Understanding Hydrolysis and Condensation Kinetics of γ-Glycidoxypropyltrimethoxysilane

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Monitoring the kinetics of hydrolysis and condensation of γ-glycidoxypropyltri-methoxy-silane (γ-GPS) was carried out by NMR spectroscopy ($^{29}Si-$, $^{13}C-$, and $^{1}H-$). The course of these reactions was followed in $2\,wt\%$ aqueous dilution conditions (26% D_2O/74% H_2O), pH 5.4, and temperatures of 26, 50, and 70°C. At ambient temperature, hydrolysis and condensation proceed at very different time scales: a few hours for the hydrolysis versus several weeks for the condensation. Distortionless Enhancement by Polarization Transfer (DEPT) sequences by $^{29}Si-$ and $^{13}C-NMR$ spectroscopy were optimized for determining the complete spectral assignment for each hydrolysis step, i.e., $RSi(OMe)_{3-n}(OH)_n$ (with $R=(CH_2OCH)CH_2OCH_2CH_2CH_2-$ and $n=1,2,3$). A pseudo-first order rate constant for the first hydrolysis step, $T0^{(OMe)3} + H_2O \rightarrow T0^{(OMe)2OH} + MeOH$, was calculated to be $0.026\,min^{-1}$. Simultaneously to the condensation reactions, we have observed epoxy ring opening of the glycidyl- group. All three processes (hydrolysis, condensation, and epoxy ring opening) are dramatically accelerated with temperature increases from 26 to 70°C. The activation energy of the epoxy ring opening leading to the formation of a diol structure at the extremity of the glycidoxypropyl- chain was estimated to be $68.4\,kJ/mol$.

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INTRODUCTION

γ-Glycidoxypropyltrimethoxysilane (*γ*-GPS) (Fig. 1) is probably one of the most widely studied and used silanes from the large family of organosilanes. Initial use for *γ*-GPS was for enhancing moisture stability of glass-fiber-reinforced plastics, which rapidly confirmed that *γ*-GPS can provide similar benefits in numerous applications where a metal oxide–adhesive interface needs improvement [1]. Since then, a large number of studies were dedicated to the understanding of mechanisms which govern *γ*-GPS chemistry either in solution or at the interface of dissimilar materials. For a good overview, the reader is encouraged to refer to a recent publication dedicated to *γ*-GPS in particular [2]. The mechanisms involved in the coupling reactions with organosilanes are related to the presence of two types of reactive moieties at their two extremities. On one end, the silyl-alkoxy groups enable the silane to react with surfaces bearing hydroxyl groups, whereas, on the other end the organic functionality (glycidyl- in *γ*-GPS, amine, methacryl-, vinyl-, etc. in other organosilanes) improves the compatibility (*e.g.*, matching solubility parameters) and possibly enables chemical reaction with organic matrices, thereby enhancing the interfacial adhesion between an organic polymer and the inorganic substrate (*e.g.*, reinforcing mineral in composites, substrates in adhesive bonding, etc.).

In any particular application where organosilanes are used, because of the inherent nature of the molecules, it is important to understand first how the chemistry in solution is influenced by factors such as, *e.g.*, concentration, pH, temperature, or the presence of catalyst. However, most of the works dealing with the chemistry of *γ*-GPS in solution were considering water/alcohol solutions, *e.g.*, typically in 80/20 to 90/10 w/w proportions, containing up to 2 wt% *γ*-GPS [2–4]. Among these studies ^{29}Si−, ^{1}H−, and ^{13}C−NMR spectroscopy was used for monitoring the evolution of species formed after hydrolysis and
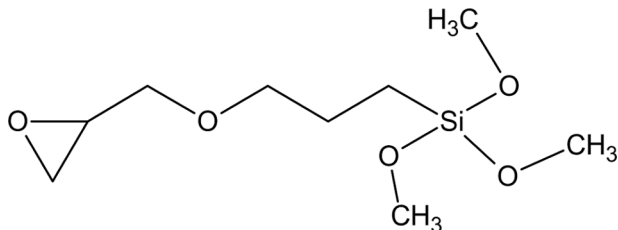
FIGURE 1 Structure of *γ*-glycidoxypropyltrimethoxysilane (*γ*-GPS) or T0$^{(OMe)3}$.

condensation reactions occurring at ambient temperature. We applied the same techniques to study the course of these reactions for 2 wt% γ-GPS pure aqueous solutions, buffered at pH ∼5.4, at temperatures of 26, 50, and 70°C. At 2 wt% concentration, the choice of this slightly acidic pH was dictated by the fact that it already accelerates the hydrolysis reaction of γ-GPS into its silanetriol corresponding monomer compared with neutral conditions, and it minimizes the rate of further condensation reactions [1] (Fig. 2). We were also interested in studying the kinetics of hydrolysis/condensation of γ-GPS in a purely aqueous solution since the trend in industrial applications is to avoid the use of any solvent, *e.g.*, in pulp and paper processing, formulation of paints and varnishes, metal pre-treatment against corrosion, etc. Finally, we were particularly interested in understanding the effect of increasing the temperature from ambient to slightly higher than ambient since, on the one hand, the reaction of hydrolysis/condensation of organosilanes is known to be strongly influenced by small temperature increases and, on the other hand, because most
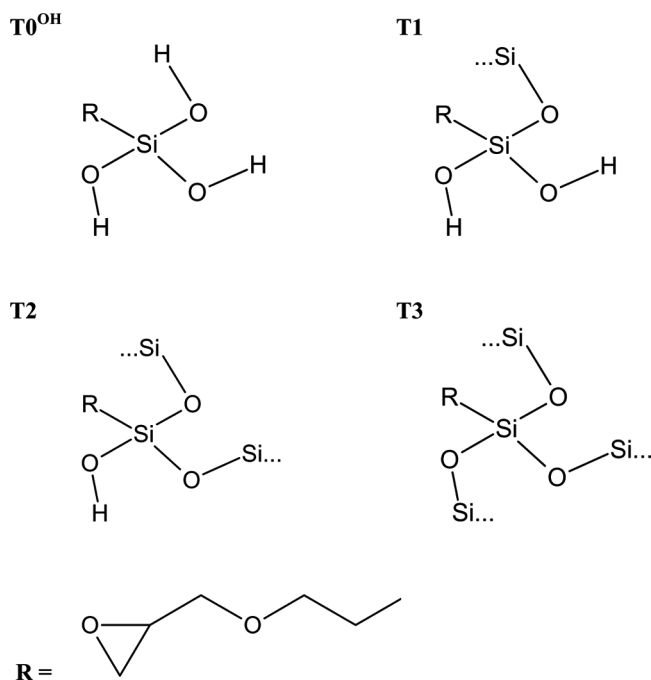

FIGURE 2 Structure of γ-glycidoxypropyltrisilanol, T0^{OH}, and corresponding T1, T2, T3 condensed species. R = γ-glycidoxypropyl-.

of the industrial processes cited above work in the range of temperature from ambient to slightly higher than ambient.

EXPERIMENTAL

Materials

γ-GPS was Z-6040 silane (Dow Corning® Midland, Michigan), USA used without further purification. Solutions of 2 wt% γ-GPS were prepared and buffered at pH $\sim$5.4 with 0.2% citric acid and 0.18% sodium hydroxide (Vel, Leuven, Belgium) 40% in water. Unless otherwise specified, NMR analyses were carried out in aqueous solution (H_2O/D_2O) at $\sim$26°C. Water used for preparing the solutions was a high purity grade produced by reverse osmosis. D_2O was 99.9 atom% D (Aldrich, Bornem, Belgium). The final solutions used for NMR spectroscopy were 26% D_2O/74% H_2O.

Experimental curves were fitted using the trendline function in Microsoft® Excel.

NMR Spectroscopy

NMR measurements were performed on a 400 MHz AVANCE spectrometer (BRUKER Biospin, Wissembourg, France). The original sample preparation of silane in 26% D_2O/74% H_2O allowed us to have a deuterated lock solvent already in the initial solution. For the ^{1}H NMR measurements we used a 5 mm tube with 0.8 ml volume solution, while ^{13}C and ^{29}Si NMR measurements were carried out using 10 mm tube with 4 ml volume solution. NMR tubes were from Wilmad® (Aldrich, Bornem, Belgium).

^{1}H NMR: All spectra were recorded using a 30° pulse angle (3.6 µs), and the relaxation delay was set to 7.6 s (acquisition plus waiting time). 72 scans were used for each spectrum. The chemical shifts were assigned referred to the water peak at 4.65 ppm.

^{13}C NMR: The Distortionless Enhancement by Polarization Transfer (DEPT)-45 sequence was applied to monitor the short time hydrolysis; each measurement lasted only 9 min (88 scans with 6.1 s relaxation delay). The sum intensity for all hydrolysis peaks for one species was constant; therefore, the DEPT sequence could be used for quantification. For the long term ring opening process the inverse gated technique was used, with a 90° pulse angle (13.1 µs) and a relaxation delay of 61.1 s. The chemical shifts were assigned referred to the methanol peak at 49.2 ppm.

^{29}Si NMR: In analogy to ^{13}C, the DEPT sequence was used for the hydrolysis. The polarization transfer by the ^{1}H nuclei is complex for [29]Si, because of the impact of different couplings: (i) ^{2}J(Si–H) with the protons of the α–CH$_2$ group (C6 position in Fig. 3), (ii) ^{3}J(Si–H) with the protons of the ß–CH$_2$ group (C5 position in Fig. 3), and (iii) ^{3}J(Si–H) with the protons of the methoxy group. In addition, there is homonuclear coupling ^{3}J(H–H) between the protons of the α and ß–CH$_2$. Brunet [5] investigated in detail the DEPT parameters for methyltriethoxysilane, and they obtained the best signal/noise ratio with the transfer time, Δ, of 59 ms, according to the ^{2}J(Si–H) of 8.4 Hz and a pulse angle, Θ of 30°. For GPS, we varied Δ and Θ and obtained for $\Delta = 54$ ms and $\Theta = 30°$ the best signal/noise ratio. The similarity with Brunet's parameter is due to the domination of the polarization transfer by ^{2}J(Si–H) in both cases. However, during the hydrolysis process the various species formed contain fewer methoxy groups and this latter phenomenon influences the polarization efficiency, similarly to what was shown by Brunet for methyltriethoxy silane [5]. This fact was reflected by a change of the sum intensity for all hydrolysis peaks; therefore, correction factors for the different hydrolysis species were used. These correction factors were calculated from ^{13}C data. The long term condensation process was followed by
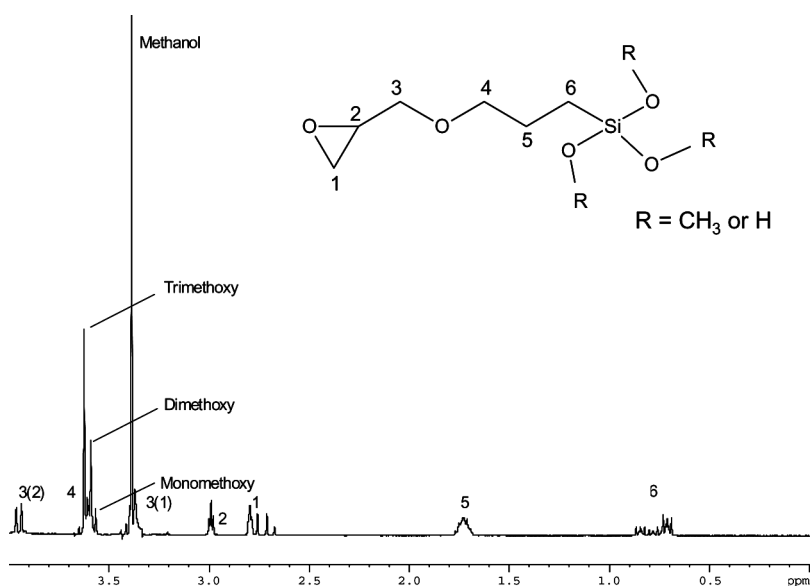

FIGURE 3 Hydrolysis of γ-GPS monitored by ^{1}H–NMR (t = 58 min, 26°C).

inverse gated measurements; the 90° pulse length was $15.0\,\mu s$ and the relaxation delay was $61.6\,s$. The chemical shifts were assigned against the spectrometer reference function for tetramethylsilane at $0\,ppm$.

RESULTS AND DISCUSSION

γ-GPS Hydrolysis kinetics

Although γ-GPS was the object of several prior works calling for various analytical techniques [2–4, 6–12] we studied the hydrolysis of γ-GPS by ^{1}H, ^{13}C DEPT-45, and ^{29}Si DEPT-30 NMR for comparing the results obtained and, using the benefits of each of them, ensuring a complete assignment of the peaks. This enabled us to understand fully the hydrolysis kinetics of γ-GPS at the conditions used. Since we were working with relatively dilute 2 wt% γ-GPS solution, DEPT enabled improvement of the sensitivity of the analyses for the ^{13}C and [29]Si measurements.

The ^{1}H spectrum of Fig. 3 allows one to distinguish between silane molecules with three, two, or one methoxy groups, taking the corresponding $-OCH_3$ peaks at $3.62\,ppm$ for $T0^{(OMe)3}$, $3.59\,ppm$ for $T0^{(OMe)2(OH)}$, and $3.57\,ppm$ for $T0^{(OMe)(OH)2}$. The completely hydrolyzed species, $T0^{(OH)3}$, has naturally no methoxy anymore and can not be observed directly, but its amount can be calculated by taking the difference with the methanol formed, the intense peak of which appears at $\sim 3.4\,ppm$ in the ^{1}H spectrum of Fig. 3. The course of γ-GPS hydrolysis by ^{1}H NMR is also indicated by the changes of intensity of the complex signal pattern corresponding to the CH_2 protons on the C6 carbon next to the Si atom between 0.5 and $1.0\,ppm$—the multiplet between 0.75–$0.90\,ppm$ is decreasing, whereas, the one between 0.60–$0.75\,ppm$ is growing. This pattern evolution was used by Abel *et al.* [11] to obtain information on the overall hydrolysis kinetics, which does, however, not allow distinguishing between the various intermediate steps. Considering the methoxy peaks centered at $\sim 3.6\,ppm$ was, therefore, the best way for resolving all species. However, there is peak overlapping between the OCH_3 signals and CH_2 protons on the C4 carbon as well as between the methanol peak and CH_2 protons on the C3 carbon. For obtaining correct results we subtracted the intensity of overlapping peaks using their theoretical intensity in relation to the other proton species of the glycidoxypropyl-group. The overall hydrolysis reaction of γ-GPS in the 2 wt% aqueous solution ($pH = 5.4$, $T = 26^\circ C$) was completed within $\sim 2\,h$ as shown by the evolution of peak intensities of the signals between 3.5–$3.7\,ppm$ (Fig. 4). The rapid disappearance of $T0^{(OMe)3}$ as well as the rapid

appearance of $T0^{(OH)3}$ fit well with a logarithmic dependence on time. The apparent first-order rate constant, $k_1^{hydrolysis}$, calculated from the slope of the straight line of Fig. 5 was found to be $0.026\,min^{-1}$ for $T0^{(OMe)3}$. From the first minutes of the hydrolysis process, the $T0^{(OMe)3}$ disappears according to a first order decay to form $T0^{(OMe)2(OH)}$ followed by $T0^{(OMe)(OH)2}$ and $T0^{(OH)3}$ species as illustrated in Fig. 4. It is only after $\sim 40\,min$ that $T0^{(OMe)2(OH)}$ and $T0^{(OMe)(OH)2}$ species start decreasing to the benefit of the silanetriol $T0^{(OH)3}$ formation. Actually, $T0^{(OMe)2(OH)}$ and $T0^{(OMe)(OH)2}$ species are only transient intermediates, which explain the complex third order equations necessary for fitting their concentration as the hydrolysis reaction evolves (Fig. 4).

The use of ^{13}C DEPT-45 to measure the hydrolysis kinetic of γ-GPS under our experimental conditions was also possible. Well separated OCH_3 peaks representing the tri-, di-, and mono-methoxy forms plus the methanol were observed (Fig. 6). The advantage of ^{13}C NMR is, however, that the course of the hydrolysis reaction can not only be monitored by the methoxy species, but also by the CH_2 units of the C4, C5, and C6 carbon positions of the glycidoxypropyl- group bonded to the central Si atom. As expected, the CH_2 of the C6 carbon next to Si shows the largest difference in chemical shift between $T0^{(OMe)3}$,
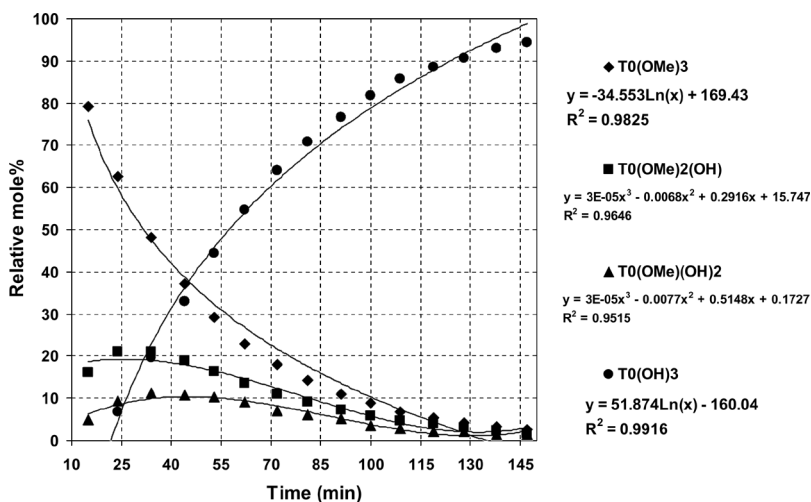

FIGURE 4 Hydrolysis kinetics of γ-GPS monitored by ^{1}H NMR. Peak intensities of the methoxy groups recorded between 3.5–3.7 ppm for $T0^{(\underline{OMe})3}$, $T0^{(\underline{OMe})2(OH)}$, and $T0^{(\underline{OMe})(OH)2}$ species. Peak intensity for $T0^{OH}$ calculated by difference with the methanol peak recorded at 3.4 ppm (T = 26°C).
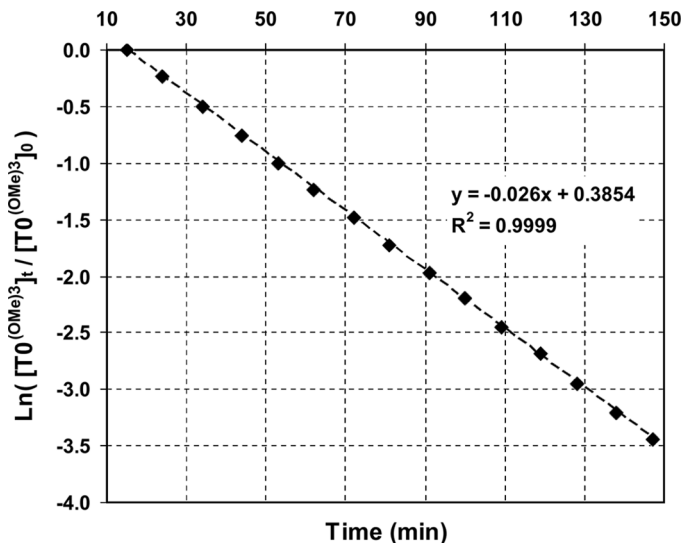
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FIGURE 5 Pseudo-first order kinetics of first hydrolysis of γ-GPS: $T0^{(OMe)3} + H_2O \rightarrow T0^{(OMe)2OH} + MeOH$. Decrease of ^1H NMR peak intensity at 3.62 ppm (Fig. 4).
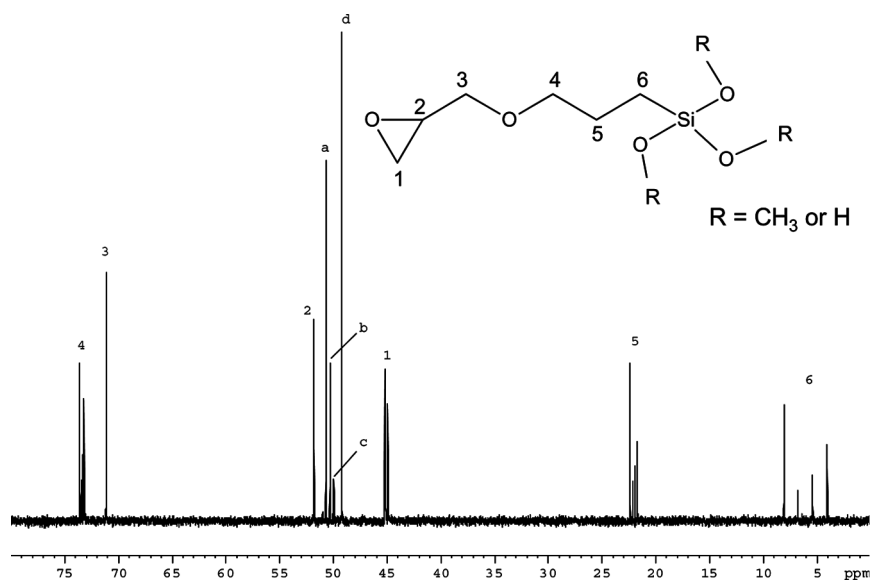

FIGURE 6 Hydrolysis of γ-GPS monitored by ^{13}C-DEPT-45 NMR (t = 38 min, 26°C). (a) $T0^{(O\underline{Me})3}$, (b) $T0^{(O\underline{Me})2(OH)}$, (c) $T0^{(O\underline{Me})(OH)2}$, and (d) $\underline{Me}OH$.

$T0^{(OMe)2(OH)}$, $T0^{(OMe)(OH)2}$, and $T0^{(OH)3}$, *i.e.*, 1.3 ppm between each hydrolysis step (4.05 to 8.09 ppm). In comparison, the CH_2 of the C5 carbon differs by just 0.2 ppm (21.75 to 22.39 ppm). The CH_2 of the C4 carbon, which has one O atom as a neighbor, shows a step-wise shift difference of 0.1–0.15 ppm. In Fig. 7 the various hydrolysis curves are shown for the C6 carbon atom next to the glycidoxypropyl-group, the chemical shifts differences of which were the largest. We should notice at this point that there was no epoxy ring opening during the first 100 min of γ-GPS hydrolysis under these experimental conditions.

In order to have all chemical shifts assignments for the different hydrolysis steps of the T0 species and for monitoring T1 species formation (Si—O—Si bridging) that starts taking place while hydrolysis is not fully completed, we also carried out ^{29}Si DEPT-30 NMR (Fig. 8). In contrast to ^{13}C NMR, there is no simple correlation between ^{29}Si shifts and hydrolysis steps, we found the two intermediate states with their chemical shift values (−37.9 and −38.0 ppm) at a lower field from the original trimethoxysilane (−38.25 ppm) and from the silanoltriol (−38.1 ppm) formed upon hydrolysis.

After DEPT method optimization, and determination of enhancement factors for the Si(T0) steps with the data issued from ^{1}H and ^{13}C analyses, we quantitatively monitored the hydrolysis as displayed in Fig. 9.
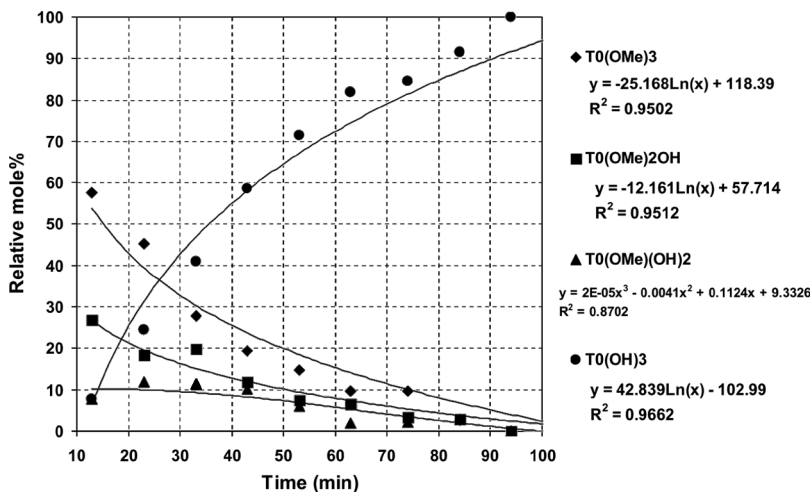

FIGURE 7 Hydrolysis kinetics of γ-GPS monitored by ^{13}C-DEPT-45 NMR on the C6 carbon next to the silicon between ∼4–8 ppm (T = 26°C).
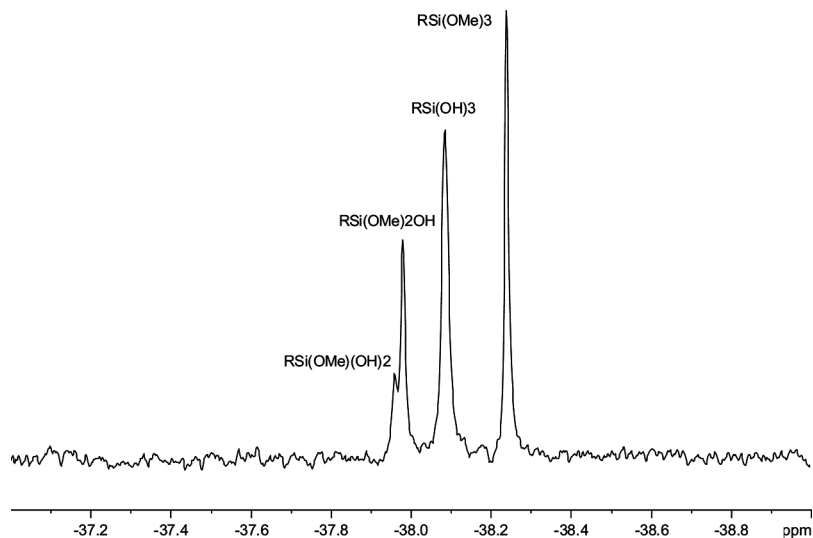
FIGURE 8 Hydrolysis of γ-GPS monitored by ^{29}Si DEPT-30 NMR (t = 53 min, 26°C).

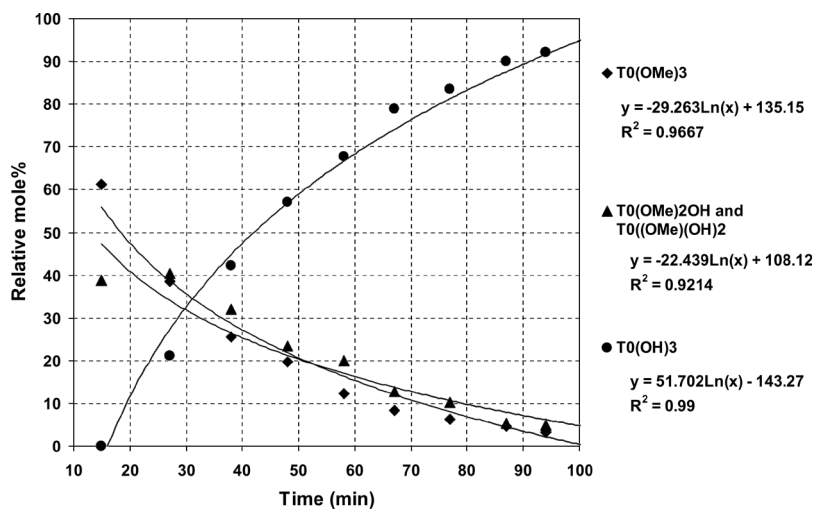**FIGURE 9** Hydrolysis kinetics of γ-GPS monitored by ^{29}Si DEPT-30 NMR. Peak intensities of $T0^{(OMe)3}$ at 38.25 ppm, $T0^{OH}$ at 38.1 ppm, and intermediates $T0^{(OMe)2(OH)}$ and $T0^{(OMe)(OH)2}$ species at 37.9–38.0 ppm (T = 26°C).

However, comparing first order kinetics for the disappearance of $T0^{(OMe)3}$ obtained from ^{1}H NMR (Fig. 4), ^{13}C DEPT-45 (Fig. 7), and [29]Si DEPT-30 (Fig. 9) NMR, the apparent first-order constants $k_1^{hydrolysis}$ were 0.026 (Fig. 5), 0.038, and 0.037 min^{-1}, respectively. This nearly 50% increase in the rate constants from ^{1}H to ^{13}C and ^{29}Si NMR are suggested as being due to, *e.g.*, (i) experimental conditions (NMR tubes size and solution volume were larger for both ^{13}C and ^{29}Si *versus* ^{1}H NMR) and (ii) differences in the signal to noise ratio between ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, which can significantly impair the accuracy of the signals integration. However, we should also notice that solvent effects between H_2O and D_2O are likely to significantly influence the hydrolysis rate constant. For instance, extrapolation of rate data from a prior study made on the γ-GPS hydrolysis in pure H_2O solution at various pH and 25°C [13] showed that the pseudo-first order rate constant was 0.055 min^{-1}. In our present study, we used a 2% dilution of γ-GPS in a 26% D_2O/74% H_2O solution. One plausible explanation for the factor of two observed in the hydrolysis rate constants between both studies is the deuterium isotope effect, *i.e.*, slowing down the rate of hydrolysis significantly.

γ-GPS Condensation Kinetics

Condensation reactions of the silanetriol ($T0^{OH}$) form of γ-GPS lead to the formation of condensed structures with one SiOSi bond (T1), two SiOSi bonds (T2), and three SiOSi bonds (T3), illustrated in Fig. 2. The only possibility to monitor the condensation of γ-GPS and to distinguish between $T0^{OH}$ (monomer species at -38.1 ppm) versus condensed T1 (-47 to -49 ppm), T2 (-55 to -60 ppm) and T3 (-60 to -70 ppm) species is ^{29}Si inverse gated NMR spectroscopy (Fig. 10). To make sure the conditions were quantitative, we used the inverse gated pulse technique. To avoid adding any chemical that could influence the kinetic parameters, we accumulated a large number of scans (1024) with, long waiting time between each scan (60 s) on our 2% aqueous solution of γ-GPS (26°C). The condensation kinetics were monitored over 2 months and the result is shown in Fig. 11. Because T0 and T1 peaks were narrow, measurements of their intensities were accurate. Peaks assigned to T2 and T3 species were broad and, hence, their integration was not very accurate, *i.e.*, their respective intensities vary significantly from one data point to another. This is the reason for summing up intensities of [T2 + T3] species in the plot of Fig. 11. One can observe that the formation of [T2 + T3] species follows a reasonably good pseudo-first order kinetic path up to the plateau starting after $\sim$1 month while the T0 and T1 species disappear.
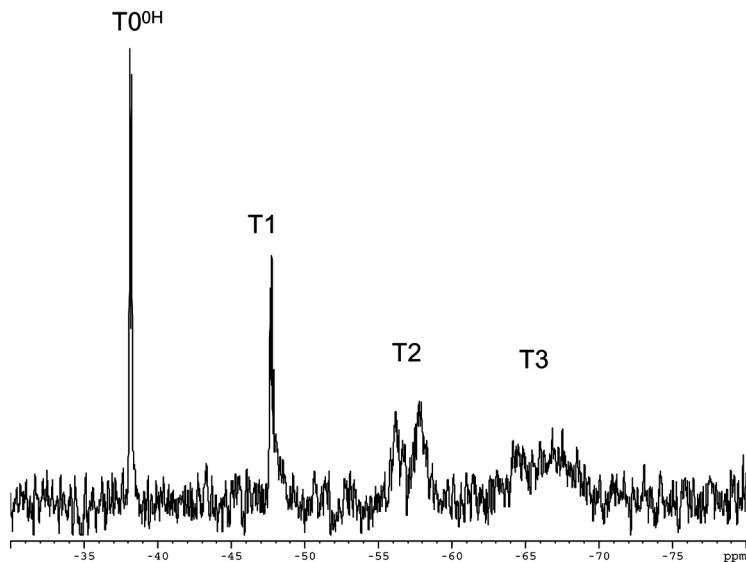
FIGURE 10 Condensation of γ-GPS monitored by ^{29}Si-inverse gated NMR (equilibrium reached after approximately 1 month at 26°C).
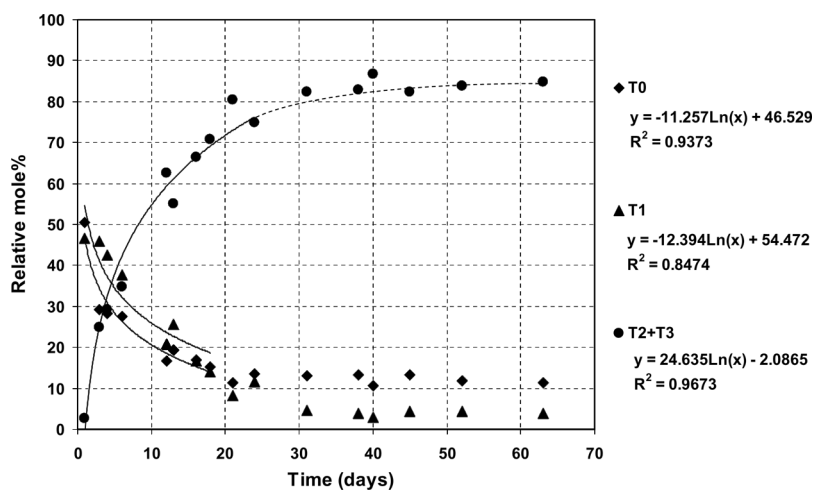

FIGURE 11 Condensation kinetics of γ-GPS with evolution of T0^{OH}, T1, T2, and T3 species monitored by ^{29}Si-inverse gated NMR (T = 26°C).

After one month, therefore, equilibrium is reached and still a significant amount of $\sim$10% T0 remains present in the solution.

Epoxy Ring Opening Kinetics

As we have seen during the hydrolysis, after $\sim$90 min all original methoxy groups of γ-GPS have been hydrolyzed and, finally, only one peak representing the silanetriol appears at -38.1 ppm in the ^{29}Si NMR spectrum (Figs. 8 and 9). As the condensation reaction of silanols proceed with time, however, a new T0 signal at -38.0 ppm, distant by 0.1 ppm from the initial silanetriol peak appears after approximately 1 day, and evolves with time up to 2 months, as shown by ^{29}Si NMR (Fig. 12). We monitored the growth of this second peak next to the initial Si(T0) peak by ^{29}Si NMR and plotted its intensity according to pseudo-first order kinetics (Fig. 13, right axis). On the other hand, we monitored the decay of the ^{13}C peak intensity at 51.8 ppm by ^{13}C NMR, corresponding to the C2 carbon atom of the epoxy ring of γ-GPS (see carbon numbering and peak assignment in Fig. 6). We then calculated the relative increase of epoxy ring opening and noticed its kinetics also follows a pseudo-first order law, similarly to the prior Si(T0) peak splitting (Fig. 13, left axis). It is indeed known that the epoxy ring undergoes a ring opening reaction under certain conditions, *e.g.*, slightly acidic in our case (pH 5.4). Interestingly, therefore, we found a straight live correlation between both processes (Fig. 14).
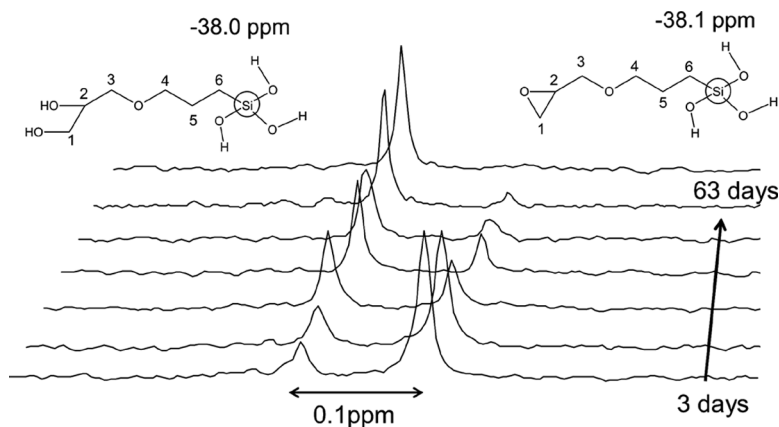

FIGURE 12 ^{29}Si(T0) peak splitting corresponding to silanetriol species, T0^{OH}, as a function of time (T = 26°C).

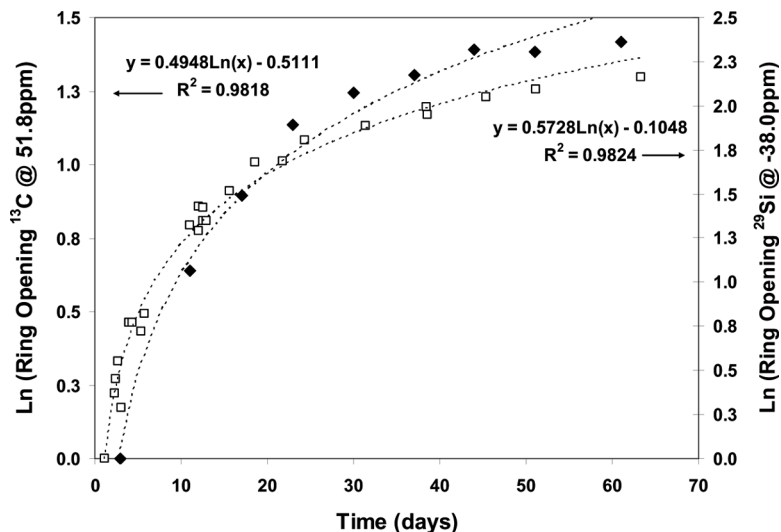*F. de Buyl and A. Kretschmer*

FIGURE 13 Kinetics of epoxy ring opening at 26°C monitored by (a) ^{29}Si-NMR on T0^{OH} peak at -38.0 ppm ($\square$) and (b) ^{13}C$-$NMR on C2 peak at 51.8 ppm ($\blacklozenge$).
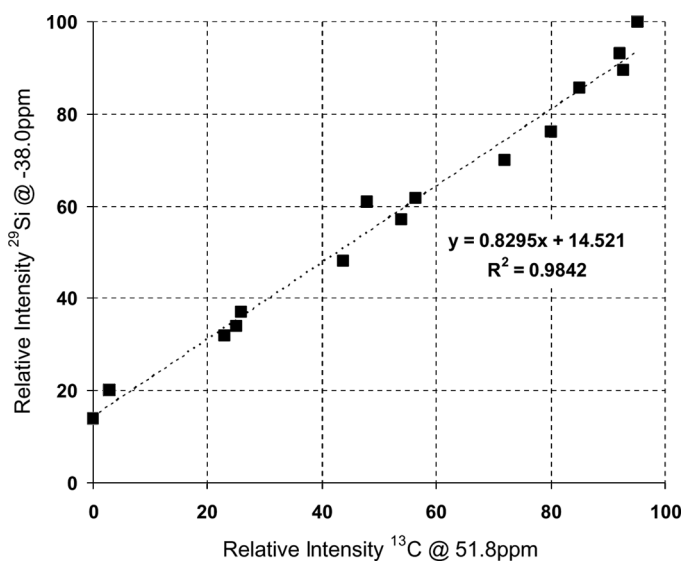

FIGURE 14 Correlation between relative intensities of ^{29}Si(T0^{OH}) peak at -38.0 ppm and ^{13}C(C2) epoxy ring peak at 51.8 ppm.

Although this phenomenon of epoxy ring opening reaction has been mentioned in prior literature, it was assigned to a variety of unknown reaction products between the diol end of the opened epoxy-ring of the γ-GPS molecule and its silanetriol form [10,12]. In our present case, we only observe one new Si(T0) peak that closely correlates with the diol formation. This suggests that specific interaction, *e.g.*, H-bonding between SiOH (silanol) and OH groups (from the diol formed by the epoxy ring opening) occurs. However we cannot say whether these interactions occur via an intra- or an inter-molecular mode.

Effect of Temperature on Hydrolysis, Condensation, and Epoxy Ring Opening Kinetics

Hydrolysis was much too fast at temperatures of 50 and 70°C to be monitored with our equipment. However, we were able to monitor the condensation reaction of T0 silanetriol species into T2 and T3 species. The condensation reaction is not pushed further with increasing temperature but an equilibrium of ~80% [T2 + T3] is reached much faster at 50 and 70°C compared with 26°C (Fig. 15). Although a limited amount of data points were available, one can notice, interestingly, that the decay of the T0 species formed were going at a similar rate
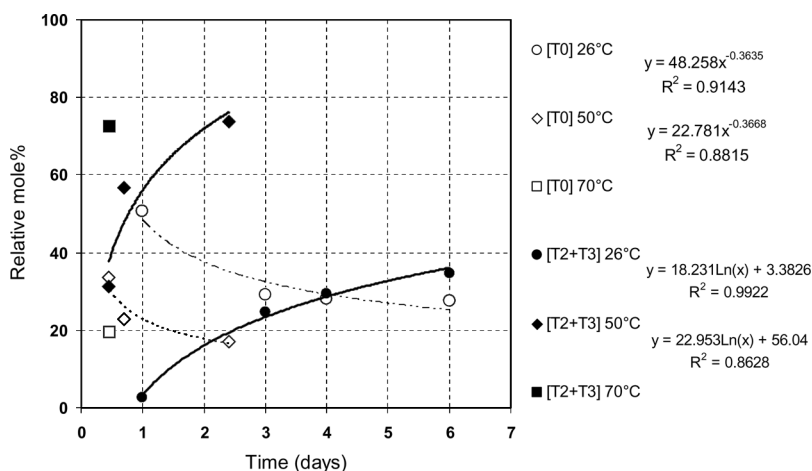

$y = 48.258x^{-0.3635}$
$R^2 = 0.9143$

$y = 22.781x^{-0.3668}$
$R^2 = 0.8815$

$y = 18.231\ln(x) + 3.3826$
$R^2 = 0.9922$

$y = 22.953\ln(x) + 56.04$
$R^2 = 0.8628$

FIGURE 15 γ-GPS condensation kinetics as a function of temperature monitored by ^{29}Si-inverse gated NMR. Decreases of T0^{OH} peak intensity at -38.1 ppm and increases of [T2 + T3] broad peak intensities (centered at -57 and -67 ppm, respectively) for the three temperatures studied (26, 50, and 70°C).

at 26 and 50°C (both exponential decays in dotted lines in Fig. 15 are parallel). However, the condensation into T2 and T3 species is significantly accelerated as temperature increases from 26°C to 50°C and 70°C. It took only 12 hours at 70°C for the solution to be composed of ~20% T0, ~8%T1, ~23%T2, and ~49%T3.
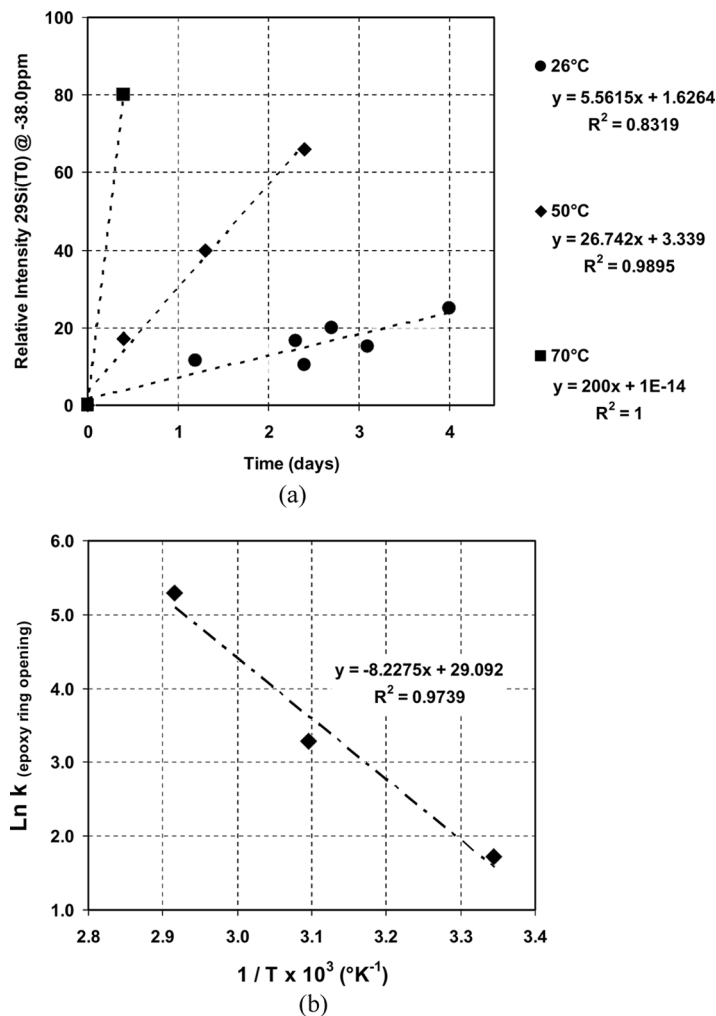
FIGURE 16 Epoxy ring opening kinetic of γ-GPS as a function of temperature monitored by ^{29}Si-inverse gated NMR. (a) Relative peak intensity increase of T0[OH] peak splitting at −38.0 pm, and (b) corresponding Arrhenius plots for the three temperatures studied (26, 50, and 70°C).

We monitored the increase of ^{29}Si peak intensity at 38.0 ppm (Fig. 12), which we have shown correlates with the epoxy ring opening reaction (Fig. 14). The epoxy ring opening phenomenon was dramatically accelerated upon increasing temperature from 26 to 70°C (Fig. 16a), recognizing, however, that for T = 70°C, only one data point was obtained and, therefore, the corresponding plot in Fig. 16a might be taken with care. However, considering the slope of the three plots of Fig. 16a, plotting them against the reverse of the absolute temperature according to Arrhenius law (Fig. 16b) we estimated the activation energy for the epoxy ring opening at $\sim$68.4 kJ/mol (*i.e.*, multiplying the gas constant R = 8.31 J/K/mol by the slope of the Arrhenius plot, 8.2275×10^3 K).

CONCLUSIONS

In conclusion, we were able to show that:

- Hydrolysis of γ-GPS to its silanetriol equivalent in a 2% aqueous solution is a fast reaction, *i.e.*, completed within about 2 h at 26°C.
- Condensation into T1, T2, and T3 oligomer species and epoxy ring opening take place at slower rate, *i.e.*, completed within about 2 months at 26°C.
- Si(T0) peak splitting into two components distant from 0.1 ppm was identified as a new parameter for monitoring epoxy ring opening of γ-GPS.
- Increasing temperature up to 50 and 70°C dramatically accelerates both processes.
- The activation energy of epoxy ring opening was estimated at $\sim$68 kJ/mol.

ACKNOWLEDGMENTS

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