REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
07-12-1997	Paper	

4. TITLE AND SUBTITLE

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

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

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5d. PROJECT NUMBER
2303

5e. TASK NUMBER
M1A3

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) AND ADDRESS(ES)

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10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)
AFRL-PR-ED-TP-1998-020

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Joseph Lichtenhan
a. REPORT **Unclassified**	b. ABSTRACT **Unclassified**	c. THIS PAGE **Unclassified**	A		19b. TELEPHONE NUMBER *(include area code)* N/A

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

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Submitted to: **Applied Organometallic Chemistry.**

ABSTRACT

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 hydrosilation 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 effects the properties of the polymer. The reactivity of the POSS-α-olefin monomers with respect to Ziegler-Natta and free radical polymerization polymerization was also examined. The reaction of POSS-α-olefins with MCPBA to give POSS-epoxides was demonstrated and the thermal stability of the POSS-epoxides determined.

INTRODUCTION

Silsesquioxane-based polymers have long been a technologically important class of materials.[1] 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.[2]

POSS reagents combine unique hybrid (inorganic-organic) chemical compositions with nano-sized cage structures that have dimensions comparable to those of most polymer segments and coils.[2a] 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 allows 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. The reactivity of the POSS-hydride, POSS-α-olefin and POSS-α-epoxide functionalities toward the synthesis of hybrid-polyolefins, -epoxides and -silicones 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.[1b,2b] 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 nanoreinforcement of polymer chains in order to enhance the mechanical, thermal and other physical properties of conventional polymer systems.[3]

Along these lines we have begun exploration of the basic transformation chemistry and polymer chemistry of polyhedral oligomeric silsesquioxane 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 Wàcker Chemie and later by Laine et al. and containing functionalities ranging from three to eight, are exclusively designed for incorporation into polymeric networks.[4]

Insert Figure 1 Here

For the present work, POSS monomers containing hydride and α-olefin functionalities were needed. These materials are readily available via the corner capping reaction of incompletely condensed POSS trisilanols ($R_7Si_7O_9(OH)_3$ R = *c*-C_6H_{11} or *c*-C_5H_9) with the appropriate silane coupling reagent. Although the synthesis of **1a** from *c*-$C_6H_{11}Si_7O_9(OH)_3$ and $HSiCl_3$ had previously been reported in the literature by several workers[5], we found that this procedure did not work well for the synthesis of **1b**. When **1b**, prepared in this way, was examined by ^{1}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}H NMR spectrum revealed a broad envelope of signals in the region around δ 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 $HSiCl_3$ were unsuccessful. Therefore, an alternative procedure involving the lithium aluminum hydride reduction of *c*-$C_6H_{11}Si_7O_{12}(Cl)$ was carried out which provided pure **1b** in 48% overall yield.

Although **1a-b** 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, $R_7Si_8O_{12}(OH)$, and $HSi(CH_3)_2Cl$ both **2a-b**, 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-b** and **2a-b** was examined.

Hydrosilation Chemistry. Hydrosilation chemistry is a common and useful synthetic method for the formation of alkyl substituted silanes.[6] 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 olefinic bearing derivatives **3-6** to be readily incorporated into olefin or silane bearing polymers as graftable nanoreinforcements.

In a first step toward exploring the amenability of these reagents to hydrosilation a series of simple model reactions were conducted. Hydrosilation reactions involving R_7Si_8H, **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 framework 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 (Pt/vinyl terminated siloxanes complex) or chloroplatinic acid, $H_2PtCl_6 \cdot H_2O$. 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 as confirmed by DEPT 90 and DEPT 135 ^{13}C NMR spectroscopy experiments. (Figure 2.)

Insert Figure 2 here.

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 $-CH_2-CH_2-$ linkage of the β-addition product, $(c\text{-}C_6H_{11})_7Si_8O_{12}CH_2CH_2Si(CH_3)_3$, were observed. Moreover, this result was confirmed for both catalyst systems. Although the hydrosilation of vinyl silanes is known to give primarily β-addition products, the preference of **1a** for β-addition with all olefins thus far studied is not surprising if one considers that the steric bulk of **1a** should favor hydrosilation to the least sterically hindered carbon atom of olefinic substrates. In contrast, related studies involving the platinum catalyzed hydrosilations of $Si_8O_{12}H_8$ with α-olefins have been shown to give both α- and β-addition.[4c,7] In cases where the olefin is also sterically encumbered, hydrosilation with **1a** becomes sluggish or does not occur at all. For example, in the reaction of **1a** and diallylbisphenol A only unreacted **1a** and diallylbisphenol A, in which the allyl groups have been isomerized to internal olefins, are isolated. In such cases the use of **2a-b** with a more accessible hydride functionality should prove to be advantageous. That **2a-b** is sterically less hindered than **1a-b** was clearly demonstrated by fact that **2a-b** undergoes hydrosilation to diallylbisphenol A in contrast to **1a-b**. A further advantage of the POSS-silanes **2a-b**, is 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-α-olefins **3a-b** and **4a-b** can be functionalized through hydrosilation with hydride containing silanes such as $HSiCl_3$ and $HSi(Cl)_2CH_3$. Since the POSS-α-olefins are readily available, this provides a complementary route to the hydrosilation of **1a-b**, that is in fact superior to procedures using **1a-b** in that the hydrosilation can often be carried out using an inexpensive, low-boiling hydride containing silanes as the solvent. Using this chemistry an entirely new series of POSS monomers, suitable for incorporation into sol-gel systems and silicones, has been developed. For example, the POSS-propyltrichlorosilane, $R_7Si_8O_{12}(CH_2)_3SiCl_3$,

can be prepared either from **1a** and allyltrichlorosilane, or from **4a** and $HSiCl_3$. Simalarly, POSS dichlorosilanes $R_7Si_8O_{12}(CH_2)_3SiCl_2CH_3$, **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 $HSiCl_2CH_3$ or $HSiCl_3$ as shown in Figure 3.

Insert Figure 3 here.

Triblock Synthesis And Characterization. The ability of both POSS-silanes and α-olefins to undergo hydrosilation chemistry provides for a facile and direct synthesis of POSS-containing siloxane triblocks via the grafting of POSS-silanes and α-olefins onto the ends of functionalized siloxane oligomers and polymers. (Figure 4.) Using this approach a series of siloxane polymers in which the length of the siloxane mid-block, 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 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.

Insert Figure 4 here.

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 via 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 ^1H 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 25-90% and were dependent on the method of isolation, with products isolated by column chromatography typically around 25%, and for 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 δ -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 readily observed in both the ^{1}H and ^{13}C NMR spectra, and their presence or absence 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-α-olefins in Figure 1 to undergo hydrosilation chemistry provides for a facile and direct synthesis of POSS-containing siloxanes with triblock, pendent and star (dendridic) 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 (Figure 4). Using this approach a series of POSS-siloxane-POSS triblock copolymers were prepared.

The series of triblock molecules and polymers in Table 1 (and Figure 4) 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.[8] Triblock systems with hard end blocks of dispersities approaching one typically exhibit very sharp melt transitions and are desirable for applications requiring narrow thermal processing windows.[8] 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 incompatible polymeric systems.[9] 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.

Insert Table 1 here.

Examination of the materials listed in Table 1 by X-ray powder diffraction revealed that all of the monomers and triblocks with short siloxane segments **1-12** are highly crystalline while compounds **13-14** are fully amorphous in nature. The X-ray diffraction patterns shown in Figure 5 are representative for the POSS macromers, and the amorphous and crystalline of POSS-silioxane-POSS triblocks. A notable observation in these diffraction patterns was the shifting of specific Bragg maxima, namely that at 8 2θ to lower 2θ 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** to that for the POSS-siloxane-POSS triblocks (i.e. **9a**) have not been fully successful. Disorder problems have led to only partial structural solutions, however the data does support that both systems crystallize in the same trigonal space group.

Insert Figure 5 here.

Analysis of the thermal transitions reported for the triblocks **9a,b** and **13a,b** 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 before in thermoplastic POSS-siloxane bead copolymers[10] 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.[11] The influence of the POSS cage and its nonreactive substituent on thermal transitions and how these interactions are affected by polymer composition and architecture are 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 length of the tether between the POSS cage and the siloxane segment on thermal properties. In **9a**, **10a** the length of the propyl tether is approximately 4.07 Å while in **11a**, **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**, **12a** being observed. For the systems studied in Table 1, 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 that the length of the siloxane segment has on thermal transitions of POSS-siloxane-POSS triblocks are shown in Figure 6. The data in Figure 6 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 Figure 6 indicate that there are two distinct types of POSS-siloxane-POSS triblocks where **9a** and **10a** are crystalline and undergo melt transitions and where **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 shows a low degree of crystallinity in X-ray diffraction experiments conducted at room temperature. Variations of **15** containing shorter siloxane midblocks 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.

Insert Figure 6 here.

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*-chloro perbenzoic acid).[2b] The reaction proceeds readily at room temperature in chlorinated solvents although gentle heating allows for completion of the reaction within 2-4 hours.

The POSS-epoxides **16-17** exhibit excellent solubilities in common organic solvents such as chloroform, THF, hexane, toluene. Their solubilities in aliphatic epoxides such as 4-vinyl-1-cyclohexene diepoxide however, only range from 1-5 % by weight. In aromatic resins such as 4,4'-isopropylidenediphenol epichlorohydrin resins, solubilities of only 1-2.5 wt % are observed.

Compounds **16-17** showed better solubilities in curatives such as diethylenetriamine 5 wt % and diethyltoluenediamine 5 wt %. While solubilities of 1-2.5

wt % were again observed in aromatic-amines such as *m*-phenylene diamine and amine terminated aromatic polymers.

In 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 onto the POSS silicon-oxygen frameworks is underway.

Insert Table 2 here.

Compounds **16-17** 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 the Shell Epolite 2330, the compounds showed irreversible exothermic transitions by DSC near 140 °C. The values for the thermal transitions of **16-17** are consistent with those reported for related T_8-POSS systems bearing polyaliphatic epoxy functionality.[12] Detailed studies into the mechanical and physical properties of these and related POSS-epoxy systems are underway.

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 systems to materials with elastomeric properties are known. The use POSS α-olefins in these types of polymerizations would result in polyolefin homopolymers or copolymers having POSS side groups and could result in new types of polymers having very desirable properties such as increased use temperatures and decreased flammability.

Along these lines a series of homopolymerization and copolymerization reactions using POSS-α-olefins and Ziegler-Natta type catalysts was carried out. Interestingly, however, all attempts to polymerize **3-6** (Figure 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 lead 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 hinderence 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 et al[13] 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.

CONCLUSION

A series of POSS silane and α-olefin monomers suitable for polymer grafting reactions have been prepared. The ability of these monomers to readily participate in typical hydrosilation chemistry has been demonstrated. Using standard hydrosilation chemistry, POSS silane and α-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 into 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-alpha-olefins into POSS-alpha epoxides and the reactivity of these epoxides to self polymerization and in reaction with amines has been demonstrated. While POSS-monoepoxides do not readily undergo self-polymerization they do exhibit normal reactivities with common amine-based curing agents in which they are soluble. The POSS-α-olefins did not participate in Ziegler-Natta type polymerizations under the conditions presented here, presumably as a result of steric hinderence caused by the inert cycloalkyl groups.

ACKNOWLEDGEMENTS

We thank the Air Force Office of Scientific Research, Directorate of Chemistry and Life Sciences and the Phillips Laboratory, Propulsion Directorate for their financial support. We thank Cheveron for providing α-olefin samples. We wish to thank Mr. Mike Carr for HPLC support and Ms. Yoshiko Otonari for support with NMR spectroscopy.

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Figure Captions

Figure 1. Monofunctionalized Polyhedral Oligomeric Silsesquioxane (POSS) Macromers.

Figure 2. Possible modes of addition for vinyltrimethylsilane to **1a-b**.

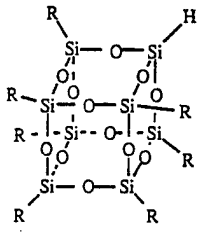
Figure 3. Synthesis of POSS monomers suitable for sol-gel type chemistry.

Figure 4. Example of the general approach to the synthesis of POSS-siloxane triblock polymers.

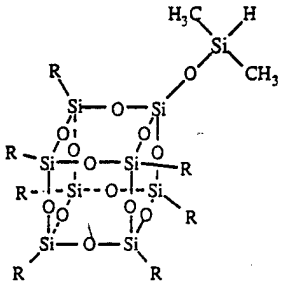
Figure 5. X-ray powder diffraction patterns of **15a** (top), **9a** (middle), and **4a** (bottom).

Figure 6. Plot of the melt transitions for **4a**, **9a**, **10a** and the softening points for **14a**, **15a**, and **13a** versus the average number of siloxane units between the POSS end groups. All data was taken from Table 1.

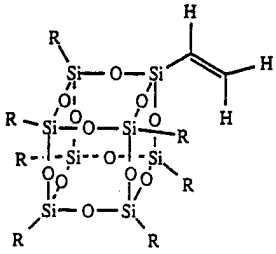
Figure 7. POSS Epoxides.



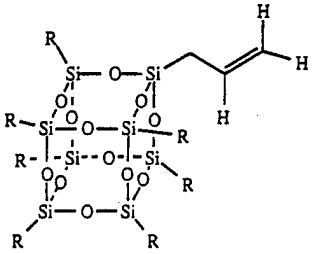
R = *c*-C_6H_{11} = **1a**
R = *c*-C_5H_9 = **1b**



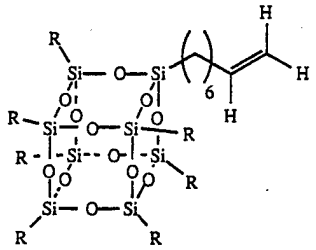
R = *c*-C_6H_{11} = **2a**
R = *c*-C_5H_9 = **2b**



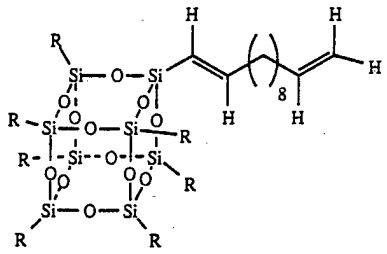
R = *c*-C_6H_{11} = **3a**
R = *c*-C_5H_9 = **3b**



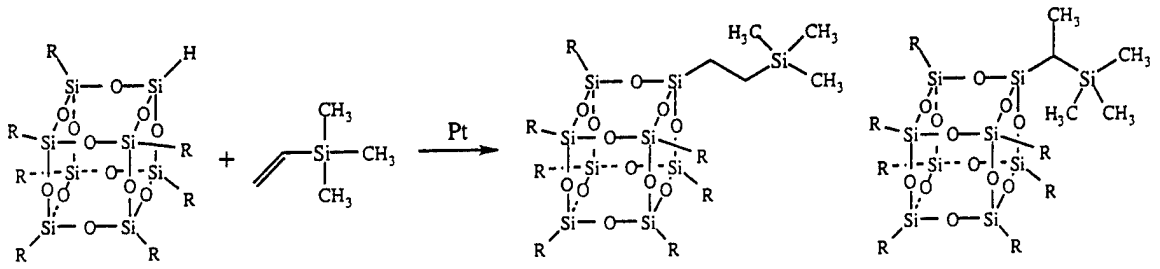
R = *c*-C_6H_{11} = **4a**
R = *c*-C_5H_9 = **4b**



R = *c*-C_6H_{11} = **5a**
R = *c*-C_5H_9 = **5b**



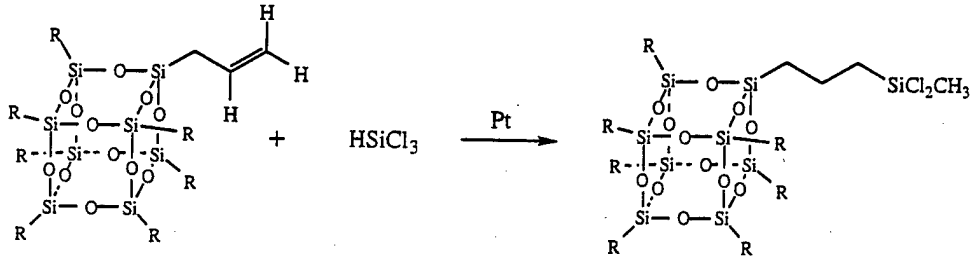
R = *c*-C_6H_{11} = **6**



R = *c*-C_6H_{11} = **1a**
R = *c*-C_5H_9 = **1b**

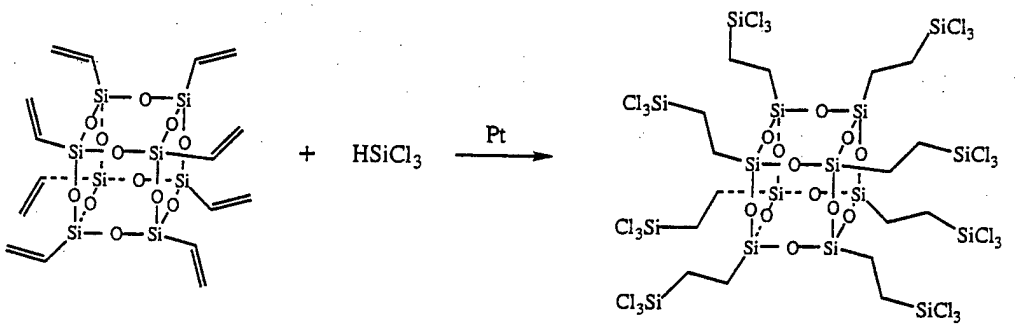
β-addition

α-addition

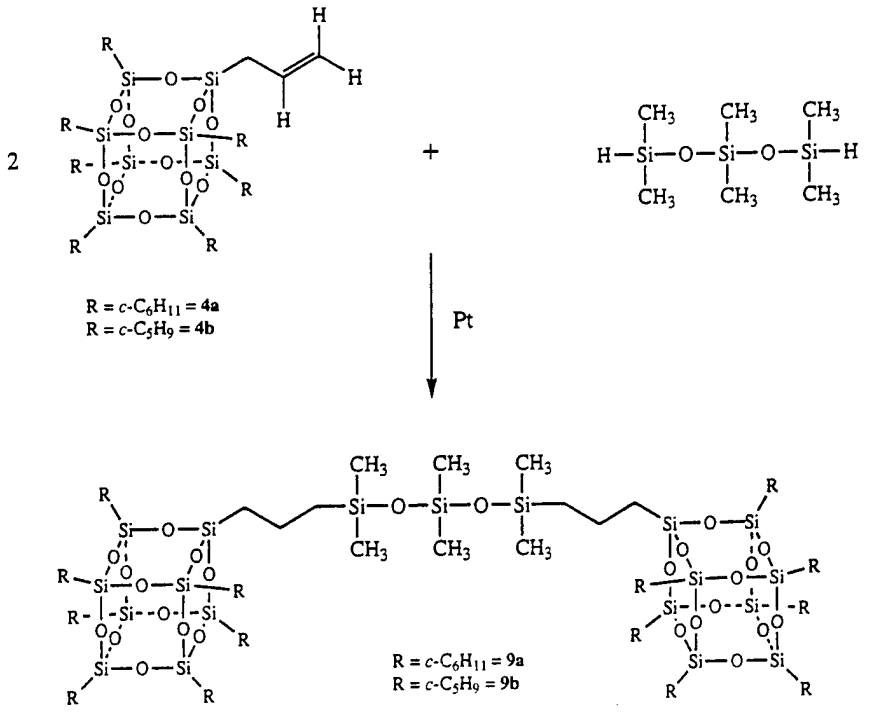


R = *c*-C_6H_{11} = 4a

R = *c*-C_6H_{11} = 7a



8


2
+
Pt
R = c-C6H11 = 4a
R = c-C5H9 = 4b
R = c-C6H11 = 9a
R = c-C5H9 = 9b

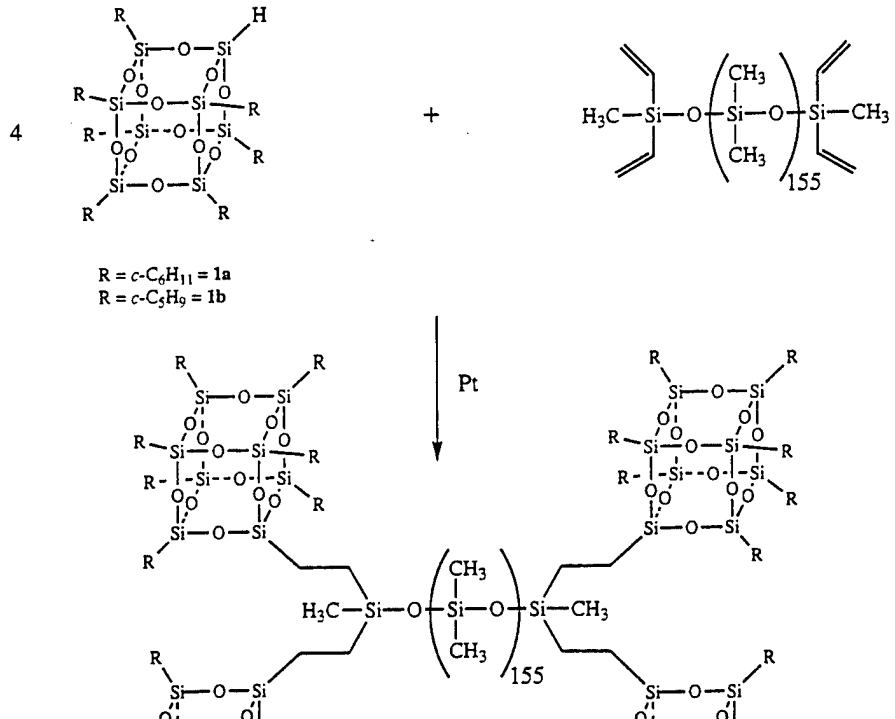
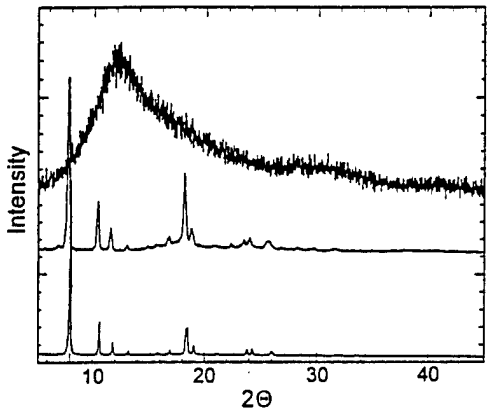
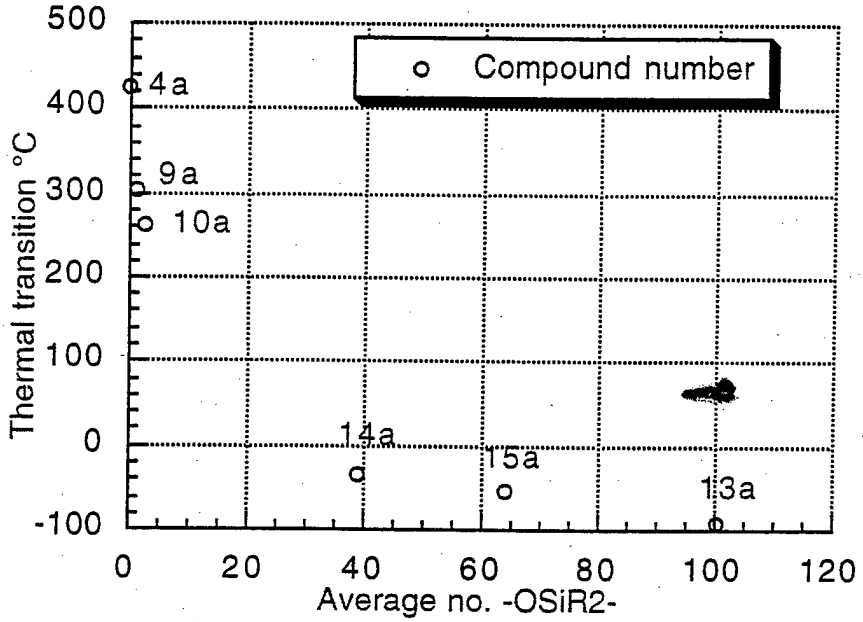

4
+
155
Pt
R = c-C6H11 = 1a
R = c-C5H9 = 1b
R = c-C6H11 = 15a

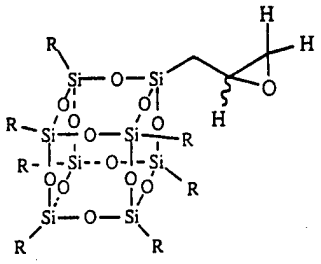
Table I. Thermal transitions for POSS monomers and triblocks.

No.	Compound	Transition °C
	POSS Macromers	
1a	$(c\text{-}C_6H_{11})_7Si_8O_{12}H$	279[a]
1b	$(c\text{-}C_5H_9)_7Si_8O_{12}H$	275[a]
4a	$(c\text{-}C_6H_{11})_7Si_8O_{12}CH_2CH{=}CH_2$	425[b]
4b	$(c\text{-}C_5H_9)_7Si_8O_{12}CH_2CH{=}CH_2$	412[b]
5a	$(c\text{-}C_6H_{11})_7Si_8O_{12}(CH_2)_6CH{=}CH_2$	358[b]
	POSS-Siloxane-POSS	
9a	$(c\text{-}C_6H_{11})_7Si_8O_{12}(CH_2)_3\text{-}SiMe_2OSiMe_2OSiMe_2\text{-}(CH_2)_3Si_8O_{12}(c\text{-}C_6H_{11})_7$	304[a]
9b	$(c\text{-}C_5H_9)_7Si_8O_{12}(CH_2)_3\text{-}SiMe_2OSiMe_2OSiMe_2\text{-}(CH_2)_3Si_8O_{12}(c\text{-}C_5H_9)_7$	221[a]
11a	$(c\text{-}C_6H_{11})_7Si_8O_{12}(CH_2)_8\text{-}SiMe_2OSiMe_2OSiMe_2\text{-}(CH_2)_8Si_8O_{12}(c\text{-}C_6H_{11})_7$	273[a]
10a	$(c\text{-}C_6H_{11})_7Si_8O_{12}(CH_2)_3\text{-}SiMe_2(OSiMe_2)_{4.6}\text{-}(CH2)_3Si_8O_{12}(c\text{-}C_6H_{11})_7$	260[a]
12a	$(c\text{-}C_6H_{11})_7Si_8O_{12}(CH_2)_8\text{-}SiMe_2(OSiMe_2)_{4.6}\text{-}(CH_2)_8Si_8O_{12}(c\text{-}C_6H_{11})_7$	255[a]
13a	$(c\text{-}C_6H_{11})_7Si_8O_{12}(CH_2)_2\text{-}SiMe_2(OSiMe_2)_{193}(OSiPh_2)_7\text{-}(CH_2)_3Si_8O_{12}(c\text{-}C_6H_{11})_7$	-92[c]
13b	$(c\text{-}C_5H_9)_7Si_8O_{12}(CH_2)_2\text{-}SiMe_2(OSiMe_2)_{193}(OSiPh_2)_7\text{-}(CH_2)_2Si_8O_{12}(c\text{-}C_5H_9)_7$	-12[c]
14a	$(c\text{-}C_6H_{11})_7Si_8O_{12}(CH_2)_2\text{-}SiMe_2(OSiMe_2)_{96}(OSiPh_2)_{31}\text{-}(CH_2)_2Si_8O_{12}(c\text{-}C_6H_{11})_7$	-54[c]
15a	$[(c\text{-}C_6H_{11})_7Si_8O_{12}CH_2CH_2]_2\text{-}SiMe(OSiMe_2)_{155}OSiMe\text{-}[CH_2CH_2Si_8O_{12}(c\text{-}C_6H_{11})_7]_2$	-36[c]

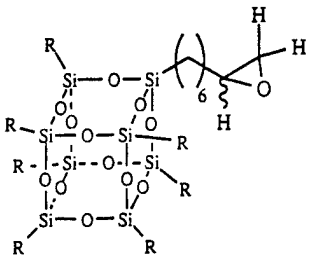
a) melt by TMA, b) decomposition, c) softening point, Me = CH_3, Ph = C_6H_5


Intensity
10
20
30
40
2Θ


Compound number
4a
9a
10a
14a
15a
13a
Thermal transition °C
500
400
300
200
100
0
-100
0
20
40
60
80
100
120
Average no. -OSiR2-



R = *c*-C_6H_{11} = **16a**
R = *c*-C_5H_9 = **16b**



R = *c*-C_6H_{11} = **17**

Table 2. Thermal properties of aliphatic POSS-epoxides.

Cmpd	[a] Self-exotherm °C	[a] Rxn-exotherm °C	[b] T_{dec} °C	[c] Char Yld. %
16a	251	143	402	31
16b	246	141	367	11

a) Irreversible polymerization by DSC. b) At 10% mass loss by TGA. c) After heating to 900 °C under N_2.

EXPERIMENTAL

General experimental protocol and procedures for the synthesis of $[(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3]$[5b,14], $[(c\text{-}C_5H_9)_7Si_7O_9(OH)_3]$[15], $[(c\text{-}C_6H_{11})_7Si_7O_{12}CH{=}CH(CH_2)_8\text{-}CH{=}CH_2]$[5a], $[(c\text{-}C_6H_{11})_7Si_7O_{12}(H)]$[5a,b], **1a**, and $[Si_8O_{12}(CH{=}CH_2)_8]$[16] appear elsewhere. Except where noted, all operations were performed under a nitrogen atmosphere either on a high vacuum line with modified Schlenk techniques or in a Vacuum Atmospheres Corporations Dri-lab. Tetrahydrofuran (THF) and diethylether were distilled from dark purple solutions of sodium benzophenone ketyl, or where noted, used directly from Triethylamine and chloroform-d[1] were vacuum transferred from calcium hydride. Chlorosilanes were purified by distillation under nitrogen or vacuum and stored under nitrogen in a glove box. Platinum tetramethyldivinylsiloxane complex in xylenes was purchased from United Technologies Inc. and used as received. All spectra were recorded on a Bruker AMX 300 (^{1}H 300.135 MHz, ^{13}C 75.475 MHz, ^{29}Si 59.624 MHz).

Differential scanning calorimetry (DSC) was carried out on a TA Instruments DSC 912 in conjunction with the Thermal Analyst 2000 data acquisition and analysis software. The instrument was operated at 10 °C/min with an atmosphere of flowing nitrogen gas. Melting or decomposition temperatures for all compounds were also determined visually in a capillary melting point apparatus. A TA Instruments TMA 2940 and the same Thermal Analyst 2000 system were used for thermomechanical analysis (TMA). Solid samples for TMA were prepared by pressing powdered materials in a 1/8" diameter mold at room temperature under a pressure of 500 psi. Oily materials were placed directly on the TMA sample platform after which they were cooled by liquid nitrogen in the TMA furnace. The TMA probe was lowered only once the sample had solidified at the starting temperature (-100 °C).

X-ray Powder Diffraction measurements were performed by a Scintag D5000 theta-theta diffractometer system using Cu K-alpha radiation (1.5406 Angstroms). Samples were prepared by grinding to 200 mesh (74 micron) where necessary and spreading thinly on a zero-background plate. Data were recorded with an intrinsic Ge detector. Integration times were typically 1 second/point with a goniometer step size of 0.02° 2Θ.

Synthesis of $(C_5H_9)_7Si_8O_{12}(H)$. Under a nitrogen atmosphere, $(C_5H_9)_7Si_8O_{12}(Cl)$ was synthesized by addition of a slight excess of tetrachlorosilane (21.35 g, 0.126 mol) to 1 litre flask containing an 800 mL THF suspension of $(C_5H_9)_7Si_7O_9(OH)_3$, (100 g, 0.114 mol) and triethylamine (38.14 g, 0.377 mol). The reaction flask was stirred under nitrogen for 12 hours, followed by filtration to remove the $HNEt_3Cl$ byproduct. The clear filtrate was transferred to a 1 litre flask equipped with a stir bar. To convert the POSS-chloride to

a hydride, excess $LiAlH_4$ (8.0 g, 0.211 mol) was added to it in 100 mg portions. The reaction was monitored by $^{13}C\{^1H\}$ NMR spectroscopy to determine when all the $(C_5H_9)_7Si_8O_{12}(Cl)$ was consumed. The diagnostic signals in the $^{13}C\{^1H\}$ NMR spectrum are from the alpha carbons of the cyclopentyl groups: $(C_5H_9)_7Si_8O_{12}(Cl)$ has three signals at 22.22, 22.16 and 21.95 (1:3:3) ppm and $(C_5H_9)_7Si_8O_{12}(H)$ has two signals at 22.26 and 22.17 (4:3) ppm. The reaction was approximately halfway done after 5 minutes, and was completed after 50 minutes. The product was isolated by filtering the cloudy solution (in air) through celite (caution: the byproducts 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 byproducts on the celite are very flammable) and reduced in volume to form a slurry. This hexanes slurry was then added to 1400 mL of methanol and stirred overnight. The product was then isolated by filtration and washed with methanol. After air drying, 49.24 g (0.0546 mol, 48 % yield) of >95 % pure $(C_5H_9)_7Si_8O_{12}(H)$ is isolated. ^1H NMR ($CDCl_3$, 300 MHz) 4.13 ppm (Si-H, with a ^{29}Si-satellite doublet $^1J_{Si\text{-}H}$ = 323 Hz, 1H); 1.78 (CH_2, multiplet, 14H); 1.58 (CH_2, multiplet, 42H); 1.00 (CH, multiplet, 7H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) 27.30, 27.04, 26.99 ppm (CH_2); 22.26, 22.17 (CH). $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 59.6 MHz) -66.42, -66.47 (SiCp, 7Si); -83.92 (SiH, 1Si).

$[(C_6H_{11})_7Si_8O_{12}OSi(CH_3)_2H]$ 2a: Procedures for the synthesis **2a-b** are identical, with a typical procedure for **2a** described below:

A solution of $ClSi(CH_3)_2H$ (1.0 g, 1.2 mL, 10.6 mmol) in THF (5 mL) was added to a solution of $(C_6H_{11})_7Si_8O_{12}OH$ (10.00 g, 9.84 mmol) and Et_3N (5.0 g, 6.9 mL, 49 mmol, 5 eq) in THF (50 mL) contained in a thick walled glass reactor. A precipitate of $Et_3N{\bullet}HCl$ formed upon addition of the chlorosilane. The reactor was sealed with a teflon plug, taken out of the glove box and the reaction mixture heated at 60 °C for 18 h. After this time, the reaction mixture was transferred to a sepratory funnel. The reaction vessel was rinsed with diethyl ether and the ether washings combined with the THF. The THF/ether phase was washed with successive portions of H_2O (2 x 50 mL), 1N HCl (2 x 50 mL), H_2O (50 mL), and sat NaCl (50 mL). The THF/ether phase was dried over $MgSO_4$, filtered and the THF/ether removed under vacuum to give 10.4 g (98%) of $(C_6H_{11})_7Si_8O_{12}OSi(CH_3)_2H$ as a white microcrystalline solid.

For **2a**: ^1H NMR (300.135 MHz, $CDCl_3$, 33 °C) δ 4.74 (sept, 1H, Si-*H*, J = 2.8 Hz), 1.74 (m, 35H, cyclohexyl-C*H*$_2$), 1.25 (m, 35H, cyclohexyl-C*H*$_2$), 0.77 (m, 7H, cyclohexyl-C*H*), 0.25 (d, 6H, Si-C*H*$_3$, J = 2.8 Hz). $^{13}C\{^1H\}$ NMR (75.475 MHz, $CDCl_3$, 33 °C) δ 27.51, 27.47, 26.92, 26.88, 26.67, 26.57 (cyclohexyl-*C*H_2), 23.22, 23.17,

23.08 (1:3:3, cyclohexyl-*C*H), 0.27 (Si-*C*H_3). $^{29}Si\{^1H\}$ NMR (59.624 MHz, $CDCl_3$, 33 °C) δ -2.97 (O*Si*Me_2H), -67.92, -68.56, -68.60 (3:3:1, cyclohexyl-*Si*), -107.6 (*Si*-$OSiMe_2H$).

For **2b:** ^1H NMR (300.135 MHz, $CDCl_3$, 33 °C) δ 4.72 (sept, 1H, $OSi(CH_3)_2H$, J = 2.8 Hz), 1.76-1.50 (m, 56H, cyclopentyl-CH_2), 1.01 (m, 7H, cyclopentyl-C*H*) 0.23 (d, 6H, $OSi(CH_3)_2H$, J = 2.8 Hz). $^{13}C\{^1H\}$ NMR (75.475 MHz, $CDCl_3$, 33 °C) δ 27.30, 27.02 (cyclopentyl-CH_2), 22.23, 22.16 (cyclopentyl-*C*H), 0.19 ($OSi(CH_3)_2H$). $^{29}Si\{^1H\}$ NMR (59.624 MHz, $CDCl_3$, 33 °C) δ 2.85 ($OSi(CH_3)_2H$), -65.83, -66.45 (3:4, cyclopentyl-*Si*), -107.7 (*Si* $OSi(CH_3)_2H$).

[(*c*-C_6H_{11})$_7$$Si_8O_{12}CH=CH_2$] 3a: Reactions were set up in air on the benchtop using dry solvents and stirred under nitrogen. Procedures for **3a-b** are the same, with a typical procedure for **3a** described below:

A solution of vinyltrichlorosilane was (9.12 g, 7.34 mL, 56.5 mmol, 1.1 eq) in Et_2O (50 mL) was rapidly added via addition funnel to a solution of [(*c*-C_6H_{11})$_7$$Si_7O_9(OH)_3$] (50.0 g, 51.4 mmol) and Et_3N (26.0 g, 36 mL, 257 mmol, 5 eq) in Et_2O (400 mL). The reaction mixture was stirred under nitrogen for 16 h. Afterwards the reaction mixture was transferred to a sepratory funnel and the Et_2O solution extracted with successive portions of H_2O (100 mL), 1M HCl (2 x 100 mL), H_2O (100 mL) and sat NaCl (50 mL). The Et_2O solution was stirred over activated charcoal and silica gel, filtered through celite and the Et_2O concentrated by rotary evaporation to give a slurry. Methanol (1L) was added to the slurry and the solid product 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, $CDCl_3$, 33 °C) δ 6.06 (dd, CH=CH_2, J = 13.3 Hz and 5.35 Hz), 6.01 (dd, CH=CH_2, J = 20.6 Hz and 5.35 Hz), 5.88 (dd, C*H*=CH_2, J = 20.6 Hz and 13.3 Hz), 1.74 (m, cyclohexyl-CH_2), 1.25 (m, cyclohexyl-CH_2), 0.77 (m, cyclohexyl-C*H*); $^{13}C\{^1H\}$ NMR (75.475 MHz, $CDCl_3$, 33 °C) δ 135.69 (*C*H=CH_2), 130.10 (CH=*C*H_2), 27.51, 27.48, 26.92, 26.86, 26.67, 26.63 (cyclohexyl-CH_2), 23.20, 23.14 (cyclohexyl-*C*H). $^{29}Si\{^1H\}$ NMR (59.624 MHz, $CDCl_3$, 33 °C) δ -68.43, -68.57 (cyclohexyl-*Si*), -80.57 (*Si*CH=CH_2).

For **3b:** ^1H NMR (300.135 MHz, $CDCl_3$, 33 °C) δ 5.97 (m, 3H, SiC*H*=CH_2), 1.78-1.50 (m, 56H, cyclopentyl-CH_2), 1.01 (m, 7H, cyclopentyl-C*H*). $^{13}C\{^1H\}$ NMR (75.475 MHz, $CDCl_3$, 33 °C) δ 135.62 (SiCH=*C*H_2), 130.16 (SiCH=CH_2), 27.33, 27.30, 27.02, 26.96 (cyclopentyl-CH_2), 22.24 (cyclopentyl-*C*H). $^{29}Si\{^1H\}$ NMR (59.624 MHz, $CDCl_3$, 33 °C) δ -66.28, -66.47 (3:4, cyclopentyl-*Si*), -80.68 (*Si*CH=CH_2).

[$R_7Si_8O_{12}CH_2CH=CH_2$] 4a-b. Reactions were set up in air on the benchtop using dry solvents and stirred under nitrogen. Procedures for **4a-b** are the same, with a typical procedure for **4a** described below:

A solution of $Cl_3SiCH_2CH=CH_2$ (9.9 g, 8.2 mL, 56.4 mmol) in THF (50 mL) was added dropwise via addition funnel to a solution of $(C_6H_{11})_7Si_7O_9(OH)_3$ (50.0 g, 51.4 mmol) and Et_3N (26.0 g, 35.8 mL, 0.257 mol, 5 eq) in THF (400 mL). A precipitate of $Et_3N{\bullet}HCl$ formed upon addition of the $Cl_3SiCH_2CH=CH_2$ solution. The reaction mixture was stirred for 16 h. After this time the reaction mixture was transferred to a sepratory funnel, the reaction flask rinsed with diethyl ether and the washing added to the THF solution. An additional 200 mL of diethyl ether was added to sepratory funnel and the THF/ether solution washed with successive portions of H_2O (100 mL), 1N HCl (2 x 100 mL), H_2O (150 mL) and sat. NaCl (100 mL). The THF/ether solution was dried over $MgSO_4$ and activated carbon, filtered and the volume of solvent reduced by rotory evaporation to give a slurry. Methanol (1 L) was added to the slurry and the solid collected and dried under vacuum to provide 47.6 g (89 %) of $(C_6H_{11})_7Si_8O_{12}CH_2CH=CH_2$ as a white solid.

For **4a:** ^1H NMR (300.135 MHz, $CDCl_3$, 33 °C) δ 5.78 (1 H, $SiCH_2CH=CH_2$), 5.00-4.90 (m, $SiCH_2CH=CH_2$) 1.74 (m, 35H, cyclohexyl-CH_2), 1.61 (br d, $SiCH_2CH=CH_2$, J = 7.8 Hz) 1.25 (m, 35H, cyclohexyl-CH_2), 0.76 (m, 7H, cyclohexyl-CH). $^{13}C\{^1H\}$ NMR (75.475 MHz, $CDCl_3$, 33 °C) δ 132.58 ($SiCH_2CH=CH_2$), 114.71 ($SiCH_2CH=CH_2$) 27.51, 27.48, 26.92, 26.67, 26.60 (cyclohexyl-CH_2), 23.20, 23.14 (4:3, cyclohexyl-CH), 19.70 ($SiCH_2CH=CH_2$). $^{29}Si\{^1H\}$ NMR (59.624 MHz, $CDCl_3$, 33 °C) δ -68.57, -68.60 (cyclohexyl-*Si*), -70.94 (*Si*$CH_2CH=CH_2$). Anal. calcd for $C_{45}H_{82}Si_8O_{12}$: C, 51.98; H, 7.95. Found: C, 51.77; H, 8.08.

For **4b:** ^1H NMR (300.135 MHz, $CDCl_3$, 33 °C) δ 5.77 (m, 1 H, $SiCH_2CH=CH_2$), 5.00-4.90 (m, $SiCH_2CH=CH_2$) 1.74-1.55 (m, 56H, cyclopentyl-CH_2), 1.01 (m, 7H, cyclopentyl-CH). $^{13}C\{^1H\}$ NMR (75.475 MHz, $CDCl_3$, 33 °C) δ 132.60 ($SiCH_2CH=CH_2$), 114.58 ($SiCH_2CH=CH_2$) 27.32, 27.02 (cyclopentyl-CH_2), 22.29 (cyclopentyl-CH), 19.73 ($SiCH_2CH=CH_2$). $^{29}Si\{^1H\}$ NMR (59.624 MHz, $CDCl_3$, 33 °C) δ -66.43, -66.49 (cyclopentyl-*Si*), -71.03 (*Si*$CH_2CH=CH_2$).

[$(R)_7Si_8O_{12}(CH_2)_6CH=CH_2$] and isomers 5a-b: Procedures for the synthesis of these monomers is identical. A detailed procedure for **5b** is given.

A solution of 1-octenyltrichlorsilane (6.17 g, 25.1 mmol, ~33% internal olefin) in THF was added to a solution of $(c\text{-}C_5H_9)_7Si_7)O_9(OH)_3$ (20.0 g, 22.8 mmol) an Et_3N

(7.63g, 10.5 mL, 3.3 eq) in THF (175 mL). A precipitate of $Et_3N{\bullet}HCl$ formed immediately upon addition of the trchlorosilane. The reaction mixture stirred for 16 h. After this time the $Et_3N{\bullet}HCl$ was removed by filtration and the solution concentrated to give a viscous residue. The residue was taken up in a minimum of THF, filtered and poured into an excess of methanol to precipitate **5b**. The precipitate was collected by vacuum filtration and dried to provide 21.36 (92%) of **5b**.

For **5a:** ^1H NMR (300.135 MHz, $CDCl_3$, 33 °C) δ 5.82 (m, C*H*=CH_2), 5.42 (m, C*H*=C*H* internal), 5.00 (m, CH=CH_2), 4.94 (m, CH=CH_2), 2.05 (m, CH_2CH=CH_2 and internal), 1.74 (m, cyclohexyl-CH_2), 1.61 (d, CH=CHCH_3, J = 5.3 Hz), 1.25 (m, cyclohexyl-CH_2), 0.77 (m, cyclohexyl-C*H*), 0.62 (t, -Si_8O_{12}-CH_2-, J = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75.475 MHz, $CDCl_3$, 33 °C) δ 139.14, 131.66, 130.86, 124.48, 123.56, and 114.07 (*C*H=*C*H_2 and internal), 33.82, 32.40, 28.83 (-*C*H_2-), 27.52, 26.94, 26.91, 26.68 (cyclohexyl-*C*H_2), 23.23, 22.85 (cyclohexyl-*C*H), 11.83 (Si*C*H_2-). $^{29}Si\{^1H\}$ NMR (59.624 MHz, $CDCl_3$, 33 °C) δ -66.07 (*Si*$(CH_2)_6$CH=CH_2), -68.58, -68.76 (cyclohexyl*Si*). Anal cacld for $C_{50}H_{92}Si_8O_{12}$: C, 54.11; H 8.35. Found: C, 53.74; H, 8.34.

For **5b:** ^1H NMR (300.135 MHz, $CDCl_3$, 33 °C) δ 5.82 (m, C*H*=CH_2), 5.41 (m, C*H*=C*H* internal), 4.96 (m, CH=CH_2), 2.05 (m, CH_2CH=CH_2 and internal), 1.76-1.51 (m, cyclopentyl-CH_2 and Si(CH_2)$_6$CH=CH_2), 0.99 (m, cyclopentyl-C*H*), 0.62 (t, -Si_8O_{12}CH_2-, J = 6.9 Hz). $^{13}C\{^1H\}$ NMR (75.475 MHz, $CDCl_3$, 33 °C) δ 139.18, 131.69, 130.90, 124.50, 123.56, and 114.07 (*C*H=*C*H_2 and internal), 33.81, 32.40, 28.83, 22.82 (-*C*H_2-), 27.36, 27.34, 27.04 (cyclopentyl-*C*H_2), 23.34 (cyclopentyl-*C*H), 11.93 (Si*C*H_2-). $^{29}Si\{^1H\}$ NMR (59.624 MHz, $CDCl_3$, 33 °C) δ -66.16 (*Si*$(CH_2)_6$CH=CH_2), -66.47, -68.62 (cyclopentyl*Si*).

Hydrosilation of 1a to give (c-$C_6H_{11})_7Si_8O_{12}CH_2CH_2Si(CH_3)_3$. A solution of Karstedt's catalyst (0.018 g) in divinyl terminated PDMS was added to a solution of (c-$C_6H_{11})_7Si_8O_{12}H$ (0.410 g, 0.410 mmol) and $(CH_3)_3SiCH=CH_2$ (0.042 g, 0.419 mmol) in CH_2Cl_2. The reaction mixture was refluxed for 18 hours. After this time the solution was concentrated to a few mL and the product purified by flash column chromatography. The fractions containing the desired product were combined and the solvent removed to provide 0.276 g (61%) of (c-$C_6H_{11})_7Si_8O_{12}CH_2CH_2Si(CH_3)_3$. ^1H NMR (300.135 MHz, $CDCl_3$, 32 °C) δ 1.74 (m, 35H, cyclohexyl-CH_2), 1.25 (m, 35H, cyclohexyl-CH_2), 0.76 (m, 7 H, cyclohexyl-C*H*), 0.52 (m, 4H, CH_2-CH_2-), 0.00 (s, 9H, Si(CH_3)$_3$). $^{29}Si\{^1H\}$ NMR (59.624 MHz, $CDCl_3$, 32 °C) δ 3.16 (*Si*$(CH_3)_3$), -66.05 (*Si*$(CH_2CH_2$-), -68.63, -68.69

(cyclohexyl*Si*). Anal Cacld for $C_{47}H_{90}Si_9O_{12}$: C, 51.32; H, 8.25. Found: C, 50.52; H, 8.17.

$[(C_6H_{11})_7Si_8O_{12}(CH_2)_3SiCl_2CH_3]$ 7: A solution of tetramethyldivinyldisiloxaneplatinium catalyst in xylenes (3 drops) was added to a slurry of **4a** (10.00 g, 9.62 mmol) in $HSiCl_2CH_3$ (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 in color. After this time the excess $HSiCl_3$ 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 dissolved in diethyl ether and the ether solution transferred to a flask containing activated carbon. The ether solution was filtered through celite to remove the activated carbon and solvent removed under vacuum to provide 10.7 g (96%) of $(C_6H_{11})_7Si_8O_{12}(CH_2)_3SiCl_2CH_3$ as a white solid. ^{1}H NMR (300.135 MHz, $CDCl_3$, 33 °C) δ 1.74 (m, 37H, cyclohexyl-C*H*$_2$ and $SiCH_2CH_2CH_2SiCl_2CH_3$), 1.25 (m, 37H, cyclohexyl-C*H*$_2$ and $SiCH_2CH_2CH_2SiCl_2CH_3$), 0.77 (m, 12H, cyclohexyl-C*H*, $SiCH_2CH_2CH_2SiCl_2CH_3$ and $SiCH_2CH_2CH_2SiCl_2CH_3$). ^{13}C{^{1}H} NMR (75.475 MHz, $CDCl_3$, 33 °C) δ 27.53, 26.94, 26.88, 26.70 (cyclohexyl-*C*H$_2$), 24.88 ($SiCH_2CH_2CH_2SiCl_2CH_3$), 23.23 (cyclohexyl-*C*H), 16.45 ($SiCH_2CH_2CH_2SiCl_2CH_3$), 15.20 ($SiCH_2CH_2CH_2SiCl_2CH_3$), 5.16 ($SiCH_2CH_2CH_2SiCl_2CH_3$). ^{29}Si{^{1}H} NMR (59.624 MHz, $CDCl_3$, 33 °C) δ 32.12 ($SiCH_2CH_2CH_2SiCl_2CH_3$), -63.37 ($SiCH_2CH_2CH_2SiCl_2CH_3$), -68.56, -68.65 (4:3, cyclohexyl*Si*).

$[Si_8O_{12}(CH_2CH_2SiCl_3)_8]$ 8: A solution of tetramethyldivinyldisiloxaneplatinium catalyst in xylenes (5 drops) was added to a heterogeneous solution of $Si_8O_{12}(CH_2{=}CH)_8$ (1.00 g, 1.58 mmol) in $HSiCl_3$ (10 mL) contained in a 50 mL, thick walled glass reactor. An immediate and very exothermic reaction proceeded. As the 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 16 h. After this time, the excess $HSiCl_3$ was removed under reduced pressure to give 2.5 g 92% of $Si_8O_{12}(CH_2CH_2SiCl_3)_8$ as an off-white solid. ^{1}H NMR (300 MHz, $CDCl_3$, 33 °C) δ 1.42 (m, 16H, $SiCH_2CH_2SiCl_3$), 0.93 (m, 16H, $SiCH_2CH_2SiCl_3$). ^{13}C{^{1}H} NMR (75.475 MHz, $CDCl_3$, 33 °C) δ 16.73 ($SiCH_2CH_2SiCl_3$), 3.37 ($SiCH_2CH_2SiCl_3$). ^{29}Si{^{1}H} NMR (59.624 MHz, $CDCl_3$, 33 °C) δ 12.86 ($SiCH_2CH_2SiCl_3$), -67.43 ($SiCH_2CH_2SiCl_3$).

Hydrosilation of 4a to give $[(C_6H_{11})_7Si_8O_{12}(CH_2)_3SiCl_3]$: A solution of tetramethyldivinyldisiloxaneplatinium catalyst in xylenes (2 drops) was added to a solution of **4a** (5.00 g, 4.81 mmol) in $HSiCl_3$ (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 18 h. After this time the excess $HSiCl_3$ 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 dissolved in diethyl ether and the ether solution transferred to a flask containing activated carbon. The ether solution was filtered through celite to remove the activated carbon and solvent removed under vacuum to provide 5.5 g (97%) of $(C_6H_{11})_7Si_8O_{12}(CH_2)_3SiCl_3$ as a white solid. ^{1}H NMR (300.135 MHz, $CDCl_3$, 33 °C) δ 1.74 (m, 37H, cyclohexyl-C*H*$_2$ and $SiCH_2CH_2CH_2SiCl_3$), 1.51 (m, $SiCH_2CH_2CH_2SiCl_3$), 1.24 (m, 35H, cyclohexyl-C*H*$_2$), 0.78 (m, 9H, cyclohexyl-C*H* and $SiCH_2CH_2CH_2SiCl_3$). ^{13}C{^{1}H} NMR (75.475 MHz, $CDCl_3$, 33 °C) δ 27.50, 27.47, 26.91, 26.84, 26.67 (cyclohexyl-*C*H$_2$), 27.30 ($SiCH_2CH_2CH_2SiCl_3$), 16.40 ($SiCH_2CH_2CH_2SiCl_3$), 14.67 ($SiCH_2CH_2CH_2SiCl_3$). ^{29}Si{^{1}H} NMR (59.624 MHz, $CDCl_3$, 33 °C) δ 12.39 (*Si*Cl$_3$), -67.70, -68.57, -68.62 (cyclohexyl-*Si*).

Synthesis of Triblocks

Triblock 9a. A solution of divinyltetramethyldisiloxaneplatinium complex (Karstedt's catalyst) (0.010 g, 2-3% platinum content) in vinyl terminated polydimethylsiloxane (PDMS) was dissolved in methylene chloride (1 mL) and added to a solution of **4a** (1.02 g, 0.98 mmol) and H-SiMe$_2$-O-SiMe$_2$-O-SiMe$_2$-H (0.133 g, 0.638 mmol) in methylene chloride (10 mL). The reaction mixture was refluxed for 18 h. Unreacted H-SiMe$_2$-O-SiMe$_2$-O-SiMe$_2$-H 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 0.667g (60%). ^{1}H NMR (300.135 MHz, $CDCl_3$, 32 °C) δ 1.73 (m, cyclohexyl-C*H*$_2$), 1.50 (m, ≡O$_3$SiCH$_2$C*H*$_2$CH$_2$Si(CH$_3$)$_2$O-), 1.25 (m, cyclohexyl-C*H*$_2$), 0.76 (m, 7H, cyclohexyl-C*H*), 0.68 (overlapping multiplets, ≡O$_3$SiC*H*$_2$CH$_2$C*H*$_2$Si(CH$_3$)$_2$O-), 0.08 (Si(C*H*$_3$)$_2$-O-Si(C*H*$_3$)$_2$-O-Si(C*H*$_3$)2-), 0.03 (s, Si(CH$_3$)$_2$-O-Si(C*H*$_3$)$_2$-O-Si(CH$_3$)2-). ^{29}Si{^{1}H} NMR (59.624 MHz, $CDCl_3$, 33 °C) δ 6.88 (*Si*(CH$_3$)$_2$-O-Si(CH$_3$)$_2$-O-*Si*(CH$_3$)$_2$-), -21.19 (Si(CH$_3$)$_2$-O-*Si*(CH$_3$)$_2$-O-Si(CH$_3$)$_2$), -66.68 (≡O$_3$*Si*-(CH$_2$)$_3$-), -68.59, -68.77 (cyclohexyl*Si*). Anal Calcd for $C_{96}H_{184}Si_{19}O_{26}$: C, 50.39; H, 8.11. Found: C, 50.00; H, 8.09.

flash column chromatography to yield 0.408g (54%) of **11a**. ^{1}H NMR (300.135 MHz, $CDCl_3$, 32 °C) δ 1.73 (m, cyclohexyl-C*H*$_2$), 1.25 (m, cyclohexyl-C*H*$_2$), 0.76 (m, cyclohexyl-C*H*)), 0.61 and 0.53 (overlapping triplets, ≡O_3SiC*H*$_2$(CH$_2$)$_6$C*H*$_2$Si(CH$_3$)$_2$O-), 0.10, 0.08, 0.06, 0.04, 0.03, and 0.02 (s, -Si(C*H*$_3$)$_2$-O-Si(C*H*$_3$)$_2$-O-Si(C*H*$_3$)$_2$-). ^{29}Si{^{1}H} NMR (59.624 MHz, $CDCl_3$, 32 °C) δ 7.49, 7.28 (-*Si*(CH$_3$)$_2$-O-Si(CH$_3$)$_2$-O-*Si*(CH$_3$)$_2$-), -21.47, -21.92 (-Si(CH$_3$)$_2$-O-*Si*(CH$_3$)$_2$-O-Si(CH$_3$)$_2$-), -66.07 (≡O_3*Si*-(CH$_2$)$_8$-), -68.65, -68.82 (cyclohexyl*Si*). Anal Cacld for $C_{106}H_{204}Si_{19}O_{26}$: C, 52.43; H, 8.47. Found: C, 51.12; H, 8.26.

Triblock 12a: A solution of divinyltetramethyldisiloxaneplatinium complex (Karstedt's catalyst) (0.010 g, 2-3% platinum content) in vinyl terminated polydimethylsiloxane (PDMS) was dissolved in methylene chloride (10 mL) and added to a solution of **5a** (0.407 g, 0.367 mmol) and H(SiMe$_2$O)$_{4.6}$SiMe$_2$H (0.106 g, 0.265 mmol) in methylene chloride (10 mL). The reaction mixture was refluxed for 18 h. Unreacted H(SiMe$_2$O)$_{4.6}$SiMe$_2$H was removed by flash chromatography and the solvent removed under reduced pressure to yield 0.432 g (90%) of **12a**. ^{1}H NMR (300.135 MHz, $CDCl_3$, 32 °C) δ 1.73 (m, cyclohexyl-C*H*$_2$), 1.25 (m, cyclohexyl-C*H*$_2$), 0.76 (m, cyclohexyl-C*H*), 0.61 and 0.54 (overlapping triplets, ≡O_3SiC*H*$_2$(CH$_2$)$_6$C*H*$_2$Si(CH$_3$)$_2$O-, J = 7.6 and 7.4 Hz), 0.05 (m, -Si(C*H*$_3$)$_2$-(O-Si(C*H*$_3$)$_2$)$_{3.6}$-O-Si(C*H*$_3$)$_2$-). ^{29}Si{^{1}H} NMR (59.624 MHz, $CDCl_3$, 32 °C) δ 7.58, 7.33 ((CH$_3$)$_2$*Si*-O-(Si(CH$_3$)$_2$-O)$_{3.6}$*Si*(CH$_3$)$_2$), -21.69, -21.72, -21.87, -22.15, and -22.32 ((CH$_3$)$_2$Si-O-(*Si*(CH$_3$)$_2$-O)$_{3.6}$Si(CH$_3$)$_2$), -66.02 (≡O_3*Si*-(CH$_2$)$_8$-), -68.59, -68.61, -68.77 (cyclohexyl*Si*). Anal Cacld for $C_{111}H_{220}Si_{22}O_{30}$: C, 50.96; H, 8.44. Found: C, 51.12; H, 8.33.

Triblock 13a. A solution of divinyltetramethyldisiloxaneplatinium complex (Karstedt's catalyst) (0.010 g, 2-3% platinum content) in vinyl terminated polydimethylsiloxane (PDMS) was added to a solution of **1a** (0.206 g, 0.206 mmol) and H_2C=CH-SiMe$_2$-(O-SiMe$_2$)$_{193}$-(O-SiPh$_2$)$_7$-CH=CH_2 (1.031 g, 0.111 mmoles) 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 removed under reduced pressure to give 0.879 g (76%) of **13a**. ^{1}H NMR (300.135 MHz, $CDCl_3$, 32 °C) δ 7.63 and 7.36 (m, -OSi(C$_6$*H*$_5$)$_2$O-), 1.75 (m, cyclohexyl-C*H*$_2$), 1.27 (m, cyclohexyl-C*H*$_2$), 0.78 (m, cyclohexyl-C*H*), 0.10 (s, -O-Si(C*H*$_3$)$_2$-O-). ^{29}Si{^{1}H} NMR (59.624 MHz, $CDCl_3$, 32 °C) δ 8.31 (-O-*Si*(CH$_3$)$_2$(CH$_2$)$_2$-), -20.79 and -21.95 (-O*Si*(CH$_3$)$_2$O-), -48.42 (-O*Si*(C$_6$H$_5$)$_2$O-), -65.95 (≡O_3*Si*(CH$_2$)$_2$-), -68.59 (cyclohexyl*Si*).

Triblock 13b. A solution of divinyltetramethyldisiloxaneplatinium complex (Karstedt's catalyst) (0.014 g, 2-3% platinum content) in vinyl terminated polydimethylsiloxane (PDMS) was added to a solution of **1b** (0.255 g, 0.283 mmol) and H_2C=CH-$SiMe_2$-(O-$SiMe_2)_{193}$-(O-$SiPh_2)_7$-CH=CH_2 (1.321 g,0.142 mmol) in methylene chloride (10 mL). The reaction mixture was refluxed for 18 h. The reaction mixture was stirred with silica gel and charcoal, filtered through Celite and the solvent removed under reduced pressure to give 1.248g (85%) of **13b**. ^{1}H NMR (300.135 MHz, $CDCl_3$, 32 °C) δ 7.65 and 7.36 (m, -OSi($C_6H_5)_2$O-), 1.77-1.56 (m, cyclopentyl-CH_2), 1.01 (m, cyclopentyl-C*H*), 0.09 (-OSi($CH_3)_2$O-). ^{29}Si{^{1}H} NMR (59.624 MHz, $CDCl_3$, 32 °C) δ 8.32 (-O-*Si*($CH_3)_2CH_2CH_2$-), -20.80, -21.73, -21.96 (-O*Si*($CH_3)_2$O-), -48.41 (-O*Si*($C_6H_5)_2$O-), -66.02 (≡O_3*Si*-($CH_2)_2$-), -66.46, -66.49 (cyclopentyl*Si*).

Triblock 14a. A solution of divinyltetramethyldisiloxaneplatinium complex (Karstedt's catalyst) (0.011 g, 2-3% platinum content) in vinyl terminated polydimethylsiloxane (PDMS) was added to a solution of **1a** (0.238 g, 0.238 mmol) and H_2C=CH-$SiMe_2$-(O-$SiMe_2)_{96}$-(O-$SiPh_2)_{31}$-CH=CH_2 (1.586 g, 0.119 mmol) in methylene chloride (10 mL). The reaction mixture refluxed for 18 h. Upon cooling the solution was filtered through activated charcoal and Celite, the solvent removed under reduced pressure to give 1.612g (88%) of **14a**. ^{1}H NMR (300.135 MHz, $CDCl_3$, 32 °C) δ 7.62 and 7.35 (m, -OSi($C_6H_5)_2$O-), 1.77 (m, cyclohexyl-CH_2), 1.26 (m, cyclohexyl-CH_2), 0.79 (m, cyclohexyl-C*H*), 0.11 (m, -OSi($CH_3)_2$O-). ^{29}Si{^{1}H} NMR (59.624 MHz, $CDCl_3$, 32 °C) δ 8.0 (-O*Si*($CH_3)_2CH_2CH_2$-), -17.03, -17.56, -18.54, -19.24, -20.04, -20.50, -20.62, -20.76, -21.47, -21.68, -21.90 (-O*Si*($CH_3)_2$O-), -44.93, -47.60, -48.19, -48.42 (-O*Si*($C_6H_5)_2$O-), -65.95 (≡O_3*Si*($CH_2)_2$-), -68.59, -68.60 (cyclohexyl*Si*). Anal Cacld for $C_{654}H_{1054}Si_{144}O_{151}$: C, 51.08; H, 6.91. Found: C, 50.44; H, 6.98.

Triblock 15a. A solution of divinyltetramethyldisiloxaneplatinium complex (Karstedt's catalyst) (0.010 g, 2-3% platinum content) in vinyl terminated polydimethylsiloxane (PDMS) was added to a solution of **1a** (0.300 g, 0.300 mmol) and (CH_2=CH)$_2$-SiMe-($OSiMe_2)_{155}$-O-SiMe-(CH=$CH_2)_2$ 0.910g (0.078 mmoles) 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 removed under reduced pressure to yield 0.948g (78%) of **15**. ^{1}H NMR (300.135 MHz, $CDCl_3$, 32 °C) δ 1.74 (m, cyclohexyl-CH_2), 1.25 (m, cyclohexyl-CH_2), 0.77 (m, cyclohexyl-C*H*), 0.08 (m, -OSi($CH_3)_2$O-). ^{29}Si{^{1}H} NMR (59.624 MHz, $CDCl_3$, 32 °C) δ -21.97 (- O*Si*($CH_3)_2$O-),

[(*c*-C_5H_9)$_7$$Si_8O_{12}$($CH_2$)$_6$$CHCH_2O$] 16b: Solid *m*-chloroperbenzoic 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**. ^{1}H NMR (300.135 MHz, $CDCl_3$, 32 °C) δ 3.03 (m, 1H, $SiCH_2CHCH_2O$), 2.78 (m, 1H, $SiCH_2CHCH_2O$), 2.45 (dd, 1H, $SiCH_2CHCH_2O$, J = 5.0 Hz, 2.7 Hz), 1.75-1.48 (m, 57H, cyclopentyl-CH_2 and $SiCH_2CHCH_2O$), 1.01 (m, 7H, cyclopentyl-C*H*), 0.59 (dd, 1H, $SiCH_2CHCH_2O$, J = 14.5 Hz, 9.2 Hz). ^{13}C{^{1}H} NMR (75.475 MHz, $CDCl_3$, 32 °C) δ 49.13, 48.17 ($SiCH_2CHCH_2O$), 27.26, 26.99 26.96 (cyclopentyl-CH_2), 22.17, 22.13 (cyclopentyl-*C*H), 17.34 ($SiCH_2CHCH_2O$). ^{29}Si{^{1}H} NMR (59.624 MHz, $CDCl_3$, 32 °C) δ -66.39, -66.45 (cyclopentyl*Si*), -70.27 (≡O_3SiCH_2-).

[(*c*-C_6H_{11})$_7$$Si_8O_{12}$($CH_2$)$_6$$CHCH_2O$] 17. A solution of *m*-chloroperbenzoic acid (MCPBA) (1.007 g 5.835 mmol) in methylene chloride (10 mL) was added to a solution of **5a** (1.474 g, 1.328 mmol) in methylene chloride (25 mL). The reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure and the resulting solid stirred with methanol for 2 days to dissolve the excess MCPBA and *m*-chlorobenzoic acid. The epoxide, (*c*-C_6H_{11})$_7$$Si_8O_{12}$($CH_2$)$_6$$CHOCH_2$, which is insoluble in methanol, was collected by vacuum filtration, washed with methanol and dried under vacuum to give 1.263g (84%) of **17.** ^{1}H NMR (300.135 MHz, $CDCl_3$, 32 °C) δ 3.04 (m, 1H, CH_2CHCH_2O), 2.89 (m, 1H, $SiCH_2CHCH_2O$), 2.74 (dd, $SiCH_2CHCH_2O$), 2.66 (m), d 2.45 (dd, H_2C-C*H*O-CH_2-), 1.72 (m, cyclohexyl-CH_2), 1.24 (m, cyclohexyl-CH_2), 0.75 (m, cyclohexyl-C*H*), 0.61 (m). ^{13}C{^{1}H} NMR (75.475 MHz, $CDCl_3$, 32 °C) δ 52.35 and 47.06 (H_2C-*C*HO-CH_2-), 32.53, 32.50, 25.83, 22.80, and 11.84 (-CH_2-), 27.51, 26.92, 26.90, 26.67 (cyclohexyl-CH_2) and 23.22 (cyclohexyl-*C*H). ^{29}Si{^{1}H} NMR (59.624 MHz, $CDCl_3$, 32 °C) δ -66.15 (≡O_3Si-CH_2-), -68.59, -68.76 (cyclohexyl*Si*).