Journal of Sol-Gel Science and Technology 26, 553–560, 2003

Smart Glasses: Molecular Programming of Dynamic Responses in Organosilica Sol-Gels

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Abstract. The stimuli-responsive behavior of a new class of sol-gel—derived materials prepared from organically-modified alkoxysilane precursors is reported. Starting from judiciously selected molecular precursors, the sol-gel reaction yields a solid state glass—a mechanically robust yet elastic material—that is capable of generating dynamic responses when subjected to different physicochemical stimuli. These materials represent an initial example of stimuli-responsive silica-based sol-gels that exhibit bulk volume changes and active mechanical responses with respect to several environmental variables including temperature, pH, salt, and solvents. These glasses incorporate an optimum balance of hydrophobic, hydrophilic, and ionic moieties in the silica-based structure and are therefore capable of showing bulk volume changes with respect to applied physicochemical stimuli.

Keywords: organosilica sol-gels, environmental sensitivity, dynamic responses

1. Introduction

Movement, motion, and related dynamic responses are distinctive features of animate objects. Conversion of different forms of energy to mechanical energy is the key factor responsible for dynamic responses associated with movement and motion in living as well as artificial systems. Consequently, materials that can convert physicochemical signals to a definite dynamic response in the form of a change in shape or size—the so-called "smart" or "intelligent" materials—are useful for many applications including design of shape memory systems, drug delivery devices, chemical valves, artificial muscle mimics, and actuators [1–4]. The generation of active mechanical responses necessitates a polyelectrolyte structure with ionizable groups, a requirement that has led to the almost universal use of organic polymer gels for design of environmentally-sensitive materials. However, the poor structural and mechanical integrity of conventional polymeric hydrogels coupled with typically long response times remain critical issues which severely limit their practical usefulness. Consequently, design of efficient response-active materials that are also mechanically stable has been a long sought-after goal. While much effort has been focused on organic polymer gel systems, examples with inorganic sol-gel analogs remain to be established.

The use of sol-gel method for synthesis of new materials is particularly appealing because the low temperature solution-based synthesis route is amenable to molecular chemistry approaches such that one can modify the structure and function of the parent silica glass by a structural modification of the precursor [5]. For design of advanced materials with useful dynamic responses, the advantage of using sol-gel—derived glasses is that the parent SiO_2 material is functionally inactive, and operationally non-responsive. Therefore, by selectively integrating specific response-active molecular units into the glass by means of chemical modification of the precursor, it is possible to introduce desired functional and operational properties into the product sol-gel [6–8].

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As such, the use of sol-gel-derived silica glasses offers a unique promise. Sol-gel glasses can be prepared by simple hydrolysis of molecular precursors and therefore considerable flexibility in synthesis is feasible [9]. However, an inherent limitation of these materials is that pristine silica sol-gels are characterized by irreversible shrinkage and solvent loss to form dried xerogels, and dynamic responses with external physicochemical stimuli are not feasible. An important criterion for environmental sensitivity is stimuli-controlled interactions of the gel network with interstitial liquid phase which is usually water. The porous water-filled sol-gel glasses are attractive for use as environmentally sensitive materials if selective interactions with solvent can be made to take place in response to an environmental stimulus. This is possible if (i) the pores of the sol-gels are enlarged sufficiently for an increased retention of the aqueous phase, and (ii) the pores of the network are made chemically-active such that they can show variable noncovalent interactions with the aqueous phase. In order to accomplish these criteria, our strategy was based on a molecular design approach involving precisely selected precursor molecules for tailoring the structure and properties of sol-gels such as pore sizes, hydrophobicity, and the overall electrostatic composition to prepare materials with an intrinsically programmed responsivity to physicochemical variables. Thus, dynamic responses are introduced in a porous silica-based glass by using organically-modified sol-gel precursors [7]. Moreover, the hydrophilicity/hydrophobicity of the sol-gels can be varied by means of using appropriate combination of precursors. The approach may be generalized to prepare a variety of novel active materials and devices with molecularly programmed "smart" responses.

In this paper, we describe a strategy to elicit dynamic responses from silica-based materials that are prepared using the sol-gel process. Starting from a judiciously selected molecular precursors, the sol-gel reaction yields a solid state glass—a mechanically robust yet elastic material—that is capable of generating dynamic responses when subjected to different physicochemical stimuli without catastrophic loss of structural integrity. The development of new materials that combine the water-rich character along with the mechanical stability of sol-gel-derived glasses is likely to provide technologically and commercially viable pathway for design of active devices.

- **$(CH_3O)_3Si(CH_2)_3NH(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$**
  Bis[3-(trimethoxysilyl)-propyl]ethylenediamine (enTMOS)
- **$(OCH_3)_3SiCH_3$**
  Methyl(trimethoxy silane) (MTMOS)
- **$Na^+O^-Si(OH)_2(CH_2)_2COO^-Na^+$**
  Carboxyethylsilanetriol, sodium salt (CEST)
- **$(CH_3O)_3Si(CH_2)_6Si(OCH_3)_3$**
  Bis(trimethoxysilyl)hexane (HexTMOS)
- **$(CH_3O)_3Si(CH_2)_3NH_2$**
  3-Aminopropyltrimethoxy silane (AMPTMOS)
- **$(CH_3O)_3Si(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2$**
  (3-Trimethoxysilylpropyl)diethylenetriamine (DienTMOS)
- **$(CH_3O)_3Si(CH_2)_3NH(CH_2)_3Si(OCH_3)_3$**
  Bis[3-(trimethoxysilyl)-propyl]amine (ATMOS)

Figure 1. Molecular formulas and abbreviations of organosilane precursors.

2. Experimental

2.1. *Synthesis of Sol-Gels*

The synthesis of sol-gels was accomplished by hydrolysis of the alkoxysilane precursors in water. The molecular formulae of different precursors used in this work are shown in Fig. 1. The samples were prepared by mixing different precursors in appropriate molar ratios. Table 1 outlines the compositions of different samples used in this study. Typical preparations involved sonicating a mixture of precursors with methanol and water. During sonication the solution becomes viscous to give rise to sol. The mixture was then poured into a polystyrene cuvette and left undisturbed at room temperature. The gelation time for these preparations varied from 15 minutes to 6–8 hours in some cases. These gels were subsequently allowed to age ambiently for 1 day prior to experimental measurements. The bulk monolithic gels have the shape of the container (i.e. cuvette) with the dimensions of 1 cm × 1 cm × 1 cm.

2.2. *Measurement of Environmental Responses*

The environmental responses of the materials were measured by monitoring the weight changes of the materials when subjected to different physicochemical stimuli. The gels were immersed in solvents, salt, and pH solutions for 24 hours prior to measurement of weight changes.

Table 1. Synthesis protocols for organically modified hybrid sol-gels.

		Amount of precursor (mL)								
Sol-gel systems	Sample	enTMOS (moles)	MTMOS sol (moles)	CEST (moles)	HexTMOS sol (moles)	AMP-TMOS (moles)	Dien-TMOS (moles)	ATMOS: MeOH (moles)	Water (mL)	Percentage mole fraction
enTMOS	S1	1.00 (1.45×10^{-3})	–	–			–	–	1.00	100 enTMOS
enTMOS + MTMOS	S2	0.50 (7.25×10^{-4})	0.0	–	–	–	–	–	0.50	100 enTMOS 0 MTMOS
	S3	0.5 (7.25×10^{-4})	0.1 (5.46×10^{-4})	–	–	–	–	–	0.22	57 enTMOS 43 MTMOS
	S4	0.5 (7.25×10^{-4})	0.2 (1.10×10^{-3})	–	–	–	–	–	0.318	40 enTMOS 60 MTMOS
	S5	0.5 (7.25×10^{-4})	0.3 (1.64×10^{-3})	–	–	–	–	–	0.417	30 enTMOS 70 MTMOS
	S6	0.5 (7.25×10^{-4})	0.40 (2.18×10^{-3})	–	–	–	–	–	0.51	25 enTMOS 75 MTMOS
	S7	0.50 (6.77×10^{-4})	0.50 (2.73×10^{-3})	–	–	–	–	–	0.61	21 enTMOS 79 MTMOS
enTMOS + CEST	S8	0.621 (8.4×10^{-4})	–	0.139 (2.33×10^{-4})	–	–	–	–	0.236	78 enTMOS 22 CEST
	S9	0.496 (6.71×10^{-4})	–	0.139 (2.33×10^{-4})	–	–	–	–	0.188	74 enTMOS 26 CEST
	S10	0.372 (5.03×10^{-4})	–	0.139 (2.33×10^{-4})	–	–	–	–	0.141	68 enTMOS 32 CEST
	S11	0.248 (3.35×10^{-4})	–	0.139 (2.33×10^{-4})	–	–	–	–	0.094	59 enTMOS 41 CEST
enTMOS + HexTMOS	S12	0.75 (1.015×10^{-3})	–	–	0.25 (3.01×10^{-4})	–	–	–	–	77 enTMOS 23 HexTMOS
	S13	0.50 (6.77×10^{-4})	–	–	0.50 (6.03×10^{-4})	–	–	–	–	53 enTMOS 47 HexTMOS
	S14	0.25 (3.38×10^{-4})	–	–	0.75 (9.04×10^{-4})	–	–	–	–	27 enTMOS 73 HexTMOS
	S15	0.0	–	–	1.00 (1.20×10^{-3})	–	–	–	–	0 enTMOS 100 HexTMOS
enTMOS + AMPTMOS	S16	1.00 (1.35×10^{-3})	–	–	–	0.104 (3.83×10^{-4})	–	–	1.00	68 emTMOS 32 AMP TMOS
enTMOS + DienTMOS	S17	0.375 (5.07×10^{-4})	–	–	–	–	0.11 (6.3×10^{-4})	–	0.375	57 enTMOS 43 DienTMOS
ATMOS	S18	–	–	–	–	–	–	0.2:0.3 (5.56×10^{-4})	0.2	100 ATMOS

3. Results and Discussion

3.1. Hybrid Sol-Gels

The hybrid gels used in this study were made by combining bis[3-(trimethoxysilyl)-propyl]ethylenediamine (enTMOS) precursor with other organosilane precursors. The enTMOS sol-gels by virtue of having a bis(propyl)ethylenediamine spacer group with a balance of hydrophobic and hydrophilic groups show expansion/shrinkage when a stimulus is applied [7]. Since the hydrophobicity of a material is a key factor that dictates the environmental responses, we prepared a series of samples by using other precursors (Fig. 1) in combination with enTMOS. In order to measure relative hydrophobicity of different compositions we used the following semi-quantitative estimate:

$$\text{Hydrophobic Estimate Value} = \frac{(\text{No. of C atoms}) \times (\%\ \text{mole fraction of precursors})}{(\text{No. of O/N atoms}) \times (\%\ \text{mole fraction of precursors})}$$

where the number of C, O, N atoms corresponds to those present in the R group of an organosilica precursor. The balance of hydrophobicity and electrostatic charges in these hybrid materials is altered as compared to the pristine enTMOS sol-gels and therefore the responses of these hybrid materials to physicochemical variables are considerably modified.

3.2. Solvent Response

The organically-modified silica sol-gels show changes in volume with respect to the interactions with solvents (Table 2). In general, solvents with high polarity provide an environment conducive to swelling (or less shrinkage) and solvents with low polarity lead to enhanced shrinkage.

3.3. pH Response

The organosilica sol-gels containing ionizable functional groups such as —NH— or —COOH exhibit responses to variations in pH of the surrounding medium (Table 3). Due to the presence of ionizable groups in the materials, protonation/deprotonation as a result of change in pH alters the electrostatic interactions and leads to volume changes. In general, it is found that the organosilica sol-gels containing amino groups undergo shrinkage at high pH while at low pH they exhibit swelling.

3.4. Salt Response

The organically-modified silica sol-gels exhibit environmental responses in the form of swelling/deswelling upon exposure to different salt solutions. Overall, the environmental responses are found to be function of the ionic strength and the nature of salt as shown in

Table 2. Response of hybrid sol-gels with respect to solvent polarity.

		enTMOS + CEST % Mole fraction CEST						
		41.0	32.0	26.0	22.0	enTMOS + DienTMOS	enTMOS	ATMOS
		Hydrophobic estimate						
Solvents	Polarity^a	2.98	3.20	3.35	3.45	3.11	4.0	6.00
		% Weight change of hybrid sol-gels						
CCl_4	32.4	−0.4	−39.6	−37.0	−34.1	−4.8	−23.6	−18.90
Toluene	33.9	−6.0	−24.2	−32.5	−24.2	−8.2	−23.0	−27.27
Ether	34.5	−31.0	−54.7	−44.1	−51.5	−13.0	−47.0	–
Acetone	42.2	−32.9	−51.5	−46.3	−43.3	−26.2	−25.6	−27.14
1-Propanol	50.7	−42.0	−44.4	−36.0	−31.8	−19.7	−10.6	−7.68
Ethanol	51.9	−27.2	−38.6	−30.2	−22.5	−8.1	−8.0	−8.60
Methanol	55.6	+0.5	−3.5	−6.4	−6.4	−10.7	−2.5	−8.00
Water	63.1	+2.2	−3.2	−4.8	−7.5	−20.3	+8.5	−5.10

[a] Values taken from *CRC Handbook of Thermophysical and Thermochemical Data* (CRC Press, Boca Raton, 1994).

Table 3. Response of hybrid sol-gels with respect to pH.

	enTMOS + CEST % Mole fraction CEST					
	32.0	26.0	22.0	enTMOS + DienTMOS	enTMOS	ATMOS
	Hydrophobic Estimate					
pH	3.20	3.35	3.45	3.11	4.0	6.0
	% Weight change of hybrid sol-gels					
1.22	+19.8	+12.1	+18.6	+24.7	−0.14	+35.0
2.44	+18.0	+5.2	+10.45	+1.5	−4.5	+31.0
2.78	+8.6	−3.9	+5.5	−5.3	−6.0	+28.0
4.15	−7.0	−8.4	+0.03	−4.0	−6.6	+9.2
5.92	−19.0	−4.7	+3.6	−6.2	−6.5	+7.5
7.00	−3.5	−10.0	+0.25	−12.5	−7.6	+2.1
8.08	−37.0	−9.3	−5.7	−13.4	−8.5	−3.2
9.33	−34.0	−10.0	−2.8	−15.0	−9	−4.7
10.83	−14.4	−10.0	−1.4	−15.2	−9.1	−4.5
11.71	−45.4	−5.6	−0.63	−15.0	−8.2	−3.0
12.27	−37.4	−3.9	−0.55	−10.0	−5.7	−2.2

Table 4. Response of hybrid sol-gels with respect to salt concentration.

	enTMOS + CEST % Mole fraction CEST				
	41.0	32.0	26.0	22.0	enTMOS + DienTMOS
Salt solutions (0.1 M)	Hydrophobic estimate				
	2.98	3.20	3.35	3.45	3.11
	% Weight change of hybrid sol-gels				
NaCl	+5.8	−19.1	−21.6	+18.9	−8.0
$MgSO_4$	−9.2	−19.6	−23.6	−19.5	−4.5
K_3PO_4	+48.3	−15.7	−12.6	−15.4	−4.3

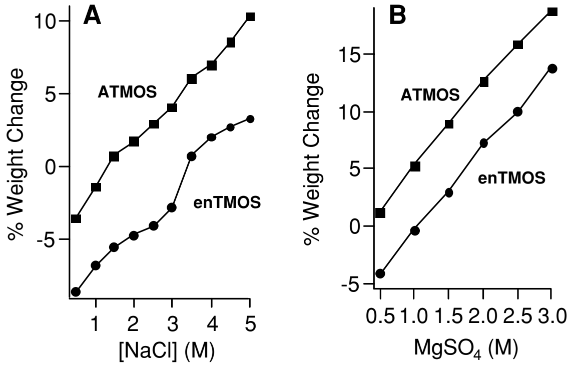

Figure 2. Response of ATMOS and enTMOS sol-gels to salt. (A) shows the response to NaCl and (B) shows the response to $MgSO_4$.

Table 4. Figure 2 shows the responses of the enTMOS and ATMOS sol-gels when exposed to different salts. For NaCl and $MgSO_4$, the swelling of the gels correlates linearly with the concentration of salts. This is possibly due to increased intake of ions along with water.

3.5. Thermal Response of Hybrid Sol-Gels

The most effective indicator of the environmental sensitivity of a material is its response to variation in temperature. 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 [10]. The thermally-regulated swelling and deswelling can be observed reproducibly with respect to variation of temperature. The molecular mechanism of thermoresponsive behavior of the enTMOS sol-gels is ascribed to thermally-induced changes in hydrophobicity and altered interactions between the organic groups present in the material which cause expulsion/intake of water [10]. In the swollen state, there exists substantial amount of water in the porous structure that is 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 of which, water is expelled from the porous structure accompanied by an overall shrinkage of the sol-gel at an elevated temperature. When the temperature is lowered, the hydrogen bonding interactions are restored and the gels undergo swelling due to 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.

Modifying the composition of the enTMOS by incorporating other organic residues in the structure leads to variation in overall thermal responses of the materials. Figure 3 shows the thermal responses of these modified hybrid sol-gels. As a part of this study we made samples by combining enTMOS with MTMOS, HexTMOS, AmpTMOS, DienTMOS, and CEST. Each of these precursors offers certain advantages to tailor the structural and functional constitution of the product sol-gels. In order to estimate the relative hydrophobicity of the these compositions we used the hydrophobic estimate as a relative measure. The unique properties of the enTMOS derive from the compositional makeup of the enTMOS sol-gels with eight hydrophobic CH_2 groups and 2 hydrophilic —NH— groups per unit. Thus, addition of MTMOS makes the resulting material more hydrophobic due to introduction of more methyl groups without altering the electrostatic or ionic constitution of the materials. Figure 3(A) shows the average weight changes of these gels as function of hydrophobic estimate and temperature. It is observed that increasing the temperature results in a greater weight change while increasing the hydrophobicity of the material leads to a decrease in overall response. Similarly, by mixing different precursors to enTMOS, the overall hydrophobicity of the material can be altered. The responses of the different samples used in this study as a function of the hydrophobic estimate value are shown in Fig. 3(B). It is seen that the average weight change in response to temperature depends on the hydrophobicity of the material. Increasing the hydrophobicity leads to a reduced volume response due to the fact that the hydrophobic compositions retain less amount of water in the pores and therefore the response is diminished.

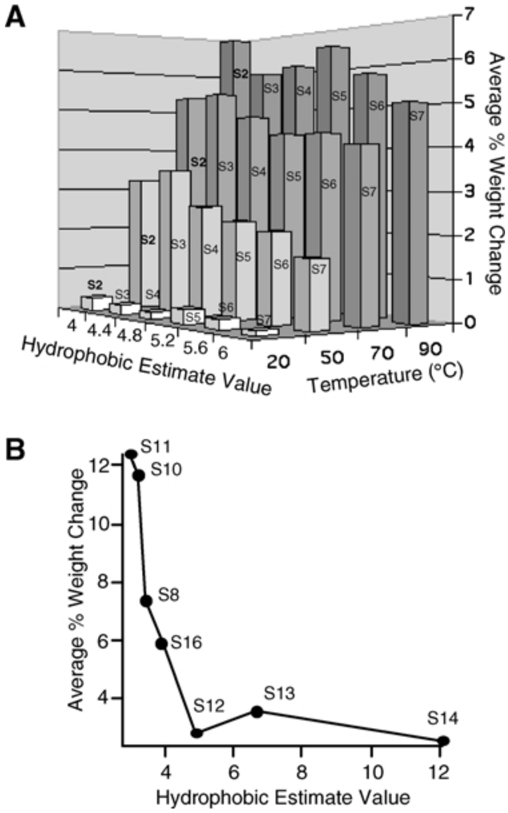

Figure 3. Average percent weight changes of hybrid sol-gels. (A) shows the variation in average % weight change of enTMOS:MTMOS sol-gels (samples 2–7) as a function of temperature and hydrophobic estimate. (B) shows the average % weight change of other hybrid sol-gel samples as a function of hydrophobic estimate.

3.6. *Molecular Programming of Environmental Responses*

Vital criteria for generating stimuli-induced dynamic responses include the occurrence of a bulk volume transition, which is initiated by alteration of noncovalent interactions within a material, and subsequent expulsion/intake of water [3]. In order to program volume modulations in the product material as a means to elicit active responses, we used a distinct molecular composition for the sol-gel precursor whose structure is given as

$$(CH_3O)_3Si(CH_2)_3NH(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$$

The overall design strategy for selecting the enTMOS precursor was based on several factors that offer unique advantages to facilitate generation of dynamic responses to different environmental variables. First, the use of alkoxodisilane precursor with a long-chain spacer unit allows formation of materials with enlarged pores. Such sol-gels are characterized by an increased retention of aqueous phase in the porous network [6]. Since the molecular mechanism of gel swelling and collapse are related to water intake and expulsion, respectively, a highly porous structure is more likely to exhibit a pronounced structural change. Second, the use of an organically-modified precursor yields sol-gels that are elastic in nature. Because of the enhanced degrees 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 when a stimulus is applied. Third, the proper combination of hydrophilic amino groups and hydrophobic organic moieties in the spacer group enables control over the noncovalent interactions of the material with water. Finally, the availability of ionizable amino groups in the precursor imparts volume sensitivity with respect to changes in pH and ionic concentration. As a combined result of these factors, the enTMOS-derived sol-gels exhibit active responses when subjected to different externally applied stimuli [7].

Additional incorporation of other functional groups in the material modifies these interactions and leads to change in dynamic responses. Thus, adding MTMOS or HexTMOS as modifiers leads to a change in overall constitution of the material making it increasingly hydrophobic. As a result, the as-prepared sol-gels contain a reduced amount of water in porous structure. Consequently, when these materials are heated the change in weight is lower as compared to pristine enTMOS sol-gels. Similarly, incorporation of other groups with $-$COOH or $-NH_2$ functionalities alters the electrostatic makeup of the materials and these materials show a modified response.

Overall, our results support the feasibility of designing stimuli-responsive glasses based on varying the hydrophobicity and the ionic content of the sol-gels by means of using precisely selected organosilane precursors. By a proper selection of precursor molecules, it is possible to incorporate different organic functional groups with variable hydrophobicity and ionic content in the glass. Further incorporation of other groups is achieved by using multiple precursors to obtain hybrid sol-gels. In this way, it is possible to introduce desired groups in the gels to tune the environmental responses. Moreover, this also allows one to control the balance of hydrophobicity and ionic content of the sol-gels. In this fashion, by using a combination of precursor molecules the volume changes of the sol-gels can be tuned selectively.

4. Conclusions

In summary, we have demonstrated the feasibility of imparting environmental sensitivity to sol-gel-derived silica-based glasses via a structural modification of the parent silica framework. The dynamic stimulus-response behavior of these solid state glasses derives from a deliberate incorporation of a response active bis-(propyl)ethylenediamine structural unit. The stimuli-responsive behavior of sol-gel—derived materials prepared from organically-modified alkoxysilane precursors is due to an optimum balance of hydrophobic, hydrophilic, and ionic moieties in the silica-based structure. An important aspect of these materials is that they combine all the essential functions of an intelligent material in a one-component monolithic unit; they are able to sense the external stimulus, translate the stimulus to mechanical energy, and generate an active dynamic response. Since the sensing-actuating mechanism is an intrinsic property of the sol-gels, the resulting monolithic device elements are simple, self-sufficient, and self-sustaining under a given applied stimulus. Conversion of different forms of physicochemical energy to mechanical energy underlies the basis of actuation, and these mechanically stable sol-gel—derived materials may find potential applications as technologically compatible intelligent systems for practical devices [11].

Finally, these materials constitute a new family of environmentally-sensitive glasses. The cost-effectiveness of raw materials for making these glasses, the ease of solution-based processability, ability to control structure and composition at a molecular level, ability to introduce several components in a single step, high homogeneity of multicomponent system, and the mechanical stability and durability of product materials are some of the attractive features that make these sol-gel—derived glasses particularly appealing from a technological standpoint. The strategy described here offers a potentially powerful approach for designing a diverse range of stimuli-responsive sol-gel materials whose properties may be tailored precisely with systematic control over both the composition of product materials and the extent of environmental sensitivity to ultimately be able to design materials with tunable active responses.

Acknowledgments

We thank Materials Technology Center, SIU for their financial support of this work.

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