

STRUCTURE OF SOL-GEL DERIVED INORGANIC POLYMERS: SILICATES AND BORATES

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Introduction

Sol-gel processing uses metal alkoxides ($M(OR)_x$) as monomeric, ceramic precursors. In alcohol/water solutions the alkoxide groups are removed stepwise by acid- or base-catalyzed hydrolysis reactions. Subsequent condensation reactions involving the hydroxyl groups yield polymeric solution species composed of M-O-M linkages. Gelation occurs by growth and linkage of polymers to form a network which spans the entire solution. Although the gel has the properties of a solid, condensation reactions continue during subsequent drying and consolidation steps. Throughout this complete process, structure is influenced by physical and chemical mechanisms which control the sequence and pattern of hydrolysis and condensation (and the reverse reactions, esterification and depolymerization).

Structures of gel-derived inorganic polymers must be considered on several length scales. First there is the local environment of the metal atom: the second nearest neighbors may be either alkyl groups, protons, or other metal atoms. On a larger length scale, oligomeric species (dimers, trimers, tetramers, etc.) may be linear, branched or cyclic. Finally, on the largest length scales, structures may be dense with well-defined interfaces, uniformly porous, or tenuous networks characterized by a fractal dimension, D [1]. (For mass fractals D relates the polymer mass to its radius according to: $M \propto r^D$, where in three-dimensions $D < 3$.)

This note summarizes the results of structural studies of silicate and borate gels both in solution and during drying and consolidation. Although many factors affect gel structure (catalytic conditions, solvent composition, water to alkoxide ratio, etc.), we emphasize those results which demonstrate how structure is influenced by the stability of the condensation products in their synthesis environment.

Structures of Polymers and Gels

Silicate polymers and gels are readily synthesized by the hydrolysis of tetraethylorthosilicate (TEOS) in acidic, neutral or basic solutions employing H_2O/OR ratios of two to over 50. As shown by the following two examples, structures on all length scales are profoundly influenced by the relative stability of the siloxane bond in the solution environment.

1) Availability of Monomer. Under most solution conditions employed for gel formation, monomer is rapidly consumed to form a distribution of oligomeric species [2]. Thereafter the only source of monomer is that produced by the hydrolytic (or alcoholic) depolymerization of siloxane bonds. Depending on the stability of the siloxane bond and hence the availability of monomer, the growth process may change significantly. For example, simulations of reaction-limited monomer cluster growth result in the formation of dense spherically expanding particles, whereas cluster-cluster growth processes, which occur in the absence of monomer, result in the formation of highly ramified fractal structures [1]. The general predictions of these simulations are experimentally realized. Silica polymers formed under conditions in which the rates of depolymerization and polymerization are comparable (e.g., the basic conditions employed by Stöber) are relatively dense spherical particles ($M \propto r^3$) [3]. Polymers formed by a two-step hydrolysis process at pH 2 where the depolymerization rate is low are weakly condensed, mass fractals ($M \propto r^D$) [1].

2) Approach to Thermodynamic Equilibrium

Depolymerization/repolymerization processes allow the system to approach thermodynamic equilibrium. Conversely, polymeric networks formed under conditions where depolymerization/repolymerization is suppressed (e.g., near

pH 2) are highly metastable. At large length scales the approach to equilibrium is manifested as ripening. Weakly crosslinked species depolymerize and preferentially condense with more highly polymerized species resulting in a reduction in surface energy. If depolymerization cannot occur, the network reflects a random sequence of condensation reactions and thus is expected to be fractal with a large interfacial area. At intermediate length scales we expect differences in the ring statistics. According to NMR investigations conducted on aqueous silicates, a typical sequence of condensation products is monomer, dimer, linear trimer, cyclic trimer, cyclic tetramer, and higher order rings [4]. If depolymerization/repolymerization occurs freely, the distribution of ring sizes might approach that achieved in the thermodynamic equilibrium of the melt (average number of silicons per ring = 6). However, if depolymerization does not occur, the most frequent ring size will be the smallest stable ring which emerges during the above sequence of condensation, i.e., the cyclic tetramer. NMR and Raman investigations of silica polymerization confirm our expectations. Cyclic tetramers are prevalent species in hydrolyzed TMOS/MeOH solutions under neutral or acidic conditions in which depolymerization is suppressed [5]. In addition, the hydrolysis and condensation of cubic octamers in which 4-fold rings comprise the six faces show no evidence of ring cleavage under neutral conditions [6]. The solution stability of cyclic tetramers is further evidenced from the Raman spectra of the corresponding dried gels. As shown by the 490 cm^{-1} vibration (labelled D1) in Fig. 1a, four-fold rings are retained in large concentrations throughout the course of gelation and drying [7]. By comparison Bunker has shown that silica polymerization in aqueous solution at pH ≥ 7 (conditions under which silica depolymerization is enhanced) results in structures containing predominantly five-fold and higher order rings [8]. On short length scales the approach to equilibrium is manifested in the distribution of non-bridging oxygens in the structure. Extensive depolymerization/repolymerization allows soluble silicate species to probe the available reactive sites on a growing polymer, promoting condensation at the most thermodynamically favored positions. Thus, under conditions where restructuring can occur, Q_4 species (silicons bonded to four bridging oxygens) are maximized relative to less stable Q_1 - Q_3 species (silicons with 1 to 3 non-bridging oxygens). Conversely, under conditions where restructuring is inhibited, the pattern of condensation is more random in solution and less fully polymerized species are retained in the final gel. For example, ^{29}Si NMR of hydrolyzed solutions of TMOS show a trend of increasing Q_4 at the expense of Q_1 - Q_3 with increasing pH [2]. MAS ^{29}Si NMR of similar systems after gelation and drying clearly shows the presence of Q_1 - Q_3 species in addition to Q_4 for gels prepared under neutral conditions [6], whereas hydrolysis of TEOS with four equivalents of water under more basic conditions results

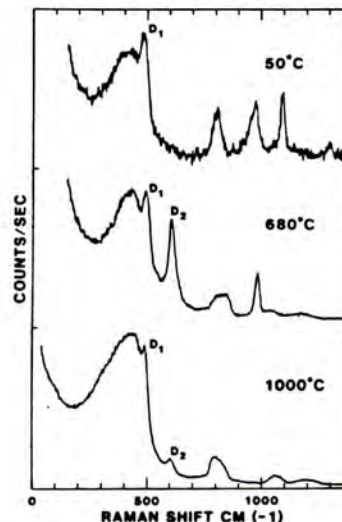


Fig. 1 Raman spectra of SiO_2 gels a) after desiccation at 50°C; b) after heating to 680°C according to: 1C/min to 350°C (10 hr hold); 1C/min to 680°C (2 hr hold); c) after densification at 1000°C (after Ref. 7)

in gels in which the relative concentrations of Q_1 and Q_2 are significantly reduced with respect to Q_4 [9].

3) **Borate Polymerization.** Borate polymers and gels are a third example of how the stability of M-O-M bonding influences solution structure of inorganic polymers. Primary structural units composed of three to eight borons arranged in various configurations of 3-fold rings (connected by bridging tetrahedral borons or borate bonds involving tetrahedral borons) are stable in aqueous solution at intermediate pH; however, gelation is not observed [10]. We believe this is due to the instability of B-O-B bonding between primary units. FTIR investigations of crystalline alkali borates indicate that B-O-B bonds linking trigonal borons contained in separate units rapidly hydrolyze upon exposure to water vapor [11]. Thus, in order to form infinite polymeric networks in a solution environment, we must either increase the kinetic stability of borate bonding or eliminate reactive molecules from the solution. Based on the results of leaching studies of borosilicate glasses [8], we expect the kinetic stability of B-O-B bonds to increase with the sequential replacement of trigonal borons with tetrahedral borons. This is consistent with our observations that in a mixed alcohol/methoxyethanol solvent there is a minimum fraction of tetrahedral borons which must be exceeded in order to form gels. Corresponding FTIR investigations of borate polymers and gels reveal that trigonal B-O-B bonding between primary units (both borons trigonally coordinated) is completely absent [11]. Fig. 2 depicts a polyborate structure based on the tetraborate primary unit which contains the minimum fraction of tetrahedral borons required to form an infinite network excluding all trigonal B-O-B bonding between units (borate bonds linking primary units contain one trigonal and one tetrahedral boron). The fraction of tetrahedral borons required for this tetraborate network (0.25) is close to the minimum fraction observed experimentally viz. 0.19 (gelation may occur without complete incorporation of boron in the network). Striking similarities between the IR spectra of partially hydrolyzed crystalline lithium tetraborate and lithia borate polymers formed near the gel point lend further support to the structural model portrayed in Fig. 2. Replacement of the mixed alcohol solvents with an aprotic solvent should also increase the kinetic stability of B-O-B bonds, because without a labile proton dissociative alcoholysis reactions are precluded. In support of this idea, replacement of methoxyethanol with THF reduces the minimum fraction of tetrahedral borons required for gelation to about 0.17. FTIR spectroscopy confirms the presence of trigonal B-O-B bonding between units.

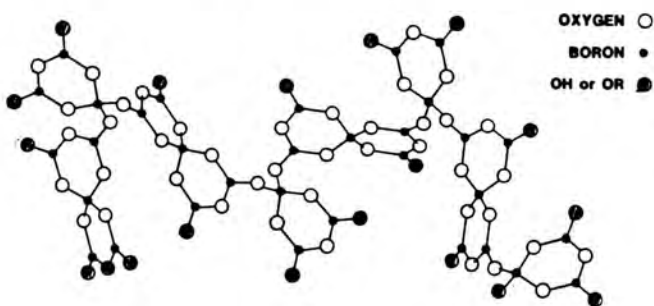


Fig. 2 Tetraborate network in which there is no trigonal: = B - O - B = bonding between units (after Ref. 11)

Gel Structure During Consolidation

Xerogels (porous solids resulting from the evaporation of solvent) are hard and glass-like. Nevertheless, during the moderate heat treatments employed for consolidation ($T < T_g$, the glass transition temperature) their structure is further modified by continued condensation reactions. Two factors distinguish condensation during consolidation from condensation in solution. First, concentrations of water and alcohol, which can undergo dissociative reactions with M-O-M bonds, are much lower during consolidation. Second, the inorganic network is more highly condensed and therefore stiffer. At the elevated temperatures employed for

consolidation the viscosity is seldom reduced below 10^{13} poises [12]. Consequently, the condensation products are well-preserved in this sterile, stiff environment in the sense that restructuring via depolymerization/repolymerization is inhibited.

The Raman spectra shown in Fig. 1 [7] succinctly illustrate the important structural changes accompanying consolidation. The most dramatic spectral feature attributable to siloxane bond formation is the behavior of the band at 608 cm^{-1} (indicated as D2 in Fig. 1). D2 is absent in the 50°C spectrum. It appears after heating to about 250°C , becomes quite intense at intermediate temperatures (Fig. 1b), and is reduced in relative intensity in the final densified gel (Fig. 1c). The structural origin of this band has been the subject of considerable controversy [13]. Our previous investigations indicate that D2 forms on the silica gel surface as the product of a significantly endothermic reaction involving predominantly isolated silanols [7]. Based on the results of ^{18}O enrichment studies and spectroscopic investigations of model compounds, we agree with Galeener's hypothesis, viz. D2 is the symmetric oxygen ring breathing mode of cyclic trisiloxanes [14]. Their absence at 50°C (Fig. 1a) indicates that cyclic trisiloxanes are unstable in most gel forming solutions due to the narrow Si-O-Si angle (130° compared to an average 145° in $v\text{-SiO}_2$) which makes Si more susceptible to nucleophilic attack. Their greatly increased relative intensity in high surface area gels dehydroxylated at intermediate temperatures (Fig. 1b) compared to conventional $v\text{-SiO}_2$ and densified silica gels (Fig. 1c) implies that, due to the lack of constraint by the matrix, trisiloxane ring formation is facile on the silica surface. Once formed trisiloxane rings are preserved until exposure to either molecules which can dissociatively chemisorb or elevated temperatures where the surface reconstructs (Fig. 1c).

In summary, insight into the structure of gels may be derived from consideration of the kinetic stability of the M-O-M bond in its synthesis environment. If restructuring is inhibited, metastable structures may persist throughout the course of gelation, drying and consolidation. Conversely, depolymerization/repolymerization processes favor the ultimate formation of thermodynamically stable structures.

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