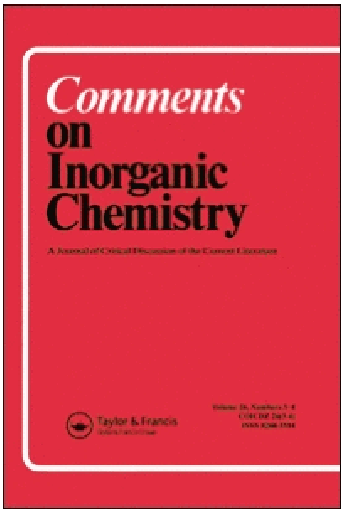

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Polyhedral Oligomeric Silsesquioxanes: Building Blocks for Silsesquioxane-Based Polymers and Hybrid Materials

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To cite this Article Lichtenhan, Joseph D.(1995) 'Polyhedral Oligomeric Silsesquioxanes: Building Blocks for Silsesquioxane-Based Polymers and Hybrid Materials', Comments on Inorganic Chemistry, 17: 2, 115 — 130
To link to this Article: DOI: 10.1080/02603599508035785
URL: http://dx.doi.org/10.1080/02603599508035785

Polyhedral Oligomeric Silsesquioxanes: Building Blocks for Silsesquioxane-Based Polymers and Hybrid Materials

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Received October 6, 1994

General methods are described for the preparation of discrete polyhedral oligomeric silsesquioxane (POSS) macromers and for their incorporation into linear polymeric systems. Depending on the type of functionality contained on the POSS macromer, macromolecular systems can be constructed with POSS units as either main chain (bead), side chain (pendant), or chain terminus groups. The preparation and polymerization chemistry for bead and pendant POSS macromers are described. The properties of the resulting polymers are discussed with respect to the overall polymer composition and architecture. Implications of the macromers as novel polymer hard blocks, polymer additives, and as non-network hybrid materials are discussed.

Key Words: *polyhedral oligomeric silsesquioxanes, linear silsesquioxane-based polymers, hybrid materials, POSS macromers, inorganic building blocks*

INTRODUCTION

The use of inorganic polyhedra as molecular building blocks for the rational design of materials is an attractive and challenging avenue

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Comments Inorg. Chem.
1995, Vol. 17, No. 2, pp. 115–130
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Printed in Malaysia

for the materials chemist. Polymerization reactions which incorporate inorganic polyhedra into polymeric form provide versatile alternative routes toward the synthesis of new inorganic and polymeric hybrid systems. Polymerizable inorganic polyhedra may also be useful for the modification of conventional hydrocarbon-based polymers.

The use of carboranes in polymerization reactions with various siloxane and acetylenic comonomers is an example where polymerizable inorganic clusters (building blocks) have been used successfully to prepare linear organic–inorganic (hybrid) polymeric systems with desirable engineering properties.[1] This cluster or "building block" approach is paralleled in organic systems by the incorporation of cubanes[2] and fullerenes[3] into various linear polymers and extended networks.

The development of additional cluster-based systems amenable to a broad range of materials applications would be of considerable interest given the continuing demand for new or retrofitted materials with enhanced properties. One class of compounds potentially suited for such development is polyhedral oligomeric silsesquioxanes (POSS). A surge of recent activity in this field has been directed primarily toward the application of POSS compounds in catalysis,[4] as nonchelating ligands,[5] as precursors to silica surfaces and interfaces,[6] as precursors to silicates,[7] and as polymerizable reagents.[8–11] We have undertaken studies aimed at the synthesis of classes of POSS molecules that are amenable to standard polymerization and grafting reactions and have subsequently begun exploration of their materials chemistry.

POSS MACROMERS

Polyhedral oligomeric silsesquioxanes are compounds with the generic formula $(RSiO_{1.5})_n$ where R = various hydrocarbons and $n = 6, 8, 10$, or higher.[12] The silicon–oxygen framework in POSS molecules generally contains multiple ring structures in which each silicon atom is bound to one organic group and three oxygen atoms to form a fully condensed polycyclic structure (Fig. 1).[13]

In general fully condensed POSS systems contain equivalent organic groups on each silicon atom, rendering them either completely functionalized with nonreactive groups, such as the cyclohex-

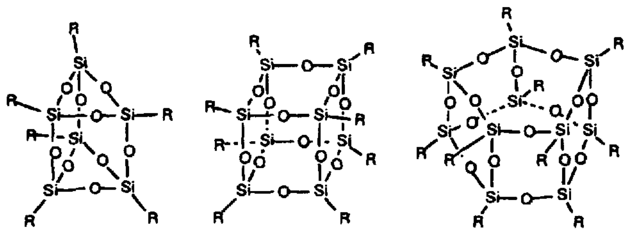

R_6T_6 R_8T_8 $R_{10}T_{10}$

FIGURE 1 Examples of fully condensed POSS systems.

yls in Cy_8T_8, or fully functionalized with reactive groups, such as the hydrides in the case of H_8T_8.

POSS systems containing incompletely condensed silicon–oxygen frameworks are also known; however, they are rarer by comparison. In addition to containing equivalent organic functionalities on each silicon atom making up the POSS silicon–oxygen framework, the incompletely condensed frameworks also contain reactive silanol functionalities. The reactivity of the silanol groups makes the incompletely condensed POSS systems (Fig. 2) of interest as models for silica supported catalysis[4] and as precursors to new families of graftable or polymerizable macromers that are useful as polymer additives and for the preparation of linear POSS-based polymeric systems.[8]

Synthetic methods which afford the preparation and isolation of both completely and incompletely condensed POSS molecules rely upon the manipulation of a variety of empirical reaction variables.

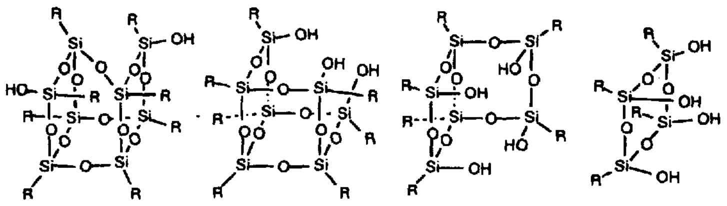

$R_8T_4D_2(OH)_2$ $R_7T_4D_3(OH)_3$ $R_8T_2D_4(OH)_4$ $R_4D_4(OH)_4$

FIGURE 2 Examples of incompletely condensed POSS systems.

The ability to selectively and rationally prepare POSS systems in a manner that affords strict control over their structure, functionality, and yield is still beyond the capability of current synthetic inorganic chemistry. For example, synthetically useful quantities of fully condensed hydride functionalized compounds (such as H_8T_8, $H_{10}T_{10}$)[9,14] and incompletely condensed POSS compounds (such as $(c\text{-}C_6H_{11})_7T_4D_3(OH)_3$ and $(c\text{-}C_6H_{11})_8T_6D_2(OH)_2$)[15] are produced in variable yields and require isolation from complex product mixtures that result from the batch hydrolysis of alkyl trichlorosilanes. Subsequent isolation and purification steps are also required, which further extends what may already be a lengthy production process.[15,16]

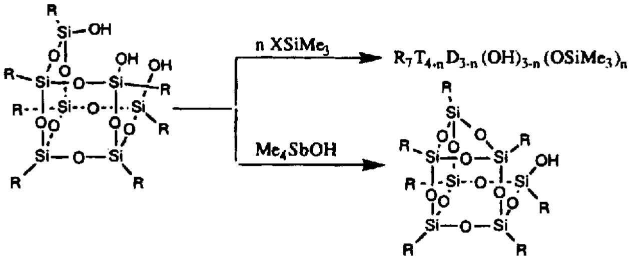
Secondary manipulations of the structure and functionality of POSS systems are also limited. Only transformations of groups attached to the silicon atoms within fully condensed POSS frameworks have been reported. These have primarily involved standard organic manipulations such as hydrogenation, chlorination, hydrosilation, esterification, acylation, epoxidation, etc. These transformations generally occur in high yield and with retention of the POSS structure (Eqs. (1) and (2)).[7,9,10,17] Selective framework manipulations in fully condensed POSS systems have not yet been reported.

$$H_8T_8 \xrightarrow[CCl_4]{Cl_2,\ h\nu} Cl_8T_8 \qquad (1)$$

$$(HOCH_2C_6H_5)_8T_8 \xrightarrow[\text{THF/pyridine}]{MeCOCl} (H_3CCO_2CH_2C_6H_5)_8T_8 \qquad (2)$$

Investigations into the chemistry of incompletely condensed POSS systems have focused on reactions of the silanol groups. Toward the synthesis of new classes of polymerizable monomers, the goal of this chemistry has been to reduce the polysilanol functionality of these systems to one or two.[18] POSS molecules with only one or two reactive functionalities are desirable for the preparation of linear POSS-based polymers and hybrid materials.

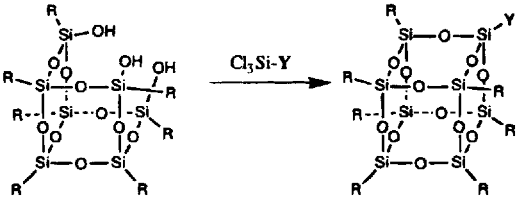
The trisilanol functionality of the $R_7T_4D_3(OH)_3$ structure shown in Fig. 2 can be fully or partially reduced through stoichiometric reactions with silanes such as $XSiMe_3$ where $X = Cl, NMe_2$ (Eq. (3)).[15b] Reactions of $R_7T_4D_3(OH)_3$ with bases capable of forming stabilized heterosiloxide bonds can promote shrinkage of POSS frameworks while also reducing the number of silanol groups (Eq. (4)).[15b,19]



(3)

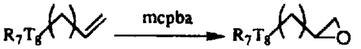
(4)

Alternatively, a method for controlling functionality and for manipulation of the silicon–oxygen framework involves corner capping POSS trisilanols with various silane coupling agents to produce fully condensed T_8 POSS compounds.[15b,20,21]



$R_7T_4D_3(OH)_3$ R_7T_8Y (5)

Through variation of the Y group on the silane, a variety of functionalities can be placed off the corner of the POSS framework (see Table I). Subsequent transformations of this group can be carried out until the desired functionality has been obtained. An example of such a modification is shown below and involves the conversion of a POSS-α-olefin into a POSS-α-epoxide after treatment with *m*-chloro-perbenzoic acid (mcpba).[21b]

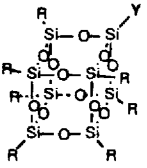


(6)

The corner capping reaction appears to be the most general and synthetically useful chemical manipulation of the silicon–oxygen framework for this incompletely condensed POSS structure. The isolated yields from these corner capping reactions average around 90% or greater when moisture is excluded from the system.

TABLE I

Partial listing of POSS R_7T_8Y molecules and reactive functionalities.

R_7T_8-Y	Y Functionalities	
 R = c-C_7H_{13} c-C_6H_{11} c-C_5H_9	silanol silane acrylic olefin epoxide	halide alcohol amine isocyanate acid/acid chloride

Improvements in the synthetic methods currently used for the preparation of POSS systems are necessary before the commercial development of these macromers and polymers can be realized. Development of synthetic routes to related polyhedral building blocks (ideally based on metallic oxides, carbides, or nitrides) are of additional interest as potential new classes of polymerizable macromers.[22]

POSS MACROMERS: "BUILDING BLOCKS TO LINEAR POLYMERS"

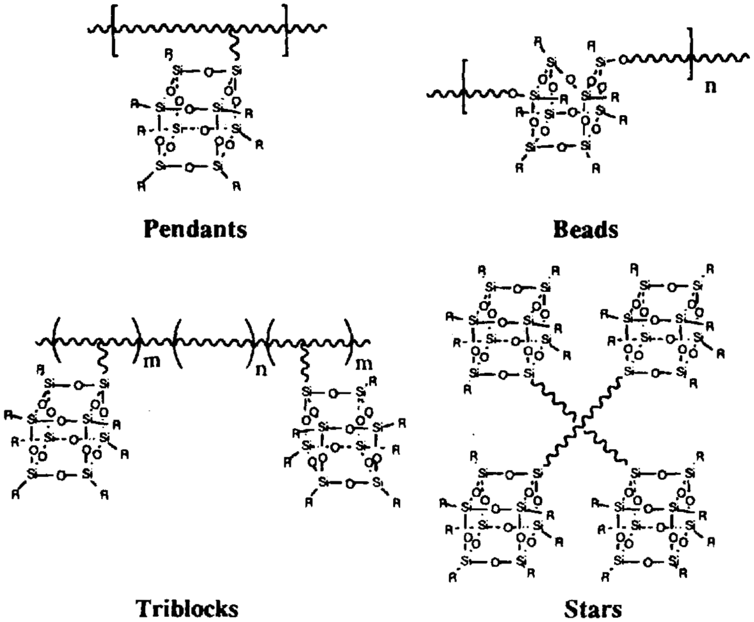
Chemically and structurally well-defined POSS macromers can be used as polymer additives or for the preparation of linear polymeric silsesquioxane-based systems.[8,21,23] The discrete structure of the POSS components in such materials enables the establishment of property relationships based on chain structure and composition. This is in contrast to that previously reported for polysilsesquioxanes for which absolute knowledge of polymeric structure is largely unknown and highly dependent on the silane reagents, reaction conditions, and degree of polymerization.[24]

In general four structural types can be envisioned for linear POSS-based polymers. These are referred to as pendant, bead, triblock, and star architectures (Fig. 3). A fifth, ladder type structure, based on two parallel polymer chains containing POSS groups as crosslinks between them (as rungs of the ladder), is also conceivable but will not be considered here.

The ability to selectively vary the polymer architecture in POSS systems enables additional control over properties and enables investigation of the role that polymer structure can play in cluster-based polymeric materials.

The linear architectures described permit the formation of a single chain structure which comprises the backbone of the polymer. This is in contrast to the ladder/polycyclic structures previously proposed for polysilsesquioxanes[24] which are composed of at least two polymer backbones (or chains) and may contain covalent crosslinks between adjacent chains (a network structure).

Significant property differences are expected between the various linear POSS-based architectures and in comparison to the polysilses-



Pendants

Beads

Triblocks

Stars

FIGURE 3 Architectures of linear POSS-based polymers.

quioxanes (Fig. 4). It is further envisioned that control of properties in POSS-based systems can be achieved in a manner similar to that used for organic-based materials, namely, through variation of polymer composition, molecular weight, tertiary structure, and processing.[25]

The POSS component in linear systems is anticipated to behave similarly to that of a conventional hard block in hydrocarbon-based polymers.[26] Through variation of the amount of hard block and soft block incorporated into a particular copolymer, physical properties such as thermoplasticity and elasticity should be attainable in POSS-based polymers. The rigidity and mass of the POSS segment is also expected to reduce intra- and intermolecular chain motions. This is in part supported by the fact that the physical size of a $(c\text{-}C_6H_{11})_8T_8$ POSS molecule is on the order of 15 Å with an approximate equivalent weight of 1000 amu.

POSS Polymer Synthesis

Depending on the type of functionality contained on the POSS macromer and on the desired polymer architecture, macromolecular systems can be constructed which contain POSS molecules as either main chain, side chain, or chain terminus groups. POSS macromers such as those shown in Fig. 5 are highly soluble in common solvents (toluene, tetrahydrofuran, chloroform, etc.) and are readily polymerized or grafted using established methods for these functional groups.

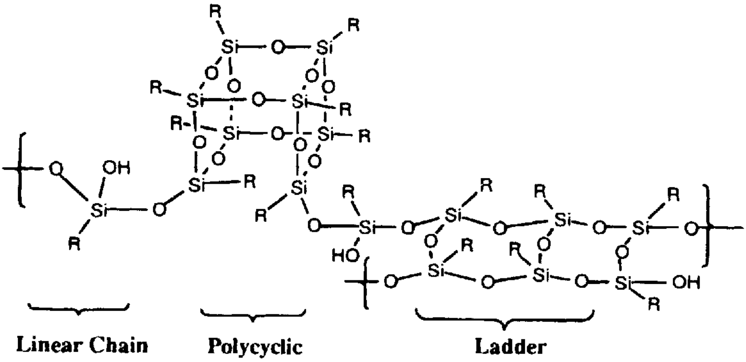
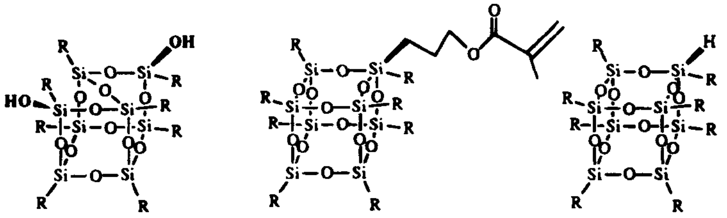


FIGURE 4 Generalized structure for polysilsesquioxanes.



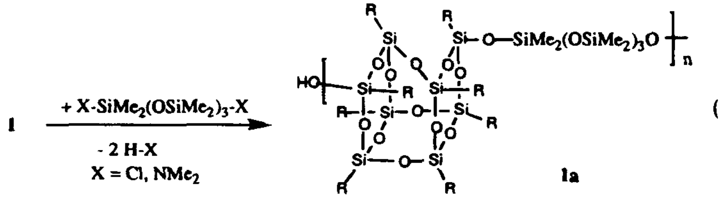
R= c-C_6H_{11}
1
"Bead Type"

R= c-C_6H_{11}, c-C_5H_9
2a,b
"Pendant Type"

R= c-C_6H_{11}, c-C_5H_9
3a,b
"Pendant Type"

FIGURE 5 Examples of polymerizable and graftable POSS macromers.

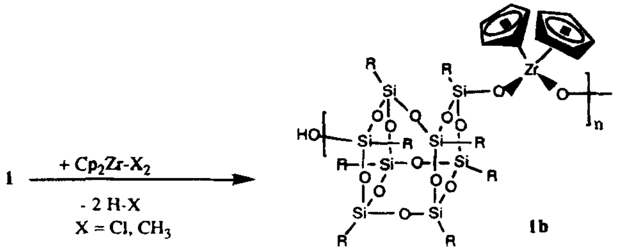
For example, macromer **1** possesses a well-defined structure and composition which includes two reactive hydroxyl groups that can be converted into additional functionalities.[27] The reaction of **1** with a variety of difunctional silane, siloxane, organometallic, and inorganic comonomers affords polymers with discrete silsesquioxane units incorporated into the polymer backbone (Eq. (7)).[8]



(7)

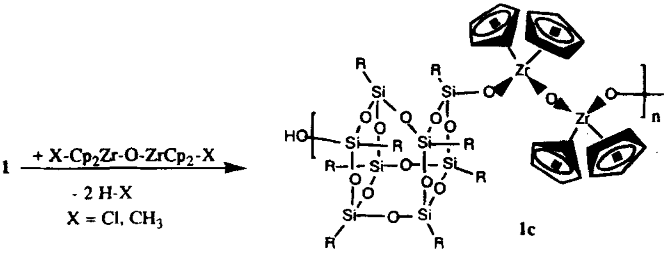
These polymerizations proceed through condensation of the reactive hydroxyl groups on **1** with the functionality on the comonomer. The formation of strong silicon–oxygen bonds in the polymer and loss of reaction byproducts may help drive these polymerizations.

Reactions of **1** with bis-dimethylamino functionalized[8] or with bis-ureidosilanes[28] and siloxanes provided highly efficient synthetic routes to POSS-siloxane copolymers. This methodology has also been extended to the synthesis of POSS-based copolymers in which the POSS segments are bridged by various inorganic and organometallic complexes (Eqs. (8) and (9)).[8a] The ability of these metal complexes to expand their coordination spheres may aid in their function as comonomeric reagents. In the case of **1b, c** the strength of the Zr–O bonds likely facilitates the incorporation of these complexes into the resulting polymeric compositions. Surprisingly, **1b** is completely insensitive to hydrolysis. This unusual stability is attributed to congestion about the Si-O-Zr bonds of this POSS–zirconocene copolymer.



1b

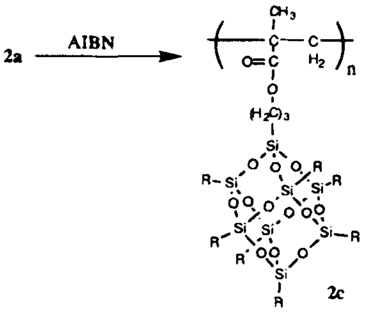
(8)



1c

(9)

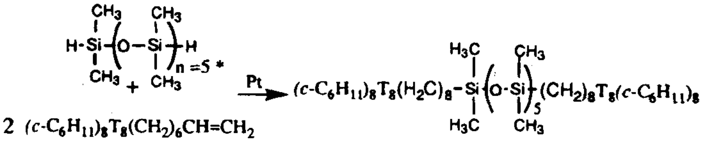
The methacrylate functionality on **2** (Fig. 5) enables these fully condensed T_8 derivatives to be polymerized using standard free radical initiators such as azobisisobutyronitrile (AIBN) (Eq. (10)).[21a] A variety of copolymerizations can also be carried out with **2** to produce a broad range of methacrylic, acrylic, and related compositions.[29]



2c

(10)

In a related approach, reactivity of the silane group on **3** (Fig. 5) allows these POSS molecules to be grafted as pendant or chain terminus groups onto vinyl functionalized polymers and reagents using common hydrosilation catalysts (e.g., Speier's or Karstedt's).[21c] Similar reactions can be carried out with olefin modified POSS compounds (**4**) to provide additional flexibility in the design and synthesis of materials with these graftable POSS macromers (Eq. (11)).



(11)

5

* oligomer average n=5

The reactions of **1–4** and the chemical manipulations mentioned previously, (Eqs. (1)–(11)) demonstrate that POSS compounds can be employed in the same manner as large organic molecules in chemical reactions and in many capacities toward the design of linear polymers.

POSS-Polymer Characterization

The high solubilities of the R_7T_8Y macromers and of POSS-based polymers readily lend them to characterization using solution NMR and GPC methods. These techniques provide information relating to structure, composition, sequence, and molecular weight. The high symmetry of POSS molecules enables structural determinations to be made in a majority of cases from ^{29}Si spectra. Molecular weight determinations for POSS-based polymers can be made from NMR spectra by taking ratios of end and repeat groups. GPC techniques coupled with refractive index and light scattering measurements also provide accurate determinations of number average (M_n) and weight average (M_w) molecular weights. The average M_n value obtained from successive measurements of an individual polymer sample is generally within 20–30% of the value measured by NMR. Excellent reproducibility for M_w ($\pm 6\%$) values have been observed.

POSS-Polymer Properties

While detailed structure–property relationships have only begun to be established for polymeric POSS-based systems,[8] initial studies suggest that POSS segments do in fact behave as (rigid) hard blocks in polymeric systems.

For example, by manipulating the relative amounts of hard and soft segments in a series of POSS–siloxane copolymers (similar to **1a**), control over thermal and mechanical properties was achieved and used to establish thermoplasticity.[8b] It was further found that decreases in the glass transition for POSS–siloxane copolymers correlated to increases in the length of the dimethylsiloxane comonomer segment (soft block).

Mechanical properties for this series were also observed to improve as the length of the comonomer segment was increased. In general the properties were observed to span a range from non-meltable, brittle plastics to flexible thermoplastics. Similar trends have been observed for POSS–methacrylic compositions.[21a,29]

Significant property differences between the various POSS-polymer architectures have also been observed (Table II). For example, while **1a** and **5** contain approximately equivalent weight percentages of dimethylsiloxane block (20%, **1a**; 16%, **5**), the observed melt transitions vary considerably. Contrary to expectations, X-ray diffrac-

TABLE II

Partial properties of POSS macromers and polymers.

Compound	M_w/M_n ($\times 10^3$)	T_g (°C)^a	T_{dec} (°C)^b
1 monomer	1.100/1.100^f	330–350	505
1a	114/28^c	135–175 (114^d)	495
1b	20/14	none	482
1c	20/15	none	514
2a monomer	1.126/1.126^f	355–385^e	416
2c	222/117^g	none	388
3a monomer	1.000/1.000^f	278–288	344
4 monomer	1.110/1.110^f	354 dec	358
5	2.651/2.651^f	242–263^h	375

(a) Visual melt/flow. (b) Represents a 10% mass loss under N_2. (c) Dp = 21. (d) By TMA. (e) Melt/polymerization by TMA. (f) Calculated values. (g) Dp = 104. (h) Crystalline melt.

tion studies on powder samples of **1a-c**, **2c** established their amorphous character while **5** showed significant crystallinity.[30] The glassy character of the POSS bead and pendant polymers (**1a-b**, **2c**) is somewhat surprising considering they are primarily composed of the highly crystalline POSS macromers.[30] The amorphous character of **1a-c**, **2c** is, however, consistent with what has been reported previously for polysilsesquioxanes (Fig. 4).[24a–d,f] The glassy nature of bead and pendant POSS polymers is thought to result either from a reduced mobility of these polymer chains or from the amorphous nature of the respective polymer backbones of which the POSS groups are a component.

Unlike polymeric hydrocarbons POSS-based polymers typically possess very high decomposition temperatures (Table II) and are very resistant to combustion. This property is thought to be associated with the preceramic nature of the silsesquioxane component, which forms a glassy layer of SiO_xC_y during pyrolysis, that may prevent or retard the diffusion of oxygen through the surface char.

POSS-based polymers can be processed into a variety of forms, including fibers, films, foams and monolithic parts using both solution and melt processing techniques. When processed, they have the appearance of clear transparent plastic with a refractive index near 1.58 and optical cut-off near 250 nm.

NON-NETWORK HYBRID MATERIALS AND POLYMER ADDITIVES

When appropriately functionalized, POSS molecules can be used as conventional organic monomers in copolymerizations to diversify the properties of conventional hydrocarbons. Additionally, the solubility and melt processability of polymeric POSS systems enable them to be blended with polymeric hydrocarbons as well as other inorganic polymers. This offers exciting prospects for property modification of numerous families of hydrocarbon polymers.[23,31] A potential advantage from the incorporation of POSS macromers and polymers into traditional polymeric materials is the enhancement of a material's resistance to combustion as described above. Furthermore, they may also be useful toward improving the resistance of materials to oxidation and degradation.[32]

CONCLUSION

The development of new classes of monomers and polymers based on inorganic polyhedra (like the POSS systems described here) can be used to enhance the development of broad new classes of materials with potential utility to material chemists, scientists, and engineers.

Acknowledgments

We gratefully acknowledge the Air Force Office of Scientific Research, Directorate of Chemistry and Life Sciences for their financial support. We thank Mr. Paul Jones for assistance with thermal analysis, Dr. Kevin Chaffee for assistance with X-ray powder diffraction experiments, Ms. Yoshiko Otonari and Cpt. Rob Mantz for NMR assistance.

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