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# Poly(ethylene glycol)-Octafunctionalized Polyhedral Oligomeric Silsesquioxane: Synthesis and Thermal Analysis

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ABSTRACT: A homologous series of PEG (various chain length)-substituted octasilsesquioxanes were prepared by the hydrosilylation of unsaturated PEGs (poly(ethylene glycol)s) with both octa(dimethylsiloxy)silsesquioxane ($Q_8M_8^H$) and octahydridosilsesquioxane ($T_8^H$). The silsesquioxane-PEGs materials were produced by the initial synthesis of a series of allyl-modified poly(ethylene glycol)s and subsequent attachment to both ($Q_8M_8^H$) and ($T_8^H$). The products were chemically characterized by Fourier transform infrared (FTIR) and nuclear magnetic resonance ($^1$H, $^{13}$C, and $^{29}$Si NMR) spectroscopy, and the properties of the allyl PEGs and their POSS hybrids were thermally characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The attachment of the PEGs onto the POSS macromonomers ($Q_8M_8^H$ and $T_8^H$) clearly demonstrated a chain-length-dependent increase in $T_g$ and a concomitant suppression of crystallization.

## Introduction

Organic−inorganic hybrid nanomaterials are of interest because they combine the properties of traditional organic polymers, such as ease of processability and toughness, with those of inorganic compounds, i.e., thermal and oxidative stability.[1] Numerous classes of hybrid nanocomposite materials have recently been developed, such as three-dimensional sol−gel materials,[2,3] pre-ceramic polymers,[4] inorganic/organic polymer blends[5] and polyhedral oligomeric silsesquioxane (POSS) nanocomposites.[1] POSS-polymers are materials that contain nanoscale, silicate cagelike segments directly bound to the polymer chains. Such newly developed nanocomposite materials show synergistic properties, as opposed to average behavior, when applying the rule of mixtures to the component phase properties.[6,7]

Polyoctahedral silsesquioxanes are unique three-dimensional nanobuilding blocks that can be used to create a wide variety of hybrid materials, where precise control of nanostructure and properties is required.[8−11] Silsesquioxanes are known to develop a random structure, a cage structure, and/or a partial cage structure.[12] The most common process used to synthesize such compounds is the hydrolytic condensation of trifunctional monomers $XSiY_3$, where X is a chemically stable organic substituent and Y is a highly reactive substituent such as Cl, alkoxy, or ethoxy. In such a synthesis, the silane monomer, which possesses three hydrolyzable groups and one organyl group, is hydrolyzed, leading to a trisilanol monomer that subsequently readily undergoes self-condensation to produce the Si−O−Si bonds of the silsesquioxane cage.[13] A number of factors are still poorly understood and must be controlled for the successful synthesis of POSS compounds. The issues include the type and concentration of the initial monomer, the nature of the solvent, the substituent X in the initial monomer, the character of catalyst used, temperature, and the rate and quantity of water addition.[14] The synthesis of the two most utilized POSS frameworks, $(HSiO_{1.5})_8$ and $[(RMe_2SiO)SiO_{1.5}]_8$, were optimized by the Agaskar and Hasegawa groups, respectively.[15−21]

POSS compounds are used as precursors in the synthesis of hybrid nanocomposites; examples include alkyl,[22] allyl alcohol, 2-allyloxyethanol,[23] epoxy,[24−26] styryl,[27,28] norbornyl,[29] mesogen,[30] methacrylate,[31] amine,[32,33] and amino- and bromophenyls.[34,35] Recently, Maitra et al.[36] synthesized oligomeric poly(ethylene oxide) (PEO)-functionalized POSS materials and studied the thermal behavior of the new hybrids.

POSS compounds can be modified into various octafunctionalized macromonomers by a hydrosilylation reaction between the terminal Si−H groups on the POSS cube with an unsaturated carbon double bond in the presence of a platinum catalyst.[37,38] If the stoichiometry is correctly controlled, hydrosilylation also offers a good method for the synthesis of monosubstituted silsesquioxanes.[39] Alternatively, end-capping of the incompletely condensed silsesquioxane precursors developed by Feher[40−43] and co-workers offers an alternative route into monofunctional silsesquioxane chemistry.

The objective of this study was to synthesize and characterize octafunctional poly(ethylene glycol) (PEG) derivatives of two different POSS structures: octa(dimethylsiloxy)silsesquioxane ($Q_8M_8^H$) and octa(hydrido)silsesquioxane ($T_8^H$), where the attached PEGs have varying chain lengths ($n = 2-6$). It should be noted that almost all POSS molecules made to date are intrinsically hydrophobic, while many commercial monomers are polar, and so dispersion of existing POSS materials in polar monomers is often difficult, leading to poor mechanical properties. Attachment of poly(ethylene glycol)s can potentially provide a solution to this issue, as they are used in a wide variety of applications because of their hydrophilic chemical structure, low toxicity, solubility in water, and lubricating properties. The POSS−PEG monomers described in this work are indeed very

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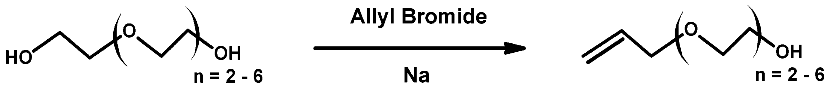
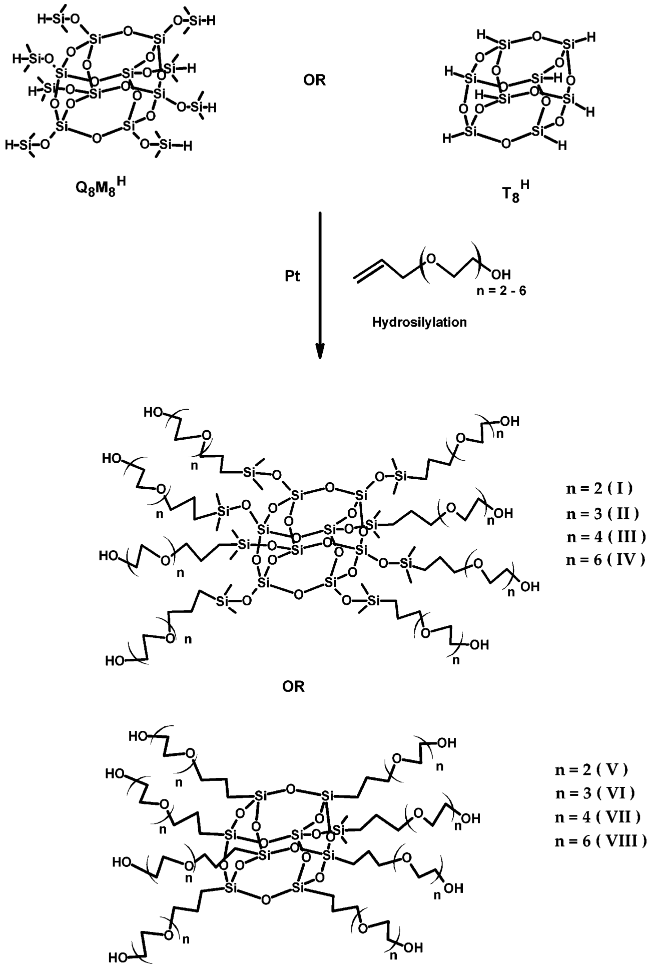
**Scheme 1. Synthesis of Ethylene Glycol Monoallyl Ethers**



**Scheme 2. Hydrosilylation of $Q_8M_8^H$ or $T_8^H$ with Ethylene Glycol Monoallyl Ethers**



hydrophilic and are readily dispersed in polar monomers. This is due to the fact that we seek to modify all corners of the POSS cage, not simply one, as is often reported.[40−43] Our approach is the synthesis of ethylene glycol monoallyl ethers of various chain lengths, followed by hydrosilylation onto octa(dimethylsiloxy)silsesquioxane ($Q_8M_8^H$) and octa(hydrido)silsesquioxane ($T_8^H$). Because of their accessible terminal OH groups, ethylene glycol monoallyl ethers described here may be further modified to give a wide variety of functional groups. The thermal behavior of the POSS starting materials, the initial PEGs themselves, and their allyl derivatives is contrasted with the resultant organic−inorganic hybrid nanocomposite materials. The potential to tailor the properties of the newly formed nanomaterials systematically, particularly with respect to their thermal stability, is of great significance. Since the chain PEG length of the above POSS−PEG materials can be varied in such a regular way, structure/property relationships can be defined, and so future nanocomposite hybrid materials for particular applications can be optimized.

## Experimental Section

**Materials.** Ethylene glycols, allyl bromide, 2,2,4-trimethylpentane, ferric chloride, methanol, toluene, hydrochloric acid, sodium dodecyl sulfate, trichlorosilane, potassium carbonate, calcium chloride, pentane, cyclohexane, and Karstedts catalyst [Pt(dvs)] were obtained from Aldrich Chemical Co. and used without further purification. Octa(dimethylsiloxy)silsesquioxane ($Q_8M_8^H$) was purchased from Hybrid Plastics. Toluene (99.5%) was purchased from Fluka, dried over $CaH_2$, and then distilled prior to use (Na/benzophenone).

**Table 1. Yields and Boiling Points for Ethylene Glycol Mono Allyl Ethers**

| monoallyl-PEG | bp of parent glycols | bp[a] | % yield | lit. % yield[b] |
|---|---|---|---|---|
| PEG(*n*=2) | 245 | 25 | 90 | 87 |
| PEG(*n*=3) | 285 | 95 | 78 | 78 |
| PEG(*n*=4) | 314 | 110 | 70 | 84 |
| PEG(*n*=6) | 217/4 mm | 160 | 76 | - |

[a] At reduced pressure ($10^{-2}$−$10^{-3}$ Torr). [b] From ref 44.

**Instrumentation.** NMR spectra were obtained on a Varian 300 NMR. Samples for $^1H$ NMR and $^{13}C$ NMR were prepared in $CDCl_3$. TMS (tetramethylsilane) was used as an internal standard for $^{29}Si$ NMR. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using TA Instruments TGA 2950 thermogravimetric analyzer and TA-DSC 2920, respectively.

**General Synthesis of Ethylene Glycol Monoallyl Ethers.** A 500 mL two-necked round-bottom flask equipped with a reflux condenser, magnetic stirrer, and thermometer before being charged with 265.3 g of diethylene glycol (2.5 mol) under argon. Sodium metal (5.75 g, 0.25 mol) was cut into small pieces, dispersed in toluene, and added to the glycol, while maintaining the temperature below 100 °C. After allowing the mixture to cool to 70 °C, 21.62 mL of allyl bromide (0.25 mol) was added, and the reaction mixture was stirred for 48 h at 60 °C. The solution was diluted to twice its volume with water and continuously extracted over 4 days using a mixture of benzene and 2,2,4-trimethylpentane (1:3). The solvent was removed under reduced pressure, and the products were purified by high-vacuum distillation ($10^{-2}$−$10^{-3}$ Torr) to yield the product as a colorless oil. The products di-, tri-, tetra-, and hexaethylene glycol monoallyl ethers were characterized by FTIR, $^1H$ NMR, and $^{13}C$ NMR. FTIR ($cm^{-1}$): $\nu = 3436$ (broad, OH), 2870 ($O-CH_2-CH_2$), 1633 ($CH_2{=}CH_2$), 1131 and 1070 (OH bending), 997 and 928 ($CH_2{=}CH_2$). $^1H$ NMR (ppm) (300 MHz, $CDCl_3$) for diethylene glycol monoallyl ether: $\delta$ 5.72−5.92 (m, $CH_2{=}CH_2CH_2$), 5.05−5.23 (m, 2H $CH_2{=}CH_2CH_2$), 3.96 (t, 2H, $CH_2{=}CH_2CH_2O$), 3.49−3.74 (m, 8H, $CH_2CH_2OCH_2CH_2$), 3.10 (br O*H*). $^{13}C$ NMR (300 MHz): 134.03 ($CH_2{=}CH_2$), 116.99 ($CH_2{=}CH_2$), 68.95−72.19 (4C $CH_2OCH_2CH_2OCH_2$), 60.99 ($CH_2OH$).

**Synthesis of Octakis(hydrido)octasilsesquioxane ($T_8^H$).** Octakis(hydrido)octasilsesquioxane was prepared following a modified procedure described by Agaskar.[15−19] In a three-necked 5 L round-bottom flask equipped with a reflux condenser, a mechanical stirrer, and a fritted gas dispersion tube, anhydrous ferric chloride (75 g, 0.46 mol) was added slowly to a rapidly stirred mixture of methanol (98.6 g), toluene (300 g), and hydrochloric acid (74.4 g, 37%). After allowing the mixture to cool, hexane (784.5 g) and sodium dodecyl sulfate (1.2 g) were added, creating a biphasic mixture. Trichlorosilane (83 g, 0.61 mol) was added with a flow of nitrogen passing through a bubbler, into the reaction vessel, with rapid stirring via the fritted gas dispersion tube. The addition took place over 5 h. The completed reaction mixture was stirred for another hour and then transferred into a separating funnel. The yellow organic layer was separated, filtered, and dried with anhydrous potassium carbonate and then with calcium chloride. The solvent was removed in a rotary evaporator until ∼150 mL remained. White needlelike crystals (3.7 g 11.6%) spontaneously formed upon cooling, which were collected, washed with pentane (5 × 5 mL), recrystallized

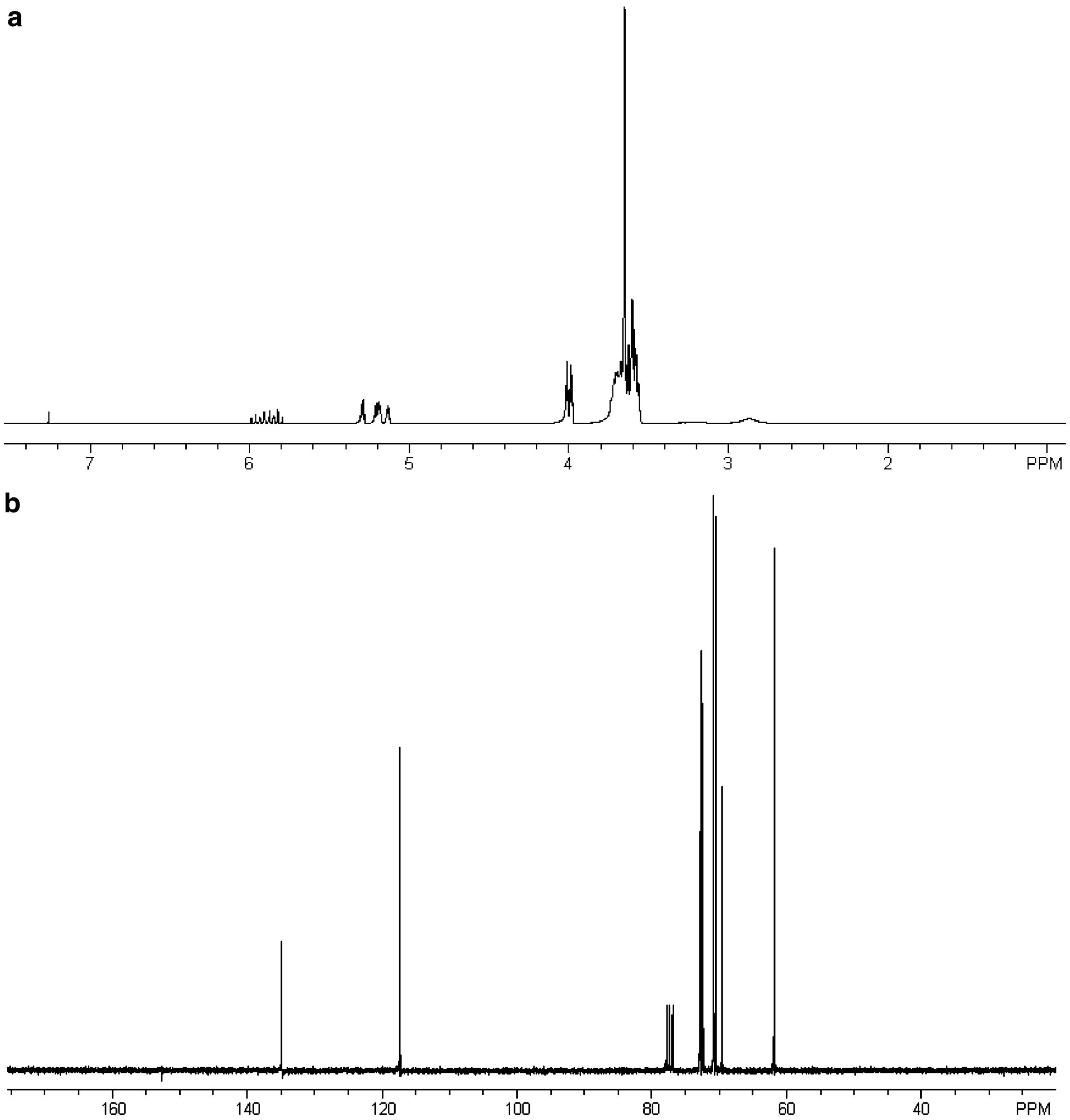


**Figure 1.** (a) $^{1}$H NMR of diethylene glycol monoallyl ether, [PEG($n$=2)]. (b) $^{13}$C NMR of diethylene glycol monoallyl ether, [PEG($n$=2)].

from cyclohexane, and dried in a 50 °C oven. The product was characterized: $^{1}$H NMR: $\delta = 4.23$ (Si−H). $^{29}$Si NMR: $\delta = -84.12$ (Si−H). FTIR (cm$^{-1}$): $\nu = 2284$, s (Si−H); 1281, s (O−Si−O) in cubic structure; 919, 907 s (O−Si−H) TGA: 98% weight loss in the temperature range from 100 to 170 °C.

**Synthesis of Octakis(diethylene glycol dimethylsiloxy)octasilsesquioxane [$Q_8M_8^{PEG(n=2)}$], (I).** 1 g of $Q_8M_8^{H}$ (0.982 mmol) was dissolved in anhydrous toluene in a 100 mL round-bottom flask under argon. Ethylene glycol monoallyl ether was added in 25% excess to the $Q_8M_8^{H}$. Karstedt's catalyst [Pt(dvs)] (0.2 mL of 2 mmol solution in toluene) was added, and an immediate increase from room temperature to 35 °C was observed. The reaction was monitored by $^{1}$H NMR. After 2 h, the disappearance of the Si−H proton shift ($\delta = 4.72$ ppm) confirmed that the hydrosilylation had gone to completion. The reaction mixture was concentrated under reduced pressure, and the excess starting ethylene glycol monoallyl ether was removed by vacuum distillation. The product $Q_8M_8^{PEG(n=2)}$ (**I**) was characterized by FTIR, $^{1}$H NMR, $^{13}$C NMR, and $^{29}$Si NMR spectroscopy. Identical hydrosilylations were conducted employing other ethylene glycol monoallyl ethers, ($n$ = 3, 4, 6), and the products $Q_8M_8^{PEG(n=3,4,6)}$ were characterized by the same spectroscopy methods employed in the synthesis of $Q_8M_8^{PEG(n=2)}$. Spectroscopy data for [$Q_8M_8^{PEG(n=2)}$], (**I**): FTIR (cm$^{-1}$): $\nu = 3448$ (broad OH), 2873 s ($O-CH_2-CH_2$), 1254 s (O−Si−O), 1092 s (O−Si−H). $^{1}$H NMR (300 MHz, CDCl$_3$) $\delta$: 3.59−3.78 (m 8H $C\mathit{H}_2C\mathit{H}_2OC\mathit{H}_2C\mathit{H}_2$), 3.45 (t 2H $Si(CH_3)_2CH_2CH_2C\mathit{H}_2$), 3.10 (br O$\mathit{H}$), 1.62 (m $Si(CH_3)_2CH_2C\mathit{H}_2CH_2$), 0.58 (t $Si(CH_3)_2C\mathit{H}_2CH_2CH_2$), 0.13 (s $Si(C\mathit{H}_3)_2$). $^{13}$C NMR for $Q_8M_8^{PEG(n=2)}$ (300 MHz, CDCl$_3$): 70.15−74.10 4C ($\mathit{C}H_2\mathit{C}H_2O\mathit{C}H_2\mathit{C}H_2$), 61.81 $\mathit{C}H_2OH$), 23.13 ($Si(CH_3)_2CH_2\mathit{C}H_2CH_2$), 13.71 ($Si(CH_3)_2\mathit{C}H_2CH_2CH_2$), −0.26 ($Si(\mathit{C}H_3)_2$). $^{29}$Si NMR (300 MHz, TMS) 12.72 ($-O\mathit{Si}(CH_3)_2$), −109.27 ($\mathit{Si}O_4$).

**Synthesis of Octakis(diethylene glycol)octasilsesquioxane ($T_8^{PEG(n=2)}$) (V).** The same procedure as for the hydrosilylation of $Q_8M_8^{H}$ was employed in the hydrosilylation of $T_8^{H}$ with ethylene glycol monoallyl ethers. 0.5 g (1.1 mmol) of $T_8^{H}$ was dissolved in anhydrous toluene in a 100 mL round-bottom flask under argon. Ethylene glycol monoallyl ether was added in 25% excess to the $T_8^{H}$. Karstedt's catalyst was added, and an immediate increase from room temperature to 30 °C was observed. The reaction was monitored by $^{1}$H NMR. After 1$^{1}/_{2}$ h, the disappearance of the Si−H proton shift ($\delta = 4.24$ ppm) confirmed that the hydrosilylation had gone to completion. The excess starting ethylene glycol monoallyl ether was removed by vacuum distillation.

The product $T_8^{PEG(n=2)}$ was characterized by FTIR, $^{1}$H NMR, $^{13}$C NMR, and $^{29}$Si NMR spectroscopy. FTIR (cm$^{-1}$): $\nu = 3405$

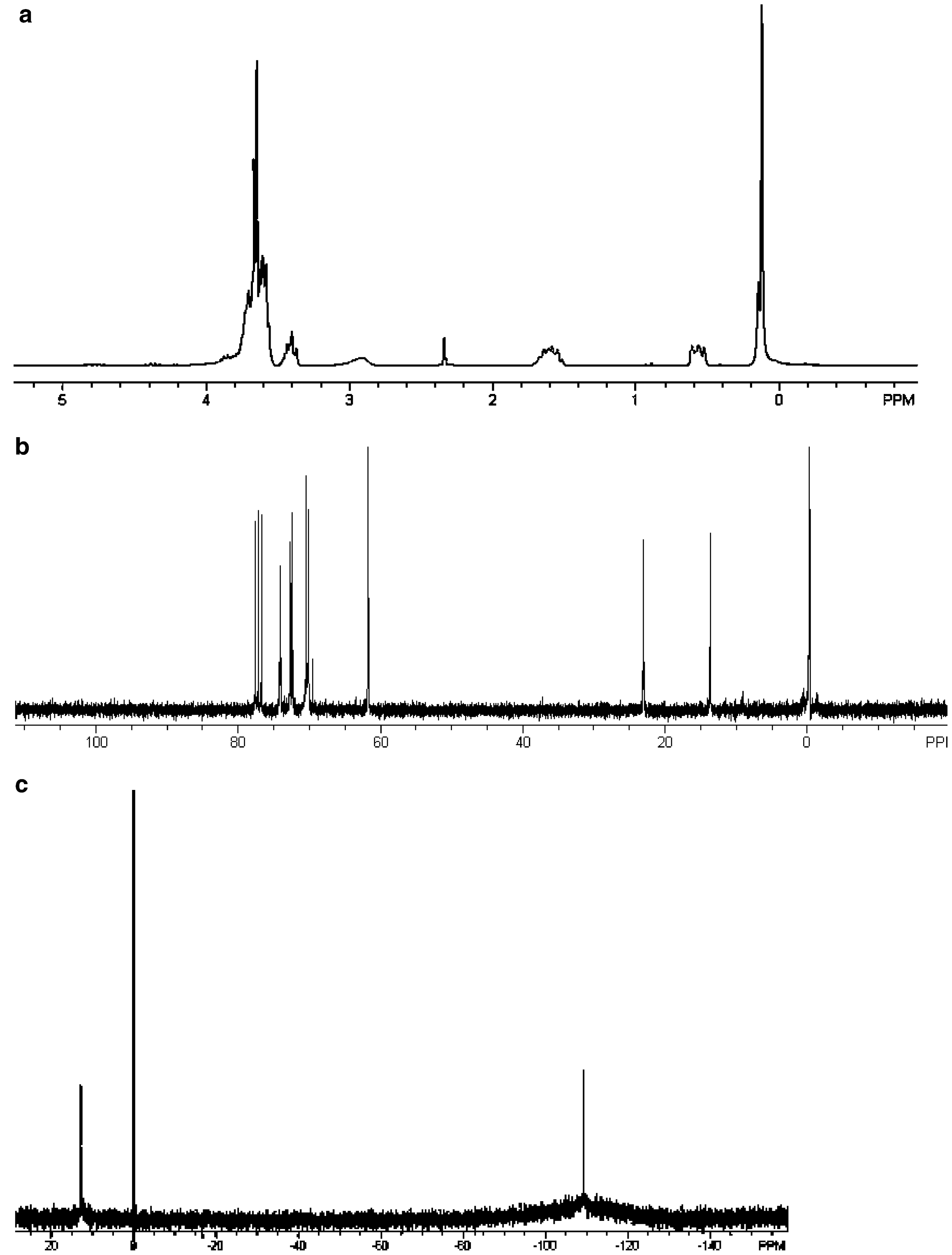


**Figure 2.** (a) $^1$H NMR spectrum of $Q_8M_8^{PEG(n=2)}$. (b) $^{13}$C NMR spectrum of $Q_8M_8^{PEG(n=2)}$. (c) $^{29}$SiNMR spectrum of $Q_8M_8^{PEG(n=2)}$.

(broad OH), 2875 s ($\mathrm{O{-}CH_2{-}CH_2}$), 1107 s (O−Si−O), 885 s (O−Si−H). $^1$H NMR (300 MHz, $\mathrm{CDCl_3}$) $\delta$: 3.59−3.66 (m 8H $\mathrm{C\mathit{H}_2C\mathit{H}_2OC\mathit{H}_2C\mathit{H}_2}$), 3.40 (t 2H $\mathrm{SiCH_2CH_2C\mathit{H}_2}$), 3.05 (br O$\mathit{H}$), 1.64 (m $\mathrm{SiCH_2C\mathit{H}_2CH_2}$), 0.60 (t $\mathrm{Si(CH_3)_2C\mathit{H}_2CH_2CH_2}$), 0.13 (s $\mathrm{Si(C\mathit{H}_3)_2}$). $^{13}$C NMR for $T_8^{PEG(n=2)}$ (300 MHz, $\mathrm{CDCl_3}$): 69.95−73.36 4C ($\mathrm{\mathit{C}H_2\mathit{C}H_2O\mathit{C}H_2\mathit{C}H_2}$), 61.61 $\mathrm{\mathit{C}H_2OH}$), 22.81 ($\mathrm{Si(CH_3)_2CH_2\mathit{C}H_2CH_2}$), 8.05 ($\mathrm{Si\mathit{C}H_2CH_2CH_2}$). $^{29}$Si NMR (300 MHz, TMS): −83.27 ($\mathrm{\mathit{Si}O_4}$).

## Results and Discussion

The synthesis of the silsesquioxane-PEGs macromonomers was achieved in three steps. Octakis(hydrido)octasilsesquioxane ($T_8^H$) was synthesized, using a modification of a procedure developed by Agaskar.[15−19] Dropwise addition of $\mathrm{HSiCl_3}$ to the $\mathrm{HCl/H_2O}$ reaction mixture in the presence of sodium dodecyl sulfate, which acted as a surfactant and ensured controlled hydrolysis occurred. The introduction of $\mathrm{HSiCl_3}$ into the biphasic reaction mixture through a fritted gas-dispersing tube resulted in improved yields.

Ethylene glycol monoallyl ethers of various chain lengths were prepared using a modified procedure developed by Jungk and Gandour.[44]

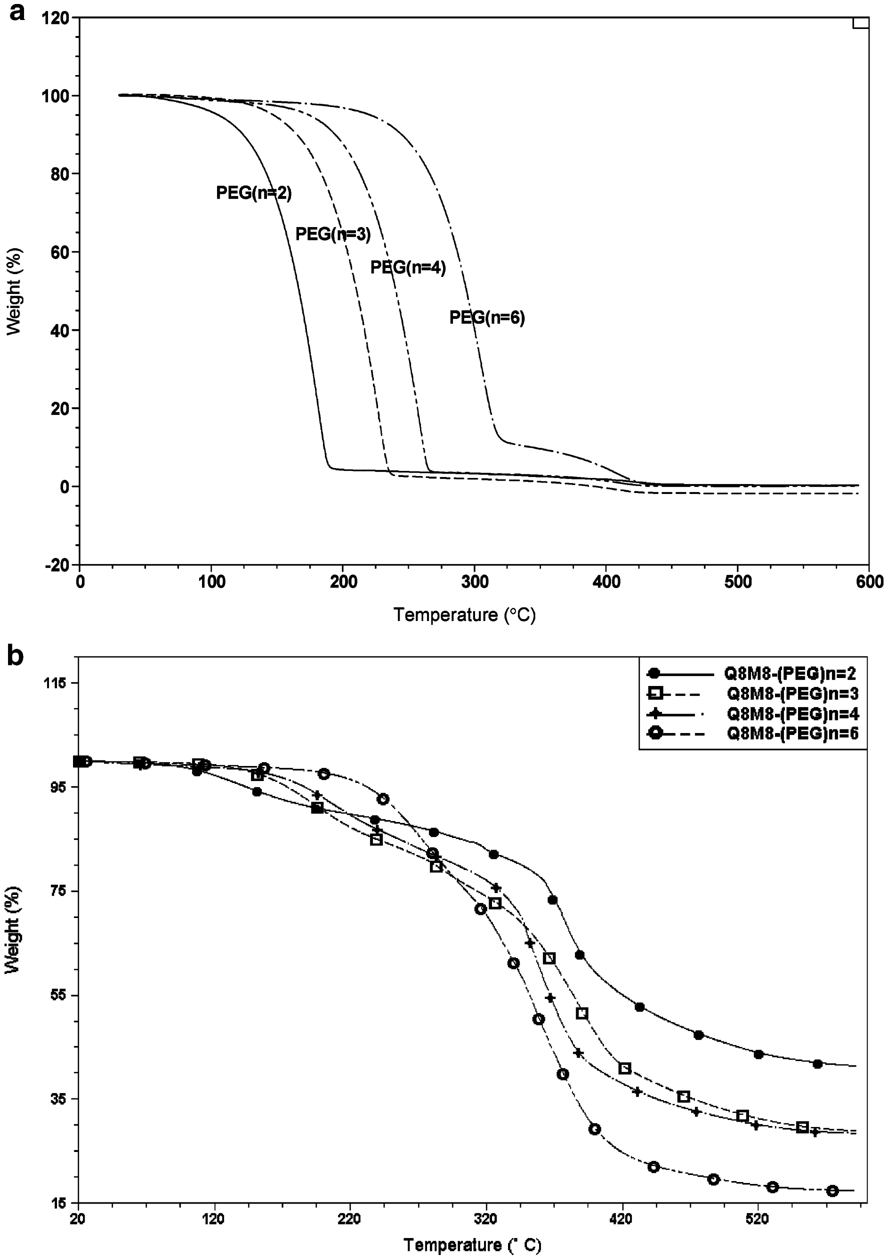


**Figure 3.** (a) TGA thermogram of allyl-PEGs ($n$ = 2−6). (b) TGA thermogram of POSS−PEGs [$Q_8M_8^{PEG(n=2-6)}$].

The reaction of sodium metal with a glycol gave a dialkoxide ion, as sodium was in considerable excess. High levels of dilution and carefully controlled stoichiometric addition of allyl bromide yielded the monoallyl−monoalkoxide ion product (Scheme 1). The crude product was diluted with water and continuously extracted using benzene and 2,2,4-trimethylpentane (1:3) for 4 days to remove the monoallyl compound from the excess parent glycol. Pure ethylene glycol monoallyl ethers were obtained by high-vacuum distillation; the yields and boiling points of the various chain length ethylene glycol monoallyl ethers are detailed in Table 1. The isolation and verification of pure, allyl-substituted glycols by such characterization are important, as any remnant of parent glycol material would interfere with isolation of the pure POSS−PEG products later. Likewise, any diallyl-substituted glycols would result in intractable, cross-linked POSS−PEG products.

The ethylene glycol monoallyl ether products were characterized by $^1$H NMR and $^{13}$C NMR spectroscopy. Figure 1a shows the $^1$H NMR spectrum of diethylene glycol monoallyl ether as a representative example. The appearance of the allyl double bond at $\delta$ = 5.85 ppm confirmed the substitution reaction had proceeded successfully. The pure ethylene glycol monoallyl ether could be effectively separated from the excess of their parent glycols by distillation, as the $^1$H NMR integration is consistent with the pure product (excess parent glycol would result in increased integrals at $\delta$ = 3.6 ppm). The integration of the allyl double bond proton to the OH proton also showed a 1:1 ratio that confirmed monosubstitution. The appearance of the double bond shift at $\delta$ = 117.3 ppm and $\delta$ = 134.5 ppm in the $^{13}$C NMR spectrum confirmed the existence of the monosubstituted allyl-functional ethylene glycols (Figure 1b). High product purity is clear, with the four carbon signals observed between $\delta$ = 65−75 ppm due only to the original glycol carbons.

The syntheses of the silsesquioxane-PEGs materials were achieved using hydrosilylation reactions. The synthesis of $Q_8M_8^{PEG(n=2-6)}$ and $T_8\ ^{PEG(n=2-6)}$ is shown in Scheme 2. Ethylene glycol monoallyl ethers of various chain lengths were covalently attached to $Q_8M_8^H$ by hydrosilylation in separate reactions. The progress of the hydrosilylaton reaction was followed by $^1$H NMR

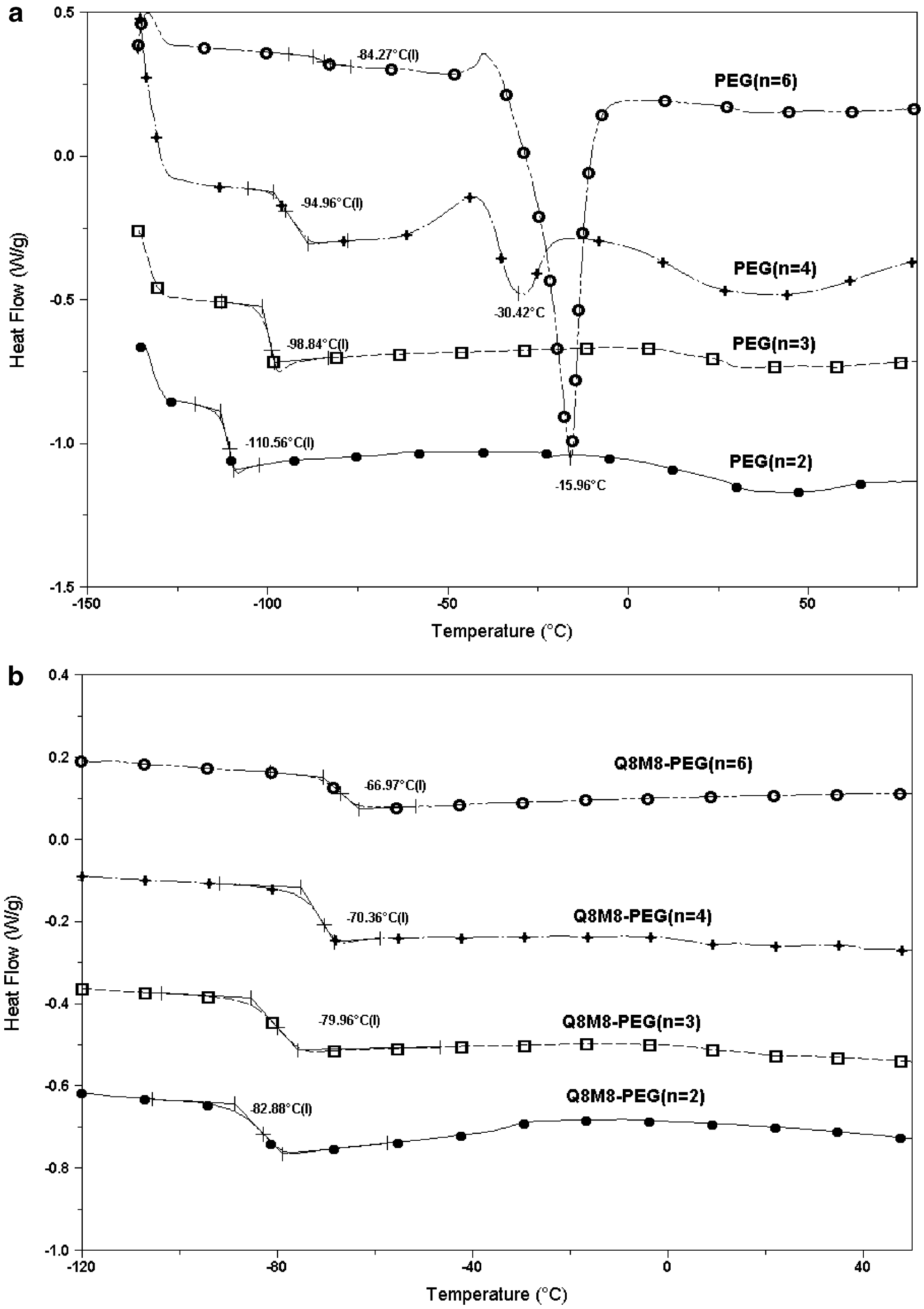


**Figure 4.** (a) DSC data for allyl-PEGs. (b) DSC data for POSS−PEGs [$Q_8M_8^{PEG(n=2-6)}$].

spectroscopy. Figure 2a shows $^1$H NMR spectrum of $Q_8M_8^{PEG(n=2)}$ as a representative example: the disappearance of Si−H bond shift at $\delta = 4.72$ ppm, concomitant with the allyl double bond shift at $\delta = 5.85$ ppm, confirms the formation of the hydrosilylation product. Further, the presence of two new proton signals (the triplet at $\delta = 0.58$ ppm and the multiplet at $\delta = 1.62$ ppm) is due to $OSi(CH_3)_2{-}CH_2{-}CH_2CH_2O$ and $OSi(CH_3)_2{-}CH_2{-}CH_2CH_2O$, respectively, and verifies the completion of the reaction. $^{13}$C NMR data (Figure 2b) likewise showed signals at $\delta = -0.26$ ppm due to $OSi(CH_3)_2{-}CH_2{-}CH_2CH_2O$ with $OSi(CH_3)_2{-}CH_2{-}CH_2CH_2O$ at $\delta = 13.71$ ppm and $\delta = 23.13$ ppm due to $OSi(CH_3)_2{-}CH_2{-}CH_2CH_2O$. The disappearance of the allyl signals of the parent glycol, at $\delta = 117.3$ and $\delta = 134.5$ ppm, in addition to the appearance of two carbons, at $\delta = 13.71$ and $\delta = 23.13$ ppm due to the unsaturated carbons of the allyl group, confirms that hydrosilylation is complete. The $^{29}$Si NMR spectrum (Figure 2c) showed two signals: the first at $\delta = -109$ ppm is due to the silicones (Q) of the silsesquioxane cage; a second signal at $\delta = 12$ ppm represents the siloxane silicon (M), shifted due to the attachment of the PEG molecule.

The products obtained (**I**−**VIII**) were colorless viscous oils, soluble in solvents such as toluene, methanol, and dichloromethane. The products were tested for their solubility in water. Not surprisingly, it was found that solubility increased with increasing chain length of the attached PEGs.

**Thermal Properties of the POSS−PEG Hybrids.** The thermal properties of the allyl-functional PEGs and octasubstituted $Q_8M_8$ and $T_8$ derivatives were studied by both TGA and DSC. TGA was used to study the thermal degradation of PEGs and their analogous POSS hybrid materials under a $N_2$ atmo-

**Table 2. TGA Results for PEGs and POSS−PEGs [$Q_8M_8^{PEG(n=2-6)}$]**

| monoallyl-PEG | decomp (°C) | POSS−PEG | 1st decomp (°C) | 2nd decomp (°C) | calcd $SiO_2$ (%) | exptl $SiO_2$ (%) |
|---|---|---|---|---|---|---|
| PEG($n$=2) | 181 | $Q_8M_8^{PEG(n=2)}$ | 164 | 394 | 35 | 35 |
| PEG($n$=3) | 227 | $Q_8M_8^{PEG(n=3)}$ | 198 | 388 | 30 | 31 |
| PEG($n$=4) | 258 | $Q_8M_8^{PEG(n=4)}$ | 208 | 385 | 27 | 26 |
| PEG($n$=6) | 305 | $Q_8M_8^{PEG(n=6)}$ | 268 | 359 | 21 | 23 |

sphere. The thermal behavior of PEG oligomers has been previously reported, where it was established that a correlation existed between melting point sensitivity and PEG polydispersity.[45,46] Because of the synthetic methods employed in this earlier work, the resultant products are mixtures of different homologous, polydisperse macromers. As shown in Figure 3a, thermograms for allyl-PEGs show only one sharp distinct decomposition event, and onset of decomposition values of these products can be found in Table 2.

Both Table 2 and Figure 3a clearly indicate that as the PEG chain length is increased, there is a distinct shift in the onset of weight loss to higher temperatures.

In contrast, POSS macromers are known for their thermal stability.[47,48] The thermal behavior of both the $Q_8M_8^H$ and $T_8^H$ PEG hybrid materials is expected to be affected by any such structural modifications. Figure 3b shows the TGA thermograms of the $Q_8M_8^{PEG(n=2-6)}$ series. Increasing peak decomposition temperature overall is consistent with an increase in the PEG molecular weight, i.e., with an increase in chain length of the attached PEGs.[22,36,49] While organic allyl-PEG derivatives exhibit a one-step decomposition, the TGA weight loss curve and first-derivative curve for the hybrid macromers (Figure 3b) indicate the presence of two distinct decompositions. The first maximum is consistent with the organic PEG component of the hybrid PEG chain, while the second peak is due to the inorganic POSS cage decomposing. The ceramic yield of $SiO_2$ for $T_8^{PEG}$ and $Q_8M_8^{PEG}$ are in good agreement with the calculated values.[25,31]

The DSC data for the allyl-PEGs ($n = 2-6$) and the octasubstituted POSS−PEGs ($n = 2-6$) silsesquioxanes display clear trends (Figure 4a,b). For example, the allyl-PEGs ($n = 2-6$) are semicrystalline compounds, and the glass transition temperature, $T_g$, of allyl glycols increases progressively with PEG chain length as would be expected for longer chain (higher molecular weight) materials. Only the tetra- and hexaethylene glycols exhibited melting points at −30.4 and −15.9 °C, respectively. The shorter chain ethylene allyl glycols were completely amorphous. However, after attachment of the PEGs ($n = 2-6$) to both of the parent silsesquioxanes making $Q_8M_8^{PEG(n=2-6)}$ and $T_8^{PEG(n=2-6)}$, any melting behavior of the allyl-PEGs disappeared, and the resultant amorphous liquids exhibit higher glass transition temperatures. $Q_8M_8$ does not show any melting before sublimation or decomposition.[36] The observed $T_g$'s resulting from the PEG chain segments attached to the inorganic POSS core increase when compared to their respective parent monoallyl ethylene glycols. Therefore, attaching PEG chains to POSS cores not only reduces PEG chain mobility, and increases $T_g$, but also disrupts intermolecular chain packing, thereby preventing crystallization (no melting behavior observed). An interesting aspect is that longer chain POSS−PEG hybrids still show an increase in glass transition, even though there is a reduced weight fraction of POSS for those larger PEG systems (from 35 wt % in POSS−$(PEG)_{n=2}$ to 23 wt % silica in POSS−$(PEG)_{n=6}$; Table 2). Thus, the glass transition of the hybrids represents an overlay of the longer PEG units motion, along with the retarding effect of the cage. The difference in the value of $T_g$ of the allyl glycols from smallest to largest is some 26 °C, while from the shortest to longest silsesquioxane PEG it is 16 °C, and thus the difference has been slightly tempered by the presence of the POSS cage.

## Conclusion

The homologous series of allyl-modified PEGs were synthesized in high yields and successfully isolated and characterized by $^1H$ NMR, $^{13}C$ NMR, and FTIR spectroscopy. The hydrosilylation reaction was employed to attach the allyl-modified PEGs onto two different POSS cages: $Q_8M_8^H$ and $T_8^H$. The $Q_8M_8$ and $T_8^H$ macromonomers were then characterized by $^1H$, $^{13}C$, and $^{29}Si$ NMR and IR spectroscopy. Thermal analysis of the homologous series of ethylene glycol monoallyl ethers revealed a chain-length-dependent increase in the onset of weight loss, while DSC data for allyl-PEGs showed that such materials are semicrystalline. As expected, the glass transition of the allyl glycols increases with chain length, and the tetra- and hexaallyl PEGs showed distinct melting points. The attachment of allyl-PEGs onto POSS cages modified the thermal properties of the newly synthesized hybrids; the POSS−PEG hybrids have increased PEG $T_g$ values, compared to their allyl-PEG counterparts, although the order of $T_g$ (higher glass transition for hybrids with longer arms) is retained. The comparatively bulky POSS cage clearly retards molecular motion and interestingly continues this inhibition, even for higher molecular weight POSS−PEG hybrids, even though the weight concentration of POSS units in higher order materials would be lower.

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