

## Molecular Growth Pathways in Silica Sol-Gel Polymerization

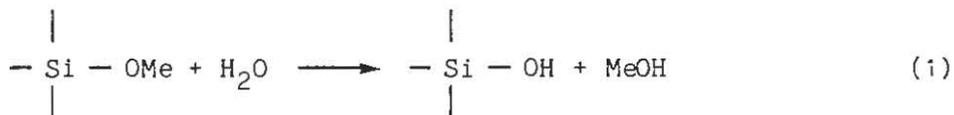
Sangeeta D. Ramamurthi

Final Seminar

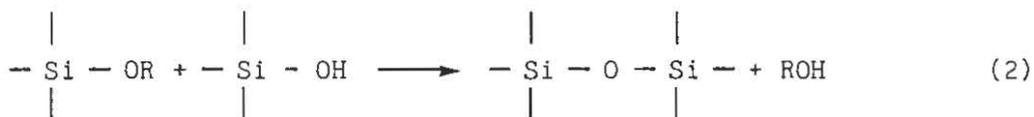
January 9, 1989

Silica sol-gel polymerization had its beginning in the early 1840's when J. J. Ebelmen first synthesized  $\text{Si}(\text{OC}_2\text{H}_5)_4$  and prepared a variety of materials including fibers, monoliths and composites from silicon alkoxides [1]. Later, the process was also utilized in fabricating materials such as microspheres [2] and films [3].

Silica sol-gel polymerization normally involves hydrolysis and condensation of silicon alkoxides in alcoholic media [1] (equations 1 and 2).



Me = methyl or other alkyl group

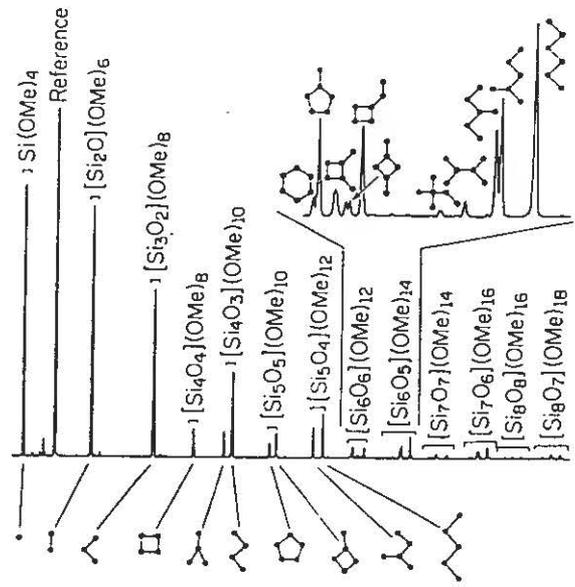
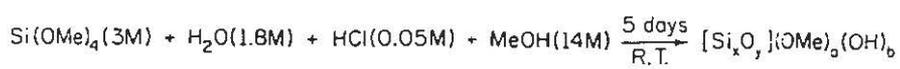


R = H or alkyl group

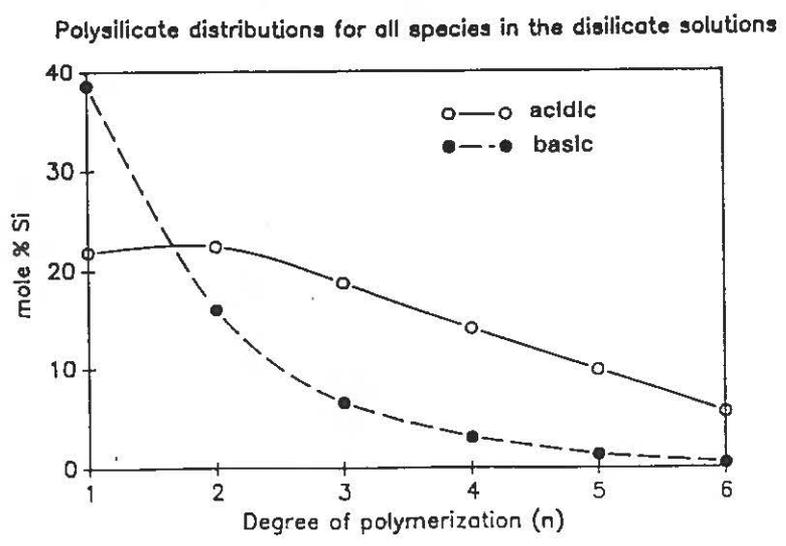
The physical properties of silica sols and gels obtained in this fashion are very sensitive to reaction conditions such as water concentration, silicate concentration, solvent and solution pH [4]. The aim of the research project was to understand the microscopic relationship between the physical properties of the materials and the reaction conditions employed.

The study of the molecular growth pathways in silica sol-gel polymerization necessitates the identification of individual polysilicate intermediates in the silicate solution. In this context, a model system with sub-stoichiometric amounts of water (i.e.  $\text{H}_2\text{O}/\text{Si}(\text{OR})_4 < 1$ ) was developed and the reaction conditions were optimized such that >90% of total silicon was present as low molecular weight polysilicates ( $1 \leq x \leq 6$  in  $\text{Si}_x\text{O}_y(\text{OCH}_3)_a$ ). An analytical protocol involving gas chromatography (GC), gas chromatography-mass spectrometry (GCMS), and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectroscopy, was developed to structurally characterize the polysilicate intermediates formed during silica sol-gel polymerization. This protocol allowed the structural identification of mono- through hexasilicate species ( $1 \leq x \leq 6$  in  $[\text{Si}_x\text{O}_y](\text{OCH}_3)_a$ ) formed during partial hydrolysis and condensation of tetramethyl-orthosilicate [5] (see Figure below).

The analytical protocol employing capillary gas chromatography was applied [6] to monitor the stoichiometry, structures and abundances of low molecular weight polysilicates ( $1 \leq x \leq 6$  in  $[\text{Si}_x\text{O}_y](\text{OCH}_3)_a$ ) formed during partial hydrolysis of methanolic tetramethylorthosilicate under acidic (HCl) and basic (KOH) conditions. The same procedure was applied to study the redistribution of methanolic hexamethyldisilicate and octamethyltrisilicate under similar reaction



conditions. The polysilicate molecular weight distributions obtained were expressed in terms of mole percent of total silicon present as a function of degree of polymerization. Under acidic conditions, the molecular size distributions showed maxima near the number average degree of polymerization, and diminished at higher and lower degree of polymerization. Under basic conditions, on the other hand, the distributions had their maxima at the monomer percent and extended to very high molecular weights, yielding distributions far broader than the ones observed under acidic conditions (see Figure below).



These features were found to be in agreement with the covalent network theories of silica gelation (Flory-Stockmayer theory) [7]. Weight fraction distributions of the type observed under acidic conditions were characteristic of linear polymers with a low degree of crosslinking. Weight fraction distributions observed under

basic conditions were characteristic of branched polymers with a high degree of crosslinking. The low degree of crosslinking obtained under acidic conditions was observed to arise from steric crowding that discouraged branching in polysilicate structures. Finally, the physical properties of the resultant materials such as bulk and skeletal densities were explained in terms of the observed molecular weight distributions and their characteristics.

#### References

1. (a) Ebelmen, J. J. Ann. de Chemie et de Phys. 1846, 16, 129.  
(b) Ebelmen, J. J. Comptes Rend. de L'Acad. de Sciences 1847, 24, 854.
2. (a) Roy, R. J. Am. Ceram. Soc. 1969, 52(6), 344.  
(b) Teichnen, S. J., Nicholaon, G. A., Vicarini, M. A., Gardos, G. E. F. Adv. Coll. Inter. Sci. 1976, 5, 245.
3. (a) Hofmann cited in Art and Archeology Technical Abstracts 1966, 6(1), 191.  
(b) Sakka, S., Kamiya, K. J. Non-Cryst. Solids 1980, 42, 403.
4. (a) M. Yamane, S. Inoue, Yasumon, A. J. Non-Cryst. Solids 1984, 63, 13.  
(b) Ulrich, D. R. Am. Ceram. Soc. Bull. 1985, 64, 1444.
5. (a) Klemperer, W. G., Ramamurthi, S. D. Poly. Pre., Am. Chem. Soc. Div. Polym. Chem. 1987, 28, 432.  
(b) Klemperer, W. G.; Mainz, V. V.; Ramamurthi, S. D.; Rosenberg, F. S. in Better Ceramics through Chemistry, edited by Brinker, C. J., Clark, D. E., Ulrich, D. R. (Mat. Res. Soc. Proc. 121, Pittsburg, PA, 1988) p. 15.
6. Klemperer, W. G.; Ramamurthi, S. D. in Better Ceramics through Chemistry, edited by Brinker, C. J., Clark, D. E., Ulrich, D. R., (Mat. Res. Soc. Proc. 121, Pittsburg, PA, 1988) p. 1.
7. (a) Flory, P. J. Principals of Polymer Chemistry (Cornell University Press, Ithaca 1953), Chapters 8 and 9.  
(b) Stockmayer, W. H. in Advancing Fronts in Chemistry edited by Twiss, S. B. (Reinhold, New York, 1945) p. 61.