Oligomeric Poly(ethylene oxide)-Functionalized Silsesquioxanes: Interfacial Effects on T_g, T_m, and ΔH_m

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Silsesquioxanes[1] have emerged as a new class of nanofillers for high-performance hybrid inorganic−organic composite applications, improving thermal properties such as decomposition and glass transition temperatures, T_g's.[2−5] Polyhedral oligosilsesquioxanes (POSS), of which the octameric structure is most common, are characterized by the formula $H_8Si_8O_{12}$ (T_8^H) for octahydridosilsesquioxane and by $(HSiMe_2O)_8Si_8O_{12}$ ($Q_8M_8^H$) for octakis(hydridodimethylsiloxy)octasilsesquioxane. They are nanosized inorganic materials with a silica core ($\approx$0.7−1.2 nm) and eight organic (R) groups on the surface, some reactive, and the remainder inert, but providing a means of controlling the solubility of the material.[6] Functionalization of $Q_8M_8^H$ or T_8^H can be achieved by the hydrosilylation reaction of Si−H groups present on the surface of the cubes in the presence of a platinum catalyst;[7,8,9−11] the products formed, $Q_8M_x^HM_{8-x}^P$ or $T_x^HT_{8-x}^P$ indicate the number ($8 - x$) and type (P) of the substituents. Examples include allyl alcohol, 2-allyloxy ethanol,[11] epoxy,[12,13] styryl,[2,3] norbornyl,[4,5] and methacrylate,[6,14] which can be used as precursors for the synthesis of hybrid, thermally, and photocurable nanocomposites.

Due to their high surface area and structure, silsequioxanes with trisilanol groups have been proposed as models for the silica surface.[15] Silsequioxanes may thus also be useful model systems for investigation of the effects of an inorganic surface on the conformation and morphological properties of grafted organic interface layers, information relevent for nanomaterials such as mesoporous or fumed silica. As the dimensions of the composite components decrease, the effects of the interface increase, and the interfacial region can in fact be considered a separate phase.

Poly(ethylene oxide) (PEO) is important as a solid polymer electrolyte in lithium ion batteries due to its ability to solvate lithium ions.[16] However, since it is a semicrystalline polymer, and ionic conduction occurs mostly in the amorphous phase,[17] the room temperature (RT) ionic conductivity of PEO is low. Since ion mobility should increase with increased free volume, and the latter increases with the number of chain ends, enhanced conductivity is expected for low molar mass or highly branched PEO compared with linear high molar mass PEO. Therefore, one approach to increasing the RT conductivity of PEO-based polymer electrolytes is by the attachment of short-chain PEO oligomers, as side chains to form "comb-shaped" or "hairy-rod" like polymeric structures,[18−28] or as "arms" from inorganic scaffolds.[29−31] However, when these ends are anchored to a stiffer surface, such as an inorganic scaffold, there may be restrictions upon chain mobility as well as on crystallization.

In the current work, we have grafted oligomeric PEO chains onto $Q_8M_8^H$. The reactions to produce the PEO-functionalized silsesquioxanes are shown in Scheme 1. The allylation reaction followed the procedure of ref 7, and the hydrosilylation reaction was carried out under anhydrous conditions until the ^1H NMR Si−H signal (4.7 ppm) disappeared; the expected peaks were well accounted for from ^1H, ^{13}C, and ^{29}Si NMR. PEOs with

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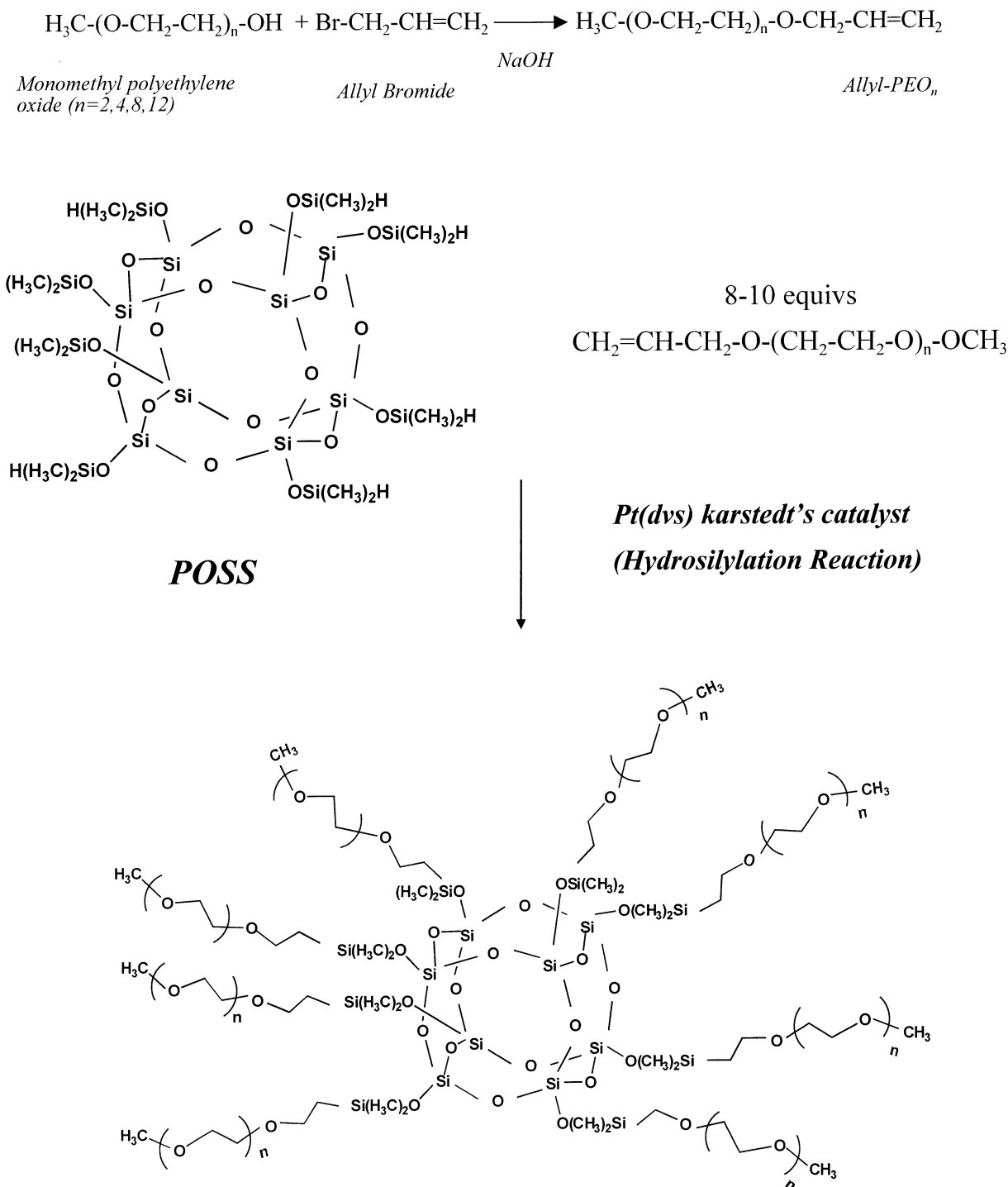(27) Yan, F.; Dejardin, P.; Frere, Y.; Gramain, P. *Makromol. Chem.* **1990**, *191*, 1197−1207.
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Scheme 1. Reaction Scheme To Prepare PEO-Octafunctionalized Silsesquioxanes

$$H_3C\text{-}(O\text{-}CH_2\text{-}CH_2)_n\text{-}OH \; + \; Br\text{-}CH_2\text{-}CH=CH_2 \longrightarrow H_3C\text{-}(O\text{-}CH_2\text{-}CH_2)_n\text{-}O\text{-}CH_2\text{-}CH=CH_2$$

<center>NaOH</center>

Monomethyl polyethylene   *Allyl Bromide*   *Allyl-PEO$_n$*
oxide (n=2,4,8,12)

POSS

8-10 equivs

$$CH_2=CH\text{-}CH_2\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}OCH_3$$

Pt(dvs) karstedt's catalyst

(Hydrosilylation Reaction)

repeat units $-(CH_2CH_2O)_n-$, with $n = 2$ (monodisperse), 4 (monodisperse), $\langle 8 \rangle$ (polydisperse), and $\langle 12.5 \rangle$ (polydisperse), corresponding, before (after) addition of the allyl group, to molar masses of 120 (160), 208 (248), 350 (390), and 550 (590) g/mol, respectively, were attached to $Q_8M_8^H$ to form $Q_8M_8^{PEO(n=2)}$, $Q_8M_8^{PEO(n=4)}$, $Q_8M_8^{PEO(n=8)}$, and $Q_8M_8^{PEO(n=12.5)}$, respectively. Unreacted allyl−(PEO)$_n$ was removed (confirmation by ^{1}H NMR and SEC), when necessary, by evacuation ($n = 2$), a silica gel column ($n = 4$), or preparative size-exclusion columns ($n = \langle 8 \rangle$, $\langle 12.5 \rangle$). All of the materials were liquids at RT. There is reasonable agreement, as shown in Table 1, between the TGA weight loss[13,32] and SEC data

Table 1. TGA^a Weight Loss and SEC^b Data for Octasubstituted Silsesquioxanes

	weight loss (wt %)		SEC results		
	calculated	TGA results	calculated M_n	PS^c equivalent M_n	M_w/M_n
$Q_8M_8^{PEO(n=2)}$	66.5	69	2297	2127	1.07
$Q_8M_8^{PEO(n=4)}$	74.5	75	3010	2816	1.32
$Q_8M_8^{PEO\;(n=8)}$	81.4	81.1	4138	4129	1.11
$Q_8M_8^{PEO\;(n=12.5)}$	86.5	85.5	5737	4500	1.19

^{a} TGA = thermogravimetric analysis. ^{b} SEC = size exclusion chromatography. ^{c} PS = polystyrene.

with the expected weight loss and molar mass data for the octasubstituted silsesquioxanes. Polydispersities >1
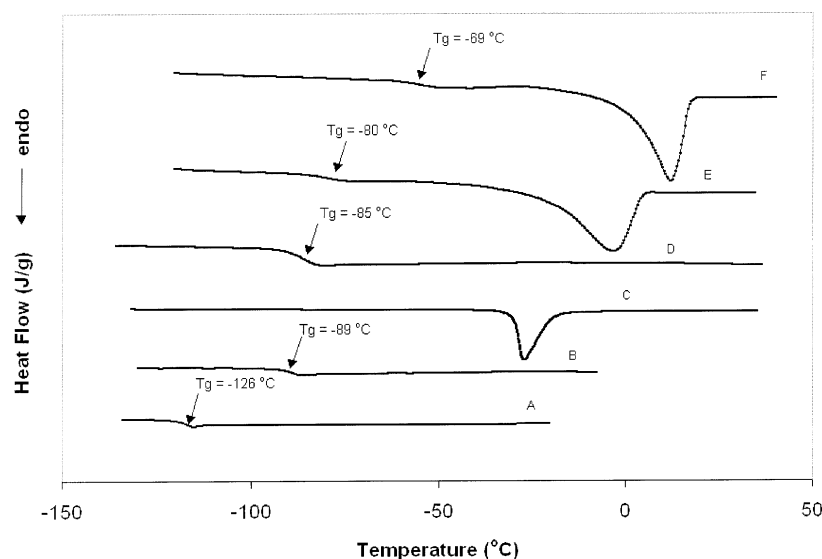
Figure 1. DSC scans (10 °C/min) for (A) allyl−PEO(*n*=2), (B) $Q_8M_8^{PEO(n=2)}$, (C) allyl−PEO(*n*=4), (D) $Q_8M_8^{PEO(n=4)}$, (E) $Q_8M_8^{PEO(n=8)}$, and (F) $Q_8M_8^{PEO(n=12.5)}$.

Table 2. Calorimetric Data for Allyl−PEOs and Octasubstituted Allyl−PEO Silsequioxanes

	DSC results			
compound	T_g (°C)	T_m (°C)	ΔH_m (J/g)	ΔC_p (J/g·K)
allyl methyl (diethylene glycol) diether, *n* = 2	−126			0.87
allyl methyl tetraglyme diether, *n* = 4		−28.3	99.7	
allyl poly(ethylene glycol) dimethyl ether (350), *n* = 8		−5.4	103.9	
poly(ethylene glycol) dimethyl ether (550), *n* = 12.5		12.9	118.4	
$Q_8M_8^{PEO}$ (*n*=2)	−89			0.85
$Q_8M_8^{PEO}$ (*n*=4)	−85			0.70
$Q_8M_8^{PEO}$ (*n*=8)	−80	−4.3	67.2[a]	0.29[a]
$Q_8M_8^{PEO}$ (*n*=12.5)	−69	11.1	69.5[a]	0.17[a]

[a] ΔH_m and ΔC_p were normalized for the wt % PEO based on TGA data.

can arise from less than octasubstitution and/or coupling of $Q_8M_8^H$.[32,33]

The calorimetric data for the allyl−PEO(*n*)s and the octasubstituted allyl−PEO(*n*) silsesquioxanes, shown in Figure 1 and presented in Table 2, demonstrate several interesting trends. Allyl−PEO(*n*=2) has a T_g of −127 °C and is completely amorphous. Octasubstitution to $Q_8M_8^{PEO(n=2)}$ raises the T_g to −89 °C. Since all of the material is amorphous, the change in heat capacity, ΔC_p, is large and comparable to that of allyl−PEO(*n*=2). Allyl−PEO(*n*=4) is completely crystalline and no T_g is observed even after rapid quenching. Upon attachment to silsesquioxane to form $Q_8M_8^{PEO(n=4)}$, melting is completely suppressed and the amorphous liquid shows a T_g at −85 °C, nearly the same as that for *n* = 2, with a large ΔC_p, about 20% lower than that for $Q_8M_8^{PEO(n=2)}$. Since $Q_8M_8^H$ does not exhibit a T_g before sublimation or decomposition, the observed T_g's arise from the PEO segments, indicating that attachment to the inorganic surface restricts the mobility of the chains and sup-

presses their crystallization. For both allyl−PEO-(*n*=⟨8⟩) and allyl−PEO(*n*=⟨12.5⟩), not shown, the samples crystallize below RT with no observable T_g, but upon octasubstitution to form $Q_8M_8^{PEO(n=8)}$ and $Q_8M_8^{PEO(n=12.5)}$, respectively, both materials exhibit a T_g and a melt temperature, T_m. The enthalpies of melting (ΔH_m's) are approximately 70% of those of the allyl−PEOs, and ΔC_p is small and decreases with an increase in chain length, due to the decreasing weight fraction of amorphous material. Since the PEO segments (*n* = 2, 4) near the surface do not crystallize, the suppression of crystallinity for the longer chains may also occur for the segments closest to the interface. However, since in $Q_8M_8^{PEO}$ (*n*=8) and $Q_8M_8^{PEO}$ (*n*=12.5) the chains are polydisperse, the possiblity that the smaller chains phase separate, and account for the low T_g, while the longer chains crystallize, cannot be ruled out. The T_g of octafunctionalized PEO silsequioxanes increases with an increase in chain length, asymptotically approaching that of high molecular weight PEO ($T_g \sim −55$ °C).

The trends for the PEO-functionalized silsequioxanes are the same as those observed for ethylene oxide side chains attached to flexible as well as rigid polymer backbones, where it has been found that T_g increased with increasing side chain length,[21,26] and the side chains did not crystallize for *n* < 5/6.[19,26] Due to this absence of crystallinity as well as the enhanced mobility of short side chains in comblike polymers, ion conductivity was observed to be highest for PEO chain lengths *n* = 5−7.[19,26] As the side chains become longer, they tend to crystallize more easily. However, in the case of a homologous series of *n*-alkanes, no suppression of crystallization was observed upon attachment to T₈, and in fact the melt temperatures increased compared with those of the neat alkanes upon octasubstitution.[34]

The current results are interesting from the point of view of characterization of the interface, in particular, the effects on T_g and T_m, as well as for implications in lithium ion battery research. Increased T_g's have previ-

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ously been observed with respect to high molecular weight base resins in proportion to the weight fraction of the POSS-comonomer.[2,4−6,35] Models have been proposed in which the polymer layer closest to the surface is immobile, and does not exhibit a T_g, and chains between POSS units exhibit increased T_g's, with the effects dependent on the amount of "constrained volume" (i.e., the volume occupied by polymer segments or chains not participating in T_g because of entropic or enthalpic effects) per POSS group.[3,4] The existence of a second, higher temperature, T_g, observed by dynamic mechanical testing, in polymer/silica composites was attributed to regions containing chains (near the particles) of reduced mobility.[36] However, for the oligomeric chain PEOs investigated here, the effect of the surface is to raise T_g directly: the chains are too short either to adsorb at a sufficient number of points on the surface to completely suppress mobility (resulting in no observation of a T_g) or to form physical cross-links with chains from other molecules (that would raise T_g).

The current investigation shows how the thermal behavior of oligomeric PEOs is affected by the silica surface. The grafting of oligomeric PEO onto $Q_8M_8^H$ resulted in a chain-length-dependent increase in T_g and suppression of crystallization. Attachment of allyl−PEO(n=2) reduced chain mobility considerably compared with the linear material as observed by a 35 °C

increase in T_g. The most dramatic effect was observed for PEO(n=4), where the originally crystalline material became completely amorphous; 4 PEO repeat units were insufficient for crystallization to occur at the surface. The PEO oligomers crystallized with increasing side chain length. Maxima in ion conductivity observed for PEO chain lengths of $n = 5−7$ have been attributed to the absence of crystallinity as well as the enhanced mobility of short side chains in comblike polymers.[19,26] The PEO-modified POSS investigated here are like dendrimers or star polymers[37] that also have a high ratio of chain ends, where for comparable molecular weights, melt viscosity is lower and free volume is greater than those for linear chains. In addition, $Q_8M_8^{PEO\ (n=2)}$ and $Q_8M_8^{PEO\ (n=4)}$, with PEO masses of 1280 and 1984, respectively, do not crystallize and have low T_g's. These materials therefore have potential as low-temperature solvents in lithium ion battery applications.

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