

Molecular Design of Organically-Modified 'Smart' Sol-Gel Materials

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ABSTRACT

The design, synthesis and stimuli-responsive behavior of organically-modified silicates (ORMOSILS) is reported. The ORMOSILS behave as 'smart' materials by undergoing structural changes at the molecular level to respond to changes in environmental variables. Typical responses in the form of swelling/shrinkage with respect to changes in temperature, pH, and salt concentrations are presented. Finally, the nature of predominant mechanism responsible for the sol-gel's behavior towards combined stimuli of high temperature and low pH is discussed.

INTRODUCTION

The recent progress in the development of materials from structural to functional, to 'smart' or 'intelligent' materials has been quite remarkable. The smart materials possess the capability to recognize changes in their environment by undergoing structural variations within their framework to take suitable action against environmental changes. Depending upon the applications and the types of environmental stimuli, there has been an extensive investigation of several kinds of 'smart' materials, such as shape-memory metals and alloys [1,2], electrorheological and magnetorheological fluids [3, 4], piezoelectric materials [2, 5], and smart polymer gels [6,7]. Among the existing 'smart' systems, the polymer gels show responses to a variety of variables, such as changes in pH, temperature, ionic and electrical potential, magnetic field, solvent polarity, and presence of organic and biomolecules. However, the organic nature of the polymeric backbone imparts them with poor mechanical properties, and under extreme environmental conditions they lose their structural integrity, thereby limiting their practical utility. Hence, a stable hybrid inorganic-organic material is required that would exhibit the responsiveness of polymer gels, and also have the mechanical stability of the inorganic systems.

In this paper, we report the environmental sensitivity of organically-modified silica sol-gels (ormosils) with inorganic-organic hybrid character. These ormosils, synthesized using the sol-gel process, incorporate the structural robustness along with environmental responsiveness. The use of sol-gel method for synthesis of new materials is particularly appealing because of the solution based synthesis route, and the use of ambient processing conditions. This process is also amenable to molecular chemistry approaches as it allows control over structure and properties of the product sol-gel by means of modifying the chemical composition of the silica precursor [8]. Hence, by selectively integrating specific response-active molecular units into the silica precursor, it is possible to introduce desired functional and operational properties into the product sol-gel. Herein, we describe a strategy to elicit dynamic responses from ormosils in response to different physicochemical stimuli. We report the responses shown by the ormosils to different concentrations of calcium chloride, along with combined stimuli of low pH and high

temperature. In addition, we also discuss suitable mechanisms for the observed behavior of the ormosils to different stimuli.

EXPERIMENTAL DETAILS

The environmentally sensitive silica sol-gels were prepared by using organically-modified silica precursors containing response-active spacer units between two silicon atoms. Precursors such as bis-[3-(trimethoxysilyl)propyl]ethylenediamine, having the chemical formula $[(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]$, abbreviated as enTMOS, and bis-[3-(trimethoxysilyl)propyl]amine, having the chemical formula $[(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]$, abbreviated as ATMOS were used to prepare the sol-gels.

Preparation of pristine ormosils. Monolithic enTMOS sol-gels were made by mixing the enTMOS precursor and water in equal volume ratio, while the ATMOS sol-gels were made by mixing ATMOS precursor, methanol and 0.04 M HCl in equal volume ratio. These sol-gels were aged for a period of 1 day before they were subjected to different experiments.

Exposure of ormosils to ionic stimulus. The above-prepared enTMOS and ATMOS sol-gels were exposed to a series of 10 mL calcium chloride solutions, with concentrations ranging from 0 to 6.5 M in 0.5 M increments for a period of one day. The weight of these sol-gels was measured before and after exposure to CaCl_2 , and the percentage response was measured in terms of the weight change after their contact with CaCl_2 solutions.

Exposure of enTMOS sol-gels to dual stimuli of pH and temperature. For this experiment, the above-prepared enTMOS sol-gels were subjected to high temperature (HT) stimulus of 80 °C in a pH 1.22, 0.1 M H_3PO_4 bath, and the weight of the sol-gel was recorded after a fixed interval of time. The weight of the enTMOS sol-gel was also measured with respect to stimulus of 80 °C (HT) in plain water, room temperature (RT) in plain water, and room temperature in pH 1.22 (0.1 M H_3PO_4) systems.

Transmission electron microscopic (TEM) measurements of ormosils. The TEM measurements were carried out on an H7100FA STEM instrument at 100 KeV incident beam. The enTMOS and ATMOS samples were dried under ambient conditions, and powdered with a mortar-pestle. Samples for TEM measurements were prepared by putting a drop of 100% ethanol suspension containing fine powders of enTMOS and ATMOS sol-gel samples onto a 200 mesh copper grid with holey formvar support films, and dried under ambient conditions before imaging.

RESULTS AND DISCUSSION

The presence of amine groups in the precursors result in rapid hydrolysis and condensation of enTMOS and ATMOS. Both enTMOS and ATMOS form porous sol-gel materials as indicated by their TEM images shown in figure 1. The texture of these sol-gels indicates network formation, and is characterized by the presence of an interconnected framework. [10] The TEM

image shows the presence of pores in the range of micro scale (1-1.5 nm) as well as mesoscale (7-12 nm).

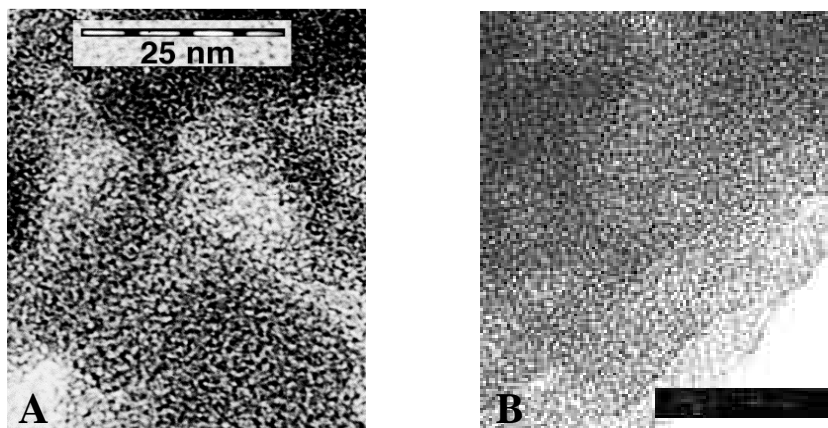


Figure 1. TEM images of a) enTMOS and b) ATMOS sol-gels.

The presence of enlarged pores in these sol-gels results in an increased capacity for water intake and retention when the sol-gels are put in an aqueous medium as compared to pristine silica gels. The intake of water molecules is facilitated by hydrogen-bonding interactions between the polar amine groups in the network of enTMOS and ATMOS sol-gels. It is the intake and expulsion of water molecules from the pores of the polymeric framework with respect to different environmental variables such as temperature, pH, ionic concentrations and electric field, which enables the sol-gels to swell and shrink, thereby generating dynamic responses to different environmental stimuli.

The environmental sensitivity of enTMOS and ATMOS sol-gels towards stimuli such as temperature, pH, electric field, and ionic concentrations of salts such as NaCl, MgSO₄, and K₃PO₄, has been already established [11,12,13]. These ormosils show swelling in low pH and increasing concentrations of NaCl and MgSO₄, and shrinkage at high pH, and in K₃PO₄. As investigated in this report, increasing the concentration of CaCl₂, showed an enormous swelling effect on the ormosils. The results of this experiment are shown in figure 2. The enhanced swelling of these ormosils in high ionic strength can be explained by the development of significant osmotic pressure in the sol-gels [13]. The movement of the ions from the outside solution into the silica framework is driven by the difference in the chemical potentials. However, once an equilibrium is established, a double layer is created whereby the protonated amine groups in the network interact favorably with the negatively charged Cl⁻ ions, which are in turn surrounded by the Ca²⁺ ions. The movement of these ions along with their respective hydration spheres results in the swelling of the sol-gels. This effect creates a critical osmotic pressure within the framework that leads to swelling of the gel [14]. The reduced swelling of enTMOS sol-gels as compared to ATMOS sol-gels may be related to its increased hydrophobic content as compared to the latter [13].

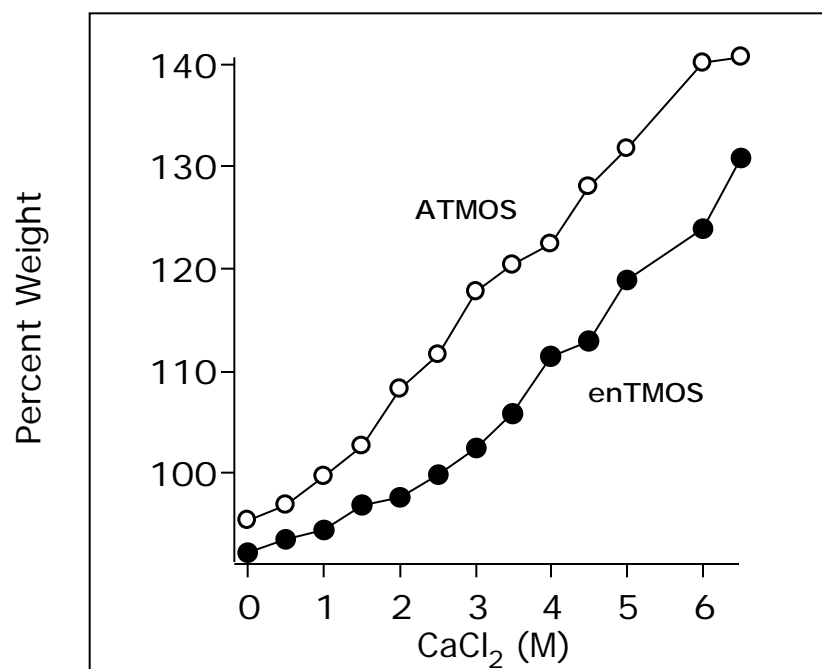


Figure 2. Percent weight of enTMOS and ATMOS sol-gels with respect to increasing concentration of CaCl₂.

In order to precisely modulate the volume responses, it is important that these materials be capable of responding to a combination of multiple stimuli. A proper control of responses can be achieved if the material undergoes these structural variations using different mechanisms. We have already established that enTMOS sol-gels exhibit volume changes through: 1) hydrogen-bonding interactions between water molecules and the hydrophilic amines and oxygens in the polymeric network under ambient conditions, which drives the intake of water molecules, and 2) enhanced hydrophobic interactions between the organic groups in the silica network at higher temperatures, which shrink the pores of the silica network and cause the expulsion of water molecules from the polymeric framework. The former is responsible for the swelling of enTMOS sol-gels at low temperature, and the latter for the deswelling of the gels at higher temperatures. The enhanced hydrophobic interactions between the organic groups at higher temperatures have been characterized by FTIR and contact angle measurements [11]. On the other hand, a disruption of hydrogen bonds with water molecules and their subsequent expulsion from the polymeric network contributes to the deswelling process. Similarly, subjecting the enTMOS sol-gels to low pH results in the protonation of the amine groups in the enTMOS network [12], which results in the development of positive charges in the sol-gel. Hence, in order to prevent electrostatic repulsion between the charged enTMOS silica polymeric chains, the sol-gel absorbs large amounts of water molecules stabilized through hydrogen-bonding interactions and undergoes swelling. Thus, subjecting the enTMOS sol-gels to dual stimuli of high temperature (forcing the gel to shrink), and low pH (allowing the gel to swell), was an interesting exercise to learn which stimulus would be predominant in controlling the response.

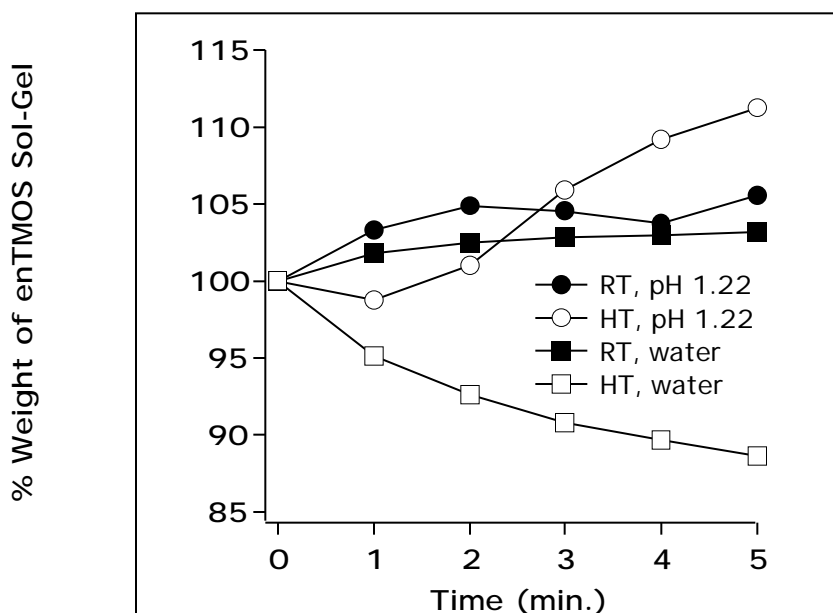


Figure 3. Kinetic profiles of response of enTMOS sol-gels to dual stimuli of high temperature (HT) at 80 °C and low pH (1.22), HT and plain water, room temperature (RT) and pH 1.22, and RT and plain water.

The results of this experiment are shown in figure 3. The results indicate that the weight of the enTMOS sol-gels increases when subjected to the combined stimuli of low pH and high temperature. Thus, the enTMOS sol-gels when placed in a low pH medium, undergo swelling at 80 °C. This makes the sol-gel take in water to screen the repulsion of the positive charges in the network. Thus, at higher temperatures, the electrostatic repulsions between the protonated amine groups predominate over the hydrophobic interactions between the organic groups. This observation shows that under the dual stimuli conditions, the low pH environment affects more dramatically than the high temperature stimulus. The increased diffusion rate of the protons inside the sol-gel network at high temperatures resulting in a rapid protonation of the amine groups may be responsible for the observed swelling. This is supported by the fact that the weight of enTMOS sol-gels in plain water at RT increases only by a minimal amount. On the other hand, as one would expect, in pH 1.22 at RT, the enTMOS sol-gel shows an increase in weight, and in plain water at high temperature, it shows a decrease in the weight. Hence under the combined stimuli of low pH and high temperature, the rate of protonation of the amines in the network is favored as compared to hydrophobic interactions. As a result, the gels exhibit swelling.

Overall, these experiments provide valuable insights into the mechanisms of environmental responses and the competition between different forces. It is particularly interesting to note that the pH effect supersedes the thermal effect. The results indicate that the environmental responses of ormosils are governed by a delicate balance of interactions and desirable responses can be introduced by means of a combination of stimuli.

CONCLUSIONS

In summary, we have demonstrated that environmental sensitivity in organically-modified silica sol-gels can be introduced by incorporation of specific response-active units into the sol-gel precursors. By selective incorporation of functional groups consisting of hydrophobic and hydrophilic moieties in the sol-gel matrix, the nature and extent of environmental responses can be tuned at the molecular level. The presence of both hydrophobic and hydrophilic components make the sol-gels respond to environmental parameters with two different mechanisms. Hence, the presence of hydrophilic amine groups contributes to the swelling of the ormosils due to water intake, while the presence of hydrophobic organic groups results in deswelling through enhanced hydrophobic interactions. The results presented herein validate the swelling of the gels due to water intake, which is introduced by means of ions such as Ca^{2+} and Cl^- or alternatively by protons. Upon subjecting the enTMOS sol-gels to dual stimuli of high temperature and low pH, the swelling of the sol-gel predominates over its shrinkage. The high temperature increases the rate of protonation of amines, which results in the development of positive charges within the matrix. In order to screen the repulsive forces between the positive charges, the sol-gel takes in water molecules and undergoes swelling. Consequently, the favorable hydrophobic interactions between the organic groups at high temperatures are more than offset by the electrostatic repulsive forces which cause the sol-gel to swell. In the long term, a detailed understanding of the competing mechanisms of swelling and shrinkage in these materials would enable selective control over the nature of these responses.

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