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# Gelation kinetics of an organically modified silicate

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The gelation of solutions containing mixtures of tetraethoxysilane (TEOS) and polydimethyl siloxane (PDMS) with isopropanol, $H_2O$, and HCl as the catalyst was studied at various temperatures in closed systems. Large variations in the gelation rates were observed with varying temperatures, and different acid and water contents. The gelation rates were found to increase with increasing temperature as well as with HCl content. However, decreasing the water concentration (the molar ratio $H_2O:TEOS < 3$) had a more significant effect in decreasing the gelation rate. Apparent activation energies were obtained from Arrhenius plots of gelation time against temperature and they were shown to change with acid content. The microstructural evolution in the final, dried gels appeared to be related to the degree of network linkage in the present system.

## 1. Introduction

Since the successful preparation of organically modified glass and ceramics via the sol–gel process, increased interest has been directed towards developing new hybrid materials [1–4]. These materials are synthesized by chemically incorporating organic polymers into an inorganic network, thus improving the resultant mechanical properties such as ductility and toughness. Additionally, the high reactivity resulting from the sol–gel route permits low-temperature processing, which gives dried gels of high surface area, and it may allow for the formation of interesting, non-equilibrium phases. An obvious advantage of this technique, compared to the more conventional high-temperature processing, is the ability to combine properties of very different materials without the problem of decomposition.

Recently, structure-related, rubber-like, organically modified silicates (ORMOSILs) have been reported [5–7], but the factors governing the formation of these ORMOSILs remained unclear. Nevertheless, the structure-related properties of gels strongly depend on the degree of the polymerization in sol–gel transformations [8, 9]. The general scheme of the sol–gel process can be viewed as a two-step reaction involving the hydrolysis reaction of metal alkoxide precursors followed by polycondensation to form a three-dimensional network. The hydrolysis reaction, in most cases, is completed in a very short time, whereas the condensation reaction progresses more slowly. Typically, these reactions occur simultaneously and depend on the type of catalyst and the experimental conditions. The role of the starting reagents [10–12], of the catalysts [13], and the temperatures [14, 15] on the gelation process of sol–gel-derived silica has been studied in great detail, but similar studies on ORMOSILs have not been reported.

In this paper, the effects of temperature, acid and water on the gelation of ORMOSILs are presented. The resultant structures and microstructures of the ORMOSILs influenced by these factors are also discussed.

## 2. Experimental procedure

TEOS and silanol terminated PDMS with molecular weights of about 1700 were obtained from the Fluka Company and from Petrach System, respectively. The gelation of solutions containing mixtures of TEOS and PDMS with isopropanol, tetrahydrofuran (THF), doubly distilled water, and HCl acid as the catalyst was studied at various temperatures in a closed system. First, a solution with a ratio of 30 g TEOS to 20 g PDMS to 15 ml isopropanol to 10 ml THF was mixed in a container and placed in a water bath to reach the desired temperature. The adjusted acidic water solution, at a desired concentration, mixed with 25 ml isopropanol at the same temperature, was then quickly added into the well-stirred solution. The reactions were studied from 20 to 70 °C. The effect of the acid on gelation was studied by changing the molar ratio of HCl to TEOS to the following values: 0.05, 0.1, 0.2, 0.3 and 0.4. The effect of water on gelation was investigated by changing the molar ratio of $H_2O$ to TEOS to the following values: 2, 3, 4, 5 and 6. The gelation time will be obtained as a function of the catalyst, water and temperature at constant concentrations of TEOS and PDMS.

The solution was stirred until its viscosity reached about $10\,N\,s\,m^{-2}$ (pre-calibrated from the stirrer

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speed), and it was then poured into a glass tube 1 cm in diameter and 8 cm long and then sealed at the same temperature. The gelation time was defined as the point when the sol did not flow upon tilting the tube under gravity and the viscosity of the solution had reached about $10^3\,\mathrm{N\,s\,m^{-2}}$. After gelation, the gels were kept at room temperature in the sealed container for two weeks and then dried in air for one week at room temperature and at 70 °C for two days. The aged gels were then heat treated at 150 °C for 24 h for bulk and apparent density measurements by the Archimedes method. The microstructures of the completely dried gels were examined by scanning electron microscopy (SEM), and X-ray diffraction (XRD) was used to examine the crystallinity.

## 3. Results and discussion

### 3.1. The reaction scheme in the sol–gel process

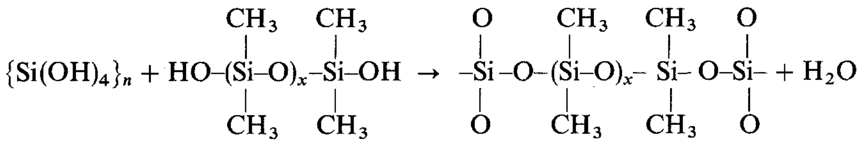
Several types of reaction in the sol–gel process, such as the hydrolysis of the alkoxides, the subsequent polymerization bonding of particles and cross-linking between these particles, are all assumed to affect the rate of the sol-to-gel transition and the gelation time. Although the exact stepwise reaction mechanisms are still unclear, the overall reactions may be represented by the following simplified reactions.

Hydrolysis:

$$\mathrm{Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH} \quad (1)$$

where R is $C_2H_5$ in the present research.

Polycondensation:



$$\{\mathrm{Si(OH)_4}\}_n + \mathrm{HO}\text{–}(\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\text{–}\mathrm{O})_x\text{–}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\text{–}\mathrm{OH} \rightarrow \text{–}\underset{\mathrm{O}}{\overset{\mathrm{O}}{\mathrm{Si}}}\text{–}\mathrm{O}\text{–}(\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\text{–}\mathrm{O})_x\text{–}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\text{–}\mathrm{O}\text{–}\underset{\mathrm{O}}{\overset{\mathrm{O}}{\mathrm{Si}}}\text{–} + \mathrm{H_2O} \quad (2)$$

Self-condensation:

$$\mathrm{2Si(OH)_4 \rightarrow SiO_2 + 2H_2O} \quad (3)$$

For the silica–gel system [10] and ORMOSILs [7], the hydrolysis reaction is completed very quickly after mixing if adequate amounts of water and catalyst are present. The extent of the reactions depends on the amount of water added, and the conditions under which the reaction is carried out. The relative rate of self-condensation with respect to polycondensation is crucial in determining the final bulk structure and, thus, the properties of the resultant materials. However, it is difficult to completely separate hydrolysis from condensation in the entire gelation process.

### 3.2. Effect of temperature

Table I shows that the bulk density, the apparent density and the porosity of the dried gels varied with the gelation temperature. The apparent density was obtained from powder of the crushed sample and may contain some micropores. Although the apparent density remained somewhat constant, the average bulk-density decreased significantly from $1.02\,\mathrm{g\,cm^{-3}}$ at 25 °C to $0.56\,\mathrm{g\,cm^{-3}}$ at 70 °C. The open porosity, calculated from the difference between the average bulk density and the apparent density, increased significantly with increasing temperature. The results are in complete contrast to the pure acid–catalyst TEOS system in which the bulk density increased as the gelation temperature increased and are directly attributable to the increased ageing at higher temperatures [15]. This indicates that the addition of PDMS has a different gelation mechanism to the pure TEOS gels.

TABLE I Bulk density, apparent density and porosity of dried gels as a function of temperature with ratios HCl/TEOS = 0.3 and $H_2O$/TEOS = 3

| Preparation temperature (°C) | Average bulk density ($\mathrm{g\,cm^{-3}}$) | Apparent density ($\mathrm{g\,cm^{-3}}$) | Open porosity (%) |
|---|---|---|---|
| 25 | 1.02 | 1.09 | 6.5 |
| 40 | 0.91 | 1.10 | 17.3 |
| 50 | 0.83 | 1.12 | 26.8 |
| 60 | 0.65 | 1.10 | 40.9 |
| 70 | 0.56 | 1.11 | 49.5 |

Fig. 1 shows that, after the ORMOSILs gels were completely dried, the microstructures varied with different gelation temperatures. During drying, the sample gelled at a higher temperature shrank less than the sample gelled at a lower temperature. The terms *cellular structure* or *foam structure*, which is an assembly of cells with solid edges or faces, can be used to describe the character of these porous microstructures. A similar foam structure has been observed in cellular plastics [16]. The cellular structure is more open at higher temperatures. The morphology of the foam structure shows that the cells becomes bigger at higher temperatures. In the present work, the samples gelled at lower temperatures showed less structural integrity, which may be a result of internal drying stresses during the gelling/drying process.

As already observed in various systems [14, 17–20], a temperature-dependent gelation can be represented by an Arrhenius equation:

$$t_{\mathrm{gel}} = A^{-1}\exp(E^*/RT) \quad (4)$$

where $t_{\mathrm{gel}}$ is the gelation time, the time taken to reach a viscosity of $10^3\,\mathrm{N\,s\,m^{-2}}$; $1/t_{\mathrm{gel}}$ can thus be considered as a rate of the overall gelation process. $E^*$ is the apparent activation energy, $R$ is the ideal gas constant, and $A$ is the usual Arrhenius constant. However, the activation energy, $E^*$, cannot be ascribed to any one of the different reactions as discussed above. This method has been used by some people to determine the activation energy of gelation for TEOS–HCl systems [14, 15, 19].

Generally, $t_{\mathrm{gel}}$ is decreased by those factors that increase the condensation rates. For example, increases in the added water, the catalyst, the temperature, and the concentration of alkoxide, and

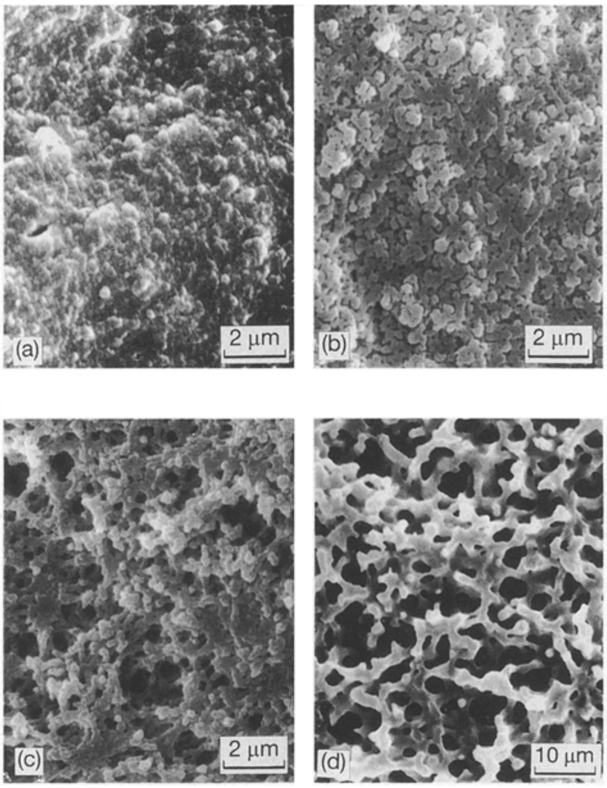


*Figure 1* SEM micrographs showing the different structural geometries obtained for different temperatures: (a) 25 °C, (b) 50 °C, (c) 60 °C, and (d) 70 °C. HCl/TEOS = 0.3 and $H_2O$/TEOS = 3.

decreases in the size of the alkoxy group can all decrease $t_{gel}$ [14, 21–24]. Figs 2 and 3 show the effect of temperature on the gelation time for different molar ratios of HCl to TEOS and $H_2O$ to TEOS, respectively. As shown, the gelation time is a function of $1/T$ and the plots are indeed linear on a logarithmic scale. No obvious shift of rate-determining steps within this temperature range is observed from the linear Arrhenius plots. The rate-determining step is usually the overall condensation reaction. Higher gelation rates at higher temperatures obviously result from the more highly energized state of the reacting molecules and the higher transport rate of condensing species.

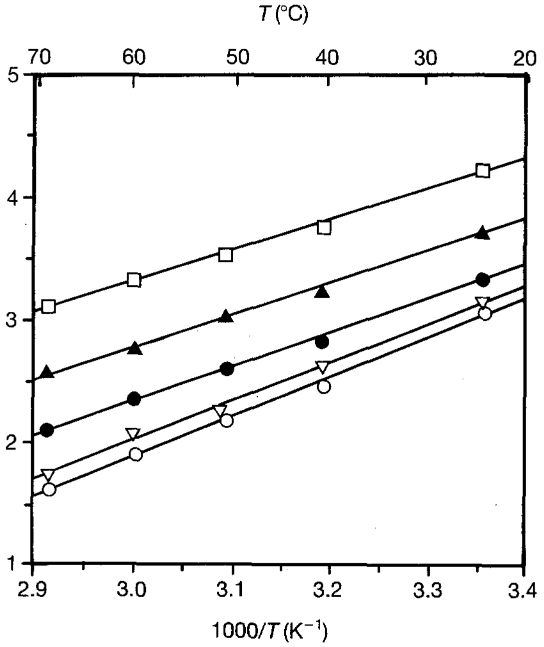


*Figure 2* Plot of gelation time versus $1/T$ for different HCl contents and a constant molar ratio of $H_2O$/TEOS = 3, for the following HCl/TEOS ratios: (□) 0.05, (▲) 0.1, (●) 0.2, (▽) 0.3, and (○) 0.4.

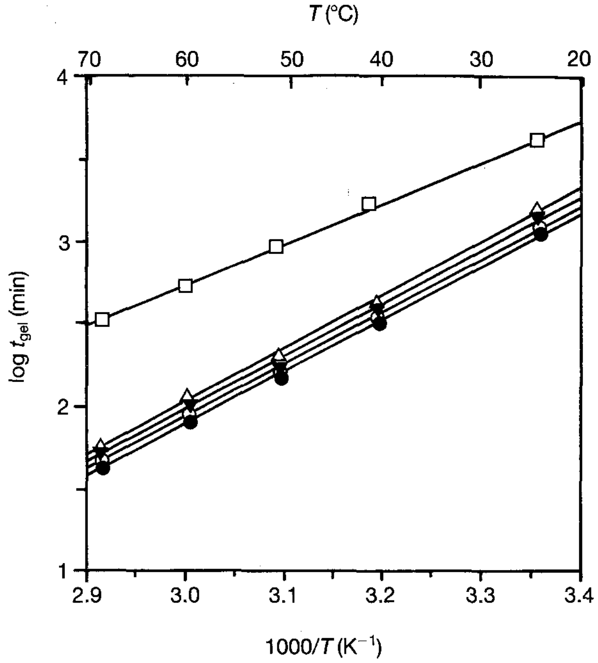


*Figure 3* Plot of gelation time versus $1/T$ for different $H_2O$ contents and a constant molar ratio of HCl/TEOS = 0.3, for the following $H_2O$/TEOS ratios: (□) 2, (△) 3, (▼) 4, (○) 5, and (●) 6.

## 3.3. Effect of HCl

Samples with higher acid contents as expected, tended to gel faster than those with lower acid contents, as shown in Fig. 2. As the acid content increased, the rate of the hydrolysis reaction increased and the mainly condensation process will be enhanced [5]. Similar results were also observed in pure silica gels within a range of pH values [25]. The apparent activation energies for different acid contents are plotted in Fig. 4. It can be seen that activation energy varies from ~ 11.7 kcal mol$^{-1}$ to ~ 14.5 kcal mol$^{-1}$ as the acid content increased. The value of the activation energy is very close to that of acid-catalyst pure silica gels from TEOS, ranging from 9 to 17 kcal mol$^{-1}$ [18, 19]. The effect of different concentrations of acid on the activation energy has not been reported. Here we found that the activation energy can be lowered when the concentration of HCl decreased. The activation energy would change little when the concentration of HCl becomes high, as shown in Fig. 2. This indicates that addition of HCl would enhance some reactions more than others. It has been reported that the copolymerization proceeded further as the acid content increased and as the reaction rates of hydrolysis and self-condensation of TEOS also increased [25]. The assumed copolymerization reaction reaches completion much faster with higher acid contents, whereas the self-condensation of TEOS becomes the determinative step in the whole process. Similar results

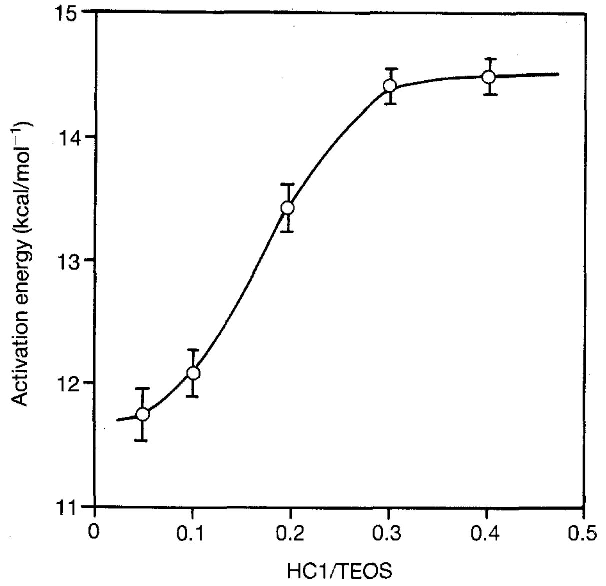


*Figure 4* Plot of the apparent activation energy versus the molar ratio of HCl to TEOS for a constant ratio of $H_2O$/TEOS = 3.

were also discovered by a $^{29}$Si NMR technique [26]. Such different reaction rates would cause a different resultant structure of the gel.

Table II shows that the bulk density, the apparent density and the porosity of the dried gels varied with different ratios of HCl to TEOS. The porosity increased significantly with increasing HCl while the apparent density remained nearly constant. The resultant microstructures due to different HCl contents are shown in Fig. 5. The gel structure becomes more open with higher acid contents which is similar to the effect of temperature. Such an acid-dependent gelation process presumably reflects a degree of networking similar to the effect of temperature. Different hydrolysis rates may result in different concentrations of reactive species, and this influences cross-linking and structure strongly [2].

Another representation of the acid-dependence gelation rate is shown in Fig. 6 in which the gelation time decreased as the HCl content increased, being a linear relation on a logarithmic scale. The slope, $n$, of the plot is about 1.2 to 1.6, and can be expressed as $t_{gel} \sim [\mathrm{HCl/TEOS}]^{-n}$. Similar results have been observed in different silica-gel systems and they show a first-order rate constant in hydrolysis and condensation reactions [25]. This indicates that HCl participates in some reactions during gelation. One suggestion is that protonated and deprotonated silanols are involved in the acid-catalysed-condensation mechanism for higher acid contents [25]. Another possible reaction is the redistribution reaction of PDMS with HCl [26].

TABLE II Bulk density, apparent density and porosity of dried gels as a function of the HCl/TEOS ratio with a ratio $H_2O$/TEOS = 3 and temperature = 60 °C

| HCl/TEOS ratio | Average bulk density (g cm$^{-3}$) | Apparent density (g cm$^{-3}$) | Open porosity (%) |
|---|---|---|---|
| 0.05 | 1.10 | 1.11 | 1.2 |
| 0.1 | 1.09 | 1.11 | 1.9 |
| 0.2 | 0.88 | 1.09 | 19.2 |
| 0.3 | 0.65 | 1.10 | 40.9 |
| 0.4 | 0.50 | 1.10 | 54.5 |

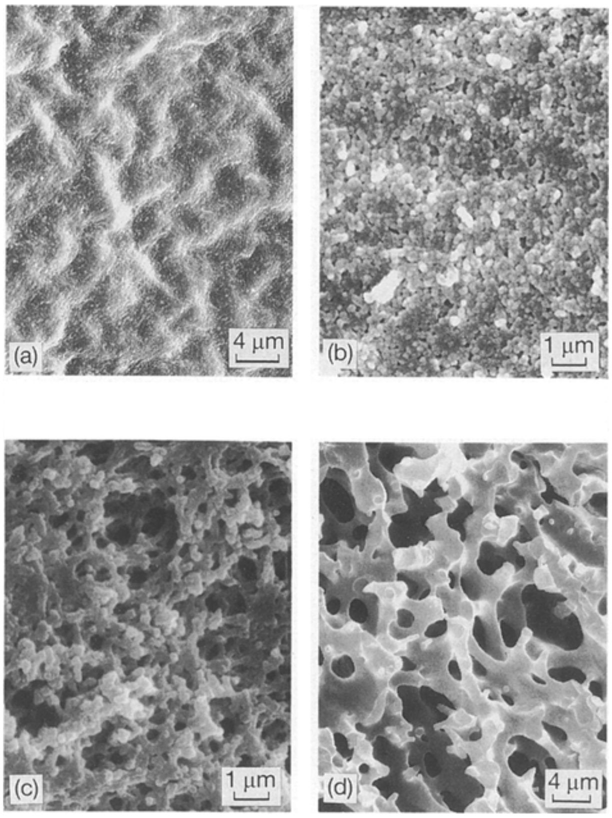


*Figure 5* The SEM microstructures for different HCl contents with a constant ratio of water/TEOS = 3; with the ratio of HCl/TEOS equal to: (a) 0.1, (b) 0.2, (c) 0.3, and (d) 0.4.

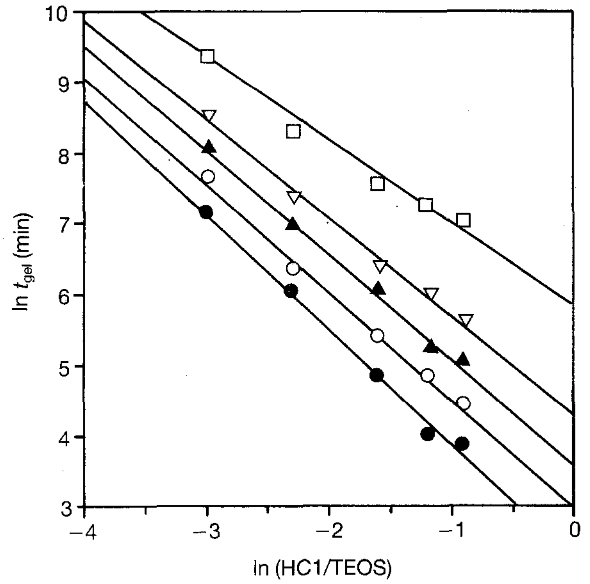


*Figure 6* Plot of the gelation time versus the molar ratio of HCl/TEOS for the following temperatures: (□) 25 °C, (▽) 40 °C, (▲) 50 °C, (○) 60 °C, and (●) 70 °C.

### 3.4. Effect of water

Water plays an important role in the hydrolysis process, as described in Reaction 1. To study the effect of water content, solutions with various amounts of water were prepared. The results, plotted in Fig. 2 as $\log(t_{gel})$ versus $1/T$, show that solutions having a water content above the stoichiometric amount, $[H_2O]/[TEOS] = 2$ in a molar ratio, have a similar reaction time. Solutions with lower water contents, e.g. $H_2O/TEOS = 2$, however, have distinctly slower gelation rates. The apparent activation energies for different water contents are plotted in Fig. 7. When the solution has higher molar ratios of $H_2O/TEOS$ ($\geq 3$) the activation energy for a constant acid content about the same value. On the other hand, for solutions prepared with $H_2O/TEOS = 2$ the activation energy is 11.2 kcal mol$^{-1}$. Similar results are observed in pure-silica systems in which the activation energies decrease with decreasing water content [19]. As shown in Reactions 1 and 2, water is consumed in the hydrolysis reaction but generated by the condensation reaction. For consistency, the amount of water added in the solution is always expressed as the percentage of water needed to complete the hydrolysis reaction. For complete hydrolysis, the ratio of $H_2O$ to TEOS should be at least four. A lower water content can defer the completion of hydrolysis and, thereafter, cause the water-forming condensation to slow down and then the hydrolysis rate becomes important to the whole reaction process. On the other hand, the hydroxyl group of PDMS may decrease the amount of water needed to complete the reactions.

Table III shows that the bulk density, the apparent density, and the porosity of the dried gels varied with the $H_2O/TEOS$ ratio. The porosity of the samples increases with increasing water content, but not so significantly as with temperature and acid content. The variations in the microstructures for different water contents are shown in Fig. 8 and result as expected in a competitive reaction between hydrolysis and condensation. As mentioned previously, the "foam" structure of ORMOSILs is unlike the structure of porous glasses which have irregular fractal-type morphologies. The competitive growth reaction between copolymerization and self-condensation is very important but it is not the only factor which shapes foam. The final foam structure depends on the rheology and surface tension of the fluids as described in producing polymer foams [27]. When surface tension is the dominant shaping force, and when it is independent of orientation, the structure minimizes the surface area for a constant cell volume. Plots of the gelation rate versus water content are shown in Fig. 9 on a logarithmic scale. When $H_2O/TEOS$ is larger than 3 the gradient is small; this indicates the necessity of water for these reactions would not greatly exceed this ratio. Similar results are observed in pure silica [14], and it can be concluded that when adequate

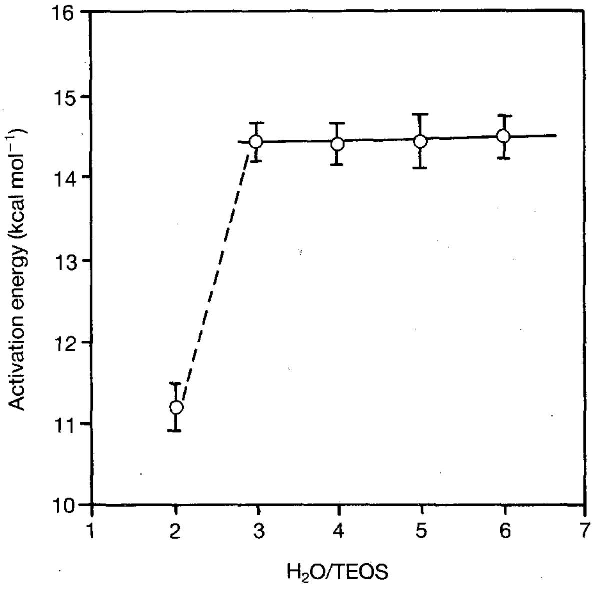


*Figure 7* Plot of the apparent activation energy versus the molar ratio of $H_2O$/TEOS for a constant ratio of HCl/TEOS = 0.3.

TABLE III Bulk density, apparent density and porosity of dried gels as a function of the $H_2O$/TEOS ratio with a ratio HCl/TEOS = 0.3 and temperature = 70 °C

| $H_2O$/TEOS ratio | Average bulk density (g cm$^{-3}$) | Apparent density (g cm$^{-3}$) | Open porosity (%) |
|---|---|---|---|
| 2 | 0.72 | 1.12 | 33.9 |
| 3 | 0.56 | 1.11 | 49.5 |
| 4 | 0.50 | 1.09 | 54.1 |
| 5 | 0.48 | 1.10 | 56.4 |
| 6 | 0.49 | 1.11 | 55.8 |

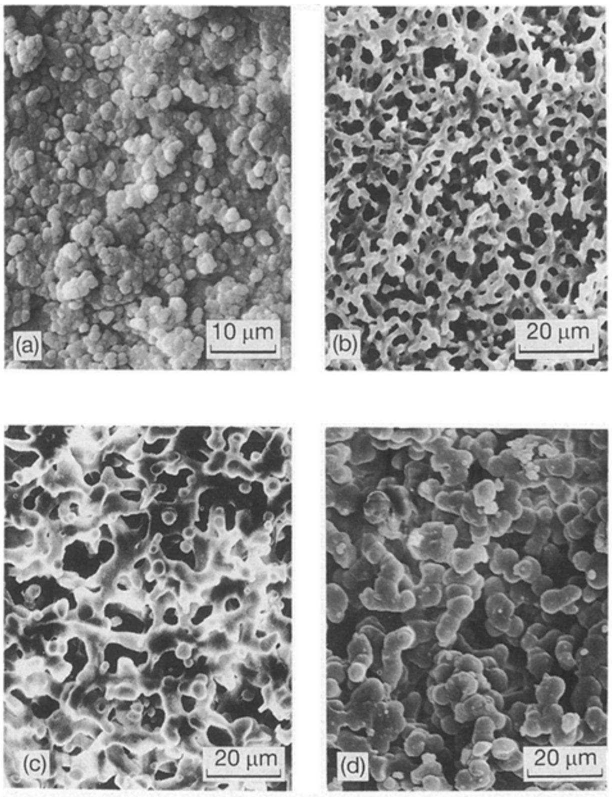


*Figure 8* SEM microstructures for different water contents with a constant ratio of HCl/TEOS = 0.3 with the ratio of $H_2O$/TEOS equal to: (a) 2, (b) 3, (c) 4, and (d) 5.

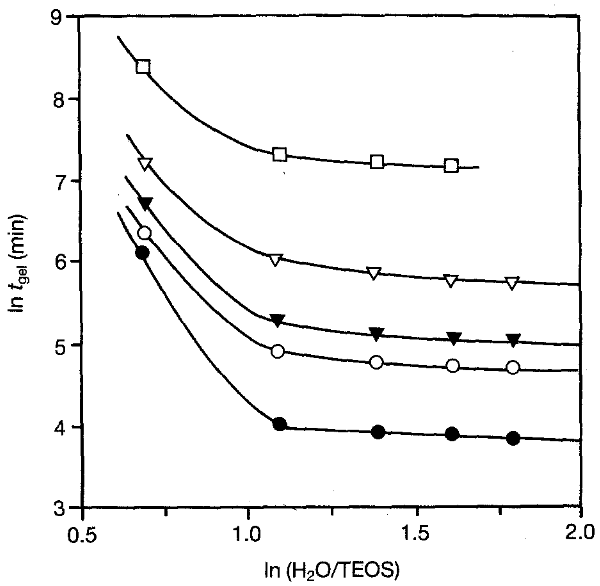


*Figure 9* Plot of the gelation time versus the molar ratio of $H_2O$/TEOS for the following temperatures: (□) 25 °C, (▽) 40 °C, (▼) 50 °C, (○) 60 °C, and (●) 70 °C.

water is present $t_{gel}$ is probably governed by condensation.

## 4. Conclusion

The results show clearly how the reaction conditions may influence the final structure of ORMOSILs. The gelation rate is a good approach to the study of the effects of these factors and was conducted by a simple tilting method. Large differences in gelation rates were observed for different temperatures, HCl contents, and water contents. The gelation rates increase with increasing temperature as well as HCl content. Water content has a more significant effect on the gelation rate when the molar ratio of $H_2O$ to TEOS is less than 3. The apparent activation energies were obtained from Arrhenius plots and show different values for different acid contents. The different microstructural evolutions for the final dried gels appear to be related to the degree of network linkage in the present system, which results in a competitive growth reaction between hydrolysis, polycondensation and self-condensation.

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