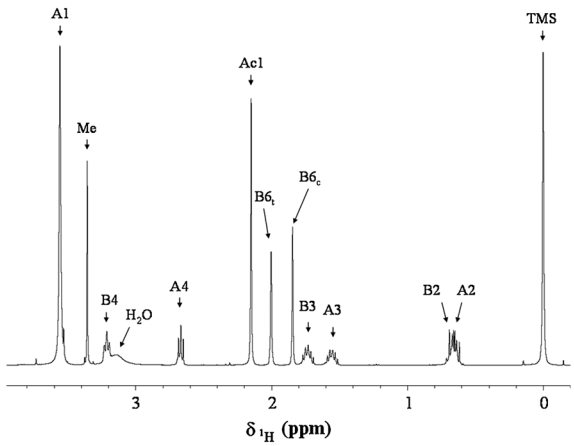

Figure 3. ^{1}H NMR spectrum of reaction solution after around 30 min from addition of 3-aminopropyltrimethoxysilane (APTMS) to acetone (A, APTMS; B, imine Schiff base; Ac, acetone; Me, methanol; TMS). The correlation between the molecule's structure and the labels attributed to NMR signals is indicated in Fig. 1.

assignment of overlapping signals in complex mixtures.[23] In fact, the HMQC-TOCSY experiment enabled the differentiation between two principal spin systems (Fig. 5), whose 2D spectrum well highlighted the C–H relations for both APTMS and Schiff base spin systems.

The spin systems were also examined by two selective 1D ^{1}H TOCSY experiments (Fig. 6), in which the choice of multiplets to be selectively irradiated was based on HMQC-TOCSY spectrum. In fact, when the A4 proton multiplet (2.6784 ppm) was selectively excited, the resulting TOCSY spectrum contained only signals of the APTMS propyl group (Fig. 6C) as compared with the simple ^{1}H spectrum of reaction mixture after 0.55 h from APTMS addition to acetone solution (Fig. 6A). Conversely, when selective excitation was addressed to the proton multiplet at 3.2156 ppm, the TOCSY spectrum revealed the spin system of the Schiff base (Fig. 6B), well in agreement with the indications of the HMQC-TOCSY spectrum. However, differently from HMQC-TOCSY, the spin system detected in the selective TOCSY spectrum of Fig. 6B included two more singlets at 2.035 and 1.839 ppm, which may be attributed to magnetically nonequivalent methyl groups bound to the imine (Fig. 1). This assignment is supported by the presence of a quaternary C N– signal at 168 ppm in the 1D ^{13}C-NMR spectrum (Fig. 4), which indicates formation of the imine. The attribution of the two singlets to imine-bound methyl groups can be reasonably justified by the relatively long mixing time (80 ms) adopted for this TOCSY experiment, which may have favoured a long-range spin-coupling magnetisation transfer even through quaternary carbons. Moreover, it is to be noted that the new spin system of imine product B showed a relevant structural analogy with the APTMS molecule (Fig. 3; Fig. S1), except for a slight down-field drift, which reflects a different chemical environment for the aminosylane in product B.

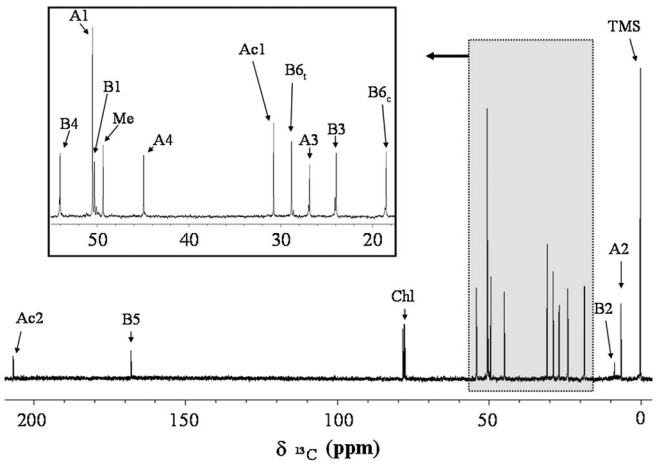

Figure 4. ^{13}C NMR spectrum of reaction solution after 0.88 h from addition of 3-aminopropyltrimethoxysilane (APTMS) to acetone. On the left-hand side, the spectral region between 57 and 16 ppm has been magnified (A, APTMS; B, imine Schiff base; Ac, acetone; Me, methanol; TMS; Chl, chloroform). The correlation between the molecule's structure and the labels attributed to NMR signals is indicated in Fig. 1.

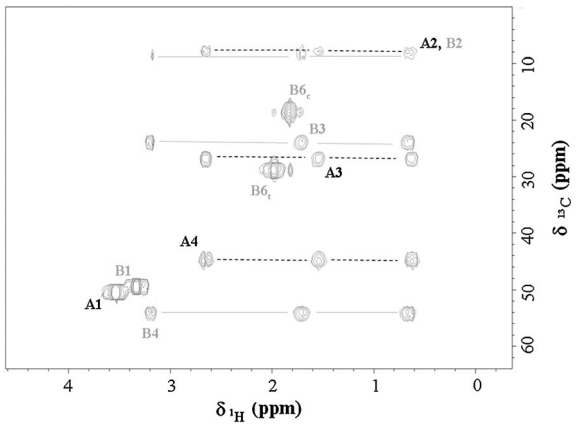

Figure 5. ^{1}H-^{13}C HMQC-TOCSY spectrum of reaction solution, acquired during the initial hours of reaction in order detect both 3-aminopropyltrimethoxysilane and reaction product where dashed black and solid grey lines indicate A and B proton spin systems, respectively.

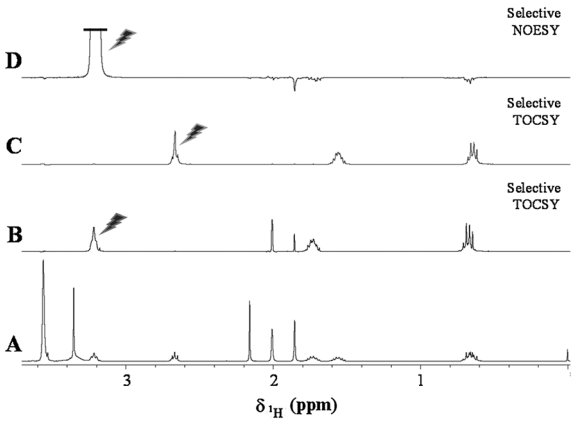

Figure 6. (A) ^{1}H NMR spectrum of reaction solution after 0.55 hs from addition of 3-aminopropyltrimethoxysilane to acetone. 1D ^{1}H TOCSY (B and C) and NOESY (D) spectra were obtained by selectively irradiating the signals indicated by the arrows.

A further structural information on the imine formed in reaction mixture was achieved by a 2D DEPT-HMQC experiment (Fig. 7). This pulse sequence reveals the number of protons bound to a carbon, because the signal phase is positive for $-CH_2$ carbons but negative for either $-CH$ or $-CH_3$ carbons. The DEPT-HMQC spectrum of the reaction mixture (Fig. 7) shows that signals for propyl carbons of both APTMS (A) and the imine product (B) had a positive phase ($-CH_2$), whereas APTMS methoxyl (A1), acetone methyl (Ac1) and both methyl groups bound to C N (B6) produced a negative phase ($-CH_3$). In order to distinguish which methyl B6 signal had an either *cis* or *trans* conformation, a NOESY experiment was conducted by selectively irradiating the B4 protons (Fig. 6D). The intense negative signal detected at 1.839 ppm in the selective NOESY permitted to unambiguously correlate this signal to the *cis* position ($B6_c$). This experiment completed the assignment of all protons (Fig. 3) and carbons (Fig. 4) for the aminosylane product B.

As the reaction proceeded after addition of APTMS (Fig. 1), NMR signal intensities showed a relevant and progressive decrease of both precursors, whereas those of the reaction product proportionally increased, and the newly formed methanol (Me) signal began to be noticed (Figs. 3, 4 and 7). Although attribution of singlet signals to A1, B1 and Me was difficult because of absence of multiplicity, DOSY experiment contributed to identify the methanol peak. DOSY NMR spectroscopy consists in a combination of pulsed field gradients that allow measurement of translational diffusion of dissolved molecules.[24–26] Moreover, spectral processing of DOSY acquisitions well suits complex samples, such as reaction mixtures, because it directly correlates translational diffusion to chemical shift in the second NMR dimension, thereby enabling separation of molecular components of a complex sample.[27] The ^{1}H DOSY spectra for APTMS alone and the reaction mixture after 66 h from addition of APTMS to reaction solution are reported in Fig. 8. In the latter spectrum, it was easy to associate methanol to the singlet signal at 3.37 ppm. In fact, methanol has a smaller hydrodynamic radius, which enables a translational diffusion significantly larger than for the DOSY projections of either APTMS product or TMS internal standard resonating at 0 ppm. Furthermore, Fig. 8 confirmed the formation of a reaction product with a hydrodynamic radius significantly larger than APTMS, as its translational diffusion was distinctly decreased. A semi-quantitative evaluation was conducted by dividing, respectively, the diffusion coefficients (log D) obtained for signals B3

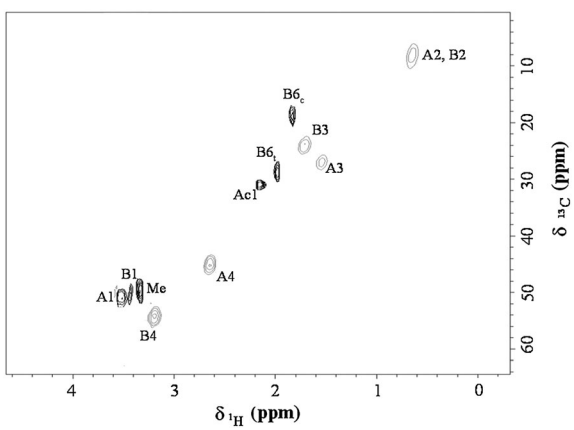

Figure 7. ^{1}H-^{13}C DEPT-HMQC spectrum of solution acquired during the initial hours of reaction. Black peaks correspond to CH_3 and CH signals, whereas grey peaks indicate CH_2 signals.

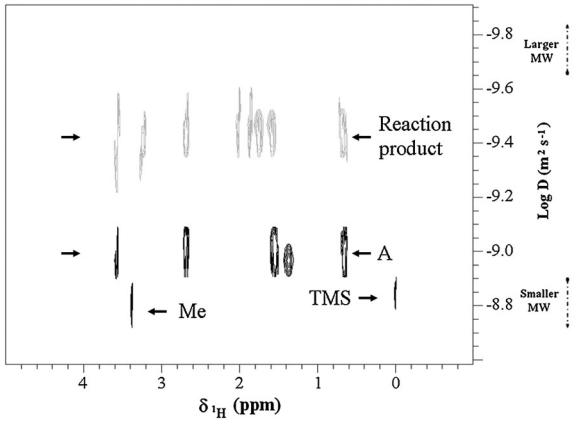

Figure 8. Proton projections of ^{1}H DOSY spectra of 3-aminopropyltrimethoxysilane without acetone (black) and of reaction mixture after 66 h from start (grey).

and B4 after 66 h from reaction start, by those for signals A3 and A4, visible at the reaction onset. These values were 0.365 for B3/A3 and 0.355 for B4/A4 and showed a pronounced decrease of diffusivity for reaction products, which was about ~ 2.8 times lower than for the reactants. This behaviour is fully consistent with the reaction mechanism shown in Fig. 1, which encompasses imine formation and consequent product coupling through silane silanols condensation.[8,14]

The ^{1}H spectra obtained at different time intervals after reaction start (0.25, 0.55, 1.27, 3.07, 11.8 and 24.5 h) showed the appearance of a broad signal at 2.45 ppm, which was progressively shifted to downfield frequencies with increasing reaction time (Fig. S3). Such broad signal may be reasonably associated to protons directly involved in chemical exchange (water, methanol, amine groups or newly formed silanols). The observed chemical shift drift, whose resonance revealed the maximum intensity within the first 12 h from reaction start, is due to the progressive and relative variation of proton populations giving rise to signal and continued with time until it reached a resonance of 4.6 ± 0.3 ppm. In addition, Fig. S3 also reveals a progressive line-broadening of product signals, which was particularly evident for B3 and B4 multiplets. Even though Fig. S3 reports spectra up to only 24.5 h from reaction start, a progressive line-broadening was observed in product signals for the following 13 days (spectra not shown). Such signal broadening must be attributed to a progressive reduction of molecular tumbling rate in reaction products,[28–30] thereby suggesting an enhanced molecular size of products as a result of increasing condensation (Fig. 2) among silane silanols.[2] However, the possible occurrence of weak interactions (H-bonds or Van der Waals forces) between amorphous oligomers[31] may moderately contribute to enhance the line broadening, due to a decrease of spin–spin relaxation times.

An evaluation of molecular changes during the reaction was achieved by integrating the main signals detected in ^{1}H spectra acquired during the first 2 weeks after reaction start (Table S1). The semi-quantitative percent of changes was reached by dividing each signal area by the area of TMS. It was found that the signal intensities for product B and methanol significantly increased as a function of time after addition of APTMS to solution, whereas the signals of APTMS and acetone concomitantly and proportionally decreased (Table S1). After about 352 h and in line with the 3 : 1 acetone to APTMS ratio, some 33% of the acetone had reacted (Table S1). However, after about 12 h of reaction time, the intensity of the broadened signal assigned to exchangeable protons, including water signal, gradually increased, whereas the reaction rate significantly slowed down. Even though this behaviour is prevalently attributed to consumption of precursors, the increasing presence of water in the reaction solution partially contributed to limit condensations, due to hydrolysis of the already condensed polymers and new release of silane silanols.[14]

Although 1D and 2D ^{1}H- and ^{13}C-NMR experiments indicated the occurrence of the step-growth polymerisation described in Fig. 1, they failed to provide unambiguous information on the extent of siloxanes condensations through Si–O–Si linkages (Fig. 2). In order to study the forms of siloxanes produced during the polymerisation phase, we thus followed the NMR changes of the involved silicon nuclei by applying ^{29}Si-NMR spectroscopy. The ^{29}Si DEPT spectra acquired after 0.25, 1.05, 5.85, 16.63 and 39.65 h from addition of APTMS to reaction solution are shown in Fig. S4. Even though the DEPT pulse sequence was designed to only provide qualitative information, several advantages resulted from its application. In fact, this sequence discriminates among different silicon-based molecules, while providing meaningful spectra with a discrete number of scans (128) in a relatively short acquisition time (18 min). Moreover, because the DEPT pulse sequence is based on indirect proton–silicon acquisition and depends prevalently on ^{1}H relaxation times, DEPT experiments are faster than those directly acquiring ^{29}Si signals with long relaxation times.

The assignment of Si signals in spectra shown in Fig. S4 were conducted on the basis of previous works.[8,32,33] At the reaction start, only the peak of APTMS was visible at −41.8 ppm. Thereafter, the silanols produced by water-induced hydrolysis (Fig. 1) began to condense through Si–O–Si linkages, which progressively increased in ever more complex systems, as shown by ^{1}H DOSY spectra. In fact, a progressive decrease of APTMS signal was accompanied after about 1 h from reaction start by the appearance of a new signal at −50.3 ppm, which is assigned to Si nuclei involved in only one siloxane linkage. After 24 h, another new signal appeared at −57.7 ppm and reached its greatest intensity after 39.65 h. This resonance is within the frequency range attributed to Si nuclei bound to two siloxanes (Fig. S4). At larger reaction times, it was observed not only an almost complete disappearance of the APTMS resonance but also a significant decrease of the −50.3 ppm signal. However, no signals were detected at −64.5 ppm, which is reported to correspond to Si nuclei linked to three siloxanes.[33] This suggests that polymerisation among units containing silanols occurred preferentially as depicted in Fig. S5. The absence of the signal at −64.5 ppm may be explained by the low stability of a four-membered siloxane ring, which may be sterically stabilised only with specific substituents.[34,35]

After 5 days of reaction, it was impossible to achieve meaningful ^{29}Si spectra, because the increased viscosity of the reaction mixture reduced even further the intrinsic low sensitivity of ^{29}Si nuclei.

Conclusions

We applied ^{1}H-, ^{13}C- and ^{29}Si-NMR spectroscopy to investigate the reactivity of acetone towards the organosilane coupling agent APTMS in chloroform. Selective TOCSY and NOESY, combined with DOSY and edited-2D HMQC-TOCSY and DEPT-HMQC, significantly contributed to simplify the spectral complexity, allowed identification of newly formed signals and facilitated the structural elucidation of molecules arising at the different

stages of reaction. NMR experiments confirmed that the course of reaction was that reported in Fig. 1 and indicated that reaction rate gradually and significantly decreased after about 12 h from addition of APTMS to acetone. The slowing down of reaction course is attributed to a less availability of APTMS and to water released during the reaction, whose increasing amount may promote the hydrolysis of siloxanes and significantly contribute to inhibit or prevent formation of larger condensation products.

In this work, we employed for the first time DOSY experiments to follow the degree of polymerisation of APTMS induced by acetone. An evidence for the occurrence of a siloxane polymerisation were indirectly provided by DOSY spectra, which revealed a significantly larger hydrodynamic radius for reaction products than for APTMS. Moreover, the detection of different siloxanes signals in ^{29}Si-NMR spectra as a function of reaction time confirmed the formation of a heterogeneous polymeric network resulting from progressive polymerisation as shown in Fig. 2.

Our results indicate that the imine formation followed by hydrolysis of methoxyls proceeded at a relatively large rate, whereas the polymerisation through mutual condensation among silanols was significantly slower. We showed that a combination of 1D and 2D multinuclear NMR experiments may be adopted to efficiently elucidate the reactivity of γ-aminopropylalkoxysilanes and can be helpful to assess the procedures fro the preparation of silicon-based resins. In particular, the DOSY-NMR pulse sequence represents a useful tool to follow the polymerisation of γ-aminopropylalkoxysilanes, especially when the overlapping signals of oligomers and polymers cannot be directly discriminated in ^{1}H spectra. In fact, DOSY-NMR spectroscopy enables us to distinguish among different compounds in a complex reaction mixture by introducing a further dimension that reflects the molecular diffusivity of mixture components.

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