

Preparation and Characterization of PEO Functionalized Silsesquioxanes as Nanofunctional Materials for Lithium Batteries

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Polyethylene oxide (PEO) has been proposed as a material for use in solid state lithium batteries due to its ability to solvate lithium ions. However, the semicrystalline nature of high molecular weight PEO makes its room temperature ionic conductivity, σ , low. In order to increase σ , several approaches have been attempted, namely, by crosslinking reactions, copolymerization, addition of nano-size fillers and by attachment of short chain PEO oligomers as side chains to form "comb-shaped" or "hairy-rod" like structures on other polymers or as "arms" from inorganic scaffolds. Chain ends or branches of PEO show enhanced conductivity compared to linear PEO of the same molecular weight, presumably due to the increase free volume created by the chain ends. However, when these ends are anchored to an inorganic surface, there may be a restriction of chain mobility. In many of these systems, the inorganic scaffold is incorporated through a sol-gel process that results in a 3-D cross-linked structure. This may make it difficult for the resultant electrolyte to be bonded to the electrodes.

Silsesquioxanes have emerged as a new class of nano-fillers for high performance composite applications. Polyhedral oligosilsesquioxanes (POSS) are nano-sized inorganic materials with a silica core and reactive functional groups on the surface. The reactive organic groups on the surface have been functionalized by many investigators for a variety of applications. Functionalization of octa(dimethylsiloxy)silsesquioxanes ($Q_8M_8^H$), ($R=HMe_2SiO$), with the general formula ($RSiO_{1.5}$) is achieved by the hydrosilylation reaction of the Si-H groups present on the surface of the cubes in the presence of a platinum catalyst. $Q_8M_8^H$ systems have been functionalized with allyl alcohol, 2-allyloxy ethanol and epoxidized, as potential precursors to hybrid nanocomposites. Methacrylate functionalized silsesquioxanes have been reported as platforms for thermally and photocurable composite materials. The functionalized materials are liquids and thus have the added advantage of easy processability.

In the current work, we have attached low molecular weight PEOs with repeat units $n = 2, 4$ and ~ 12.5 to octa(dimethylsiloxy) silsesquioxane. The molecular weight of the $n = 12.5$ is approximately 550. These materials can be used as model systems to understand the silica/PEO interface and be investigated for use as a component of polymer electrolytes for lithium battery applications. The attachment of short chain PEOs to silsesquioxanes, which are inorganic particles of high surface area, may provide insight on the nature of the effects of the substrate on the chain mobility and crystallinity near the interface. Short chain PEOs tethered to silsesquioxanes may suppress crystallization of high molecular weight PEO or be used in alternate/suitable polymer hosts.

The PEO functionalized silsesquioxanes were synthesized by preparation of the allyl PEOs from monomethoxy PEOs and allyl bromide, followed by the

hydrosilylation reaction with $Q_8M_8^H$ in the presence of platinum catalyst. They were characterized by 1H , ^{13}C , ^{29}Si NMR, GPC and thermogravimetric analysis (TGA). Differential scanning calorimetry (DSC) was used in order to elucidate the effects of the interface and chain length of the PEO segment on the degree of crystallinity (as measured by the enthalpy of melting, ΔH_m) and glass transition temperature, T_g .

The TGA and GPC results are summarized in Table I. The calculated molecular weight (MW) and polydispersity index (PDI) are obtained using polystyrene (PS) standards.

Table I: Molecular Weight Results

	TGA % wt loss		Calc. MW	GPC Results	
	Calc.	Exptl.		PS M_n	PDI
$Q_8M_8^{PEO(n=2)}$	66.5	69	2297	2127	1.07
$Q_8M_8^{PEO(n=4)}$	74.4	75.0	3010	2816	1.32
$Q_8M_8^{PEO(n=12.5)}$	86.5	85.5	5737	4500	1.19

The TGA and GPC results show reasonable agreement with the predicted values.

The DSC results for the starting materials, model compounds and PEO functionalized silsesquioxanes are summarized in Table II.

Table II: DSC Data

	$T_g(^{\circ}C)$	$T_m(^{\circ}C)$	$\Delta H_m(J/g)$
mono methyl (diethyleneglycol) ether	-116.6		
allyl methyl (diethylene glycol) diether	-127		
tetraglyme		-27	
allyl methyl tetraglyme diether		-40	
Polyethylene glycol (PEG) dimethyl ether (MW =550)		12.9	118.4
$Q_8M_8^{PEO(n=2)}$	-89		
$Q_8M_8^{PEO(n=4)}$	-72.6		
$Q_8M_8^{PEO(n=12.5)}$	-57.2	11.1	78.4

Both the mono methyl (diethyleneglycol) ether and allyl methyl (diethylene glycol) diether, with PEO repeat units of $n = 2$ are amorphous with low values of T_g . When attached to the silsesquioxane, T_g increases about $30^{\circ}C$. Tetraglyme and allyl methyl tetraglyme diether ($n = 4$) are completely crystalline and do not exhibit a glass transition. When attached to silsesquioxane, the melt transition is suppressed and is replaced by a T_g . Low molecular weight (550) PEG does not exhibit a T_g , but when attached to silsesquioxane exhibits a T_g similar to high molecular weight PEO and a normalized ΔH_m (to take into account the presence of SiO_2) less than that of the unattached PEG. These results suggest that the PEO segments close to the silica interface are prevented from crystallizing. In addition, the 8 PEO segments, each with a molecular weight of 550, attached to the silsesquioxane core act like a dendrimer whose chains overlap and thus behave like high molecular weight PEO in terms of mobility (i.e. T_g).

