SILSESQUIOXANES: SYNTHESIS, REACTIVITY AND APPLICATIONS IN MATERIALS CHEMISTRY

Abstract

The study of the chemistry of silsesquioxanes comprising Si–O bonds has been primarily applied in field of inorganic silica and organosiloxane in which the repeating $RSiO_{1.5}$ unit governs. Silsesquioxane has various benefits such as thermal, chemical stability and optical transparency from inorganic silica and solubility, ease of functionalization of organic groups to achieve the desired properties, ease of processing, less toxicity and biocompatibility from organosiloxanes. Silsesquioxanes are typically subdivided into two classes such as completely condensed silsesquioxanes and incompletely condensed silsesquioxanes. Polyhedral oligomeric silsesquioxanes are nanoscale building blocks that have been employed in template-free methods leading to the development of hybrid materials through "bottom-up" approaches. The construction of hierarchical structures by that unique functionalization followed by self-assembling of POSS molecules performs a significant role in materials chemistry. Hierarchical superstructures formed by POSS derivatives can be used in applications related to oil/water separations and flame retardant materials.

Keywords: Silsesquioxanes, Materials chemistry, silanols

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I. INTRODUCTION

The chemistry of silicates, silanes, and silanols has been governed by silica and its minerals, notably the SiO_2 unit, which in turn plays an essential part in the silicone industries. Additionally, silicon-oxygen compounds are exceptional in terms of their chemistry and wide range of accessibility in the form of crystalline silicates, which are made up of $[SiO_4]^{4-}$ tetrahedrons [1]. In addition, siloxane is an organosilicon compound formed by the R_2SiO unit in which R is an organic group. In order to produce this class of siloxanes, silane precursors such as organoalkoxysilanes ($R'_nSi(OR)_{4-n}$) undergo hydrolysis followed by polycondensation reaction of silanols. R' denotes an organic substituent that is unable to be hydrolysed, leading to hybrid materials that contain both an organic and an inorganic portion of the siloxane bridges (–Si–O–Si–) networks.

Following the hydrolysis of silane, a reactive group of silanol has been produced on the exterior of silica, and this group is essential to the chemistry of siloxanes [2-4]. These silanols are categorised into three different silanol types, including isolated (a single silanol group attached to the same silicon atom), vicinal (one silanol group connected to an identical silicon atom and possible hydrogen bonds) and geminal (two silanol groups bound to the same silicon atom) as shown in **Figure 1**. These silanols form linear, cyclic, and spherical variations of polysiloxane as they become condensed [5]. The construction of structurally unique two- and three-dimensional metallasiloxanes is additionally rendered due to the nature of these silanols [6-8]. The siloxane compounds have a structure in which silicon atoms are linked to one another by oxygen atoms, with each silicon atom owning a single half-share in each oxygen atom due to the connection between each oxygen atom and two silicon atoms. The exact structure that forms have the generic formula for an organosiloxane, $R_nSiO_{4-n/2}$, where n=1, 2, and 3, and this unit gives its siloxane structure. The nomenclature of siloxane chemistry is based on organic groups and oxygen atoms bonded to the Si atom. Accordingly, the symbols M (mono-substituted), D (di-substituted), T (tri-substituted), and Q (quaternary or tetra-substituted) are used when Si is attached to one, two, three, and four oxygen atoms respectively, their scientific frameworks are represented by $R_3SiO_{0.5}$, R_2SiO, $RSiO_{1.5,}$ and SiO_4 (**Figure 2**) [6-12].

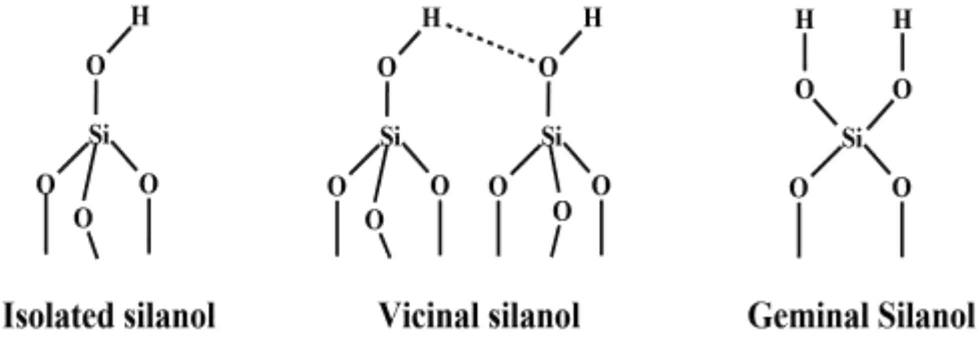


Figure 1: Different types of silanols

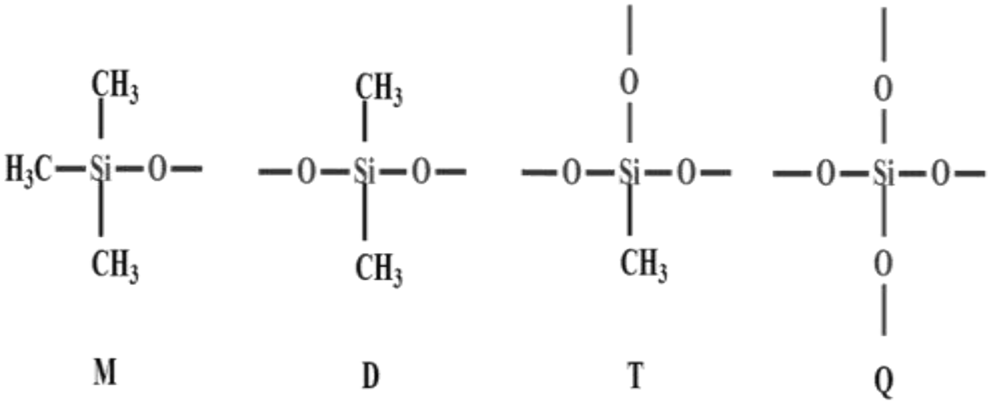


Figure 2: Basic siloxane structural units

II. HISTORY OF SILSESQUIOXANES

Silsesquioxane, one of the siloxane compound, was first discovered in 1946 by Scott as the product represented by $(CH_3SiO_{1.5})n$ from the thermolysis of the polymeric products obtained from hydrolysis of methyltrichlorosilane [13]. Generally, trifunctional silane precursors were used in synthesizing the silsesquioxane frameworks. Barry *et. al.* discovered the molecular structure of many organosilsesquioxanes in 1955 using single-crystal X-ray diffraction techniques. They were the initial experiments to demonstrate how completely condensed silsesquioxane molecules take on a cubic or hexagonal prismatic form [14]. The following year, Sprung and Guenther used the exact same procedure to develop a compound containing the formula $(CH_3SiO_{1.5})_8OSiCH_3(OC_4H_9)$ [15], establishing this area of silicon chemistry. Brown and Vogt proposed a better approach for synthesising completely and partially condensed silsesquioxanes in 1965 [16]. After studying the polycondensation of cyclohexyl trichlorosilane using an acetone/water combination. At the start of their reaction, the predominant outcomes were larger oligomers carrying silanol groups and dimers $[RSi(OH)_2ORSi(OH)_2$, R=cyclohexyl]. In contrast to the completely condensed $R_6Si_6O_9$ without any remaining silanol groups, the cubic shape of incompletely condensed silsesquioxanes trisilanol $(R_7Si_7O_9)(OH)_3$ was generated over a period of time (days to months) [17].

As reported by Barry and Gilkey a few years later, many crystalline silsesquioxane frameworks built upon the formulae $R_6Si_6O_9$, $R_8Si_8O_{12}$, and $R_{12}Si_{12}O_{18}$ can be established from easily accessible organyltrichlorosilanes ($RSiCl_3$ with R = Me, Et, *i*-Pr, *i*-Bu, Cy, Ph) [18-19]. Polyhedral oligomeric silsesquioxanes (POSS) serve as the common name for these completely condensed structures, which are distinguished by cages with well-defined polyhedral geometries (such as cubic or prismatic) [20]. However, the development of POSS and its applications had far less success due to the lack of analytical assistance for chemical characterizations. At the same time, silicone-related experiments were making great progress. Despite three decades of research, the availability of different trifunctional silanes (such as $MeSiCl_3$, $PhSiCl_3$, and vinyl-$SiCl_3$), and the ability to synthesize diverse POSS compounds in virtually quantitative amounts, there have been no significant commercial applications for POSS. Feher *et. al.* described the silsesquioxane chemistry using cyclopentyl and cycloheptyl trichlorosilanes as starting materials in the 1990s. Nevertheless, no completely condensed products were found in this specific instance. Trisilanol $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ is the only product of the hydrolytic polycondensation of cyclopentyl trichlorosilane, which is one of the basic units of silsesquioxane chemistry. Trisilanol was then employed in finding several metal and silsesquioxane-based derivatives, as well as applications in catalysis and materials science [21].

To use POSS-containing polymers as the building blocks for hybrid inorganic/organic materials, Joseph D. Lichtenhan established a research programme at Edwards Air Force Base (California, USA) in the early 1990s. Few years later, Joseph D. Lichtenhan and his colleagues understood the way to scale up the synthetic procedures and rapidly determined several uses for POSS-containing polymers in military applications [22-24]. In the course of their research, they also developed their POSS production skills to a stage where they were able to offer samples of POSS to other researchers who were interested in implementing POSS. Afterward, in the latter part of the 1990s, they departed Edwards Air Force to founding Hybrid Plastics, Inc., a company that is currently known as the market pioneer in POSS production and applications [25]. Since 1985, POSS has served as a new model for the more intricate Si–O and Si–O–M structures in applications of materials science and technology, with the development of the POSS based on their structures and chemical and physical properties. POSS is distinct from other silicon compounds in terms of both structure and characteristics, which makes it special in silicon chemistry [26-27].

III. NOMENCLATURE AND STRUCTURE OF SILSESQUIOXANES

Silsesquioxanes is a class of inorganic-organic hybrid compound in which tetrahedral units of SiO_4 are linked together oligomerically by the Si-O bond to make a cage structure. This cage-like molecule has an internal Si- O core and organic groups around it. The chemical structure of silsesquioxane is based on the basic formula $(RSiO_{1.5})_n$ (n=6, 8, 10, 12...). At the molecular level, the inorganic core-shell hybridized and the peripheral organic groups can be further functionalized as needed [27-30]. The term "silsesquioxane" is derived from the Latin prefix "sesqui," which means "one and a half," and refers to the number of oxygen atoms in each molecular unit. It has the empirical formula $(RSiO_{1.5})_a(H_2O)_{0.5b}$ or, after being reconfigured, $R_aSi_aO_{(1.5a\ 0.5b)}(OH)_b$, where R can be hydrogen or organic functional groups. According to the formula, the numbers a and b are integers (a = 1, 2, 3; b = 0, 1, 2, 3). The number of R groups linked to the Si atom is denoted using the symbol a, whereas the total amount of OH groups are denoted with the symbol b [31, 32]. A small unit of silsesquioxane is indicated by the prefix "oligo" which contains three oxygen atoms and an organic group attached to the Si atom. The architecture of the silsesquioxane is based on the oligomeric linkage of $RSiO_{1.5}$ and their substituents are organized tetrahedrally around the silicon vertices to form an oligo silsesquioxane and the cage structures are created by T (tri-substituted) siloxane unit. Based on the synthesized products of silsesquioxanes can be self-arranged into four different basic structures: Open cage(incompletely condensed silsesquioxanes), closed cage(completely condensed silsesquioxanes), random and ladder silsesquioxanes (**Figure 3**) [33].

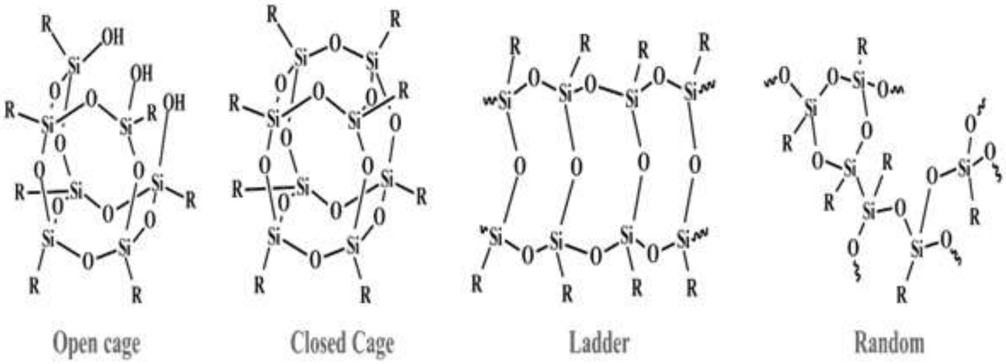


Figure 3: Basic structures of silsesquioxanes

While the enormous research progress on various structures of silsesquioxanes, most attention has particularly been focused on the cage structure. Generally, octahedral silsesquioxanes are represented as a8b0 which is highly stable due to the double four-member ring of Si_4O_4. The fundamental structure of silsesquioxane frameworks is tetrahedral units with silicon bonded to three oxygens and one R-group. Oxygen atoms are able to serve as bridges that connect two silicon atoms comprised of various tetrahedral units. The tiniest particles of silsesquioxane units are known as polyhedral oligomeric silsesquioxane (POSS), which has been named after silsesquioxane structures with completely condensed cages [34]. POSS cages were 1- to 3-nanometer sized 3-D structures with a Si-to-Si distance of 0.5 nm with a predicted R-to-R diagonal range of 1.5 nm. These organic substituents on the POSS outer layer make them compatible with solubility and chemical reactions. The rigidity and heat capacity of POSS compounds improve their mechanical and thermal properties. Each functional group is located in its own octant, orthogonal to one another in three dimensions (**Figure 4**) [35-37].

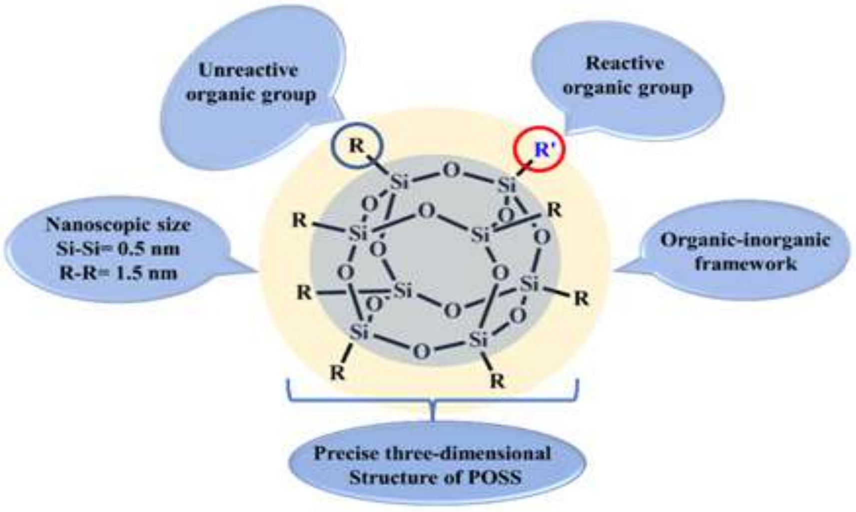


Figure 4: Architecture of silsesquioxane

IV. TYPES OF SILSESQUIOXANES

In accordance with the general formula mentioned above, wherein ($b=0$ or $b\neq 0$), silsesquioxanes are classified into two distinct categories: 1. Completely condensed silsesquioxanes and 2. Incompletely condensed silsesquioxanes.

1. **Completely Condensed Silsesquioxanes (anb0):** All of the Si-O linkages at each of the molecule vertices are present in these completely condensed silsesquioxanes. These entirely condensed structures are enclosing cages, such as cubic and prismatic structures, with a predetermined geometry. Additionally, their organic substituents are attached to the silicon vertices compared to the relative stabilities of the various completely condensed silsesquioxanes structures. The Si-O-Si symmetry ring is essential for the framework's cage-like structure. a6b0, a6b0, a10b0, and a12b0 are completely condensed cages based on the Si-O ring that will form when the RSiO units are connected together (**Figure 5**) [38-40].

   The dominant driver in silsesquioxane chemistry is the a8b0 cage structure out of these completely condensed compounds. In this case, the smallest tetrahedral silsesquioxane units are oligomerized to produce polyhedral structures, called polyhedral oligomeric silsesquioxane (POSS) when these silsesquioxanes form structurally completely condensed cages. The Si_4O_4 ring in a8b0 has features that include numerous Si-O-Si rings connected in a proven 3-D molecular skeleton, and these molecules are also known as spherosiloxanes since their polyhedral assemblies are topologically equivalent to a sphere [41]. This is a consequence of the Si_4O_4 ring's durability. The many different POSS geometries precisely define an inorganic-organic hybrid framework with an inorganic silicon and oxygen $(SiO_{1.5})_8$ core surrounded by organic groups [42].

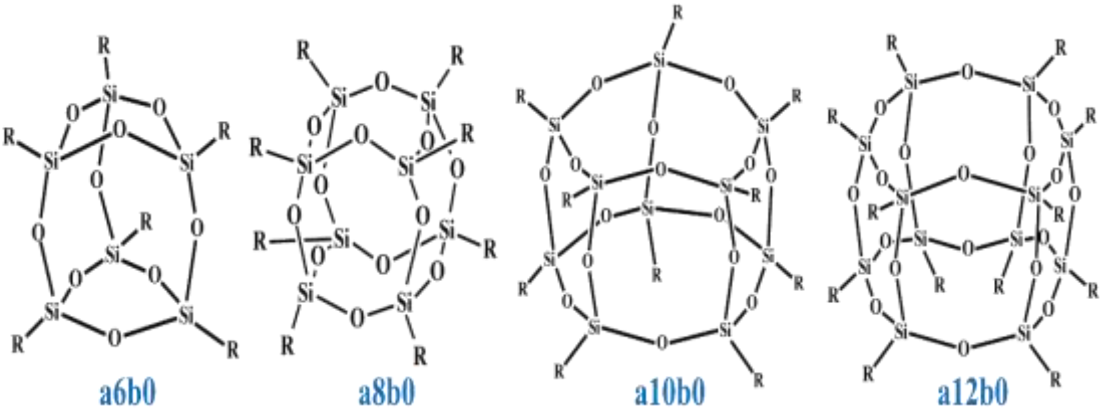
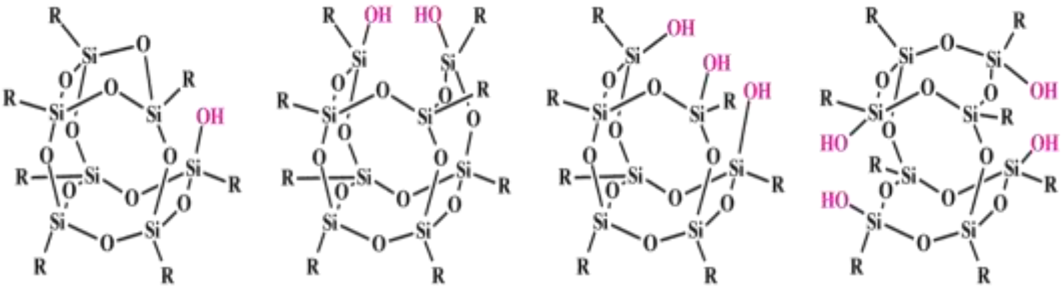

a6b0 a8b0 a10b0 a12b0

Figure 5: Completely condensed silsesquioxanes

2. **Incompletely Condensed Silsesquioxanes (anbn):** Tetrahedral units with an R-group, three oxygen atoms, and one silicon atom attached form the structural basis of silsesquioxane frameworks. All oxygen acts as a bridging atom between two tetrahedral units in the case of completely condensed formations [43]. The Si□O□Si bonds formed here, however, do not entirely use the oxygen involved for bridging in the types of incompletely condensed silsesquioxane, and some of the Si–OH groups are present in these type components as shown in **Figure 6**.



a7b1 a8b2 a7b3 a8b4

Figure 6: Incompletely condensed silsesquioxanes

Additionally, incompletely condensed silsesquioxane containing silanol is a versatile precursor for mono, di, and tri-substituted POSS and metal silsesquioxane. Its fascinating promise as ligands in homogeneous analogues of silica-supported catalysts, analogues for hydroxylated silica surfaces, and components of structure for the systematic development of geometrically well-defined Si-O-M clusters has additionally been developed [44].

V. SYNTHESIS OF SILSESQUIOXANES

The preferred and frequently employed synthetic process for synthesizing oligomeric silsesquioxanes involves the hydrolytic condensation of monosilane $RSiX_3$ (where R is H or an organic group and X = Cl, OMe, OEt...) [45-47]. There are two steps in the reaction: The monosilane first undergoes hydrolysis to produce the equivalent trisilanol, $RSi(OH)_3$. Typically, the first step response happens extremely quickly. The second step involves the trisilanol molecules partially or completely condensing, which might result in various silsesquioxane species (**Scheme 1**).

Several intermediates are created throughout the condensation reactions. **Figure 7** shows the proposed mechanism of development of the silsesquioxane in the form of incomplete and complete cages *via* hydrolysis of monosilane followed by condensation reaction. Several factors can influence this hydrolytic condensation reaction, including the nature of the organic group (R), the nature of the reactive group (X), the concentration of the starting precursor monosilane $RSiX_3$, the amount as well as the rate of water addition, the reaction of the solvent, the temperature of the reaction, reaction the pH level, and reaction time [48-51].

Hydrolysis of Monosilane

$$RSiX_3 + 3H_2O \longrightarrow RSi(OH)_3 + 3HX$$

Condensation of Trisilanol

$$aRSi(OH)_3 \rightleftharpoons (RSiO_{1.5})_a(H_2O)_{0.5b} + (1.5a - 0.5b)H_2O$$

Scheme 1: Hydrolytic condensation reactions of monosilane

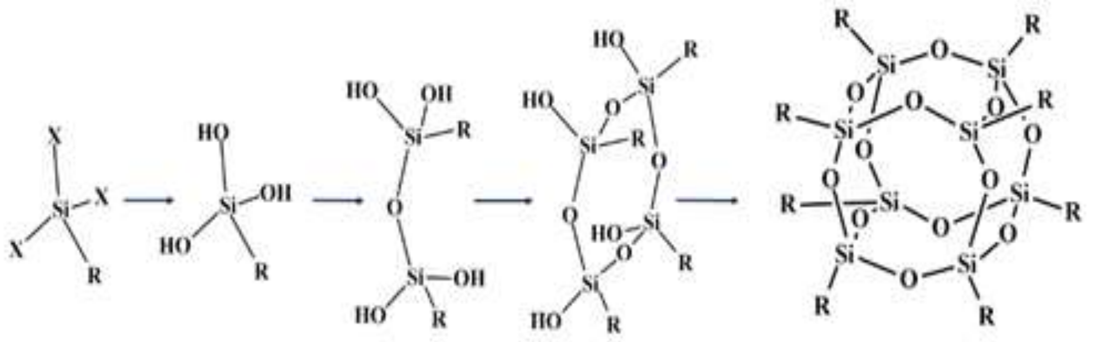


Figure 7: Proposed mechanism for hydrolytic condensation reactions

VI. CHARACTERIZATIONS

1. **Nuclear Magnetic Resonance (NMR) Spectroscopy:** NMR techniques are suitable for investigating a minimum of three types of nuclei in silsesquioxane structures: ^{1}H, ^{13}C, and ^{29}Si. Each of these three NMR spectra has valuable data for silsesquioxane species characterization. Incompletely condensed silsesquioxanes are analyzed using ^{1}H NMR spectroscopy to count the silanol groups present and determine whether they are hydrogen bound to other silanol groups and also provide structural proton of the aryl and alkyl from the organic groups of silsesquioxane cage. The most effective method for characterizing silsesquioxanes is ^{29}Si NMR spectroscopy.

   The ^{29}Si NMR spectrum of a silsesquioxane reveals the details of the framework's symmetry and how its symmetry and environment of Si atoms. For example, the a7b3 silsesquioxane (c-$C_6H_{11})_7Si_7O_9(OH)_3$) ^{29}Si NMR spectrum shows three distinct peaks with integral ratios of 3:1:3, which is consistent with the molecule's C3v symmetry. These peaks contain silanol groups; peaks at lower shifts (-68/-70 ppm) are created by Si atoms that are largely connected to other Si atoms *via* oxygen bridges, whilst peaks at higher shifts (about -60 ppm) are triggered by Si atoms that are bound to an OH group. In addition, the kind of R-group attached to the silicon influences peak position, but the gap between peaks from silicons with a variety of OH groups is essentially consistent (10 ppm per OH group). For instance, silsesquioxane (c-$C_6H_{11})_6Si_6O_9$ produced a single peak at -56 ppm when it was completely condensed, but (c-$C_6H_{11})_8Si_8O_{12}$ produced a single peak at -69 ppm when it was less strained [52].

2. **Mass Spectrometry:** The identification of unknown silsesquioxane structures and the investigation of the type of species produced during silsesquioxane synthesis are both made possible by mass spectrometry (MS) [53,54]. A range of ionization methodologies, comprising electro-spray ionization (ESI), the pressure of air chemically ionization (APCI), turbo ion-spray (TISP), as well as matrix-assisted laser desorption ionization (MALDI), could be used for the study [55-57].

3. **Fourier Transform Infrared (FT-IR) Spectroscopy:** Many different vibrations are capable of being observed in the IR spectrum of silsesquioxanes, such as the Si-O-Si asymmetric stretches at 1100-1140 cm^{-1} or 1057-1085 cm^{-1} in the context of strained geometry [58,59] as well as the silicon-oxygen framework's deformational vibrations,

ranging between the 360 and 600 cm^{-1}. The chemical composition of the R-group has an enormous impact on the nature of Si-R vibrations.

For example, silsesquioxanes with a hydrogen atom as the R-group exhibit a typical Si-H stretching mode in the range of 2100 to 2300 cm^{-1}, whereas the O-Si-H bending vibration occurs in the range around 800 to 900 cm^{-1}. In the vicinity of 3600 cm^{-1}, incompletely condensed silsesquioxanes may exhibit a sharp band caused by free Si–OH, whereas hydrogen-bound silanol species are predicted to exhibit a broader band at lower wavenumber [60,61].

4. **Single Crystal X-Ray Diffraction:** Single crystal X-ray diffraction is widely used for identifying the structure of silsesquioxanes. The main limitation regarding the technique's application is the sometimes-challenging crystallization of silsesquioxanes. Considering this practical disadvantage, many silsesquioxane structures have crystallographic data that can be used to provide accurate data about the lengths of Si–O and angles of Si–O–Si bonds. The crystal structures of POSS compounds can be very well analyzed using X-ray diffraction, the Si–O bond length in POSS ranges from 1.60-1.63 Å and the Si–O–Si bond lengths from 3.05-3.2 Å [62,63].

VII. PROPERTIES OF SILSESQUIOXANES

While the enormous research progress on various structures of silsesquioxanes, most attention has particularly been focused on the cage structure. Generally, cubic silsesquioxanes are represented as a8b0 which is highly stable due to the double four-member ring of Si_4O_4 [64]. As a result, inorganic-organic hybrid molecules seen in **Figure 8** are correctly represented by the POSS's precise structures. Higher thermal stability is provided by its high stiffness, Si–O–Si inorganic core, and chemical inertness. These organic substituents on the POSS outer layer make them compatible with solubility and chemical reactions. POSS does not produce volatile components as byproducts, making them odorless and environmentally beneficial in contrast to conventional organic compounds. Additionally, POSS substituents are designable, making them a flexible building block for a range of applications [65,66].

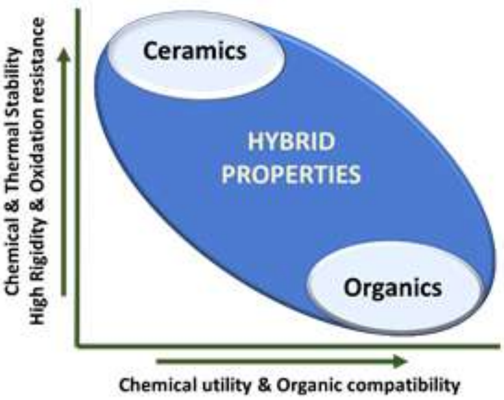


Figure 8: Comparison graph illustrating the characteristics of organic-inorganic hybrid property of POSS

VIII. REACTIONS OF SILSESQUIOXANES

1. **Reactions of Completely Condensed Silsesquioxanes:** In answer to the requirement for POSS derivatives, POSS containing a diverse spectrum of reactive and inert substituents were developed. POSS derivatives are produced *via* a reaction of completely condensed POSS substituted with H, alkyl, and aryl groups, which opens up a wide area of research in hybrid materials. Several organic functional groups, including alcohols, esters, phenols, epoxides, alkoxysilanes, styrene, fluoroalkyls, chlorosilanes, halides, etc., are present on the siloxane cages [67]. **Figure 9** shows architectures of the non-functional, mono, and octa-functional substituted polyhedral oligomeric silsesquioxanes, and these are used to develop new POSS materials *via* covalent and non-covalent interactions (**Table 1**) [68].

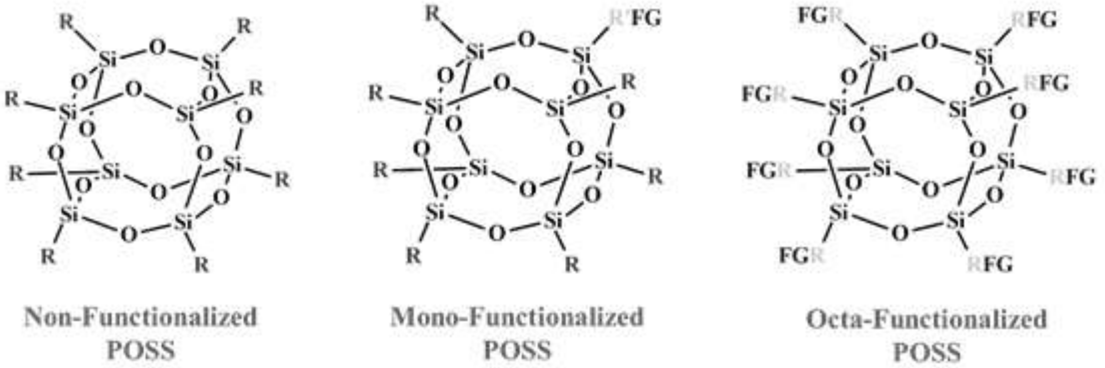

Non-Functionalized POSS
Mono-Functionalized POSS
Octa-Functionalized POSS

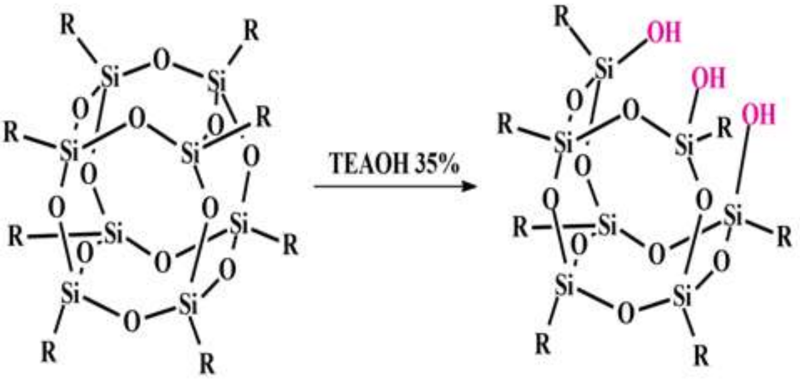
Figure 9: Non-functional and Functional substituted polyhedral oligomeric silsesquioxanes

Table 1: Non, Mono, and Octa functional POSS

S. No	Non-Functionalized POSS		Mono-Functionalized POSS		Octa-Functionalized POSS	
	Compounds	R	Compounds	R & R'FG	Compounds	R'FG
1	$(Ph)_8POSS$	R-phenyl	*i*-BuPOSS-$(CH_2)_3NH_2$	R-*i*-Bu R'-$CH_2)_3NH_2$	$POSS(C_2H_3)_8$	$CH=CH_2$
2	$(CH_3CH_2CH_2)_8POSS$	R-n-propyl	*i*-BuPOSS-$(CH_2)_3SH$	R-*i*-Bu R'-$(CH_2)_3SH$	$POSS[(CH_2)_3NH_2]_8$	$(CH_2)_3NH_2$
3	$(CH_3)_8POSS$	R-CH_3	Ph-POSS-$(CH_2)_3NH_2$	R-Ph R'-$CH_2)_3NH_2$	$POSS[(CH_2)_3Cl]_8$	$(CH_2)_3Cl$
4	$(C_6H_{11})_8POSS$	R-c-C_6H_{11}	c-C_6H_{11}POSS-H	R- c-C_6H_{11} R'-H	$POSS(C_6H_4NH_2)_8$	$C_6H_4NH_2$
5	$(C_2H_5)_8POSS$	R- C_2H_5	*i*-Bu-POSS-$C_6H_4NH_2$	R-*i*-Bu R'- $C_6H_4NH_2$	$POSS(OSiMe_2H)_8$	$OSiMe_2H$
6	(-*c*-$C_5H_9)_8$POSS	R-*c*-C_5H_9	*i*-Bu-POSS C_2H_3	R-*i*-Bu R'-CH=CH_2	$POSS(C_6H_5COOH)_8$	COOH
7	(*i*-Bu)$_8$POSS	R-*i*-Bu	(-*c*-$C_5H_9)_8$POSS-$(CH_2)_3Cl$	R-*c*-C_5H_9 R'-$(CH_2)_3Cl$	$POSS[(CH_2)_3SH]_8$	$(CH_2)_3SH$
8	(*i*-Octyl)$_8$POSS	R-*i*-Octyl	(-*c*-$C_5H_9)_8$POSS-$(CH_2)_3NH_2$	R-*c*-C_5H_9 R'-$CH_2)_3NH_2$	$\{POSS[(CH_2)_3NH_3]_8\}Cl_8$	$(CH_2)_3NH_3^+Cl^-$

2. **Building Blocks for Self-assembly:** The most significant feature of POSS is its capacity to functionalize the silicon edge alongwith an extensive number of organic groups, which permits bottom-up approach for building nanocomposites that have different architecture and fulfilling the efficiency necessities of the materials in various purposes. Lamellar and micelle structures are the most typical architecture of self-assembly of POSS based nanocomposite [69-71].

3. **Cleavage of Si–O–Si Bonds :** On the other hand, Si–O–Si bonds in fully condensed structures are cleaved in corner-cleavage reactions (**Scheme 2**). The process of cleaving widely available POSS ($R_8Si_8O_{12}$) by reacting it with a potent acid (HBF_4/BF_3, CF_3SO_3H, or CH_3SO_3H) or a base Et_4NOH, TEAOH to produce several incompletely condensed silsesquioxanes [72,73].



Scheme 2: Corner-cleavage reaction

4. **Reactions of Incompletely Condensed Silsesquioxanes :** Because of the presence of silanol groups, the incompletely condensed silsesquioxanes are effective solubility alternatives for both silica and silicate-based surfaces of materials [74]. With a large silicon-oxygen framework, these silsesquioxanes should have adequate similarities in electronic properties of silica. The silanol group that are capable of reacting strongly with alkoxy or halo silane in order to produce both completely and incompletely condensed silsesquioxanes, with various structural isomers [75,76].

5. **Corner Capping Reactions:** The corner capping reaction is a simple method to generate a wide range of monosubstituted silsesquioxanes with reasonable yields. It involves reacting incompletely condensed a7b3 with a chlorosilane in the presence of a base to produce completely condensed mono-substituted silsesquioxane [77,78]. The vicinal silanols, which enable multidentate coordination with the metal centre, tend to be the best candidates for grafting metal ions. Similarly, trisilanols in a7b3 makes it simple to simulate vicinal silanols. A couple of the groups made up of silanols can react with methyltrichlorosilane [CH_3SiCl_3] to reduce the number of silanol groups that are available to coordinate the metal ions (**Scheme 3**).

Scheme 3: Corner capping reaction

6. Chemistry of Metal-Silsesquioxanes

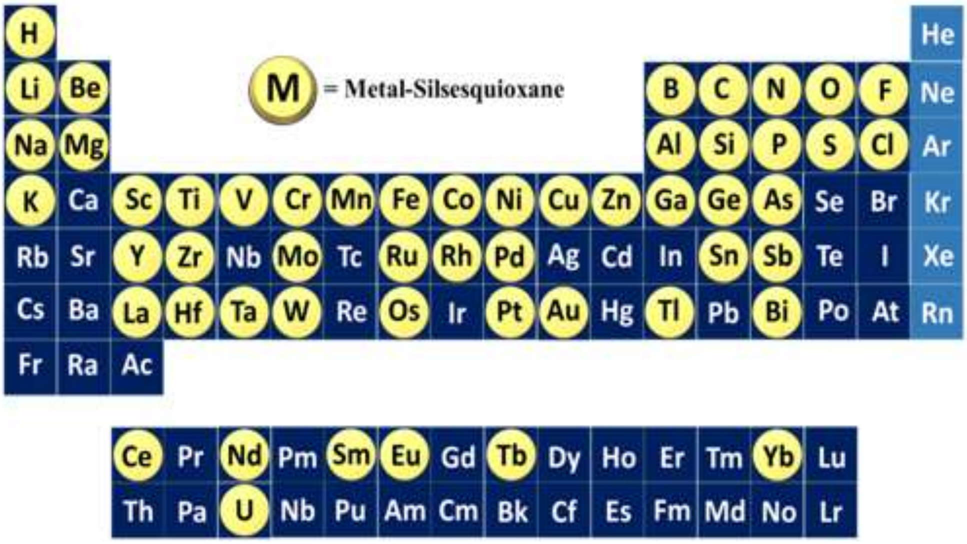


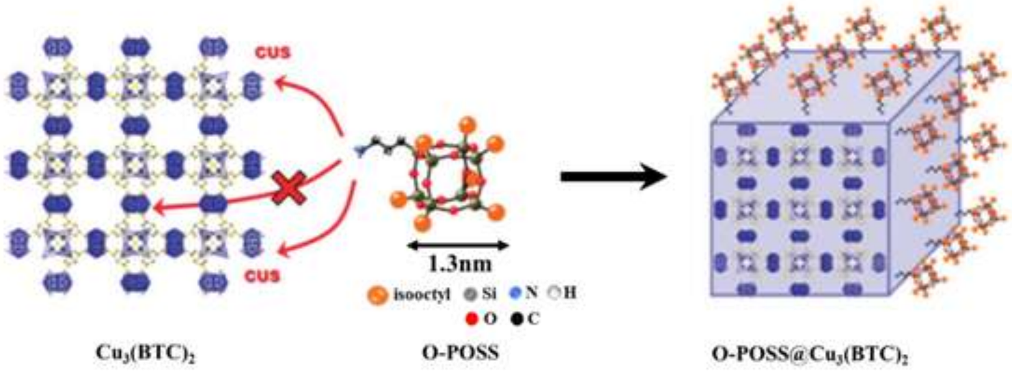
Figure 10: Elements (inside circle) that have been incorporated in silsesquioxane complexes

By the end of the 1980s, Feher *et. al.* explored the usage of silsesquioxane compounds as ligands for the main group and transition-metal compounds [78], proposing silsesquioxanes as prototypes for industrial silica supports. Additionally, the persistent O-Si-O bridges in silsesquioxanes are sufficient to mimic the silica surface and have the potential to interact with a metal centre. Silsesquioxanes are easily silylated to imitate the multiple silanol groups that may be located on a silica surface. Incompletely condensed silsesquioxane including mono, di, or trisilanol are able to be employed as adaptable pioneers for minimizing partially or completely condensed structures with Si–O or Si-O-M scaffolding. A list of the elements that are used in silsesquioxane chemistry is shown in **Figure 10**. The Si –OH containing silsesquioxanes have also been employed to develop hetero- and metal-silsesquioxanes in which a transition metal and main-group metal are incorporated into the silsesquioxane cage [79]. Since the invention of silsesquioxanes, a variety of elements from the entire periodic table have been used in a rich coordination chemistry.

IX. APPLICATIONS OF SILSESQUIOXANES

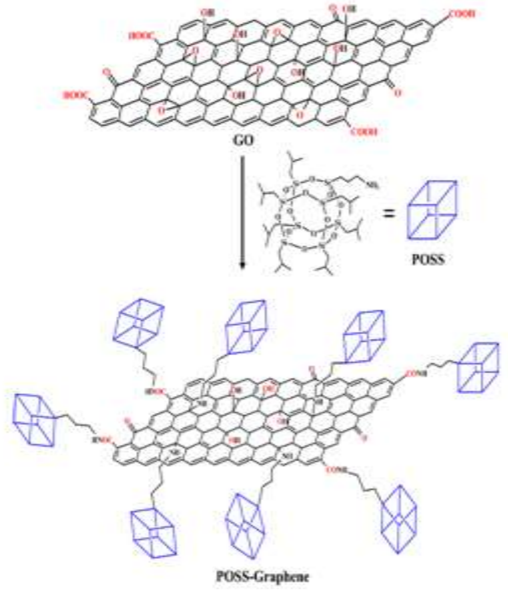
1. **POSS As Sorbent Materials For Absorption and Oil-Water Separation:** The rapid increase in pollution levels in seas and polluted rivers by crude oil, petrochemical byproducts, and toxic organic solvents is turning into a serious global concern that environmental and ecological issues [80,81]. Many conventional approaches such as booming, skimming, absorption, in situ burning, dispersants, and bioremediation have been used to mitigate oil spills from marine bodies and the oil industries to solve this growing problem. Sorption is the most promising approach to water purification. Although prominent absorbents including zeolites, activated carbon, organoclays, and natural fibers have challenges with environmental compatibility, low absorption rates, poor recycling, and other problems. These materials also absorb water in addition to oils which reduces the separation's selectivity and effectiveness. A lotus leaf, a fish scale, and a butterfly wing are examples of bio-inspired surfaces that might serve as inspiration for the need to design exceptionally liquid-repellent surfaces. As improved sorbent materials for oil-water separation, numerous polymers containing hydrophobic surfaces were synthesized and they were coated with cotton fabric, meshes, and foams to build a filter membrane [82]. However, the breakdown or noticeable changes in the intrinsic wettability of polymeric/nanostructures and nanocomposites make the majority of manufactured super wetting surfaces unsustainable [83]. To preserve highly textured structures with continuous chemical compositions for their practical uses, the development of strong and extremely wet surfaces has, up until now, principally concentrated on sustaining highly textured structures. To strengthen the mechanical and chemical resilience of super wetting surfaces, it is strongly advocated to utilize structurally stable and without losing their original nature components to create superhydrophobic hybrid materials [84-86]. Due to the robust silica core and polyfunctionality of the nano-POSS, POSS is a desirable precursor in the creation of hybrid materials with novel and possibly lucrative features. Because of their distinct structures, the organically modified POSS stands to be developed at a low cost and provide a reliable starting point for the synthesis of complex functional materials [87].

   The complementary roles of surface energy and roughness on nonwetting surfaces of fluoroalkyl POSS has led to produce superhydrophobic surfaces, exhibiting superficial contact angles with water more than 150^o and low contact angle hysteresis. Nevertheless, superoleophobic surfaces show contact angles more than 150^o with organic solvents containing significantly lower surface tensions than that of water that are very rare. The re-entrant textures of fluoroalkyl POSS permit for the accessibility of creating really nonwetting surfaces which can preserve the Cassie state with water and several organic solvents. In addition, the re-entrant surface curvature can be employed to plan surfaces which show extremely resistance to wetting from several solvents with low surface tension, comprising decane and octane [88]. Lately, Copper trimesate [$Cu_3(BTC)_2$] has been selectively functionalized using aminopropyl isooctyl POSS to generate a hydrophobic environment around its outer unsaturated copper sites which increases its stability against humidity (**Scheme 4**) [89].



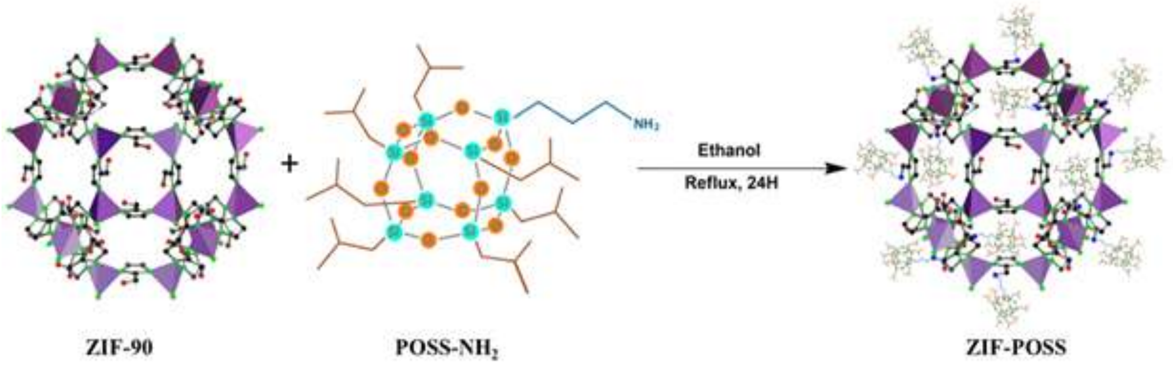
Scheme 4: Schematic of the surface modification of $Cu_3(BTC)_2$ with O-POSS. Reproduced from ref. no. 89. Reprinted with permission from Copyright © 2015 The Royal Society of Chemistry

The newly formed O-POSS@$Cu_3(BTC)_2$ can be employed for applications in the adsorption and separation of gases molecules in the presence of fairly huge amounts of moisture. A POSS-PMMA copolymer was synthesized by free-radical polymerization reaction of methyl methacrylate (MMA) with (propyl methacrylate)$(isobutyl)_7Si_8O_{12}$ (MA-POSS). Smooth fibers of this copolymer exhibited a water contact angle of 165^o with a sliding angle of 6^o. The isobutyl groups on POSS support to reduce the surface free-energy and also, such with increasing remarkable non-wetting functions which is very useful in the growth of aquatic devices for several purposes [90]. POSS-Graphene inorganic-organic hybrid materials were synthesized by condensation reactions of amine functionalized POSS and epoxy and carboxyl groups in graphene oxide via the amide formation by covalently bonding (**Scheme 5**). The superhydrophobic nature of resultant POSS-graphene with air or water contact angles closed to 157° can be employed to generate liquid marbles standing apart on hydrophobic or hydrophilic surfaces as a miniaturized device [91].



Scheme 5: Schematic Representation of the Route to POSS-Modified Graphene

A simple and fluorine-free strategy for constructing a superhydrophobic ZIF-POSS hybrid material was developed through imine bond formation between the free aldehyde-functional group in zeolitic imidazolate frameworks (ZIF-90) and polyhedral oligomeric silsesquioxane containing amine groups (POSS-NH_2) (**Scheme 6**). The resultant ZIF-POSS hybrid material showed a remarkably high-water contact angle of 157° and consequently displayed a high sorption selectivity and best absorbance for organic solvents from the mixture of water-organic solvents. Therefore, ZIF-POSS@PDA@Sponge is effectively exploited for the removal of a sequence of organic solvents from water mixtures with very high separation efficiency of more than 96% over 25 cycles of separation [92].



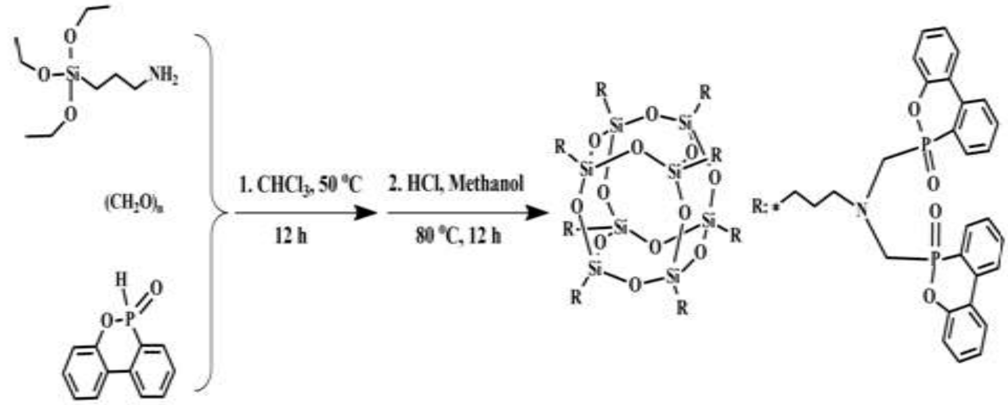
Scheme 6: Synthesis of the ZIF-POSS hybrid material

2. **POSS As Flame Retardant Materials:** Fire safety is a significant feature for consideration in the production of consumer products, buildings construction and infrastructures. Therefore, wide effort has been capitalized in the progress of materials with flame retardant properties for superior safety guarantee against fire threats to the universal community [93]. In literature, Cost-effective ways of manufacturing DOPO and their derivatives have been applied for developing halogen free flame retardants and have certainly facilitated its recent commercial manipulation. In the chemistry of POSS as flame retardant, POSS-bisDOPO compound was synthesized by reaction of aminopropylisobutyl POSS (POSS-NH_2) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and employed as co-additive with tetra-n-butyl titanate.

The UL-94 ratings and LOI value of the EP composite with a loading of 5% POSS-bisDOPO achieved V-0 grade and 31.0%, respectively. The SEM results showed that the residual char of the EP composites produced a honeycombed inner layer and incessant compact outer layer, which was beneficial to generate fruitful physical barrier to avert the penetrating of the high temperature and oxygen [94].

The progress on the growth of a multi elements flame retardant depends mainly on the design and synthesis of flame retardants containing a mixture of elements including Si, P and N. The POSS derivative called octa-(N,N-(bis-(9,10-dihydro-9-oxa-10-phosphaphenanthene-10-yl)methyl) aminopropyl) silsesquioxane (ODMAS) was synthesized through a Kabachnik–Fields reaction followed by hydrolysis condensation using (3-Aminopropyl)triethoxysilane (APTES)), polyoxymethylene(POM) and 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) (**Scheme 7**). ODMAS was homogeneously mixed with epoxy resins, confirming in a completely translucent composite material.

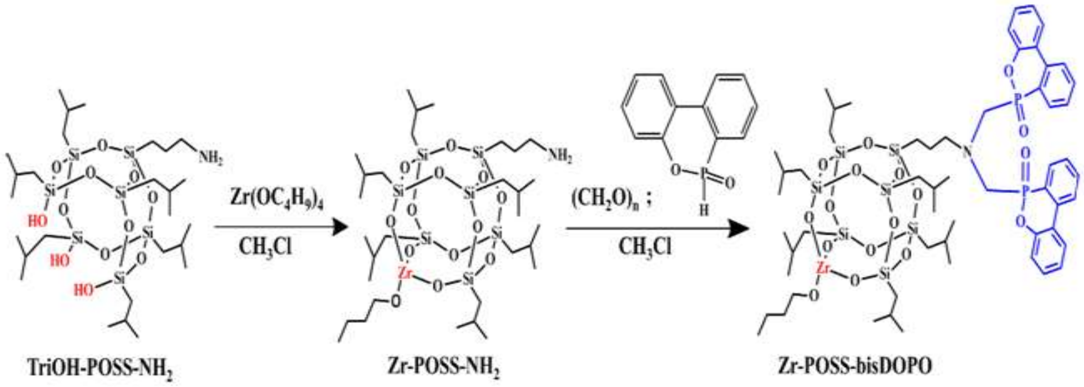
The addition of ODMAS into epoxy matrix attends improved flame resistance, including the enlarged char yield at 800 ^{o}C and decreased rate of mass loss. Furthermore, the LOI value is remarkably improved to 37.5%, and the ODMAS materials are categorized as V0 rating in the UL-94 test. The significant enhancement in the fire resistance is primarily ascribed to the hierarchical structure of the produced char that represented as an excellent barrier to safe-guard the inner layer epoxy matrix from extra burning [95].



Scheme 7: Synthetic route of ODMAS

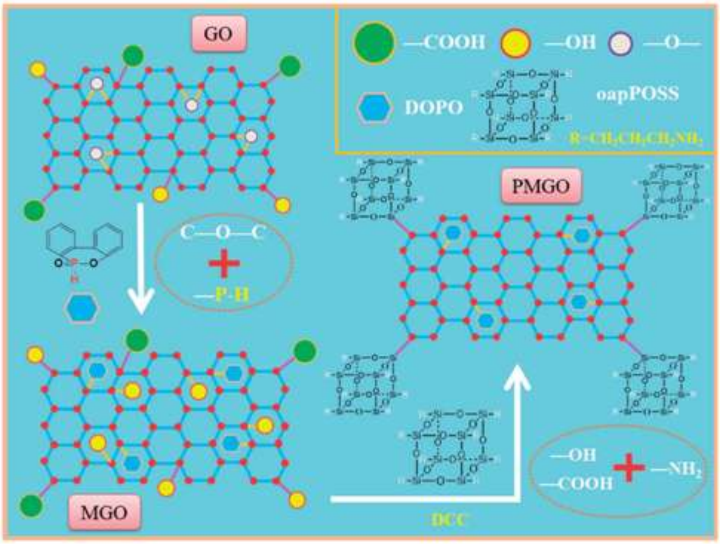
A zirconium-polyhedral oligomeric silsesquioxane-bisocta-(N,N-(bis-(9,10-dihydro-9-oxa-10-phosphaphenanthene-10-yl) methyl)aminopropyl) derivative named as Zr–POSS–bisDOPO was synthesized by the corner-capping and Kabachnik–Fields reactions followed by hydrolysis condensation using (3-Aminopropyl)triethoxysilane (APTES), polyoxymethylene (POM) and 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) (**Scheme 8**). Zr–POSS–bisDOPO was added into epoxy resin to produce EP/Zr–POSS–bisDOPO that revealed upright flame retardant effect, enhanced the LOI values from 24.6% (EP-0) to 29.8% (EP-4), and noticeable intumescent chars were formed.

The exceptional capability of char formation was mostly ascribed to the catalytic effect from Zr, Si of Zr-POSS. The char and volatile product investigation demonstrated that the flame retardant Zr–POSS–bisDOPO formed phosphorus-containing free radicals and completed the chain reactions in the gases phase. Simultaneously, the Si–O and Zr–O units were conserved in the solid phase, promoting the formation of char [96].



Scheme 8: Synthetic route of Zr–POSS–bisDOPO

A novel halogen-free flame retardant PMGO was synthesized by the reaction between octaminopropyl silsesquioxane, graphene oxide and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide and then employed as an intumescent flame retardant (IFR) to improve the flame retardancy of polypropylene (PP) (**Scheme 9**). The experimental results show that the thermal and flame retardant properties of these composites are remarkably enhanced by adding 5 wt% PMGO as well as 20 wt% IFR. In comparison with neat PP, the heat release rate and total heat release of these composites are lessened 61.5% and 40.2%, respectively. As per the char layer results and TG analysis, the enrichment in flame retardancy is primarily ascribed to the outstanding intumescent char layers along with in height strength and thermal stability produced by the combined effect of PMGO and IFR. In addition, the introduction of phosphorous, silicon and nitrogen hydrophilic groups did not show the undesirable effects on the external hydrophobicity of flame retardant PP materials which might increase its scope of application [97].



Scheme 9: The synthetic route and structure of PMGO. Reproduced from ref. no. 97. Reprinted with permission from Copyright © 2018 The Royal Society of Chemistry

X. CONCLUSIONS

The main objective of this book chapter is to explicate the important features of polyhedral oligomeric silsesquioxanes. We have discussed the main synthetic approaches used to prepare completely and partially condensed polyhedral oligomeric silsesquioxanes such as hydrolytic condensation reactions, Corner capping and Corner cleavage reactions. A concise illustration of the spectroscopic and structural characterization techniques utilized to analyse the properties of silsesquioxanes is too reported here. The arena of silsesquioxane and their materials chemistry has extended greatly in additional of the last 20 years yielding exhilarating progresses in their synthesis and application in oil/water separations and flame retardant properties, which is a recommendation of the richness of the chemistry of these inorganic-organic hybrid materials. Several opportunities are still unknown; both in synthesis of different silsesquioxane materials and in their applications, and the readers will find inspiration for developing the new route to innovation and exhilarating traditions of silsesquioxane.

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