Functionalized Polyhedral Oligosilsesquioxane (POSS) Macromers: New Graftable POSS Hydride, POSS α-Olefin, POSS Epoxy, and POSS Chlorosilane Macromers and POSS–Siloxane Triblocks

Edward G. Shockey,¹ Alan G. Bolf,¹ Paul F. Jones,² Joseph J. Schwab,¹* Kevin P. Chaffee,² Timothy S. Haddad¹ and Joseph D. Lichtenhan²
¹Hughes STX Corporation, Phillips Laboratory, Propulsion Directorate, Edwards AFB, CA 93524-7680, USA
²Phillips Laboratory, Propulsion Directorate, Edwards AFB, CA 93524-7680, USA

A series of polyhedral oligomeric silsesquioxanes (POSS) monomers bearing silane or α-olefin substituents have been prepared and their chemistry explored. Both the POSS silanes and α-olefin monomers readily participate in hydro-silation chemistry and have been used as starting materials for the preparation of POSS sol–gel-type reagents. Similarly, POSS silanes and α-olefins are reactive towards silane- and olefin-functionalized polymers, which makes them useful as grafting reagents. The utility of these reagents as graftable monomers was demonstrated by synthesis of a series of POSS–siloxane–POSS triblock polymers. Thermal and X-ray diffraction (XRD) characterization of the triblock polymers was performed in order to examine how the length of the siloxane segment affects the properties of the polymer. The POSS α-olefin monomers were found to be unreactive with respect to Ziegler–Natta polymerization. The reaction of POSS α-olefins with m-chloroperbenzoic acid (MCPBA) to give POSS epoxides was demonstrated and the thermal stability of the POSS epoxides determined. Copyright © 1999 John Wiley & Sons, Ltd.

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INTRODUCTION

Silsesquioxane-based polymers have long been a technologically important class of materials (for reviews on polymeric silsesquioxanes, see Refs 1–3). The recent establishment of broad classes of monomeric reagents based on well-defined polyhedral oligomeric silsesquioxanes (POSS), coupled with the development of bulk-scale preparative methods of these monomers, affords a new chemical technology for the modification of properties in nearly all thermoset and thermoplastic materials.4,5

POSS reagents combine unique hybrid (inorganic–organic) chemical compositions with nano-sized cage structures that have dimensions comparable with those of most polymer segments and coils.4 Thus incorporation of POSS reagents into polymer chains can be used to modify the local structure and chain mobility in polymeric materials. Furthermore, the wide variety of functional groups and the solubility of POSS reagents in both organic solvents and comonomers also allow them to be easily employed as comonomer feedstocks and graftable reagents.
In this work we report the synthesis, spectroscopic and thermal characterization of the title POSS macromers (Fig. 1). The reactivity of the POSS hydride, POSS \( \alpha \)-olefin and POSS \( \alpha \)-epoxide functionalities towards the synthesis of hybrid polyolefins, epoxides and siloxanes is also reported.

RESULTS AND DISCUSSION

Starting from incompletely condensed polyhedral oligomeric silsesquioxanes (POSS), a tremendous number of new chemical reagents and monomers from which to conduct basic and applied polymer and chemical research has been developed. More recently, interest in this new class of chemicals has been directed toward the development of a fundamental understanding of how to utilize the three-dimensional nature of these molecules for nano-reinforcement of polymer chains in order to enhance the mechanical, thermal and other physical properties of conventional polymer systems.

Along these lines we have begun exploration of the basic transformation chemistry and polymer chemistry of polyhedral oligomeric silsesquixoxane monomers bearing hydride, olefin and epoxy functionalities. The octameric systems developed and utilized in this study bear one reactive functionality and seven inert and solubilizing groups, such as cyclohexyl or cyclopentyl. POSS molecules bearing only one or two reactive functionalities are useful for the preparation of both thermoplastics and crosslinked polymers while the related systems, developed by Wacker Chemie and later by Laine and co-workers and containing functionalities ranging from three to eight, are exclusively designed for incorporation into polymeric networks, for examples of polyhedral oligomeric silsesquioxanes with polyfunctionality, see Refs 8–10.

For the present work, POSS monomers containing hydride and \( \alpha \)-olefin functionalities were needed. These materials are readily available via the corner capping reaction of incompletely condensed POSS trisilanols [R7Si7O9(OH)3; R = \( \text{c-C}_6\text{H}_{11}\) or \( \text{c-C}_5\text{H}_9\)] with the appropriate silane coupling reagent. Although the synthesis of 1a from \( \text{c-C}_6\text{H}_{11}\text{Si}_{7}\text{O}_{9}(\text{OH})_3\) and HSiCl3 had previously been reported in the literature by several workers, we found that this procedure did not work well for the synthesis of 1b. When 1b, prepared in this way, was examined by \(^1\text{H} \) NMR spectroscopy the integrated intensity of the hydride resonance relative to the cyclohexyl proton resonances was consistently 33% too low. Closer analysis of the \(^1\text{H} \) NMR spectrum revealed a broad envelope of signals in the region around \( \delta = 4 \) ppm, which gave an integrated intensity equal to that of the missing...
intensity for the hydride resonance of 1b. All further attempts to either purify or cleanly prepare 1b by corner capping the trisilanol with HSiCl₃ were unsuccessful. Therefore, an alternative procedure involving the lithium aluminum hydride reduction of c-C₆H₁₃Si₇O₁₂(Cl) was carried out which provided pure 1b in 48% overall yield.

Although 1a and 1b were potentially useful reagents for grafting reactions via hydrosilation, we were concerned that the hydride functionality might be sterically inaccessible; we were also interested in developing a more facile and higher-yielding synthetic route to a POSS hydride monomer. Starting from the monosilanol, R₇Si₈O₁₂(OH), and HSi(CH₃)₂Cl both 2a and 2b, with a more accessible hydride functionality, could be prepared in essentially quantitative yield. With the complementary POSS hydrides readily available the hydrosilation chemistry of 1a, 1b, 2a and 2b was examined.

### Hydrosilation chemistry

Hydrosilation chemistry is a common and useful synthetic method for the formation of alkyl-substituted silanes. It is also an industrially important process for the preparation of addition cured silicones. The use of standard hydrosilation chemistry should allow for both the silane-bearing compounds 1 and 2 along with the olefin-bearing derivatives 3–6 to be readily incorporated into olefin- or silane-bearing polymers as graftable nano-reinforcements.

In a first step toward exploring the amenability of these reagents to hydrosilation, a series of simple model reactions were conducted. Hydrosilation reactions involving R₇Si₈H (1a) were particularly interesting because it was thought that the silane functionality might be sterically inaccessible since it is attached directly to the silicon–oxygen frame-work of the POSS cage and could therefore be shielded by the adjacent cyclic alkyl groups.

The hydrosilation reactions in this study were catalyzed using either Karstedt’s catalyst (platinum/vinyl-terminated siloxanes complex) or chloroplatinic acid, H₂PtCl₆·H₂O. Both catalysts were found to be effective for the hydrosilation of 1a with vinyltrimethylsilane. Furthermore, the reaction was found to proceed with exclusive formation of the β-addition product (scheme 1) as confirmed by DEPT 90 and DEPT 135 ¹³C NMR spectroscopy experiments. Along with the resonances for the methylene and methine carbons of the cyclohexyl groups, only the resonances for the methyl carbons of the trimethylsilyl group and those of the

[Scheme 1 Possible modes of addition for vinyltrimethylsilane to 1a and 1b.]

that they can be hydrosilated directly to reagents having active hydrogens, such as phenols and alcohols without using protecting groups.

Reagents for sol–gel and silicone synthesis

In addition to the hydrosilation chemistry of POSS silanes, POSS \( \alpha \)-olefins \( 3a, 3b, 4a \) and \( 4b \) can be functionalized through hydrosilation with hydride-containing silanes such as HSiCl$_3$ and HSi(Cl)$_2$CH$_3$. Since the POSS \( \alpha \)-olefins are readily available, this provides a complementary route to the hydrosilation of \( 1a \) and \( 1b \) that is in fact superior to procedures using \( 1a \) and \( 1b \) in that the hydrosilation can often be carried out with inexpensive, lowboiling hydride-containing silanes as the solvent. Using this chemistry an entirely new series of POSS monomers, suitable for incorporation into sol–gel systems and siloxanes, has been developed. For example, the POSS propyltrichlorosilane \( R_2Si_8O_{12}\)(CH$_2$)$_3$SiCl$_3$ can be prepared either from \( 1a \) and allyltrichlorosilane, or from \( 4a \) and HSiCl$_3$. Similarly, POSS dichlorosilanes \( R_2Si_8O_{12}(CH_2)_2SiCl_2CH_3 \) (7) and the octafunctional POSS trichlorosilane, \( Si_8O_{12}(CH_2CH_2SiCl_3)_8 \) (8), are easily prepared from \( 4a \) or \( Si_8O_{12}(CH=CH_2)_8 \) and HSiCl$_2$CH$_3$ or HSiCl$_3$, as shown in Scheme 2.

**Scheme 2** Synthesis of POSS monomers suitable for sol–gel-type chemistry.

**Triblock synthesis and characterization**

The ability of both POSS silanes and \( \alpha \)-olefins to undergo hydrosilation chemistry provides for a facile and direct synthesis of POSS-containing siloxane triblocks via the grafting of POSS silanes and \( \alpha \)-olefins onto the ends of functionalized siloxane oligomers and polymers (Scheme 3). Using this approach a series of siloxane polymers in which the length of the siloxane mid-block and the length of the alkyl tether between siloxane and POSS, as well as the number of POSS groups on the ends of the siloxane mid-block, were prepared and the effects of each of these variables on the properties of the polymers was investigated.

It is also interesting to note that, in the synthetic approach taken here, the use of well-defined, monodisperse difunctional siloxanes will lead to the formation of triblock polymers that are themselves monodisperse. This ability to form monodisperse triblock polymers leads to highly crystalline materials.

Crude product mixtures containing unreacted POSS monomer proved difficult to purify since the solubilities of the POSS macromers and the POSS triblocks are not significantly different, especially for triblocks with short siloxane segments, e.g., \(-SiMe_2-O-SiMe_2-O-SiMe_2-\). Product mixtures containing unreacted POSS monomer could only be purified by column chromatography.
which resulted in lower yields. Therefore, the grafting reactions were typically carried out using a slight excess of the functionalized siloxane, which was easily removed by stirring the crude product mixtures with activated charcoal and silica gel. The progress of the reactions was conveniently followed by $^1$H NMR spectroscopy and the disappearance of the POSS olefin or hydride resonances taken as completion of the reaction. Although NMR spectroscopy of the crude reaction products indicated high yields of the desired products, isolated yields of the products ranged from 54 to 90% and were dependent on the method of isolation, with products isolated by column chromatography typically around 60%; other methods typically resulted in yields of 60–90%.

Since POSS monomers have distinct NMR spectra, characterization of the POSS triblocks was most easily accomplished by NMR spectroscopy. The cycloalkyl groups of the POSS monomers give rise to a series of ubiquitous resonances in both the $^1$H NMR and $^{13}$C NMR spectra which are indicative of their presence. The $^{29}$Si NMR spectra of the silicon atoms of all the POSS compounds bearing cycloalkyl groups have resonances at approximately $\delta = -68$ ppm which are separated by no more than 1 ppm and are very diagnostic for the presence of these monomers. As stated above, hydridic and olefinic resonances for the reactive side chains are readily observed in both the $^1$H and $^{13}$C NMR spectra, and their presence or absence is used to determine the extent of reaction. Taken along with the $^{29}$Si NMR spectra in which the observed shifts in the resonances for the unique silicon atoms containing the reactive functionalities change significantly, the $^1$H and $^{13}$C NMR spectra provide unambiguous evidence for the formation of triblock polymers.

### Thermal characterization of triblocks

The ability of the POSS silanes and POSS $\alpha$-olefins in Fig. 1 to undergo hydrosilation chemistry provides a facile and direct synthesis of POSS-containing siloxanes with triblock, pendant and star (dendritic) architectures. POSS siloxanes with triblock and star architectures are easily prepared by grafting POSS olefins or POSS silanes onto the ends of telechelic siloxane oligomers and polymers (Scheme 3). Using this approach a series of POSS–siloxane–POSS triblock copolymers were prepared.

The series of triblock molecules and polymers in Table 1 (and Scheme 3) can be considered as the simplest versions of triblock polymers possible where each of the end blocks is monodisperse. In these systems the POSS end-groups function as the ‘hard’, crystallizable or glassy, reinforcing segments, while the middle siloxane block functions as a ‘soft’, amorphous segment. In such systems the POSS segments have been presumed to function in the same manner as, for example, the hard styrenic blocks in organic thermoplastics and thermoplastic elastomers such as styrene–butadiene–styrene (SBS), or styrene–siloxane–styrene systems. Tri-block systems with hard end-blocks of dispersities approaching unity typically exhibit very sharp melt transitions and are desirable for applications requiring narrow thermal processing windows. In previous preliminary work we have shown that using POSS as an end-group in main-chain liquid-crystalline polymer systems can have a marked effect on lowering the interfacial tension between

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Table 1. Thermal transitions for POSS monomers and triblocks

<table>
<thead>
<tr>
<th>No of Compd</th>
<th>Formula</th>
<th>Transition temp. ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>POSS macromers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1a</td>
<td>(c-C$<em>6$H$</em>{11}$)$_7$Si$<em>8$O$</em>{12}$H</td>
<td>279$^a$</td>
</tr>
<tr>
<td>1b</td>
<td>(c-C$_5$H$_9$)$_7$Si$<em>8$O$</em>{12}$H</td>
<td>275$^a$</td>
</tr>
<tr>
<td>4a</td>
<td>(c-C$<em>6$H$</em>{11}$)$_7$Si$<em>8$O$</em>{12}$CH$_2$CH=CH$_2$</td>
<td>425$^b$</td>
</tr>
<tr>
<td>4b</td>
<td>(c-C$_5$H$_9$)$_7$Si$<em>8$O$</em>{12}$CH$_2$CH=CH$_2$</td>
<td>412$^b$</td>
</tr>
<tr>
<td>5a</td>
<td>(c-C$<em>6$H$</em>{11}$)$_7$Si$<em>8$O$</em>{12}$CH$_2$CH=CH$_2$</td>
<td>358$^b$</td>
</tr>
<tr>
<td><strong>POSS–siloxane–POSS</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9a</td>
<td>(c-C$<em>6$H$</em>{11}$)$_7$Si$<em>8$O$</em>{12}$(CH$_2$)$_7$SiMe$_2$O SiMe$_2$OSiMe$_2$OSiMe$_2$–(CH$_2$)$<em>3$SiO$</em>{12}$–(c-C$<em>6$H$</em>{11}$)$_7$</td>
<td>304$^a$</td>
</tr>
<tr>
<td>9b</td>
<td>(c-C$_5$H$_9$)$_7$Si$<em>8$O$</em>{12}$(CH$_2$)$_7$SiMe$_2$O SiMe$_2$OSiMe$_2$OSiMe$_2$–(CH$_2$)$<em>3$SiO$</em>{12}$–(c-C$_5$H$_9$)$_7$</td>
<td>221$^a$</td>
</tr>
<tr>
<td>10a</td>
<td>(c-C$<em>6$H$</em>{11}$)$_7$Si$<em>8$O$</em>{12}$(CH$_2$)$_3$SiMe$_2$O SiMe$_2$OSiMe$_2$OSiMe$_2$–(CH$_2$)$<em>3$SiO$</em>{12}$–(c-C$<em>6$H$</em>{11}$)$_7$</td>
<td>260$^a$</td>
</tr>
<tr>
<td>11a</td>
<td>(c-C$<em>6$H$</em>{11}$)$_7$Si$<em>8$O$</em>{12}$(CH$_2$)$_3$SiMe$_2$O SiMe$_2$OSiMe$_2$OSiMe$_2$–(CH$_2$)$<em>3$SiO$</em>{12}$–(c-C$<em>6$H$</em>{11}$)$_7$</td>
<td>255$^a$</td>
</tr>
<tr>
<td>12a</td>
<td>(c-C$<em>6$H$</em>{11}$)$_7$Si$<em>8$O$</em>{12}$(CH$_2$)$_3$SiMe$_2$O SiMe$_2$OSiMe$_2$OSiMe$_2$–(CH$_2$)$<em>3$SiO$</em>{12}$–(c-C$<em>6$H$</em>{11}$)$_7$</td>
<td>273$^a$</td>
</tr>
<tr>
<td>13a</td>
<td>(c-C$<em>6$H$</em>{11}$)$_7$Si$<em>8$O$</em>{12}$(CH$_2$)$_3$SiMe$_2$O SiMe$_2$OSiMe$_2$OSiMe$_2$–(CH$_2$)$<em>3$SiO$</em>{12}$–(c-C$<em>6$H$</em>{11}$)$_7$</td>
<td>92$^c$</td>
</tr>
<tr>
<td>13b</td>
<td>(c-C$_5$H$_9$)$_7$Si$<em>8$O$</em>{12}$(CH$_2$)$_3$SiMe$_2$O SiMe$_2$OSiMe$_2$OSiMe$_2$–(CH$_2$)$<em>3$SiO$</em>{12}$–(c-C$_5$H$_9$)$_7$</td>
<td>12$^c$</td>
</tr>
<tr>
<td>14a</td>
<td>(c-C$<em>6$H$</em>{11}$)$_7$Si$<em>8$O$</em>{12}$(CH$_2$)$_3$SiMe$_2$O SiMe$_2$OSiMe$_2$OSiMe$_2$–(CH$_2$)$<em>3$SiO$</em>{12}$–(c-C$<em>6$H$</em>{11}$)$_7$</td>
<td>54$^c$</td>
</tr>
<tr>
<td>15a</td>
<td>(c-C$<em>6$H$</em>{11}$)$_7$Si$<em>8$O$</em>{12}$(CH$_2$)$_3$SiMe$_2$O SiMe$_2$OSiMe$_2$OSiMe$_2$–(CH$_2$)$<em>3$SiO$</em>{12}$–(c-C$<em>6$H$</em>{11}$)$_7$</td>
<td>36$^c$</td>
</tr>
</tbody>
</table>

$^a$ Melt by TMA.
$^b$ Decomposition.
$^c$ Softening point.
incompatible polymeric systems.\textsuperscript{19,20} A full report of this work will be forthcoming.

The series of triblocks in Table 1 vary in four different aspects: (1) the nature of the $R$ group on the POSS cage, (2) the length of the alkyl tether between POSS and the siloxane block, (3) the length of the siloxane mid-block, and (4) the number of POSS groups on the chain-ends of the siloxane block. The effects of each of these variables on the properties of the polymers relative to their respective thermal transitions and powder diffraction patterns has been investigated.

Examination by X-ray powder diffraction of the materials listed in Table 1 revealed that all of the monomers and triblocks with short siloxane segments ($1\text{--}12$) are highly crystalline, whereas compounds $13$ and $14$ are fully amorphous in nature. The X-ray diffraction patterns shown in Fig. 2 are representative of the POSS macromers, and the amorphous and crystalline POSS–siloxane–POSS triblocks. A notable observation in these diffraction patterns was the shifting of specific Bragg maxima, namely that at $8^\circ 2\theta$ to lower $2\theta$ values in the crystalline triblocks (9a) relative to the corresponding monomers (4a). The shifting of these maxima corresponds to an increase in the unit cell size, with the space group apparently unchanged. Such an increase does seem reasonable based on the necessity to accommodate the short siloxane linkage between the two POSS cages in 9a in a crystalline environment. Attempts to perform single-crystal diffraction studies to compare the packing between POSS monomers such as 4a with that for the POSS–siloxane–POSS triblocks (i.e. 9a) have not been fully successful. Disorder problems have led to only partial structural solutions, although the data do support the fact that both systems crystallize in the same trigonal space group.

Analysis of the thermal transitions reported for the triblocks 9a, 9b, 13a and 13b reveal that systems bearing cyclohexyl substituents on the POSS cages show thermal transitions that are roughly 80 °C higher than for the systems in which the POSS cages bear cyclopentyl groups. This trend has been observed previously in thermoplastic POSS–siloxane bead copolymers;\textsuperscript{21} however, the opposite trend has been observed in thermoplastic POSS–styryl systems with high POSS loadings and at all loading levels in linear POSS–acrylic copolymer systems.\textsuperscript{22,23} The influence of the POSS cage and its nonreactive substituent on thermal transitions and how these interactions are affected by polymer composition and architecture will be the subjects of future studies.

Comparison of the thermal transitions between triblocks 9a and 11a and between 10a and 12a provides insights into the influence of the length of the tether between the POSS cage and the siloxane segment on thermal properties. In 9a and 10a the length of the propyl tether is approximately 4.07 Å whereas in 11a and 12a the octane tether is roughly 10.56 Å. It is apparent from Table 1 that increasing the tether length results in an overall decrease in the melt transition, with specific decreases of 31 °C between 9a and 10a and of only 5 °C between 11a and 12a being observed. For the systems studied in

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2}
\caption{X-ray powder diffraction patterns of 15a (top), 9a (middle) and 4a (bottom).}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{Plot of the melt transitions for 4a, 9a and 10a and the softening points for 14a, 15a and 13a versus the average number of siloxane units between the POSS end-groups. All data were taken from Table 1.}
\end{figure}
The influence of the tether length on packing and crystallinity appears to be important yet is secondary in magnitude to the influence that the seven nonreactive substituents contained on the cage have on such transitions.

The results of a similar examination of the influence of the length of the siloxane segment on thermal transitions of POSS–siloxane–POSS triblocks are shown in Fig. 3. The data in Fig. 3 and in Table 1 reveal that as the length of the siloxane group between the POSS end-groups increases, the resulting thermal transition in the POSS–siloxane–POSS system decreases. The data in Fig. 3 indicate that there are two distinct types of POSS–siloxane–POSS triblocks: 9a and 10a are crystalline and undergo melt transitions whereas 13a–15a are amorphous and undergo softenings. Within each series, a decrease in the thermal transition can be correlated to the increased number of siloxane linkages located between the POSS cages. It is not possible to determine from this series the exact composition necessary for the preparation of a semicrystalline POSS–siloxane–POSS system; however, 15 does show a low degree of crystallinity in X-ray diffraction experiments conducted at room temperature. Variations of 15 containing shorter siloxane mid-blocks and an increased number of POSS-segments incorporated at the chain-ends may be sufficient to drive phase separation and crystallization of the POSS end-groups.

Table 1. Influence of the Tether Length on Packing and Crystallinity

Table 2. Thermal Properties of Aliphatic POSS Epoxides

<table>
<thead>
<tr>
<th>Compd</th>
<th>Self-exotherm (°C)</th>
<th>Rxn exotherm (°C)</th>
<th>$T_{\text{dec}}$ (°C)</th>
<th>Char yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16a</td>
<td>251</td>
<td>143</td>
<td>402</td>
<td>31</td>
</tr>
<tr>
<td>16b</td>
<td>246</td>
<td>141</td>
<td>367</td>
<td>11</td>
</tr>
</tbody>
</table>

*Irreversible polymerization by DSC.

$^b$ At 10% mass loss by TGA.

$^c$ After heating to 900 °C under N$_2$.

POSS–epoxides

As has been reported in a previous review on this subject, POSS α-olefins can be readily converted into POSS α-epoxides through the use of common epoxidizing agents such as MCPBA (m-chloroperbenzoic acid). The reaction proceeds readily at room temperature in chlorinated solvents although gentle heating allows for completion of the reaction within 2–4 h.

The POSS epoxides 16 and 17 (Fig. 4) exhibit excellent solubilities in common organic solvents such as chloroform, THF, hexane and toluene. Their solubilities in aliphatic epoxides such as 4-vinyl-1-cyclohexene diepoxide, however range from only 1 to 5 wt%. In aromatic resins such as 4,4’-isopropylidenediphenyl epichlorohydrin resins, solubilities of only 1–2.5 wt% are observed.

Compounds 16 and 17 showed better solubilities in curatives such as diethylenetriamine (5 wt%) and diethyltoluenediamine (5 wt%), but solubilities of only 1–2.5 wt% were again observed in aromatic amines such as m-phenylenediamine and amine-terminated aromatic polymers.

In an attempt to increase the solubility these POSS epoxides in aromatic-based epoxy resins, the incorporation of compatibilizing, nonreactive aromatic substituents and reactive aromatic epoxy functionalities on the POSS silicon–oxygen frameworks is under way.

Compounds 16 and 17 did prove to be reactive in that each of the compounds was observed to undergo an exothermic self-polymerization near 250 °C (Table 2). This temperature was well below the onset of mass loss due to decomposition, which was observed to occur near 370 °C. In reaction with aromatic amines commonly used as curatives, such as Shell Epolite 2330, the compounds showed irreversible exothermic transitions by differential scanning calorimetry (DSC) near 140 °C. The values for the thermal transitions of 16 and 17 are consistent with those reported for related T_{α}-POSS systems bearing polyaliphatic epoxy functional-
Polymerization of POSS α-olefins

The polymerization of olefins with appropriate transition-metal catalysts can efficiently produce a wide variety of polyolefin materials having a range of properties. For example, polyolefin polymer properties ranging from highly crystalline, rigid polyolefins and Ziegler–Natta-type catalysts was carried out. Interestingly, however, all attempts to polymerize 3–6 (Fig. 1) failed. Although reactions involving homopolymerization of 3–6 lead only to the recovery of unreacted monomer, addition of 1-hexene to the active reaction mixture led to rapid formation of poly(1-hexene) with little or no incorporation of POSS monomer. This result clearly demonstrates that POSS α-olefins 3–6 do not poison or inhibit catalyst activity and that even in the presence of an active polymerization catalyst, 3–6 are resistant to polymerization. Similar results were obtained in all attempts to carry out the copolymerization of POSS α-olefins with α-olefins. The success of the platinum-catalyzed hydrosilation reactions suggests that POSS macromers can coordinate to a metal center and react with less-hindered, linear oligomers and polymers, but in the case of polymerization with Ziegler–Natta-type catalysts steric hindrance at the metal center prevents propagation. These results are in contrast to the successful polymerizations of monofunctionalized POSS α-olefins with propene and ethylene reported by Frey and co-workers, in which POSS macromers bearing seven inert ethyl groups were used in place of the seven cycloaliphatic groups present on the POSS macromers used in this work.

EXPERIMENTAL

General experimental protocol and procedures for the synthesis of [(c-C₅H₉)₇Si₇O₉(OH)₃].{[(c-C₅H₉)₇Si₇O₉(OH)₃]}{[(c-C₅H₉)₇Si₇O₉(OH)₃]}{[(c-C₅H₉)₇Si₇O₉(OH)₃]}{[(c-C₅H₉)₇Si₇O₉(OH)₃]}{[(c-C₅H₉)₇Si₇O₉(OH)₃]}{[(c-C₅H₉)₇Si₇O₉(OH)₃]}

Synthesis of [(c-C₅H₉)₇Si₈O₁₂(H)]

Under a nitrogen atmosphere, [(c-C₅H₉)₇Si₈O₁₂(Cl)] was synthesized by addition of a slight excess of tetrachlorosilane (21.35 g, 0.126
mol) to a 1-liter flask containing 800 ml of a tetrahydrofuran (THF) suspension of [(c-
C₆H₁₂)₇Si₉O₉(OH)₃], (100 g, 0.114 mol) and triethylamine (38.14 g, 0.377 mol). The reaction flask was stirred under nitrogen for 12 h, followed by filtration to remove the HNEt₃Cl by-product. The clear filtrate was transferred to a 1-liter flask equipped with a stir bar. To convert the POSS chloride to a hydride, excess LiAlH₄ (8.0 g, 0.211 mol) was added to it in 100-ml portions. The reaction was monitored by 13C{¹H} NMR spectroscopy to determine when all of the [(c-
C₆H₁₂)₇Si₈O₁₂(Cl)] was consumed. The diagnostic signals in the ¹³C{¹H} NMR spectrum are the z-carbons of the cyclopentyl groups: [(c-
C₆H₁₂)₇Si₈O₁₂(Cl)] has three signals at 22.22, 22.16 and 22.15 ppm; [(c-
C₆H₁₂)₇Si₈O₁₂(H)] has two signals at 22.26 and 22.17 ppm (4:3). The reaction was approximately half complete after 5 min, and was completed after 50 min. The product was isolated by filtering the cloudy solution (in air) through Celite (caution: the by-products on the Celite are very flammable) and evaporating the filtrate to dryness. The crude product was then extracted with 400 ml of warm hexanes, filtered through Celite (caution: the by-products on the Celite are very flammable) and reduced in volume to form a slurry. This slurry was then dispensed from a Kilo-Lab cylinder. Procedures for the synthesis 2a and 2b are identical, with a typical procedure for 2a described below.

Procedures for the synthesis 2a and 2b are identical, with a typical procedure for 2a described below.

A solution of ClSi(CH₃)₂H (1.0 g, 1.2 ml, 10.6 mmol) in THF (5 ml) was added to a solution of [(c-
C₆H₁₂)₇Si₈O₁₂OH] (10.00 g, 9.84 mmol) and Et₃N (5.0 g, 6.9 ml, 49 mmol, 5 equiv) in THF (50 ml) contained in a thick-walled glass reactor. A precipitate of Et₃N·HCl formed upon addition of the chlorosilane. The reactor was sealed with a Teflon plug, then taken out of the glove box and the reaction mixture was heated at 60 °C for 18 h. After this time, the reaction mixture was transferred to a separatory funnel. The reaction vessel was rinsed with diethyl ether and the ether washings were combined with the THF. The THFether phase was washed with successive portions of H₂O (2 x 50 ml), 1 M HCl (2 x 50 ml), H₂O (50 ml), and satd NaCl (50 ml). The THFether phase was dried over MgSO₄, filtered, and the THF ether was removed under vacuum to give 10.4 g (98%) of [(c-
C₆H₁₂)₇Si₈O₁₂(OSi(CH₃)₂H) as a white microcrystalline solid.

For 2a: ¹H NMR (300.135 MHz, CDCl₃, 33 °C): δ = 4.74 (sept, 1H, Si—H, J = 2.8 Hz), 1.74 (m, 35H, cyclohexyl—CH₂), 1.25 (m, 35H, cyclohexyl—CH₂), 0.77 (m, 7H, cyclohexyl—CH), 0.25 (d, 6H, Si—CH₃, J = 2.8 Hz). ¹³C{¹H} NMR (75.475 MHz, CDCl₃, 33 °C): δ = 27.51, 27.47, 26.92, 26.88, 26.67, 26.57 (cyclohexyl—CH₂), 23.22, 23.17, 23.08 (1:3:3, cyclohexyl—CH), 0.27 (Si—CH₃). ²⁹Si{¹H} NMR (59.624 MHz, CDCl₃, 33 °C): δ = −2.97 (OSiMe₂H), −67.92, −68.56, −68.60 (3:3:1, cyclohexyl—Si), −107.6 (Si—OSiMe₂H).

For 2b: ¹H NMR (300.135 MHz, CDCl₃, 33 °C): δ = 4.72 (sept, 1H, OSi(CH₃)₂H, J = 2.8 Hz), 1.76–1.50 (m, 56H, cyclopentyl—CH₂), 1.01 (m, 7H, cyclopentyl—CH) 0.23 (d, 6H, OSi(CH₃)₂H, J = 2.8 Hz). ¹³C{¹H} NMR (75.475 MHz, CDCl₃, 33 °C): δ = 27.30, 27.02 (cyclopentyl—CH₂), 23.23, 23.16 (cyclopentyl—CH), 0.19 (OSi(CH₃)₂H). ²⁹Si{¹H} NMR (59.624 MHz, CDCl₃, 33 °C): δ = 2.85 (OSi(CH₃)₂H), −65.83, −66.45 (3:4, cyclopentyl—Si), −107.7 (SiOSi(CH₃)₂H).

**Synthesis of [(c-
C₆H₁₁)₇Si₈O₁₂CH=CH₂] 2a**

Reactions were set up in air on the benchtop using dry solvents, and were stirred under nitrogen. Et₂O was dispensed from a Kilo-Lab cylinder. Procedures for 2a and 2b are the same, with a typical procedure for 2a described below.

A solution of vinyltrichlorosilane (9.12 g, 7.34 ml, 56.5 mmol, 1.1 equiv.) in Et₂O (50 ml) was added rapidly via an addition funnel to a solution of [(c-
C₆H₁₂)₇Si₈O₁₂OH] (50.0 g, 51.4 mmol) and Et₃N (26.0 g, 36 ml, 257 mmol, 5 equiv.) in Et₂O (400 ml). The reaction mixture was stirred under nitrogen for 16 h. Afterwards the reaction mixture was transferred to a separatory funnel and the Et₂O solution extracted with

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successive portions of H₂O (100 ml), 1 M HCl (2×100 ml), H₂O (100 ml) and satd NaCl (50 ml). The Et₂O solution was stirred over activated charcoal and silica gel, filtered through Celite and the Et₂O was concentrated by rotary evaporation to give a slurry. Methanol (1 l) was added to the slurry and the solid product was collected by vacuum filtration and dried to provide 43.26 g (82%) of 3a as a white solid.

For 3a: ¹H NMR (300.135 MHz, CDCl₃, 33 °C): δ = 6.06 (dd, CH=CH₂, J = 13.3 and 5.35 Hz), 6.01 (dd, CH=CH₂, J = 20.6 and 5.35 Hz), 5.88 (dd, CH=CH₂, J = 20.6 and 13.3 Hz), 1.74 (m, cyclohexyl—CH₂), 1.25 (m, cyclohexyl—CH₂), 0.77 (m, cyclohexyl—CH). ¹³C(¹H) NMR (75.475 MHz, CDCl₃, 33 °C): δ = 68.43, -68.57 (cyclohexyl—Si), 26.67, 26.63 (cyclohexyl—CH₂), 23.20, 23.14 (cyclohexyl—CH). ²⁹Si(¹H) NMR (59.624 MHz, CDCl₃, 33 °C): δ = -68.43, -68.57 (cyclohexyl—Si). 68.60 (cyclohexyl—Si). 66.43, 66.49 (34.4, cyclohexyl—Si).

**Synthesis of [R₇Si₈O₁₂CH₂CH=CH₂] 4a and 4b**

Reactions were set up in air on the benchtop using dry solvents and stirred under nitrogen. THF was dispensed from a Kilo-Lab® cylinder. Procedures for 4a and 4b are the same, with a typical procedure for 4a described below.

A solution of Cl₅SiCH₂CH=CH₂ (9.9 g, 8.2 ml, 56.4 mmol) in THF (50 ml) was added dropwise via an addition funnel to a solution of [(C₆H₁₂)₇SiΟ₉(OH)₃] (50.0 g, 51.4 mmol) and Et₃N (26.0 g, 35.8 ml, 0.257 mol, 5 equiv.) in THF (400 ml). A precipitate of Et₃N·HCl formed upon addition of the Cl₅SiCH₂CH=CH₂ solution. The reaction mixture was stirred for 16 h. After this time the reaction mixture was transferred to a separatory funnel, the reaction flask was rinsed with diethyl ether and the washings were added to the THF solution. An additional 200 ml of diethyl ether was added to the separatory funnel and the THF/ether solution washed with successive portions of H₂O (100 ml), 1 M HCl (2×100 ml), H₂O (150 ml) and satd NaCl (100 ml). The THF/ether solution was dried over MgSO₄ and activated carbon, then filtered, and the volume of solvent was reduced by rotary evaporation to give a slurry. Methanol (1 l) was added to the slurry and the solid was collected by vacuum filtration and dried to provide 47.6 g (89%) of [(C₆H₁₁)₇SiΟ₁₂CH₂CH=CH₂] as a white solid.

For 4a: ¹H NMR (300.135 MHz, CDCl₃, 33 °C): δ = 5.78 (1H, SiCH₂CH=CH₂), 5.00–4.90 (m, SiCH₂CH=CH₂), 1.74 (m, 35H, cyclohexyl—CH₂), 1.61 (br d, SiCH₂CH=CH₂, J = 7.8 Hz) 1.25 (m, 35H, cyclohexyl—CH₂), 0.76 (m, 7H, cyclohexyl—CH). ¹³C(¹H) NMR (75.475 MHz, CDCl₃, 33 °C): δ = 132.58 (SiCH₂CH=CH₂), 114.71 (SiCH₂CH=CH₂), 27.51, 27.48, 26.92, 26.67, 26.60 (cyclohexyl—CH₂), 23.20, 23.14 (4.3, cyclohexyl—CH₂), 19.70 (SiCH₂CH=CH₂). ²⁹Si(¹H) NMR (59.624 MHz, CDCl₃, 33 °C): δ = -68.57, -68.60 (cyclohexyl—Si), -70.94 (SiCH₂CH=CH₂). Analysis: Calcd for C₆H₁₂Si₈O₁₂: C, 51.98; H, 7.95. Found: C, 51.77; H, 8.08%.

For 4b: ¹H NMR (300.135 MHz, CDCl₃, 33 °C): δ = 5.77 (m, 1H, SiCH₂CH=CH₂), 5.00–4.90 (m, SiCH₂CH=CH₂), 1.74–1.55 (m, 56H, cyclopentyl—CH₂), 1.01 (m, 7H, cyclopentyl—CH). ¹³C(¹H) NMR (75.475 MHz, CDCl₃, 33 °C): δ = 135.62 (SiCH₂CH₂), 130.16 (SiCH₂CH₂), 27.33, 27.30, 27.02, (cyclopentyl—CH₂), 22.24 (cyclopentyl—CH). ²⁹Si(¹H) NMR (59.624 MHz, CDCl₃, 33 °C): δ = -66.29, -66.47 (34.4, cyclohexyl—Si), -80.68 (SiCH₂CH₂).

**Syntheses of [R₇Si₈O₁₂(CH₂)₆CH=CH₂] and isomers 5a and 5b**

Procedures for the synthesis of these monomers are identical. A detailed procedure for 5b is given.

A solution of 1-octenyltrichlorosilane (6.17 g, 25.1 mmol, ~33% internal olefin) in THF was added to a solution of [(C₆H₁₂)₇SiΟ₉(OH)₃] (50.0 g, 51.4 mmol) and Et₃N (26.0 g, 35.8 ml, 0.257 mol, 5 equiv.) in THF (400 ml). A precipitate of Et₃N·HCl formed upon addition of the Cl₅SiCH₂CH=CH₂ solution. The reaction mixture was stirred for 16 h. After this time the reaction mixture was transferred to a separatory funnel, the reaction flask was rinsed with diethyl ether and the washings were added to the THF solution. An additional 200 ml of diethyl ether was added to the separatory funnel and the THF/ether solution washed with successive portions of THF (175 ml). A precipitate of Et₃N·HCl formed immediately upon addition of the tetrachlorosilane. The reaction mixture was stirred for 16 h. After this time the Et₃N·HCl was removed by filtration and the solution concentrated to give a viscus residue. The residue was taken up in a minimum of THF, filtered and poured into an excess of methanol to precipitate 5b. The pre-
cipated was collected by vacuum filtration and dried to provide 21.36 g (92%) of 5b.

For 5a: 1H NMR (300.135 MHz, CDCl3, 33 °C): δ = 5.82 (m, CH2=C=H), 5.42 (m, CH2=CH=CH internal), 5.00 (m, CH2=CH2), 4.94 (m, CH2=CH), 2.05 (m, CH2CH=CH2 and internal), 1.74 (m, cyclohexyl—CH3), 1.61 (d, CH2CH3, J = 5.3 Hz), 1.25 (m, cyclohexyl—CH2), 0.77 (m, cyclohexyl—CH), 0.62 (t, Si8O12—CH2J, J = 6.9 Hz). 13C{1H} NMR (75.475 MHz, CDCl3, 33 °C): δ = 139.14, 131.66, 130.86, 124.48, 123.56, 114.07 (CH—CH2 and internal), 33.82, 32.40, 28.83 (CH3), 27.52, 26.94, 26.91, 26.68 (cyclohexyl—CH3), 23.23, 22.85 (cyclohexyl—CH), 11.83 (SiCH2). 29Si{1H} NMR (59.624 MHz, CDCl3, 33 °C): δ = −66.07 (Si(CH2)2CH2CH3), −68.58, −68.76 (cyclohexyl—Si). Analysis: Cacld. for C50H92Si8O12: C, 54.11; H, 8.35. Found: C, 53.74; H, 8.34%.

For 5b: 1H NMR (300.135 MHz, CDCl3, 33 °C): δ = 5.82 (m, CH2=CH2), 5.41 (m, CH2=CH=CH internal), 4.96 (m, CH2=CH), 2.05 (m, CH2=CH=CH2 and internal), 1.76–1.51 (m, cyclopentyl—CH2 and Si(CH2)2CH=CH2), 0.99 (m, cyclohexyl—CH3), 0.62 (t, Si8O12—CH2J, J = 6.9 Hz). 13C{1H} NMR (75.475 MHz, CDCl3, 33 °C): δ = 139.18, 131.69, 130.90, 124.50, 123.56, 114.07 (CH2=CH and internal), 33.81, 32.40, 28.83, 22.82 (CH3), 27.56, 27.34, 27.04 (cyclohexyl—CH2), 23.34 (cyclohexyl—CH), 11.93 (SiCH3). 29Si{1H} NMR (59.624 MHz, CDCl3, 33 °C): δ = −66.16 (Si(CH2)2CH2CH3), −68.47, −68.62 (cyclohexyl—Si).

Hydrosilation of 1a to give (c-C6H11)7Si8O12CH2CH2Si(CH3)3

A solution of divinyltetramethyldisiloxane-platinum complex (Karstedt’s catalyst) (0.018 g) in divinyl-tetramethylpolysiloxane (PDMS) was added to a solution of [(c-C6H11)7Si8O12H] (0.410 g, 0.410 mmol) and (CH3)3Si=CH2 (0.042 g, 0.419 mmol) in CH2Cl2. The reaction mixture was refluxed for 18 h. After this time the solution was concentrated to a few milliliters and the product was purified by flash column chromatography. The fractions containing the desired product were combined and the solvent was removed to provide 0.276 g (61%) of [(c-C6H11)7Si8O12CH2CH2Si(CH3)3). 1H NMR (300.135 MHz, CDCl3, 32 °C): δ = 1.74 (m, 35H, cyclohexyl—CH2), 1.25 (m, 35H, cyclohexyl—CH2), 0.76 (m, 7H, cyclohexyl—CH2), 0.52 (m, 4H, CH2—CH2), 0.00 (s, 9H, Si(CH3)3). 29Si{1H} NMR (59.624 MHz, CDCl3, 32 °C): δ = 3.16 (Si(CH3)3), −66.05 (Si(CH2)2), −68.63, −68.69 (cyclohexyl—Si). Analysis: Cacld. for C57H96Si8O12: C, 51.52; H, 8.25. Found: C, 50.52; H, 8.17%.

Synthesis of [(c-C6H11)7Si8O12(CH2)3SiCl2CH3] 7

A solution of tetramethyldivinylsiloxane–platinum catalyst in xylenes (3 drops) was added to a slurry of 4a (10.00 g, 9.62 mmol) in HSiCl2CH3 (25 ml) contained in a 30 ml thick-walled glass reactor. The reaction vessel was sealed with a Teflon plug, taken out of the glove box and placed in an oil bath kept at 60 °C for 18 h. Almost immediately upon heating the reaction mixture became homogeneous and the solution became pale yellow brown. After this time the excess HSiCl3 was removed under vacuum to give a foamy off-white solid. The reaction vessel with the solid was taken into the glove box, the solid was dissolved in diethyl ether and the ether solution was transferred to a flask containing activated carbon. The ether solution was filtered through Celite to remove the activated carbon and the solvent was removed under vacuum to provide 10.7 g (96%) of [(c-C6H11)7Si8O12(CH2)3SiCl2CH3] as a white solid. 1H NMR (300.135 MHz, CDCl3, 33 °C): δ = 1.74 (m, 37H, cyclohexyl—CH2 and SiCH2CH2CH2, SiCl2CH3), 1.25 (m, 37H, cyclohexyl—CH2 and SiCH2CH2CH2SiCl2CH3), 0.77 (m, 12H, cyclohexyl—CH), 2.48 (SiCH2CH2SiCl2CH3), 23.93 (cyclohexyl—CH), 16.45 (SiCH2CH2SiCl2CH3), 15.20 (SiCH2CH2SiCl2CH3), 5.16 (SiCH2CH2SiCl2CH3), 29Si{1H} NMR (59.624 MHz, CDCl3, 33 °C): δ = 32.12 (SiCH2CH2SiCl2CH3), −63.37 (SiCH2CH2SiCl2CH3), −68.86–68.65 (4:3, cyclohexyl—Si).

Synthesis of [Si8O12(CH2)3SiCl2CH3] 8

A solution of tetramethyldivinylsiloxane–platinum catalyst in xylenes (5 drops) was added to a heterogeneous solution of [Si8O12(CH2=CH)3] (1.00 g, 1.58 mmol) in HSiCl3 (10 ml) contained in a 50 ml thick-walled glass reactor. As the immediate and very exothermic reaction proceeded, the solution became homogeneous. The reaction vessel was sealed with a Teflon plug, taken
out of the glove box and heated to 60 °C for 16 h. After this time, the excess HSICl3 was removed under reduced pressure to give 2.5 g (92%) of Si8O12(CH2CH2SiCl3)8 as an off-white solid. 1H NMR (300 MHz, CDCl3, 33 °C): δ = 1.42 (m, 16H, Si(CH2)2SiCl3), 0.93 (m, 16H, Si(CH2)2SiCl3), 134C[1H] NMR (75.475 MHz, CDCl3, 33 °C): δ = 16.73 (Si(CH2)2SiCl3), 3.37 (SiCH2CH2SiCl3). 29Si[1H] NMR (59.624 MHz, CDCl3, 33 °C): δ = 12.86 (SiCH2CH2SiCl3), –67.43 (SiCH2CH2SiCl3).

Hydrosilation of 4a to give [(c-C6H11)2Si8O12(CH2)3SiCl3]

A solution of tetramethyldivinylsiloxane–platinum catalyst in xylene (2 drops) was added to a solution of 4a (5.00 g, 4.81 mmol) in HSICl3 (10 ml) contained in a 30 ml thick-walled glass reactor. The reaction vessel was sealed with a Teflon plug, taken out of the glove box and placed in an oil bath kept at 60 °C for 16 h. After this time, the excess HSICl3 was removed under vacuum to give a foamy off-white solid. The reaction vessel was filtered through Celite and the solvent was removed under reduced pressure to yield 2.01 g (92%). 1H NMR (300.135 MHz, CDCl3, 33 °C): δ = 1.73 (m, cyclohexyl–CH2), 1.50 (m, =O2Si(CH2)2CH2Si(CH3)2O), 1.25 (m, cyclohexyl–CH2), 0.76 (m, 7H, cyclohexyl–CH), 0.68 (overlapping multiplets, =O2Si(CH2)2CH2CH2Si(CH3)2O, 0.98 (Si(CH3)2–O–Si(CH3)2–O–Si(CH3)2, 0.03 (s, Si(CH3)2–O–Si(CH3)2–O–Si(CH3)2, 23Si[1H] NMR (59.624 MHz, CDCl3, 33 °C): δ = 6.88 (Si(CH3)2–O–Si(CH3)2–O–Si(CH3)2), 21.19 (Si(CH3)2–O–Si(CH3)2–O–Si(CH3)2), –66.68 (=O2Si(CH3)2), –68.59, –68.77 (cyclohexyl–Si). Analysis: Calcd for C96H184Si19O26: C, 50.39; H, 8.11. Found: C, 50.00; H, 8.09%.

Triblock 9b

A solution of Karstedt’s catalyst (0.010 g, 2–3% platinum content) in vinyl-terminated PDMS was dissolved in methylene chloride (1 ml) and added to a solution of 4a (1.93 g, 2.05 mmol) and HSiMe2–O–SiMe2–O–SiMe2H (0.222 g, 1.06 mmol) in methylene chloride (25 ml). The reaction mixture was refluxed for 72 h. Unreacted HSiMe2–O–SiMe2–O–SiMe2H was removed by stirring the reaction mixture over silica gel and activated charcoal for several hours. The reaction mixture was filtered through Celite and the solvent was removed under reduced pressure to yield 2.01 g (94%). 1H NMR (300.135 MHz, CDCl3, 32 °C): 1.83–1.50 (m, cyclopentyl–CH2 and =O2Si(CH2)2CH2Si(CH3)2O), 0.98 (m, cyclopentyl–CH2), 0.67 (m, =O2Si(CH2)2CH2Si(CH3)2O, 0.07 (Si(CH3)2–O–Si(CH3)2–O–Si(CH3)2), 0.02 (s, Si(CH3)2–O–Si(CH3)2–O–Si(CH3)2), 23Si[1H] NMR (59.624 MHz, CDCl3, 33 °C): δ = 6.91 (Si(CH3)2–O–Si(CH3)2–O–Si(CH3)2), –21.12 (Si(CH3)2–O–Si(CH3)2–O–Si(CH3)2), –66.44 (=O3Si–(CH3)3), –66.50, –66.67 (cyclopentyl–Si).

Triblock 10a

A solution of Karstedt’s catalyst (0.010 g, 2–3% platinum content) in vinyl-terminated PDMS was dissolved in methylene chloride (1 ml) and added to a solution of 4a (0.579 g, 0.557 mmol) and H(SiMe2O)4SiMe2H (0.116 g, 0.289 mmol) in methylene chloride (10 ml). The reaction mixture was refluxed for 18 h. The reaction mixture was stirred with silica gel and activated carbon and
filtered through Celite. The solvent was removed by rotary evaporation and the residue dried to give 0.496 g (72%) of 10a. \(^1H\) NMR (300.135 MHz, CDCl\(_3\), 32 °C): \(\delta = 1.74\) (m, cyclohexyl—CH\(_2\)), 1.49 (m, \(\equiv O Si(CH_2)_2CH_2Si(CH_3)_2O\)), 1.24 (m, cyclohexyl—CH\(_2\)), 0.76 (m, 7H, cyclohexyl—CH), 0.68 (overlapping triplets, \(\equiv O Si(CH_2)_2CH_2Si(CH_3)_2O\)), 0.07 and 0.05 (m, Si(CH\(_3\)_2—O—Si(CH\(_3\)_2)), 28Si[\(^1H\)] NMR (59.624 MHz, CDCl\(_3\), 32 °C): \(\delta = 7.09, 7.05\) (Si(CH\(_3\)_2—O—Si(CH\(_3\)_2)), 6.30—O—Si(CH\(_3\)_2)), −1.58, −21.70, −21.95, −22.09 (Si(CH\(_3\)_2—O—(Si(CH\(_3\)_2)), −66.70 (\(\equiv O Si(CH_3)_2\)), −68.61, −68.79 (cyclohexyl—Si)). Analysis: Calcd for C\(_{96}\)H\(_{200}\)Si\(_{22}\)O\(_{30}\): C, 48.99; H, 8.11. Found: C, 49.39; H, 7.85%.

**Triblock 11a**

Solid H\(_3\)PtCl\(_4\)\(_2\)\(_4\)\(_2\)\(_2\)\(_2\)O (0.5 mg) was added to a solution of 5a (0.686 g, 0.618 mmol) and HSiMe\(_2\)—O—SiMe\(_2\)—O—SiMe\(_2\)—H (0.065 g, 0.31 mmol) in tetrahydrofuran (10 ml). The reaction mixture was heated to reflux for 48 h. The product was purified by flash chromatography using hexane as the eluent, which removed the unreacted HSiMe\(_2\)—O—SiMe\(_2\)—O—SiMe\(_2\)H as well as the unreacted 5a containing internal olefins. Removal of the solvent gave 0.408 g (54%) of 11a. \(^1H\) NMR (300.135 MHz, CDCl\(_3\), 32 °C): \(\delta = 1.73\) (m, cyclohexyl—CH\(_2\)), 1.25 (m, cyclohexyl—CH\(_2\)), 0.76 (m, cyclohexyl—CH)), 0.61 and 0.53 (overlapping triplets, \(\equiv O Si(CH_2)_2CH_2Si(CH_3)_2O\)), 0.10, 0.08, 0.06, 0.04, 0.03, 0.02 (s, Si(CH\(_3\)_2)—O—Si(CH\(_3\)_2)), 28Si[\(^1H\)] NMR (59.624 MHz, CDCl\(_3\), 32 °C): \(\delta = 7.49, 7.28\) (Si(CH\(_3\)_2)—O—Si(CH\(_3\)_2)), −21.47, −21.92 (Si(CH\(_3\)_2)—O—Si(CH\(_3\)_2)), −66.07 (\(\equiv O Si(CH_3)_2\)), −68.65, −68.82 (cyclohexyl—Si)). Analysis: Calcd for C\(_{111}\)H\(_{220}\)Si\(_{22}\)O\(_{30}\): C, 50.96; H, 8.44. Found: C, 51.12; H, 8.33%.

**Triblock 12a**

A solution of Karstedt’s catalyst (0.010 g, 2–3% platinum content) in vinyl-terminated PDMS was added to a solution of 1a (0.206 g, 0.206 mmol) and H\(_2\)C—CHSiMe\(_2\)—(O—SiMe\(_2\))\(_{32}\)—(O—SiPh\(_2\))—CH\(_2\)=CH\(_2\) (1.031 g, 0.111 mmol) in methylene chloride (10 ml). The reaction mixture was refluxed for 18 h. Upon cooling, the reaction mixture was filtered through activated charcoal and Celite and the solvent was removed under reduced pressure to give 0.879 g (76%) of 12a. \(^1H\) NMR (300.135 MHz, CDCl\(_3\), 32 °C): \(\delta = 7.63, 7.36\) (m, cyclohexyl—CH\(_2\)), 1.27 (m, cyclohexyl—CH\(_2\)), 0.78 (m, cyclohexyl—CH)), 0.10 (s, −O—Si(CH\(_3\)_2)—O—), 28Si[\(^1H\)] NMR (59.624 MHz, CDCl\(_3\), 32 °C): \(\delta = 8.31\) (−O—Si(CH\(_3\)_2)(CH\(_3\)_2)), −20.79, −21.95 (−O—Si(CH\(_3\)_2(O)—), −48.42 (−O—Si(CH\(_3\)_2(O)—), −65.95 (\(\equiv O Si(CH_3)_2\)), −68.59 (cyclohexyl—Si)). Analysis: Calcd for C\(_{106}\)H\(_{204}\)Si\(_{19}\)O\(_{26}\): C, 51.12; H, 8.33%.

**Triblock 13a**

A solution of Karstedt’s catalyst (0.014 g, 2–3% platinum content) in vinyl-terminated PDMS was added to a solution of 1a (0.255 g, 0.283 mmol) and H\(_2\)C—CHSiMe\(_2\)—(O—SiMe\(_2\))\(_{32}\)—(O—SiPh\(_2\))—CH\(_2\)=CH\(_2\) (1.321 g, 0.142 mmol) in methylene chloride (10 ml). The reaction mixture was refluxed for 18 h, then stirred with silica gel and charcoal, filtered through Celite and the solvent was removed under reduced pressure to give 1.248 g (85%) of 13a. \(^1H\) NMR (300.135 MHz, CDCl\(_3\), 32 °C): \(\delta = 7.65, 7.36\) (m, −O—Si(CH\(_3\)_2(O)—), −1.77–1.56 (m, cyclopentyl—CH\(_2\)), 1.01 (m, cyclopentyl—CH\(_2\)), 0.09 (−O—Si(CH\(_3\)_2(O)—), 29Si[\(^1H\)] NMR (59.624 MHz, CDCl\(_3\), 32 °C): \(\delta = 8.32\) (−O—Si(CH\(_3\)_2)(CH\(_3\)_2)), −20.80, −21.73, −21.96 (−O—Si(CH\(_3\)_2(O)—), −48.41 (−O—Si(CH\(_3\)_2(O)—), −66.02 (\(\equiv O Si(CH_3)_2\)), −66.46, −66.49 (cyclohexyl—Si)).
**Triblock 14a**

A solution of Karstedt’s catalyst (0.011 g, 2–3% platinum content) in vinyl-terminated PDMS was added to a solution of 1a (0.238 g, 0.238 mmol) and H₂C≡CH·SiMe₂·(O·SiMe₂)₉(O·SiPh₂)ₙ·CH=CH₂ (1.586 g, 0.119 mmol) in methylene chloride (10 ml). The reaction mixture was refluxed for 18 h. Upon cooling, the solution was filtered through activated charcoal and Celite, and the solvent was removed under reduced pressure to give 1.612 g (88%) of 14a. ¹H NMR (300.135 MHz, CDCl₃, 32 °C): δ = 7.62 and 7.35 (m, —O—Si(CH₃)₂—O—), 7.17 (m, cyclohexyl—CH₂), 1.26 (m, cyclohexyl—CH₃), 0.79 (m, cyclohexyl—CH₂), 0.11 (m, —O—Si(CH₃)₂—O—), 29Si(¹H) NMR (59.624 MHz, CDCl₃, 32 °C): δ = 8.0 (—O—Si(CH₃)₂CH₂CH₂), −17.03, −17.56, −18.54, −19.24, −20.04, −20.50, −20.62, −20.76, −21.47, −21.68, −21.90 (—O—Si(CH₃)₂—O—), −44.93, −47.60, −48.19, −48.42 (—O—Si(CH₃)₂—O—), −65.95 (≡O,Si(CH₂)₂), −68.59, −68.60 (cyclohexyl—Si). Analysis: Calcd for C₆₈H₁₄₅Si₈O₁₂éCH₂CHCH₂O: C, 40.44; H, 6.98%.

**Triblock 15a**

A solution of Karstedt’s catalyst (0.010 g, 2–3% platinum content) in vinyl-terminated PDMS was added to a solution of 1a (0.300 g, 0.300 mmol) and (CH₂≡CH)₂SiMe—(OSiMe₂)₁₅—O·SiMe(CH=CH₂) (0.910 g, 0.078 mmol) in methylene chloride (10 ml). The reaction mixture was refluxed for 18 h. Upon cooling, the reaction mixture was filtered through activated charcoal and Celite and the solvent was removed under reduced pressure to yield 0.948 g (78%) of 15. ¹H NMR (300.135 MHz, CDCl₃, 32 °C): δ = 1.74 (m, cyclohexyl—CH₂), 1.25 (m, cyclohexyl—CH₃), 0.77 (m, cyclohexyl—CH₂), 0.08 (m, —O—Si(CH₃)₂—O—), 29Si(¹H) NMR (59.624 MHz, CDCl₃, 32 °C): δ = −21.97 (—O—Si(CH₃)₂—O—), −68.60, −68.97 (cyclohexyl—Si). Analysis: Calcd for C₆₅₅H₁₀₂₆Si₁₄₄O₁₅₁: C, 50.44; H, 6.91. Found: C, 50.44; H, 6.98%.

**Transition-Metal catalyzed polymerization of POSS macromers**

Catalysts were prepared from both TiCl₄ and a commercial product comprising titanium supported on magnesium chloride (Lynx 705; Catalyst Resources). TiCl₄ and Al(C₆H₅)₃ were mixed in toluene and stirred for various lengths of time before addition of the monomer(s). In this case, fine, black, solid particles formed which were kept in suspension by stirring. When Lynx 705 was used, monomer(s) and Al(C₆H₅)₃ were dissolved in toluene before adding the Lynx 705 powder. The aluminum/titanium molar ratio was between 10:1 and 400:1 for Lynx 705 and TiCl₄ catalyst mixtures with Al(C₆H₅)₃. Polymerizations were carried out at various temperatures between ambient and 95 °C to observe any effect temperature may have had on the product. All reagents and solvent were dried and degassed and polymerizations were conducted under a nitrogen atmosphere. Products were isolated by pouring the solutions into methanol with vigorous stirring to cause instantaneous precipitation. Products were characterized by ¹H and ²⁹Si NMR spectroscopy and size-exclusion chromatography.

**Epoxidation of POSS macromers**

[(c-C₆H₁₁)₅SiO₁₂(OCH₂CH₂O)₁₆]a

Solid m-chloroperoxybenzoic acid (MCPBA) (0.68 g, 3.9 mmol) was added to a solution of 4a (2.01 g, 1.93 mmol) in methylene chloride (25 ml). The reaction mixture was stirred for 3 days. The methylene chloride was removed from the reaction mixture by rotary evaporation and the resulting solid was stirred with methanol for 24 h. The epoxide, 16a, which is insoluble in methanol, was collected by vacuum filtration, washed with methanol and dried under vacuum to give 1.263 g (62%) of 16a. ¹H NMR (300.135 MHz, CDCl₃, 32 °C): δ = 3.04 (m, SiCH₂CH₂O₂CH₂O), 2.79 (m, SiCH₂CH₂O₂CH₂O), 2.47 (m, SiCH₂CH₂O₂CH₂O), 1.42 (m, SiCH₂CH₂O₂CH₂O, J = 14.6 and 4.1 Hz), 1.23 (m, cyclohexyl—CH₂), 0.77 (m, cyclohexyl—CH₂), 0.60 (m, SiCH₂CH₂O₂CH₂O, J = 14.5 and 9.2 Hz). 13C(¹H) NMR (75.475 MHz, CDCl₃, 32 °C): δ = 49.13 and 48.29 (SiCH₂CH₂O₂CH₂O), 27.48, 27.25, 26.89, 26.84, 26.66, 26.62 (cyclohexyl—CH₂), 23.17, 23.10 (cyclohexyl—CH), 17.36 (CH₂). ²⁹Si(¹H) NMR (59.624 MHz, CDCl₃, 32 °C): δ = −68.51, −68.56 (cyclohexyl—Si), −70.03 (≡O,Si(CH₂)₂).

[(c-C₆H₁₃)₅SiO₁₂(OCH₂CH₂O)₁₆]b

Solid m-chloroperoxybenzoic acid (MCPBA) (20.0 g, 116 mmol) was added to a solution of 4b (25.0 g, 26.5 mmol) in methylene chloride (650 ml). The reaction mixture was kept at a constant 30 °C and stirred for 24 h. The reaction mixture was concentrated to approximately half the original volume, poured into a large excess of methanol and stirred
for 30 min. The epoxide, 16b, which is insoluble in methanol, was collected by vacuum filtration, washed with methanol and dried under vacuum to give 94% of 16b. 1H NMR (300.135 MHz, CDCl3, 32 °C): δ = 3.03 (m, 1H, SiCH2CHCH2O), 2.78 (m, 1H, SiCH2CHCH2O), 2.45 (dd, 1H, SiCH2CHCH2O, J = 5.0 and 2.7 Hz), 1.75–1.48 (m, 57H, cyclopentyl—CH2), 0.59 (dd, 1H, SiCH2CHCH2O, J = 14.5 and 9.2 Hz). 13C{1H} NMR (75.475 MHz, CDCl3, 32 °C): δ = 49.13, 48.17 (SiCH2CHCH2O), 27.26, 26.99, 26.96 (cyclopentyl—CH2), 22.17, 22.13 (cyclopentyl—CH), 21.34 (SiCH2CHCH2O). 29Si{1H} NMR (59.624 MHz, CDCl3, 32 °C): δ = −66.39, −66.45 (cyclopentyl—Si), −70.27 (≡O3SiCH2).

[(c-C6H11)7Si8O12(CH2)6CHCH2O]17

A solution of MCPBA (1.007 g, 5.835 mmol) in methylene chloride (10 ml) was added to a solution of 5a (1.474 g, 1.328 mmol) in methylene chloride (25 ml). The reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure and the resulting solid was stirred with methanol for 2 days to dissolve the excess MCPBA and make the epoxide, 16b, which is insoluble in methanol, was collected by vacuum filtration, washed with methanol and dried under vacuum to give 1.263 g (84%) of 17. 1H NMR (300.135 MHz, CDCl3, 32 °C): δ = 3.04 (m, 1H, CH2CHCH2O), 2.89 (m, 1H, SiCH2CHCH2O), 2.74 (dd, SiCH2CHCH2O), 2.66 (m), 2.45 (dd, H2CCCH2O), 1.72 (m, cyclohexyl—CH2), 1.24 (m, cyclohexyl—CH2), 0.75 (m, cyclohexyl—CH), 0.61 (m). 13C{1H} NMR (75.475 MHz, CDCl3, 32 °C): δ = 52.35 and 47.06 (H2CCCH2O), 32.53, 32.50, 25.83, 22.80, 11.84 (CH2), 27.51, 26.92, 26.90, 26.67 (cyclohexyl—CH2), 23.22 (cyclohexyl—CH). 29Si{1H} NMR (59.624 MHz, CDCl3, 32 °C): δ = −66.15 (≡O3SiCH2), −68.59, −68.76 (cyclohexyl—Si).

CONCLUSION

A series of POSS silane and z-olefin monomers suitable for polymer grafting reactions have been prepared. The ability of these monomers to participate readily in typical hydrosilation chemistry has been demonstrated. Using standard hydrosilation chemistry, POSS silane and z-olefin monomers were not only used to prepare new POSS reagents for use in sol–gel systems, but their ability to participate in grafting reactions to appropriately functionalized siloxane polymers to produce a series of POSS–siloxane triblocks was also demonstrated. The utilization of POSS molecules as hard segments in simple POSS–siloxane–POSS triblocks is capable of producing both crystalline and amorphous systems. The number of POSS groups incorporated in the hard segment and the type of nonreactive substituents located on the POSS cages have a large influence on thermal transitions, as does the length of the mid-block. The conversion of POSS z-olefins into POSS z-epoxides and the reactivity of these epoxides in self-polymerization and in reaction with amines has been demonstrated. Although POSS monoepeoxides do not readily undergo self-polymerization they do exhibit normal reactivities with common amine-based curing agents in which they are soluble. The POSS z-olefins did not participate in Ziegler–Natta-type polymerizations under the conditions presented here, presumably as a result of steric hindrance caused by the inert cycloalkyl groups.

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