

FLUORESCENCE STUDIES FOR *IN SITU* MONITORING OF THE HYDROLYSIS AND POLYMERIZATION REACTIONS OF ORGANICALLY –MODIFIED TETRAMETHYLORTHOSILICATE

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ABSTRACT

Monitoring of hydrolysis and condensation polymerization reactions of tetramethylorthosilicate-organosiloxane have been carried out. Proton transfer from the excited state of 8-hydroxy-1,3,6-pyrenetrisulfonic acid trisodium salt (pyranine) to surrounding water molecules was used as a sensitive fluorescence method for following the kinetics of water consumption during the early stages of the sol-gel polymerisation process. Changes in water/silane ratio, type of organosiloxane, mol ratio of organosiloxane to silica precursor and pH affected markedly the kinetic behavior of the hydrolysis and condensation reaction of tetramethylorthosilicate.

Keywords: hydrolysis, polymerisation, fluorescence, pyranine, tetramethylorthosilicate, organosiloxane.

INTRODUCTION

The sol-gel process based on the hydrolysis and polycondensation reactions of metal alkoxides and/or reactive metal salts has been widely used as an important process for the synthesis of glasses in recent years. Various starting compounds have been used to prepare the silica gel. The most frequently used starting materials are silicic acid [1] and alkoxy silanes, particularly tetramethoxysilane [2] and tetraethoxysilane [3]. It was reported that the hydrolysis rates of different alkoxy silanes depend on the alkyl group, and the hydrolysis and condensation mechanisms of alkoxy and organo-alkoxy silanes have been studied in detail [4-6].

The relative rates of hydrolysis and condensation are important for gel formation. These reactions determine mainly the rate of gelation and the ultimate structure, density and specific surface area of the gel [7]. Some variables including the type of alkoxy silanes and their functionality, the catalyst and its concentration, the molar ratio of H₂O/alkoxide and the reaction temperature influence these reaction sequences [7-9]. These variables control the polymerization growth and aggregation of the silica species throughout the transition from the sol to the gel state [1,7-9]. There have been many studies of reaction kinetics, structural evolution and thermodynamics of the sol-gel reaction of tetraalkoxy silanes [10-11]. The experimental techniques include NMR [12-14], chromatography [15], infrared and Raman

spectroscopy [16-19]. These studies, however, generally do not detail initial fast changes in the early stages of the sol-gel process. Fluorescence methods using pyranine as a photoprobe developed by Kaufman *et al.* [20] and followed by Wasiucionek and Breiter [21] have been shown to be sensitive for monitoring the early stages of sol-gel reactions of tetramethylorthosilicate (TMOS). However, up till recently very little work has been reported on the early stages of sol-gel reactions of organically-modified TMOS. This paper will show that sol-gel reactions of hybrid TMOS-methyl trimethoxysilane (MTMOS) and TMOS-hydroxyl terminated poly(dimethylsiloxane) (PDMS) can also be monitored *in situ* by fluorescence techniques, enabling substituent effects to be examined. Factors affecting the hydrolysis and condensation polymerization are also discussed in this paper.

EXPERIMENTAL SECTION

Tetramethylorthosilicate derived gels were prepared by mixing TMOS, Si(OCH₃)₄ 1 mL, deionized water 0.48 mL containing 10⁻⁵ M pyranine and methanol 0.81 mL containing 10⁻⁵ M pyranine at room temperature. Dilute HCl solution, 25 μL of HCl 0.15 M, was added as catalyst. All the reactants were mixed at room temperature until a homogeneous solution was obtained. Solutions were then left to gel at room temperature in disposable cuvettes covered with paraffin film. The molar composition of the gels is [TMOS] : [water] : [methanol] = 1 : (2, 4, 8, 15, 20) : 3

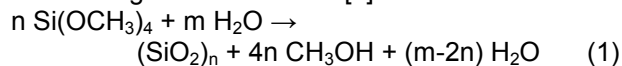
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The preparation of organically-modified silicate gels followed similar procedures to the TMOS derived materials as described above, except that the organosiloxanes were mixed with TMOS during the hydrolysis and co-condensation. The organosiloxanes used in this study are methyl trimethoxysilane, MTMOS, and hydroxyl-terminated poly(dimethylsiloxane), PDMS (MW 300). In general, the silica precursors were mixed with deionized water in methanol using HCl as catalyst at [organosiloxane]: [TMOS]:[H₂O]:[MeOH]:[HCl] molar ratio of $x:1-x:4:3:0.001$ where x ranged from 10 to 30 mol% for either MTMOS and 2.5 to 20 wt% for PDMS. The reactants were mixed at room temperature. The resultant homogeneous sol was then left to gel at room temperature in disposable cuvettes sealed with paraffin film.

Fluorescence spectra were collected on an LS 50 B Perkin Elmer Luminescence Spectrometer with an Xe lamp at room temperature. Excitation was set at 390 nm and emission was collected from 400 nm to 600 nm in 1 nm increments using 4 nm slits in both excitation and emission paths.

RESULT AND DISCUSSION

The overall chemical reaction for the formation of a silica gel from TMOS is [7]



It is seen from equation (1) that water plays an important role in the sol-gel reactions. Although the process is much more complex in reality, changes in water content have been used qualitatively to detect the hydrolysis and condensation reactions during sol formation [20-21]. This approach was

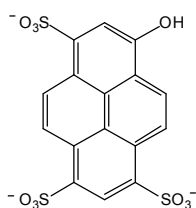
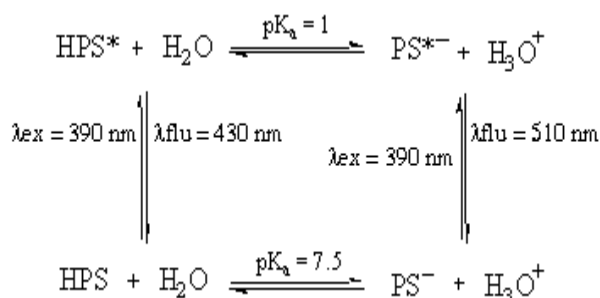


Figure 1 Pyranine (or HPS)



Scheme 1 Proton transfer in pyranine [20, 22-25]

applied for in situ monitoring of the hydrolysis and condensation reactions of TMOS sol-gels in this study. A simple fluorescence method was devised utilizing pyranine (HPS, 8-hydroxy-1,3,6-pyrenetrisulfonic acid trisodium salt) as photoprobe (Figure 1). Pyranine was chosen due to its high sensitivity to trace amounts of water and ability to perform over a wide range of pH values. The principles of the use of this molecule as a water detector can be seen from Scheme 1.

There are two sets of equilibria, the dissociation of HPS in the ground state, and the dissociation of excited states of HPS*. The dissociation of HPS to PS⁻ can be induced only under basic conditions which shift the reaction to the right. When HPS is excited (at $\lambda_{\text{ex}} = 390 \text{ nm}$), the HPS* becomes an acid of medium strength. In this condition, HPS* is capable of transferring a proton to a water molecule, forming PS^{*-}. Since HPS* and PS^{*-} fluoresce at different wavelengths ($\lambda_{\text{flu}} = 430 \text{ nm}$ and 510 nm , respectively), the ratio of fluorescence intensities at these wavelengths can be calibrated against known water concentrations [20].

The study of hydrolysis and condensation reactions in this work was carried out by using the method of Wasiucionek and Breiter with some modifications [21]. Calibration curves were first prepared by measuring the fluorescence spectra of three series of water-methanol solutions corresponding to pH values of 2, 5 and 7. The fluorescence spectra of pyranine in water-methanol mixtures at pH 5 are shown in Figure 2. The ratio of the intensities of emission peaks at 510 nm and 430 nm is a measure of the extent of proton transfer to water [20]. The calibration curves for water-methanol solutions at pH 2, pH 5 and pH 7 are presented in Figure 3. The curves are compared well with those reported in the literature, for methanol-water at pH 2 [21] and pH 6 [20].

The hydrolysis and condensation reactions of TMOS can be detected from changes in water content, obtained from the calibration curves (Figure 3). Figure 4 displays the effect of water/TMOS ratio (r) on the observed water content as a function of time. The initial period of the sol-gel process is separated into 2 regions. First is a fast decrease of the water content indicating hydrolysis and second is a slow increase of the relative water content correlating with condensation of hydrolyzed groups [21]. The rate of hydrolysis increases with increasing r value. For sols with $r = 2$ and 4 , the rate of decrease of the water content was somewhat slower and the times necessary to reach the minimum were about 5 minutes. Additionally, higher values of r caused more complete hydrolysis of monomer before significant condensation occurred.

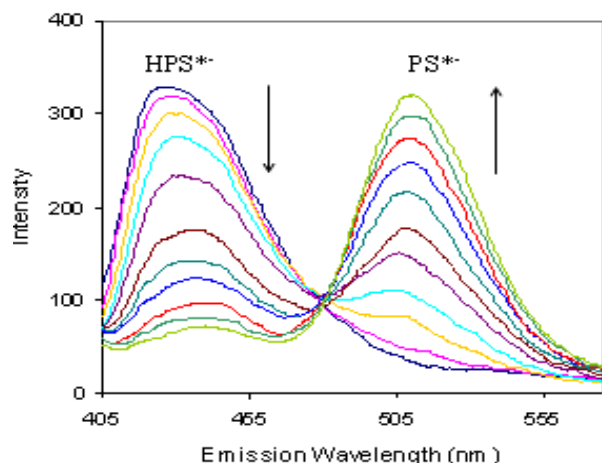


Figure 2 Fluorescence spectra of pyranine in water-methanol mixtures at pH 5. Arrows show the changes as the water content increases from 0 – 100 mol%.

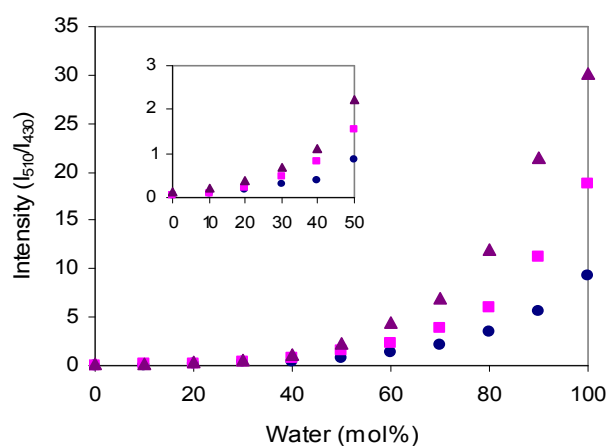


Figure 3 Calibration curves for water-methanol solutions at pH 2 (●), pH 5 (■) and pH 7 (▲); inset shows the lower water contents on an expanded scale.

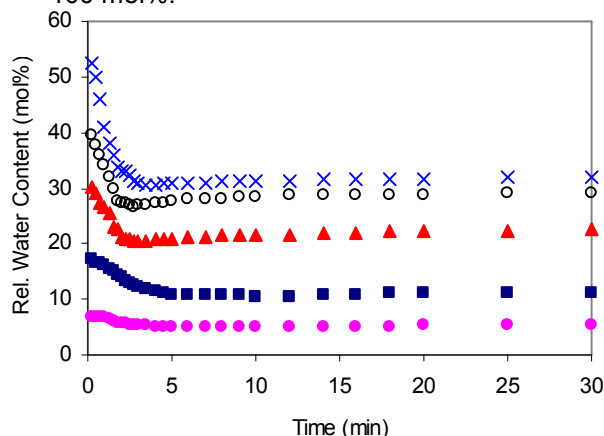


Figure 4 Effect of water/TMOS (r) ratio on the changes of relative water content at pH 2. (●) $r = 2$, (■) $r = 4$, (▲) $r = 8$, (○) $r = 10$ and (x) $r = 20$

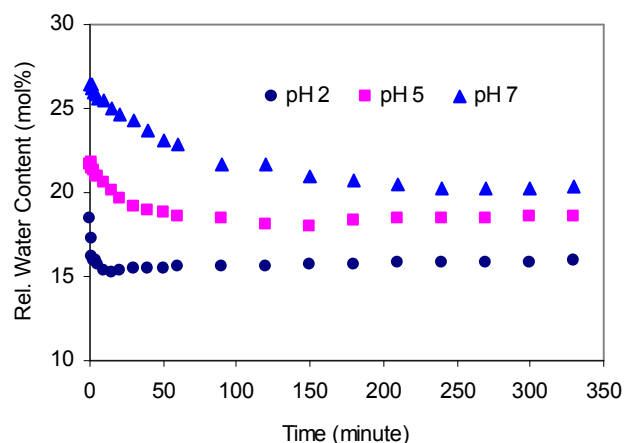
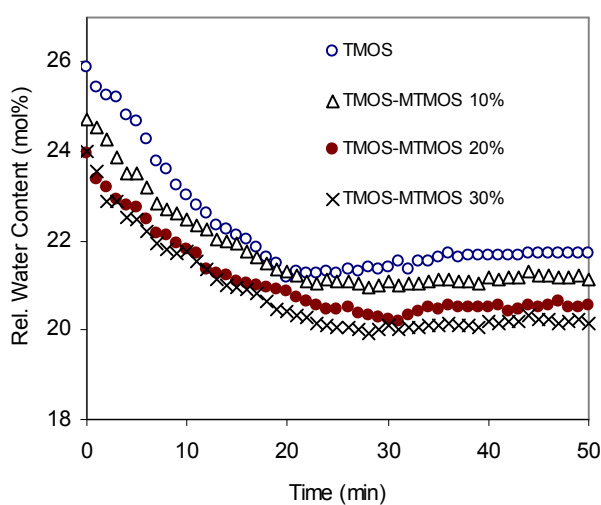
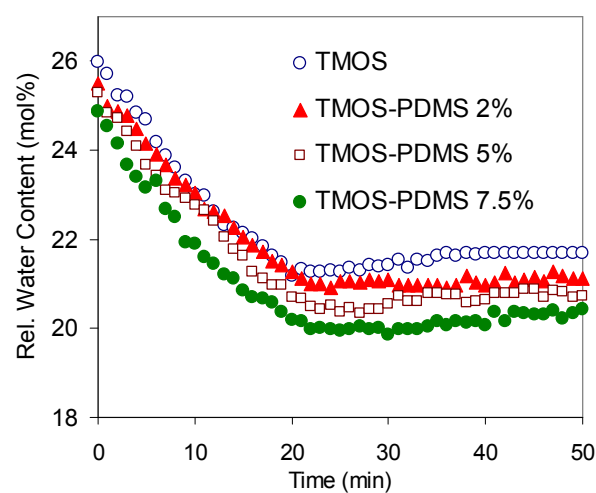


Figure 5 Effect of pH on the changes of water content at water/TMOS ratio = 4

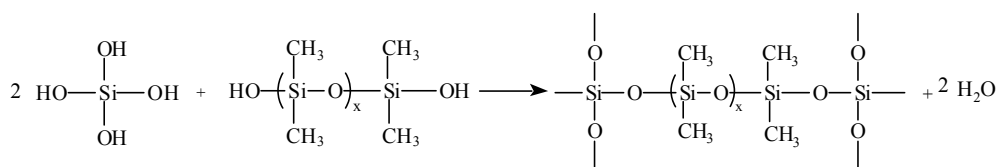


(a)



(b)

Figure 6 Effect of incorporation of (a) MTMOS and (b) PDMS on the changes of relative water content at pH 5



Scheme 2 Co-condensation of TMOS with PDMS

These results are in accordance with those reported in the literature [21]. In this study, however, increase of the water content in the second region is very slow and is not as clearly observed as the early stages of condensation (shown in Figure 4) which was measured within 30 minutes. This is far from the gelation time, which is typically about 81 hours.

The results are consistent with water consumption for the overall sol-gel reaction of TMOS (equation 1) which implies that two equivalents of water are needed to convert $\text{Si}(\text{OCH}_3)_4$ to SiO_2 . For the complete hydrolysis of $\text{Si}(\text{OCH}_3)_4$, 4 equivalent of water are needed if no condensation were to take place. Increasing r generally favors the formation of silanol groups over Si-O-Si groups [7, 26], since in principle the condensation is reversible. This is also consistent with the concept stated by Schubert and Husing [26] that there are only mixtures of hydroxylated species $[\text{SiO}_x(\text{OH})_y(\text{OR})_z]_n$ ($2x+y+z=4$) formed in sols with $r < 2$. It is considered that lower water content, $r \leq 2$ favors the condensation reaction, and higher water content, $r \geq 2$ favors the hydrolysis reaction.

The effect of pH on the hydrolysis and condensation reactions is presented in Figure 5 which shows a slower rate of decrease in water content in the first region (hydrolysis) at higher pH. As found in the water/TMOS ratio studies, the changes in water content in the second region are not clearly observed here either because of their gelation times which are still far longer than the reaction times under investigation (except for pH 7 which gels in 162 minutes).

Modification of sol-gel silica materials by incorporation of organic groups via covalent bonding changes the behavior of the hydrolysis and condensation reactions. Figure 6 shows the effect of incorporation of MTMOS, $(\text{CH}_3\text{Si}(\text{OCH}_3)_3)$ and PDMS (polydimethylsiloxane) on the changes of water content at pH 5. It should be noted that in these fluorescence experiments all reactions were performed in closed cuvettes, which do not have any evaporation, so any changes were due to relative water content. The graphs show that the rate of both hydrolysis and condensation decrease in the presence of MTMOS. In general, however,

there is no significant difference in the rate of hydrolysis with increasing concentration of the organosilane. This supports the hypothesis that when organically modified alkoxides are reacted, the hydrolytically stable groups change the reactivity of silicon atom to which they are directly bonded, resulting in slower sol-gel reactivity [7,26]. In the sol-gel reactions of the TMOS-MTMOS system, co-condensation should be dominant due to the steric repulsion between alkyl groups and the greater mobility of TMOS species. In addition, in the presence of relatively large amounts of TMOS, hydrolyzed MTMOS molecules are more likely to co-condense with TMOS rather than condensing themselves.

Very similar behaviour to TMOS-MTMOS was found for the TMOS-PDMS system. When PDMS is introduced to the pure TMOS system, the mechanism of hydrolysis of TMOS remains the same, but polycondensation reactions become complicated. It was noted that the acid reaction schemes that lead to the formation of PDMS-modified silica must consist of both hydrolysis and self condensation of TMOS and also co-condensation between PDMS and TMOS as shown in Scheme 2 [27-30].

CONCLUSION

Fluorescence method was developed for *in situ* monitoring of reaction processes during hydrolysis and polymerization reactions of organically-modified tetramethylorthosilicate. The fluorescent dye pyranine is sensitive to the proton acceptor characteristics of the solvent changes in the solvent composition during these processes. The hydrolysis and condensation reactions are greatly influenced by water to precursor ratio, type of organosiloxane, mol ratio of organosiloxane to silica precursor and pH. The fluorescence *in situ* method enables ready monitoring of the sol-gel reactions. This enables the effect of added organosiloxane precursors to be easily investigated. Incorporation of MTMOS and or PDMS to TMOS changes the behavior of the sol-gel reaction.

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