

Effect of silica and water content on the glass transition of poly(ethylene glycol) monomethylether–silica gel–lithium perchlorate ormolytes

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Abstract

The effect of silica and water content on the glass transition temperature, T_g , of MPEG2000–silica–LiClO₄ ormolytes was assessed by differential scanning calorimetry (DSC). The sol–gel synthesized ormolytes consisted of various amounts of poly(ethylene glycol) monomethylether (M.W. = 2000 g/mol; i.e., MPEG2000) tethered to silica gel through the hydroxyl terminus via a urethane linkage. DSC features corresponding to physisorbed and hydrogen-bonded water, as well as the glass transition of the polyether, were identified. Both silica and LiClO₄ raise the T_g and suppress crystallization of the polyether component. Water plasticizes the polyether and stoichiometrically solvates and sequesters Li⁺, thereby, lowering T_g .

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1. Introduction

Organic–inorganic composite materials are currently being intensively studied due to their potential use in ambient to moderate temperature, solid-state electrolyte, lithium ion batteries [1,2]. Polyethers are the most popular organic component in these composites because they dissolve a variety of lithium salts to a concentration of 2 M by forming lithium–polyether complexes. However at room temperature, these complexes either crystallize when using high molecular weight polymers, resulting in low ionic conductivity (10^{-7} to 10^{-8} S/cm), or remain as a liquid when using low molecular weight oligomers, leading to creeping or bleeding [3]. To enhance the conductivity and mechanical properties of these materials while minimizing creeping and bleeding, we have

focused on the study of oligoether–silica hybrids formed by sol–gel synthesis.

It has been shown that the crystallinity of high molecular weight polyether-based systems can be greatly reduced by the addition of inorganic fillers such as alumina [1,3] or silica [4], giving increased ionic conductivity. New ionic conduction paths and phases, which have lower energy barriers for ion transport, are thought to form at the silica–polyether interface, consistent with the fact that the conductivity enhancement increases with the interfacial area [5–7]. Polyethers incorporated in a silica matrix via sol–gel synthesis would not only suppress crystallization, but would also maximize the interfacial contact between the organic and inorganic components. In addition, the silica component should impart rigidity to the material.

Composite materials can be prepared by physically mixing the polyether with the inorganic phase [8–10], homogeneously entrapping the polyether in an inorganic sol–gel [11–13], or covalently binding the polyether to an inorganic sol–gel [14,15]. The latter organic–inorganic hybrid, often called an *ormolyte* (organically modified electrolyte), has the

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advantage of mitigating creeping, bleeding and evaporation of low molecular weight oligomers incorporated in the hybrid. Oligoethers, which tend to be more conductive than high molecular weight polyethers, can then be utilized in these applications.

Our hybrids consist of polydisperse poly(ethyleneglycol) methyl ether having an average M_n of 2000 g/mol (i.e., MPEG2000), tethered to the silica framework at the hydroxyl terminus via a urethane linkage. This leaves one end of the oligoether free to vacillate and facilitate ion-hopping. The hybrid is doped with lithium perchlorate in a ratio of 1 lithium ion per 9 polyether oxygen atoms (Li:EO = 1:9), which was previously found to give optimum conductivity in polyether–LiClO₄ solutions [16]. Apart from an FT-IR study by Gonçalves [14] and an ionic conductivity study by Lee et al. [15], little work has been done on singly-tethered hybrids compared to those in which the polyether was tethered at both ends and used to cross-link the silica [2,17–20].

The effect of the micro-scale structure and overall composition of these materials has great influence over the mechanical and thermal characteristics, most notably, the glass transition temperatures, T_g , of the polyether. The T_g controls the lower temperature limit of conduction in these materials, thus, it is desirable to keep it as low as possible. The purpose of this investigation was to examine the effect of silica, lithium perchlorate and water content on the glass transition temperature of these ormolytes, and to ascertain how each component interacts with each other. Li⁺-free ormolytes and Li⁺-doped ormolytes can be made without difficulty using the sol–gel method [21]. The acid-catalyzed sol–gel reaction of triethoxysilane-derivatized MPEG (MPGSC2000) with tetraethylorthosilicate (TEOS) yields solid electrolyte materials in which the polymer phase is covalently linked to an inorganic silica backbone. The thermal properties of these materials were studied by differential scanning calorimetry.

2. Experimental

2.1. Reagents

All starting materials were reagent grade and used without further purification. ω -Methoxy poly(ethylene glycol)-3-triethoxysilylpropylcarbamate (MPGSC2000) was prepared

by the stoichiometric reaction of poly(ethylene glycol) monomethyl ether ($M_n = 2000$; Aldrich; i.e. MPEG2000) and 3-isocyanatopropyl triethoxysilane (Gelest) in THF. The reaction mixture was capped with a drying tube and refluxed at 67 °C for 8 h. The product was then flash evaporated and washed with hexane. Any hexane remaining after extraction was removed by rotary evaporation. The completion of the reaction was confirmed by FT-IR, where disappearance of the isocyanato vibrational band at 2270 cm⁻¹ was correlated with the appearance of a urethane vibrational band at 1720 cm⁻¹. The direct correlation of the two bands indicated that there was a negligible amount of water present, and hence very little carbamate formation, during the reaction.

2.2. Sample preparation

Ormolyte samples were prepared by the sol–gel reaction of MPGSC2000 with tetraethyl orthosilicate (TEOS) under acid-catalyzed conditions as follows. Approximately 1 g of MPGSC2000 was dissolved in 2 mL ethanol prior to the addition of varying amounts of TEOS (Aldrich) to reach the desired polyether to SiO₂ ratio as seen in Table 1. To this solution was added a mixture containing 1 mL of a 2 M HCl solution and a precalculated amount of LiClO₄ to reach a Li⁺ to polyether oxygen ratio of 1:9. The mixture was shaken until it was homogeneous. The sol was allowed to crosslink for approximately 24 h at room temperature, or until gelled. Remaining water, ethanol and HCl were pumped off in a vacuum oven under dynamic vacuum at room temperature for 72 h, but are denoted ‘undried’ samples because they still retain about 7–8 wt% water unless they are heated at 120 °C for some time.

2.3. Differential scanning calorimetry (DSC)

The resulting gel was lightly ground and crimped shut in non-hermetic DSC pans. DSC was performed on a TA Instruments Model 2920 equipped with a chiller at an average heating rate of 10 K min⁻¹ under a dynamic nitrogen atmosphere (50 mL min⁻¹). Pure indium metal was used for all temperature and enthalpy calibrations of the instrument. Undried samples were scanned from 60 to 200 °C. ‘Dried’ samples were obtained by scanning undried samples from room temperature to 120 °C where they were held isothermally

Table 1
The names and compositions of the MPEG2000-Silica-LiClO₄ ormolytes

Sample	SiO ₂ (wt%)	Li/[EO]	H ₂ O ^a , undried (wt%)	H ₂ O ^b excluding SiO ₂ (wt%)
40% SiO ₂ – Li	40	0/9	n/a	n/a
20% SiO ₂ + Li	20	1/9	7.3	8.0
25% SiO ₂ + Li	25	1/9	5.3	6.3
35% SiO ₂ + Li	35	1/9	6.1	8.0
40% SiO ₂ + Li	40	1/9	4.8	6.8
50% SiO ₂ + Li	50	1/9	4.1	6.8

^a Estimates based on the area under the DSC curves, assuming $\Delta H_{\text{desorb}} \approx \Delta H_{\text{vap}} = 44 \text{ k J mol}^{-1}$ (see text).

^b Percent water by mass if the mass of SiO₂ is excluded from the calculation.

for 20–40 min to remove adsorbed water. These were then scanned from -60 to 200 °C to obtain glass transition data. Glass transition temperatures are reported at the inflection of the transition during the heating cycle.

3. Results and discussion

3.1. Physically adsorbed water

DSC was employed to study the glass transition temperatures of the ormolytes. A thermogram of the Li^+ -added ormolytes can be seen in Fig. 1, with silica content ranging from 20 to 50% by weight. A broad endothermic peak, due to the removal of physisorbed water [22], appears around 100 °C and becomes significantly diminished after the sample is dried in the calorimeter at 120 °C for 20 min prior to the scan (Fig. 2). A similar peak is present in the thermogram of air-exposed silicic acid and in silica gel derived from hydrolyzed TEOS, but it is not present in pure MPEG2000 (Fig. 3a) or in pure MPGSC2000 (Fig. 3b). The variability in the height and po-

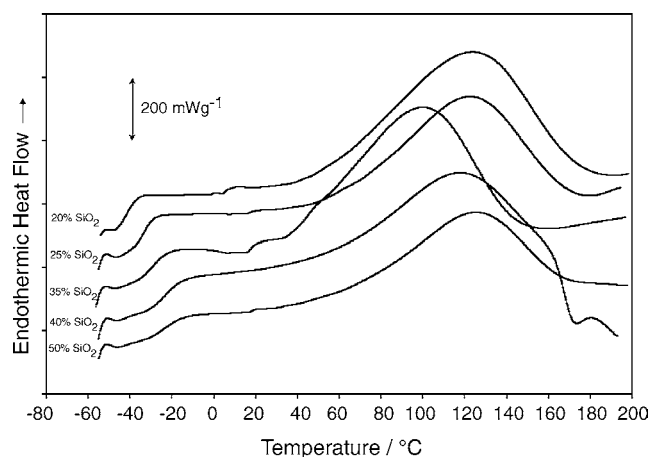


Fig. 1. DSC thermograms of the undried MPEG2000-silica- LiClO_4 ormolytes containing varying wt% of silica, as indicated.

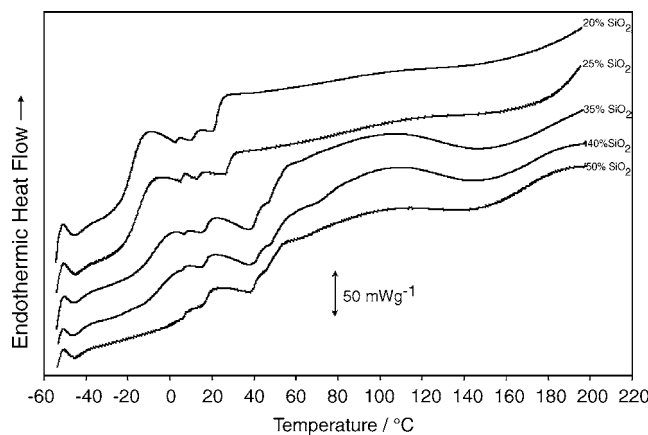


Fig. 2. DSC thermograms of the dried MPEG2000-silica- LiClO_4 ormolytes containing varying wt% of silica, as indicated.

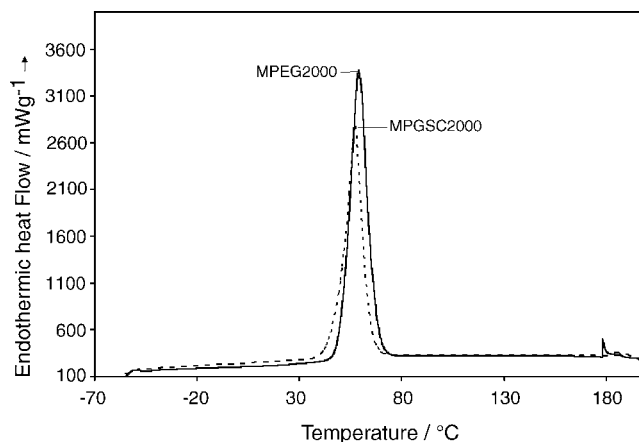


Fig. 3. DSC thermograms of: (a) poly(ethylene glycol) monomethylether (M.W. = 2000 g mol^{-1} ; i.e. MPEG2000); (b) ω -methoxy poly(ethylene glycol) 3-triethoxysilylpropyl carbamate (MPGSC2000).

sition of this peak depends on the water content in the sample and the rate at which the DSC pan allows the outflow of gases. The anomalous appearance of the DSC thermogram for the 35 wt% silica sample in Fig. 1 demonstrates this point, as the sample contains unusually large amounts of water, probably adsorbed from the air. The water content of the samples can, in fact, be estimated from the area under the peak since the energy required to remove water in these types of materials is roughly equal to the heat of vaporization of the water [23] i.e.,

$$\text{wt\% H}_2\text{O} = \frac{(6 \times 10^{-5} \times A \times MW_{\text{H}_2\text{O}})}{(\beta \times \Delta H_{\text{vap}})}$$

where A is the area under the DSC curve in mW g^{-1} , $MW_{\text{H}_2\text{O}}$ the molar mass of water, β the average heating rate in K min^{-1} , and ΔH_{vap} the enthalpy of vaporization of water in kJ mol^{-1} . The result of such estimates is shown in Table 1. The values are slightly over-estimated because silica and salt raise the heat of desorption/vaporization by about 20% for the amount of water in these samples.

3.2. Hydrogen-bonded water

Other features appear between 0 and 55 °C that increase in temperature as the amount of silica increases (Fig. 2). They generally have a peaked shape but are broader on the higher temperature side. These features are attributed to transitions of water hydrogen-bonded to the silica, and may be related to the 15 , 30 , 45 , and 60 °C thermal anomalies reported in the literature for water-containing silica samples [24–26]. These anomalies are thought to originate from the construction and destruction of ice-like clusters of water molecules. The features are absent from the DSC of MPEG2000 and MPGSC2000 (Fig. 3), but similar features do appear in pure silicic acid, commercial silica gel and in TEOS-derived silica gel. The position and appearance of the features change significantly with the history of the silica. For example, when a

sample of silicic acid is dried at 120 °C for 20 min in the DSC and subsequently scanned from –10 to 120 °C, the features are absent; however, a following scan from –60 to 120 °C causes the features to appear. One last scan from –10 to 120 °C again shows no features. Since no phase transitions appear below –10 °C during the scan to –60 °C at 10 °C/min, the silica must undergo a slow, undetectable phase change. According to Staszczuk [26], water freezes at –20 °C in silica gel pores and this supports our observations.

Heating a sample of silicic acid to 300 °C causes shifts in the temperature at which these features occur, but does not eliminate them. Thus, it is suspected that the transitions are affected by further condensation of vicinal silica hydroxyl groups, which is known to occur at around 170 °C [22].

3.3. Polyether melting/crystallization

The DSC thermograms of MPEG2000 and MPGSC2000 respectively exhibit strong endothermic peaks at 59.4 and 57.2 °C due to the melting of polyether (Fig. 3). The lower melting point of the latter reflects the poorer crystal packing of the terminal triethoxysilane group. In the Li⁺-free ormolytes, the melting peak of the polyether moiety, which occurs at 47.9 °C, is greatly diminished (Fig. 4). From the area under the melting peak, and the reported 203 J/g heat of melting of 100% crystalline poly(ethyleneoxide) [27], it is estimated that the 1.7% of the polyether is crystallized in the ormolyte as compared to 97% in pure MPEG2000. The 10 °C drop in melting point from that of MPEG2000 suggests that the tethered end is unable to participate in crystallization, leaving only the free end to crystallize. The Li⁺-added ormolytes do not exhibit melting peaks for the polyether. As in other poly(ethylene glycol) solutions of lithium salts, the lithium ion raises the viscosity of the polyether, thereby, suppressing crystallization and promoting glassing. Such viscosity increases are due to the formation of temporary cross-links

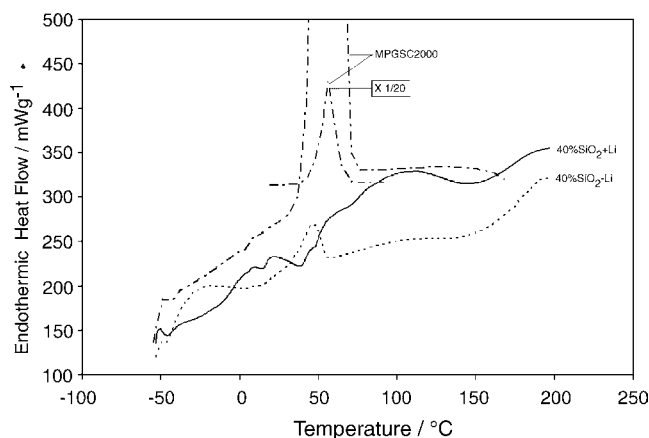


Fig. 4. A comparison of the DSC thermograms of dried, Li⁺-free MPEG2000-silica ormolyte containing 40 wt% silica (40% SiO₂–Li), dried, Li⁺-added MPEG2000-silica ormolyte containing 40 wt% silica (40% SiO₂+Li), and MPEG2000.

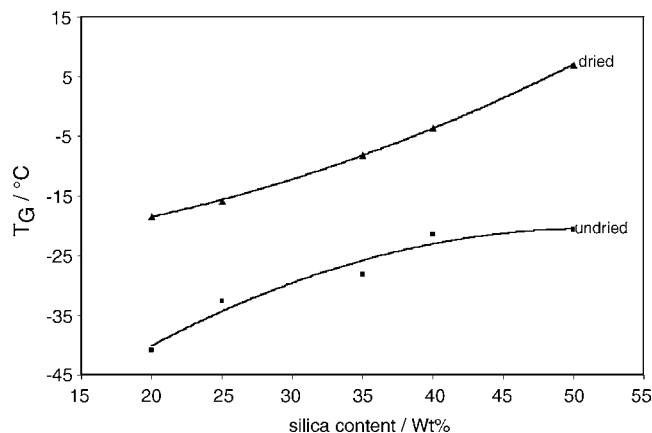


Fig. 5. The glass transition temperature of dried, and undried, Li⁺-added MPEG2000-silica ormolytes as a function of silica content.

between the polyether chains [28] and the reduction of the polyether's partial molar volume as the polymer solvates Li⁺ [29,30]. The latter affects viscosity in a manner similar to a physical compression [31].

3.4. Polyether glass transition

A sigmoid in the DSC thermogram, ranging from –20 to 10 °C in the dried samples (Fig. 2), and ranging roughly 20 °C lower in the undried samples (Fig. 1), is assigned to the glass transition of the MPEG moiety. This assignment is supported by the fact that the intensity of the feature scales with the MPEG content (Table 2), and because it is absent from the thermogram of MPEG-free silica gel. This transition shifts to higher temperature with greater silica content, and increases more for the dried samples than for the wet ones (Table 2, Fig. 5). As would be expected, the T_g for the dried samples, when extrapolated to 0 wt% in Fig. 5, approaches that of a silica-free LiClO₄–MPEG2000 solution having a Li:[EO] ratio of 1:9 ($T_g = -29$ °C).

The elevation of the polyether T_g with added silica appears to be caused by a mechanism similar to that of added lithium salts [29]. Attractive forces between the polymer and the polar or charged inorganic component directly restrict polymer segmental motions and cohesively decrease the free volume of the mixture. Moreover, the effect of Li⁺ and silica on T_g appears to be additive.

As mentioned earlier, the undried ormolyte samples show a T_g that is about 20 °C lower than that of the dried samples. Solutions of LiClO₄ in MPEG2000 having a Li:[EO] ratio of 1:9 exhibit a 2 °C drop in T_g per wt% of water added [32]; thus, a 20 °C drop in T_g corresponds to 10 wt% water in these solutions. If one considers, hypothetically, that the silica in the undried ormolyte is a non-interacting filler, the wt% of water in the LiClO₄–MPEG2000 portion would be, at most, 7–8 wt% (Table 1). Thus, only 7–8% water is required in the ormolytes to cause the same 20 °C drop in T_g drop as 10 wt% in silica-free LiClO₄–MPEG2000 solutions. The silica in the ormolytes, therefore, enhances the

Table 2

DSC data for the dried, Li:[EO] = 1:9, MPEG2000-Silica-LiClO₄ ormolytes. Silicic acid is also shown for comparison

Sample	Glass transition of PEG (°C)				Adsorbed water transitions ^a (°C)
	Dry		Wet		
	<i>T_g</i> (°C)	ΔC_p	<i>T_g</i> (°C)	ΔC_p ^b	
20% SiO ₂ +Li	-18.4	0.56	-40.9	0.65	2.5, 10.3, 21.0
25% SiO ₂ +Li	-15.8	0.52	-32.6	0.58	5.0, 13.2, 26.7
35% SiO ₂ +Li	-8.2	0.40	-28.2	0.56	6.6, 16.1, 41.1, 38.9, 47.1
40% SiO ₂ +Li	-3.6	0.23	-21.4	0.59	5.8, 15.7, 41.8, 39.1, 47.9
50% SiO ₂ +Li	7		-20.7	0.45	6.7, 16.7, 38.9, 45.4, 51.6
Silicic Acid	n/a				11.6, 24.4, 53.9

^a The onset temperatures of the adsorbed water transitions are reported.^b The changes in specific heat capacity, ΔC_p , from the glass state to the liquid state are reported in units of J g⁻¹ K⁻¹.

T_g-lowering ability of water. In fact, our data suggest that the *T_g*-lowering ability increases in proportion to the amount of silica present. A possible explanation for this is that water preferentially binds to silica and inhibits the *T_g*-raising association of polyether and silica. Since a larger portion of the polyether is associated with silica at high silica: polyether ratios, water has a greater effect for ormolytes having a higher wt% of silica.

The depression of *T_g* by water in LiClO₄-MPEG2000 solutions is due to a combination of plasticization and the solvation of Li⁺ by water [33]. The *T_g* is observed to be more dependent on water content than suggested by the Fox equation,

$$\frac{1}{T_g} = \frac{\text{wt\% } A}{T_g(A)} + \frac{\text{wt\% } (B)}{T_g(B)}$$

which predicts the *T_g* of polymer, A, mixed with a plasticizer, B.¹ On the other hand, the *T_g* is observed to be less dependent on water content than is expected by the stoichiometric removal of Li⁺ by complexation with water, assuming a 1:4 (Li⁺:H₂O) molar ratio. Thus, the *T_g* suppression appears to be a combination of the two effects.

4. Conclusion

Our studies have shown that the degree of crystallinity is suppressed from 97% in pure MPEG2000 to about 1.7% in the Li⁺-free, MPEG2000-silica ormolyte by the inclusion of 40 wt% silica. The addition of LiClO₄ to the ormolyte in a 1:9 Li⁺:EO ratio completely removes the remaining crystallinity.

During a heating scan, the DSC thermograms of the MPEG2000-silica-LiClO₄ ormolytes exhibit a polyether glass transition, a desorption endotherm for weakly bound water, and several transitions that may be due to the destruction of ice-like water clusters. These latter transitions persist despite heating the samples at 120 °C prior to the scan, and

only appear after the sample is cooled below -20 °C, where water in silica-gel pores reportedly freezes. Similar transitions have been previously noted for samples of silicic acid impregnated with salt solutions.

The effect of Li⁺ and silica content on the ormolyte's *T_g* appears to be additive. Both raise the *T_g* of the incorporated polyether due to the restriction of the polymer's segmental motion by dipole-dipole and ion-dipole interactions, and by the cohesive contraction of the material. Addition of water decreases the ormolyte's *T_g* by a combination of plasticization, sequestering of lithium ions by complexation, and by inhibiting silica-polyether associations by preferentially binding to the silica.

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¹ The *T_g* of water is commonly quoted as -137 °C, and this value was used in the assessment. Higher values for the *T_g* of water have been suggested by [34], which would make *T_g* even less sensitive to water through plasticization.

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