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Communications

Effect of pH on the Gelation Time of Hexylene-Bridged Polysilsesquioxanes

Douglas A. Loy,* Brian Mather,[†]
Andrei R. Straumanis,[†] Colleen Baugher,[†]
Duane A. Schneider,[†] Arturo Sanchez,[†] and
Kenneth J. Shea[‡]

Polymers and Coatings Group, MST-7,
Los Alamos National Laboratory,
Los Alamos, New Mexico 87545,
Properties of Organic Materials Department,
Sandia National Laboratories,
Albuquerque, New Mexico 87185-0888,
Department of Chemistry, University of California,
Irvine, California 92717

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The pH of the sol−gel polymerizations of alkoxysilanes is generally recognized as the single most important reaction and processing parameter affecting the porosity, density, strength, transparency and chemical structure of the resulting gels.[1,2] Much of this relationship can be traced to the dependence of the reaction mechanism and rate on the pH of the sol−gel solution.[3] Sol−gel polymerizations involve hydrolysis of alkoxysilanes to silanols that subsequently condense to siloxane bonds linking monomers into a growing network and, eventually, a gel (Scheme 1). Siloxane bond formation at pH below the isoelectric point of the silanol involves catalysis by protonation of the hydroxyl group. Condensations at pH greater than the isoelectric point involve deprotonation to form a nucleophilic silanolate. Although hydrolysis rates of alkoxysilanes have been well studied, condensation rates, due to the myriad number of reactive intermediates that form during the sol−gel polymerization, are difficult to determine. Instead, gelation times of alkoxysilanes are often characterized as the inverse of the "average" condensation rate for a sol−gel system. The pH−gelation time relationship has been characterized for both silicic acid[4] and tetraalkoxysilane sol−gels[5,6] as exhibiting a maximum in gelation time near the isoelectronic point (pH 2) and the most rapid gelation occurring at pH 4. Yet, the relationship between pH and gelation time has never been determined for organotrialkoxysilanes, an important class of compounds useful for coatings,[7] composite coupling,[8] and formation of hybrid organic−inorganic materials.[9,10] This is because the hydrolysis and condensation products of most organotrialkoxysilanes phase separate as resins, crystals, or precipitates rather than forming gels.[10]

We first focused on the sol−gel polymerization of methyltrimethoxysilane, one of the few organotrialkoxysilanes that forms gels with base or acid catalysts in a

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* To whom correspondence should be addressed at Los Alamos National Laboratory. Tel: 505-665-1696. E-mail: daloy@lanl.gov.

[†] Sandia National Laboratories.

[‡] University of California.

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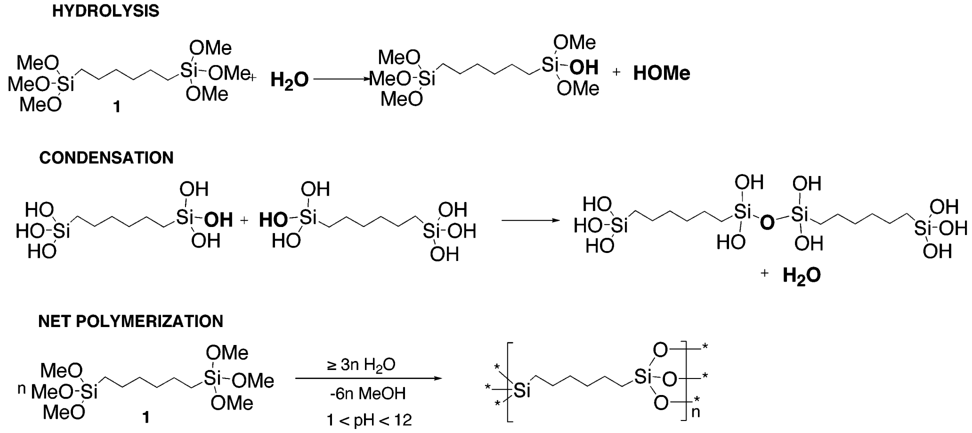
Scheme 1. Hydrolysis and Condensation of 1,6-Bis(trimethoxysilyl)hexane (1)



reasonably short time.[10] However, it was not possible to prepare polymethylsilsesquioxane gels except at high or low pH regardless of monomer or water concentration. The key to studying the effects of pH on the gelation of the alkyl-substituted silsesquioxanes was to use 1,6-bis(trimethoxysilyl)hexane **1**.[11] This organically bridged monomer has an alkylene substituent with electronic and steric characteristics similar to those of alkyl groups, but that is long enough to prevent intramolecular cyclization reactions from interfering with gelation.[12,13] The hexa-functional monomer is known to readily form gels with acid or base catalysts at monomer concentrations as low as 0.2 M[11,14,15] in aqueous methanol solutions amicable to accurate pH measurements.

Sol−gel polymerizations of **1** were conducted with 24 equivalents of water for each equivalent of monomer to accommodate the 3−6 equivalents of water consumed by the reaction and still provide more than the 5% aqueous content needed for accurate pH measurements.[6] Monomer concentration was optimized to 0.6 M (10 mL total volume) to allow gelation of all of even the slowest sol−gel polymerizations in less than 2 months. Solutions were prepared with potassium chloride or potassium phthalate and borate buffers added to establish a constant ionic strength (0.386 M) across the pH range and stabilize the pH of the more alkaline samples.[6] Elemental analyses on the resulting gels revealed that less than 20 ppm boron was detected, and phosphorus, if present, was below levels of detection. Polymerizations of **1** were performed in triplicate at 20 different points between pH 1 and 12. Reactions were performed under inert atmosphere to prevent dissolution of carbon dioxide. Acidity was monitored during the polymerization process using a Denver Instruments Co. model 225 pH meter equipped with a pH/ATC electrode and was found to be in good agreement with calculated pH.

Sol−gel polymerizations of **1** yielded gels in as little as 15 min at pH 11.7 and a maximum gelation time of 660 h at pH 5 (Figure 1). Gelation was recorded as the time when the solution would not flow when the vial was turned on its side. In contrast to the pH−gelation time results for silica,[6] the plot of gelation times versus pH for the sol−gel polymerization of **1** is a simple bell curve anchored by short gelation times under acidic and basic conditions and rising to a gelation time maximum at pH 4.5. This is also the optimum pH for maximizing shelf life for aqueous dispersions of silane coupling agents. The fact that the first condensation reaction of a silsesquioxane, alkylSi$(OH)_3$, has a reaction rate minimum near pH 4.5[16,17] suggests that the pH−gelation time maximum may not accurately reflect the average of all condensation rates or that the current model for siloxane substituent effects on silanol acidities and condensation reaction mechanism[5] may not be accurate. Analogous experiments with 0.4 M and 0.8 M monomer reveal that gelation rates increase with increasing concentration,[18] but that the pH−gelation time curves have the same shape and maxima between pH 4.5−5. Examination of sol−gel solutions of **1** (0.4 M in MeOH, 24 equiv H_2O) at pH 4.5 with ^{29}Si NMR (Figure 2)[19] revealed that condensation to form the first siloxane T^1−T^1 bonds is so slow that no T^1 silicons were observed after 24 h and total condensation was only 34% complete after 720 h. Persistence of the T^1 peak and the slow appearance of the T^2 peak suggest that the second condensation reaction rate is comparable to the first. Thus, the slow rate of gelation appears to be the direct result of the slow rates of condensation at pH 4.5. Examination of the gels with solid state ^{29}Si NMR before and after drying reveal that the degrees of condensation are similar to those of gels that form within a few hours at lower pH. Phase separation of resins or precipitates instead of gels between pH 7−11 occurs across the same pH range where silica gels will not form without the addition of salts to provide Columbic shielding between negatively charged colloids.[4] Interestingly, phase separation of the hexylene-bridged polysilsesquioxanes seems

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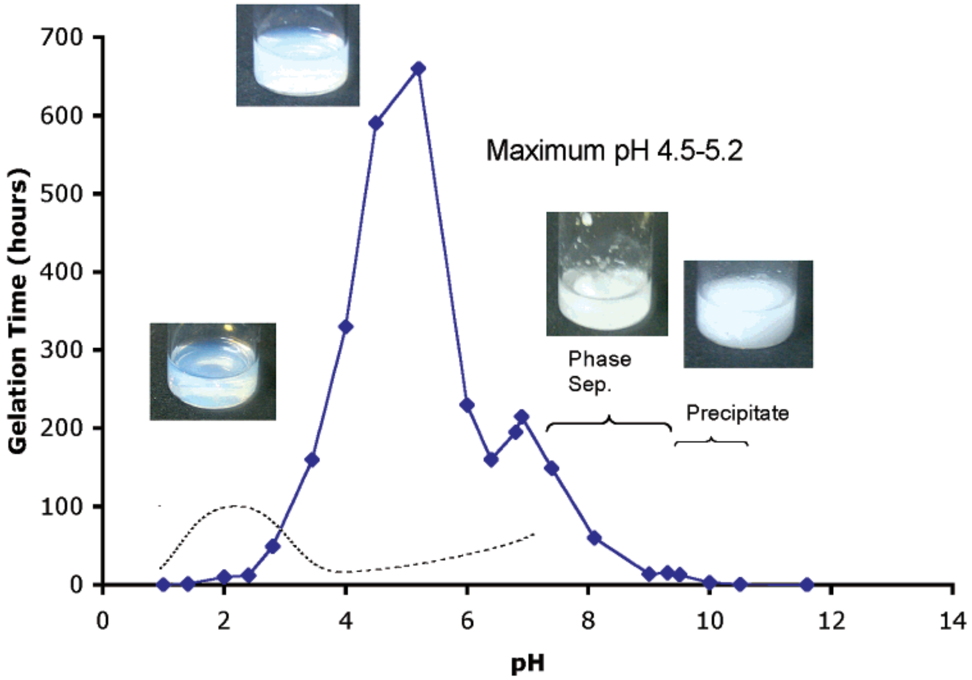

Figure 1. Plot of pH−gelation time for the sol−gel polymerizations of **1** (0.6 M in methanol, 25 °C). The dashed line is the pH gelation time curve for tetramethoxysilane (2.0 M in methanol, 60 °C).[6]

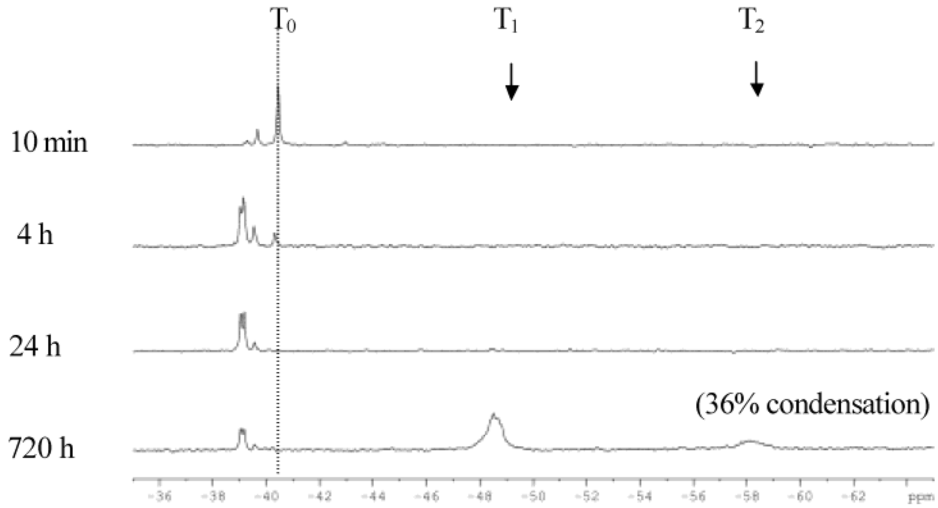

Figure 2. Solution ^{29}Si NMR spectra for the sol−gel polymerization of **1** at pH 4.5 in methanol showing the slow hydrolysis and condensation chemistry over 1 month. The relative positions of the peaks due to the hydrolysis of **1** are similar to those observed by Alam et al.[19]

to occur at times that fit in the gelation time curve. Serendipitously, in all of our investigations of bridged polysilsesquioxanes[10−15] we had originally formulated our sol−gel experiments with bridged monomers with catalyst concentrations approximating pH 1.5 for acid-catalyzed polymerizations and pH 12.4 for base-catalyzed polymerizations such that gels rather than precipitates were obtained.

Besides being useful to researchers intending to prepare polysilsesquioxane gels, the pH−gelation time profile for alkyl-substituted polysilsesquioxanes poses more questions regarding the importance of substituent effects on the sol−gel process.[5] Additional investigations on the effects of pH on the porosity and chemical structure of hexylene-bridged xerogels and more detailed investigations of substituent effects on condensation and gelation rates for organotrialkoxysilanes are underway.

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