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Thermoresponsive Glasses: Temperature-Controlled Rapid Swelling and Deswelling of Silica-Based Sol–Gels**

By *Mukti S. Rao* and *Bakul C. Dave**

Conversion of different forms of energy to mechanical energy is the fundamental basis of actuation, movement, and motion. Materials that can translate an applied stimulus and produce a definite response in the form of change in shape or size—the so-called "smart" or "intelligent" materials—have been the focus of several studies.[1–4] Environmentally sensitive materials of this type include polymeric hydrogels,[5] polypeptides,[6] and protein-based materials,[7] which have been shown to undergo bulk volume transitions in response to different applied stimuli. In general, a common characteristic of these materials is an increase in hydrophobicity of the material at an elevated temperature which results in compression strain and overall volume shrinkage due to expulsion of solvent.[1–7] Consequently, thermally induced responsivity is a critical index of environmentally sensitive materials.

Herein, we report temperature-regulated swelling and shrinkage of organically modified silica sol–gels. These sol–gels undergo bulk shrinkage at high temperature and swell when the temperature is lowered. The swelling–deswelling is reversible and the kinetics of the bulk transition are fast such that overall changes take place within 2–3 min. Vibrational spectroscopy results indicate that the molecular mechanism of bulk volume transition is associated with increased hydrophobic interactions of the organic spacer group and consequent expulsion of water at elevated temperature. The interactions of the material with water are restored upon lowering the temperature, which results in reswelling due to intake of water within the porous structure of the sol–gel.

The sol–gel method of synthesis of glasses begins from molecular precursors,[8] and therefore, it is possible to use molecular chemistry approaches to tailor the structure and properties of the parent silica sol–gel by a selective choice of the precursor.[9,10] Our strategy for making a thermo-responsive sol–gel involves the use of an organically modified bis[3-(trimethoxysilyl)propyl]-ethylenediamine (enTMOS) precursor whose structure is given as $(CH_3O)_3Si(CH_2)_3NH(CH_2)_2NH(CH_2)_3$-$Si(OCH_3)_3$.

The sol–gels were prepared by hydrolysis of the enTMOS precursor followed by gelation in a polystyrene cuvette. Typical preparation involves mixing an equal volume of enTMOS precursor (1 mL, 1.45 mmol) and water (1 mL, 55.5 mmol). Upon addition of water, hydrolysis and condensation of the siloxane units give rise to a solid porous sol–gel. The freshly formed sol–gels were allowed to age for one day. These aged materials were used for all the experimental data reported in this paper.

The enTMOS sol–gels, when placed in a water bath and heated to 80 °C, exhibit a bulk volume shrinkage and reswell when the temperature is lowered to 20 °C (Fig. 1). The thermally regulated swelling and deswelling can be observed reproducibly with respect to variation of temperature. An average swelling/deswelling of ±6 % of the original weight is

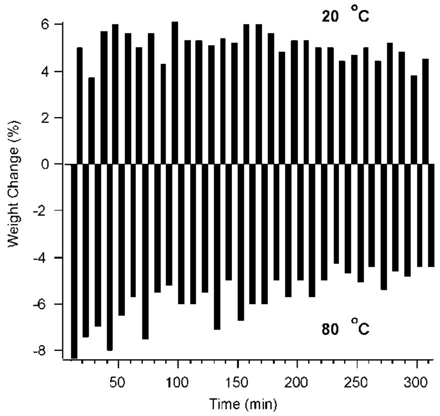

Fig. 1. Percent weight change of enTMOS sol–gels as a function of sequential variation of temperature between 20 and 80 °C. The gels were placed into a water bath kept at 20 and 80 °C, respectively, for intervals of 5 min prior to measuring the weight change.

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observed with respect to thermal variations. It is important to note that this weight change corresponds to 2 mol of water molecules per mole of enTMOS unit. The kinetics of thermal response are shown in Figure 2 (middle panel). It is seen that the swelling and deswelling responses strongly correlate with temperature variation. The response of the material to thermal variations is quite rapid and the overall bulk changes take place within 2–3 min.

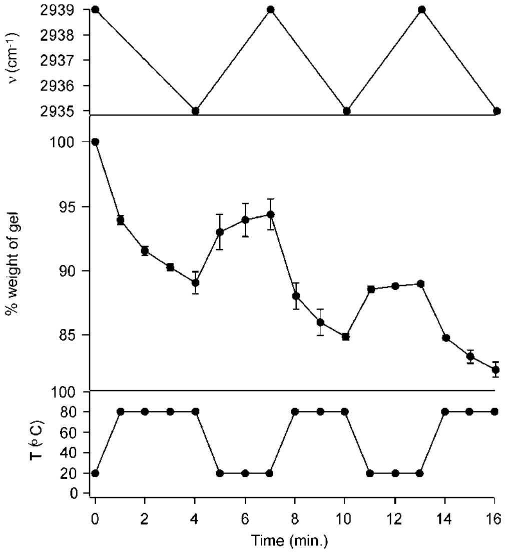

Fig. 2. Correlation of weight change of the enTMOS sol–gels with frequency of the asymmetric methylene stretching mode. Bottom panel shows the variation of temperature as function of time. Middle panel shows the percent weight of the enTMOS sol–gels with respect to applied thermal changes. Top panel shows the variations in frequency of the $\nu_{as}(CH_2)$ mode as the enTMOS sol–gels undergo swelling/deswelling.

Infrared vibrations of methylene groups have been shown to be quite informative and both the frequency and intensity of the CH_2 vibrational modes exhibit subtle variations that correlate with packing order, lateral chain–chain interactions, and hydrophobicity.[11,12] Specifically, the asymmetric stretch of the CH_2 groups is found to be a particularly sensitive probe of local microenvironment and hyrodrophobicity around CH_2 units.[13–15] It is found that the $\nu_{as}(CH_2)$ mode occurs at lower energies as the hydrophobicity of the surrounding environment is increased, due to chain–chain interactions. In order to probe the molecular nature of events associated with thermally induced bulk transitions, Fourier transform infrared (FTIR) spectroscopy was employed[16] to monitor the structural changes of the CH_2 moieties present in the enTMOS sol–gels with respect to temperature variations. As shown in Figure 2 (top panel), the $\nu_{as}(CH_2)$ mode occurs at 2939 cm^{-1} in the swollen samples while it downshifts to 2935 cm^{-1} when the samples undergo deswelling at 80 °C. This change in frequency of the $\nu_{as}(CH_2)$ mode can be observed consistently and reproducibly with respect to temperature variations.

The thermal response of the sol–gels is due to the overall change in hydrophobicity of the material as a result of the change in temperature. In order to evaluate the changes in hydrophobicity with respect to temperature variation, contact angle measurements were performed on the enTMOS sol–gels. Water contact angle is a quite sensitive indicator of hydrophobicity and as the hydrophobicity of a material increases a concomitant increase in contact angle is observed.[17] Figure 3 shows the variation in contact angle for enTMOS sol–gels as a function of temperature. As can be seen, the contact angle remains constant between 10–40 °C and then there is a sharp transition centered at 50 °C. At 60 °C, a saturation value is obtained. These results are in excellent agreement with a thermally induced transition in structure and properties of the materials. Thus, overall the thermally induced transition of the enTMOS sol–gels from the hydrophilic to hydrophobic state is very well-defined and occurs within a 10 °C temperature change. The changes in contact angle are fairly reproducible and can be repeated for several cycles (see Fig. 3, inset).

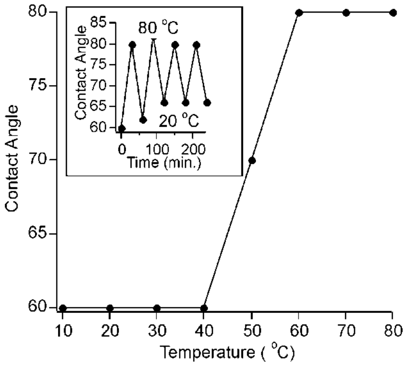

Fig. 3. Changes in contact angle of enTMOS sol–gels as a function of temperature change from 10 to 80 °C. Inset shows variations in contact angle after cooling (20 °C) and heating (80 °C) the samples successively for a period of 30 min.

Based on the results, the molecular mechanism of thermoresponsive behavior of the enTMOS sol–gels can be ascribed to thermally induced changes in hydrophobicity and altered interactions between the organic groups present in the material that cause expulsion/intake of water. Figure 4 shows the molecular units present in the enTMOS sol–gel according to their affinity for water; the hydrophilic groups are represented

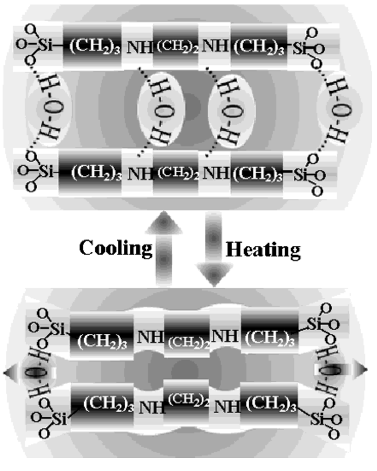

Fig. 4. Schematic depiction of molecular mechanism of dynamic responses associated with thermally regulated swelling and shrinkage of the enTMOS sol–gels.

by gray while the hydrophobic organic groups are represented by a darker shade. In the swollen state, there exists substantial amounts of water in the porous structure that are most likely stabilized by hydrogen bonding interactions with the hydrophilic siloxane and amino groups. In the collapsed state, the hydrophobic interactions between the organic functionalities predominate. As a result, water is expelled from the porous structure accompanied by an overall shrinkage of the sol–gel at an elevated temperature (Fig. 4). When the temperature is lowered, the hydrogen bonding interactions are restored and the gels undergo swelling due to the intake of water. Thus, the thermal responses of enTMOS sol–gels originate mainly due to specific movement of molecular domains restricted to the spacer group as a result of variations in noncovalent interactions. Consequently, the observed volume changes are relatively smaller as compared to organic polyelectrolytic hydrogels.[1–5] However, such a localized response suggests that the enTMOS sol–gel system possibly undergoes minimal entropic losses due to short-range movement of sol–gel network during the conversion of thermal energy to mechanical energy. This is consistent with the rapid responses observed for the enTMOS system indicating a more efficient conversion of energy to useful work.

It is important to note that the parent SiO_2 material is nonresponsive to environmental stimuli, and the selective integration of bis(propyl)ethylenediamine molecular unit introduces the dynamic responses into the product enTMOS sol–gels. Vital criteria for generating temperature-induced swelling/shrinkage include the occurrence of a bulk volume transition, which is initiated by alteration of non-covalent interactions within the material, and subsequent expulsion/intake of water.[1–7] The enTMOS precursor offers unique advantages that facilitate the generation of thermally induced responses. Firstly, the use of alkoxodisilane precursor with a long-chain spacer unit allows the formation of materials with enlarged pores. Such sol–gels are characterized by an enlarged porosity[10] and increased retention of the aqueous phase in the porous network. Since the molecular mechanism of gel swelling and collapse are related to water intake and expulsion, respectively,[1–7] a highly porous structure is more likely to exhibit a pronounced structural change. Secondly, the use of an organically modified precursor yields sol–gels that are elastic in nature. Because of the enhanced degree of translational freedom at the molecular level due to elasticity, the enTMOS-derived materials can undergo a volume change, without catastrophic destruction, to enable expansion/shrinkage of the sol–gel network with respect to changes in temperature. Finally, the proper combination of hydrophilic amino groups and hydrophobic organic moieties in the spacer group enables control over the non-covalent interactions of the material with water at a given temperature. It is important to note that the thermoresponsive behavior of the enTMOS sol–gels derives from a balance of hydrophobic and hydrophilic residues in the precursor. This is supported by the fact that sol–gels prepared using the precursor $(CH_3O)_3Si(CH_2)_6Si(OCH_3)_3$, which contains only hydrophobic residues in the spacer group, show an irreversible shrinkage at higher temperature and do not exhibit swelling when the temperature is lowered.

In summary, the feasibility of imparting thermal responsivity to sol–gel derived silica-based glasses is demonstrated. Starting from a judiciously selected molecular precursor, the sol–gel process is used to prepare an organically modified glass—a mechanically robust yet elastic material—that is capable of generating active responses when subjected to thermal variations. An important aspect of these materials is that they combine all the essential functions of an intelligent material in a one-component monolithic unit which is capable of generating a thermoreversible response in a self-sustaining manner. The stimulus-response behavior in these glasses derives from a deliberate incorporation of a response-active bis(propyl)ethylenediamine structural unit containing hydrophobic and hydrophilic moieties. Finally, the strategy of integrating a specific response-active unit for molecularly engineering the properties of sol–gels offers a potentially powerful approach for designing a range of materials by a structural modification of silica framework to program dynamic stimuli-responsive behavior in sol–gels.

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Colloidal Isopressing: A New Shape-Forming Method

By *Benjamin C. Yu* and *Frederick F. Lange**

Ceramic components, ranging from silicon nitride turbocharger rotors used in high-performance automobiles, to translucent aluminum oxide tubes used in high efficiency yellow sodium lamps, are formed by molding a powder into the

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