# Preparation of Highly Crystalline Octavinyl Silsesquioxane Building Blocks via Sol-Gel Technique

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## ARTICLE INFO

## ABSTRACT

Polyhedral oligomeric silsesquioxanes (POSSs) are a class of hybrid materials with a unique structure and properties originated from a combination of organic functional groups and inorganic silica core. Not well-defined synthesis process generally suffers from multistep, complex and especially time-consuming procedure from days to weeks and months. Consequently, in the present study, the effect of various parameters on the synthesis of octavinyl POSS (OV-POSS) nanostructure such as temperature, monomer concentration, reaction time, and rate of monomer addition are investigated. Finally, OV-POSS crystallization is produced under optimal condition through single-step hydrolytic condensation of vinyltrimethoxysilane (VTMS) with 72% yield and a high crystallinity (above 90%) during a reduced time interval of 5 h at 60 °C at a 20 µl.min$^{-1}$ monomer addition rate. Morphology and size of the as-prepared samples are characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses. Also, the chemical structure is predicted using nuclear magnetic resonance (NMR), FTIR, and EDX.

## INTRODUCTION

Recently, hybrid organic/inorganic materials have received a great deal of attention due to taking advantage of organic and inorganic constituents. Generally, organic materials show high flexibility, light weight, processability and toughness with a low thermal stability. However, inorganic materials exhibit low thermal conductivity, high thermal and oxidative resistance and on the other hand, poor toughness and processability.

Polyhedral oligomeric silsesquioxanes (POSSs) are a class of hybrid materials as a 3D nanostructured molecule with the general formula $(RSiO_{1.5})_{2n}$, where R is the organic part and can be hydrogen, alkyl, aryl or halogen and n is the number of repeating units (Fig. 1). The silica cage

leads to high thermal, mechanical and oxidative stability, while the organic fraction improves the solubility of POSS building blocks in organic solvents, and also generates the compatibility with
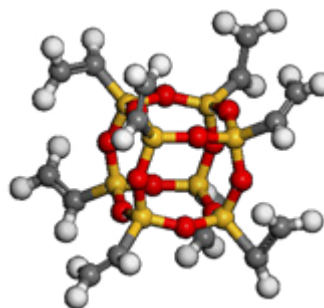


Fig. 1. Structure of octahedral silsesquioxane.

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different polymeric matrices. The silica core and organic functional groups represent a spheroid 1-2 nm in diameter with a volume of < 2 nm$^3$ [1, 2].

Hydrolytic condensation of three functional monomers (XSiY$_3$), where Y is a highly reactive substituent such as methoxy, ethoxy or Cl, and X is a chemically stable group such as vinyl, phenyl and various alkanes, is the most common technique for the POSS preparation (Eq. 1). Hydrolytic condensation of XSiY$_3$ is a complex and multistep time-consuming process producing various polymers, oligomers and polyhedral silsesquioxanes depending on the operating conditions [3].

$$nXSiY_3 + 1.5nH_2O \rightarrow (XSiO_{1.5})_n + 3nHY \qquad (1)$$

Due to the underdeveloped chemistry of silsesquioxanes and lack of straight forward route, synthesis of these compounds was delayed for decades with low yield values [1, 4]. Generally, synthesis and characterization of silsesquioxanes was initiated by Scott et al. in 1946 [5]. High Mw dimethyl silicon was prepared through hydrolysis of a mixture of dimethyldichlorosilane and methyltrichlorosilane. Finally, cyclic siloxane compounds with general formula (CH3SiO1.5) n were isolated by increasing the temperature. Since then, studies on silsesquioxanes and POSS compounds were developed rapidly by several groups such as Feher's group on chemical modification of silicon frameworks [6-11] and Lichtenhan's group on some applications [12-14].

Vinyl-POSS (OV-POSS) compounds consist of unsaturated vinyl groups attached to silicon located at cage vertices where the number of vinyl groups can be controlled by the concentration of monomers. Due to the presence of reactive vinyl groups, Vi-POSS is one of the most interesting POSS compounds. Functional compounds can be co-polymerized with other organic mono-mers through free radical polymerization, hydrosilylation reactions and atom transfer radical polymerization to obtain organic–inorganic hybrid nanocomposites or as cross-linking agents in order to improve thermal and mechanical properties of various matrices by forming a 3D network [15, 16]. Recently, OV-POSS compounds have been utilized in various applications such as cross-linkers [17], dielectric films [18], hybrid nanocomposites [19] for electron lithographic manufacture of semiconductor microreliefs [20].

Synthesis of OV-POSS nanostructures was initiated by Andrianov in 1978 through hydrolysis of ViSiCl$_3$. The nanoparticles produced were isolated at <10% yield [21]. Baney et al. (1995) [22] hydrolyzed ViSi(OC$_2$H$_5$)$_3$ in anhydrous alcohol as solvent under acidic conditions. A white crystalline powder was isolated upon filtration, washing and recrystallization with 18% yield. Following this study, Bonhomme et al. (1997) [23] hydrolyzed ViSi(OC$_2$H$_5$)$_3$ in a solution of water and HCl as a catalyst without any solvent. After several days at room temperature, transparent OV-POSS crystals were isolated. Aging the remaining liquid led to the formation of a transparent gel turning into xerogel via heating. Also, Harrison & Hall [24] used ethanol for ViSiCl$_3$ hydrolysis in an ice bath for 3 days. A white crystalline powder was obtained with a 20.5% yield. Dare et al. (2006) utilized a modified technique to produce different POSS compounds including OV-POSS [25]. Methanol and amberlite ion-exchange resin were used as solvent and catalyst, respectively. Due to reusability of the resin, Vi-POSS yield reached 41% in the 3$^{rd}$ cycle. Also, Gao et al. (2005) [26] improved Vi-POSS yield up to 80% using tetramethylammonium hydroxide as the catalyst using ViSi(OC$_2$H$_5$)$_3$ in methanol. Monofunctional POSS compounds including propyl and vinyl groups were synthesized by Chen et al. (2010) [27]. They used (C$_3$H$_7$)Si(OCH$_3$)$_3$ and ViSi(OCH$_3$)$_3$ as precursors of cohydrolysis and cocondensation for the synthesis of monofunctional POSS in methanol under acidic conditions. After 3 days, crystals were separated, and washed with methanol and THF. The as-prepared POSS nanostructures were obtained with a 32% yield. Bifunctional POSS building blocks were synthesized by Chen et al. (2012) [28] using (C$_3$H$_6$Cl)Si(OCH$_3$)$_3$, (C$_3$H$_7$) Si(OCH$_3$)$_3$ and ViSi(OCH$_3$)$_3$ in ethanol under acidic conditions. After 3 days, POSS compounds with vinyl, propyl and 3-chloropropyl periphery groups were synthesized with 31 to 32% yields. Chen et al. (2009) [29] synthesized Vi-POSS using ViSi(OCH$_3$)$_3$ in acetone as a solvent under acidic conditions, with a 33% yield. Afterwards, they modified the as-prepared POSS by diethyl ether and activated carbon being incorporated into PDMS to fabricate room temperature volcanized (RTV) silicon rubbers. Penso et al. (2015) [30] utilized two different heating conditions in the OV-POSS synthesis procedure. In their study, ViSi(OC$_2$H$_5$)$_3$ was hydrolyzed in acetone in acidic media and the solution was heated to 40 °C using microwave oven

and conventional heating. Microwave radiation led to a rapid temperature rise resulting in the reduction of reaction time in comparison with conventional heating. It was observed that the reaction rate of $ViSi(OC_2H_5)_3$ heating was ~47 times higher than those with conventional heating.

Hydrolytic poly-condensation of $XSiY_3$ comprises of two reactions (Eq. 2, 3(a) and 3(b)) during which various cross-linked intermediate networks such as random structures, ladder type polymers, cages and partial cage structures can be isolated.

Several parameters affect the final structure and yield the POSS compounds including monomer concentration [1, 2], solvent type [2, 20], pH [2], amount of water [2] and synthesis procedure [20]. Generally, these factors are inter-dependent and their interactions increase the complexity of POSS synthesis process. In the present study, effect of synthesis parameters such as temperature, monomer concentration, synthesis time and also the rate of monomer addition on yield and crystallinity were investigated. It was observed that decreasing the rate of monomer addition led to increase the yield and size of the as-prepared compound. The prepared samples were characterized using FTIR, NMR, TEM and XRD, SEM and FE-SEM analyses to determine the morphology, crystallinity and chemical composition. Finally, OV-POSS compounds were successfully synthesized with a high yield (72%) and crystallinity (>90%) in a reduced time interval of 5 h.
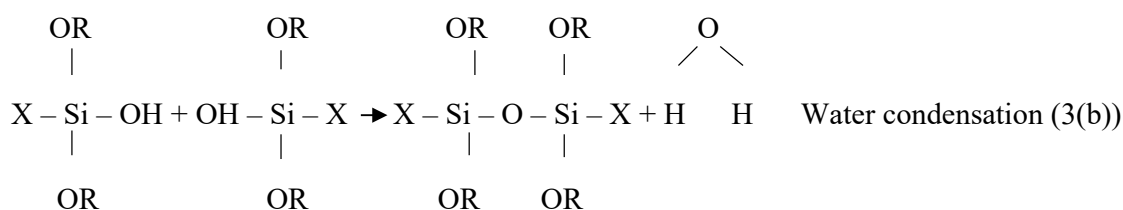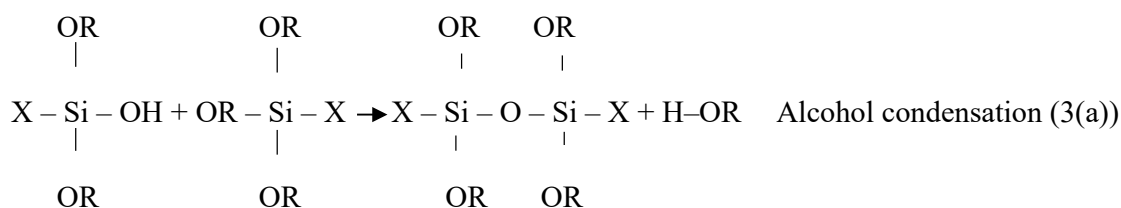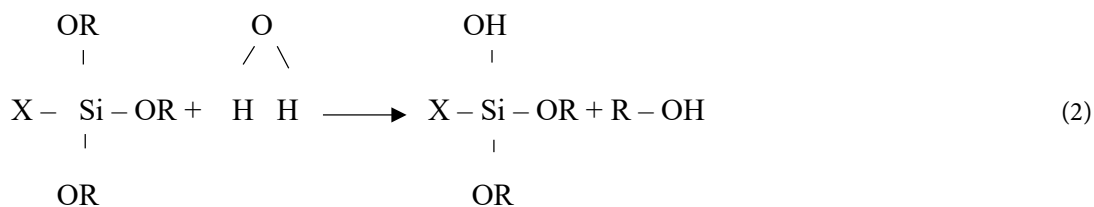
## MATERIALS AND METHOD
### Materials

Vinyltrimethoxysilane (98% purity) (VTMS), butanol ($C_4H_{10}O$), hydrochloric acid 36% (HCl), ethanol ($C_2H_6O$), methanol ($CH_4O$) and acetone ($C_3H_6O$) were purchased from Merck Co. All the reagents were of analytical grade and used without further purification. Also, deionized water was used for preparing the solutions.

### Characterization techniques

*Fourier transform infra-red spectroscopy (FTIR)* was performed using Nicolet Magna 550 spectrometer at room temperature (25 °C) to characterize the chemical composition of POSS, giving information on various chemical bonds, and also used for the detection of POSS functional groups. *X-ray diffraction (XRD)* was taken to characterize the crystalline structure using Panalytical Xpert PRO X-Ray Diffractometer (Holland) with Cu (λ= 0.154 nm) irradiation at 40 kV and 30 mA in the 2θ= 5-90° range to determine crystallinity. The XRD results could be also used to

$$\begin{array}{cccc}
OR & O & OH & \\
| & /\backslash & | & \\
X-Si-OR + & H\quad H \longrightarrow & X-Si-OR + R-OH & \qquad (2)\\
| & & | & \\
OR & & OR &
\end{array}$$

$$\begin{array}{ccccc}
OR & OR & OR & OR & \\
| & | & | & | & \\
X-Si-OH + OR-Si-X \rightarrow & X-Si-O-Si-X + H{-}OR & \quad \text{Alcohol condensation (3(a))}\\
| & | & | & | & \\
OR & OR & OR & OR &
\end{array}$$

$$\begin{array}{ccccc}
OR & OR & OR & OR & O\\
| & | & | & | & /\backslash\\
X-Si-OH + OH-Si-X \rightarrow & X-Si-O-Si-X + H\quad H & \quad \text{Water condensation (3(b))}\\
| & | & | & | & \\
OR & OR & OR & OR &
\end{array}$$

measure the crystallite size. *Field emission scanning electron microscopy (FESEM)* of the POSS sample was obtained using Mira3-Tescan XMU operated at 15 kV to define POSS morphology. Furthermore, *scanning electron microscopy (SEM)* (TESCAN-VEGA3) operated at 30 kV and *transmission electron microscopy (TEM)* using Philips CM30 (Holland) apparatus were performed to illuminate POSS morphology. *Nuclear magnetic resonance (NMR)* spectroscopy was carried out using a Bruker AVANCE III (300 MHz) spectrometer in $CDCL_3$ as a solvent to investigate the structure of POSS compounds. The H- and C-NMR characterizations were also performed.

**EXPERIMENT**
*Synthesis of Octavinyl-POSS*

Octavinyl POSS was synthesized through modifying the procedure reported by Chen et al. [28] with butanol as solvent. In order to investigate the effect of initial monomer concentration, three different solutions were prepared using various solvent/monomer ratios. Typically, 0.3, 0.4 and 0.536 M VTMS solutions were prepared using 1.458 g deionized water, 34.51, 24.67 mL and 17.2 mL butanol for each solution and 1.5 mL concentrated hydrochloric acid were added sequentially to a 250-mL flask and mixed. Then, 1.8 ml vinyltrimethoxysilane (VTS) was added in a dropwise manner to the flask over a period of 15-90 min while vigorously stirring. The water/VTMS ratio was kept constant at 6.88. The effect of temperature was also studied by refluxing each solution in an oil bath at 28, 40, 50 and 60 °C. Then, mixtures were refluxed at the mentioned temperatures at different time intervals in the 2-72 h range while stirring until gradually turning turbid and a white crystalline precipitate appeared. Finally, the crystallites were collected, dissolved in acetone and recrystallized. The white product was washed twice with a solution of methanol/ethanol (1:1) and dried under vacuum for 24 h at 100 °C.

**RESULTS AND DISCUSSION**
*Effect of monomer concentration and temperature*

POSS nanostructures tend to form at both low temperatures and low concentrations [1, 20, 31]. So, according to Voronkov and Lavrent'yev [20], 0.3, 0.4 and 0.536 M of monomer concentrations and 28-60 °C temperature range were selected in order to find the optimal POSS formation conditions. Different concentrations were prepared using various

amounts of solvent while the water/monomer ratio was kept constant at 6.88 M. According to Chen et al. [28], solutions were hydrolyzed under 60, 50 and 40 °C for 72 h. Fig. 2 (a-c) represents XRD spectra of compounds synthesized at different concentrations. Several sharp peaks with high intensity illustrate the crystalline structure of the as-prepared samples. The peak located at 2θ = 9.65° determines the crystallite size, and other peaks represent the crystal structure. It can be inferred from the spectra that increasing temperature does not have a significant effect on the amorphous content. According to the results, no precipitate was appeared at the ambient temperature (28 °C). This can be attributed to the reduction of reaction rate at low temperatures. On the other hand, precipitates appeared sooner at higher temperatures. Figs. 3(a-c) indicate XRD spectra of samples synthesized at 0.3, 0.4 and 0.5 M concentrations at different temperatures. All spectra illustrate high crystallinity with various peak ratios which can be related to the growth of special facets. In case of Fig. 3(a), the characteristic peak located at ~ 9.7° is related to the crystallite size. XRD profile of samples synthesized at 0.4 M at different temperatures is shown in Fig. 3(b). Traces of amorphous phase can be seen on the XRD spectra synthesized at 40 °C which tends to decrease at higher temperatures. The diffraction pattern of samples synthesized at 0.536 M at different temperatures is depicted in Fig. 3(c). Presence of several sharp peaks indicates the formation of highly crystalline products with no significant amorphous phase. From XRD spectra, it can be concluded that all compounds exhibit identical main peaks with varying intensities and amorphous phase content with temperature and concentration. Table 1 represents crystallite size using Scherrer Eq. and yield determined using the ratio of the obtained POSS to its stochiometric amount. The compound synthesized using 0.4 M solution under 60 °C shows the highest crystallinity without the presence of significant amorphous phase and the smallest crystallite size.

*Effect of reaction time*

POSS structures prepared by Chen et al. [28] were synthesized through 3 days. In order to investigate the reaction time effect and determine the optimal point, a 0.4 M solution at 60 °C was considered to react at various time intervals initiated from the first precipitate appearance until 3 days. According to the results, the mixture turned
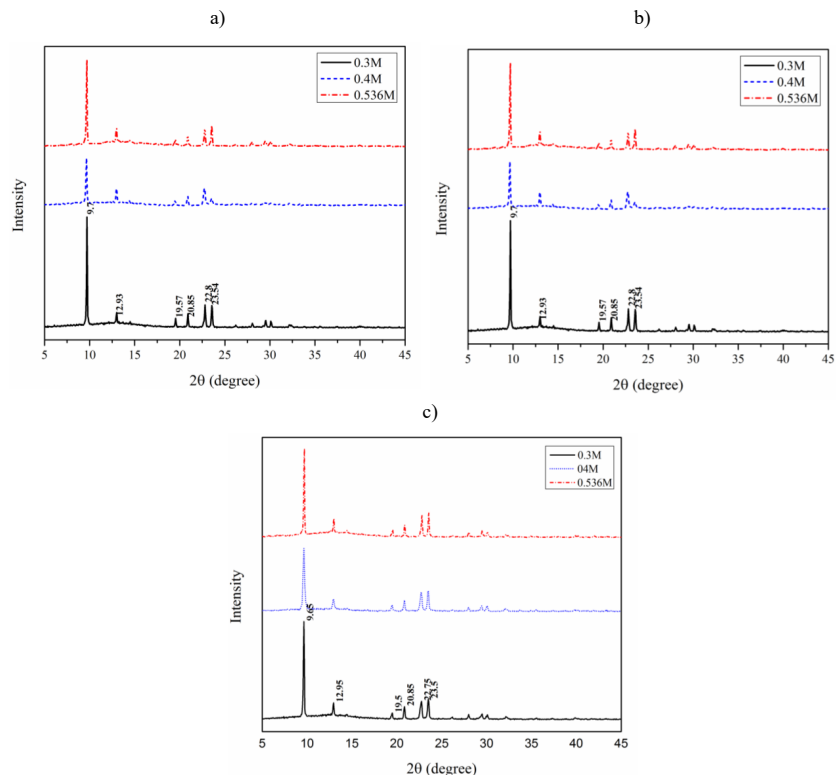
a)

b)



c)



Fig. 2. XRD spectrum of POSS samples prepared using different concentrations at (a) 40 °C, (b) 50 °C and (c) 60 °C.
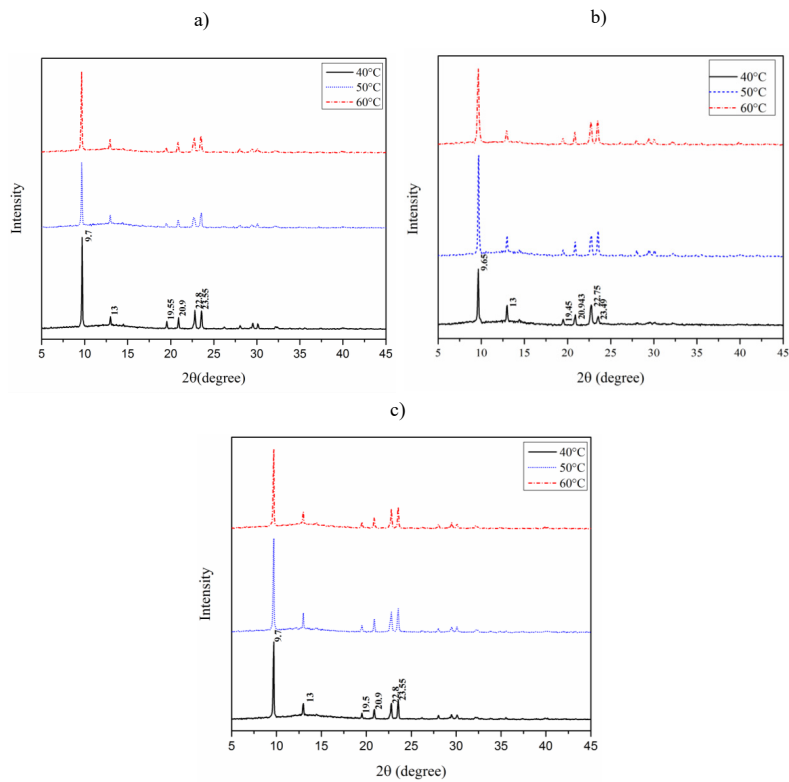
a)

b)



c)



Fig. 3. XRD spectrums of POSS synthesized at (a) 0.3 (b) 0.4 & (c) 0.536 M solutions at various temperatures.

Table 1. Crystallinity, yield and crystallite size of the as-prepared compounds through various temperatures and concentrations hydrolyzed in 72 h.

|  | Temp. (°C) | Conc. (mol/L) | Crystallite size (nm) | Yield (%) | Crystallinity (%) |
|---|---|---|---|---|---|
| A₁ | 40 | 0.300 | 79.47 | ~ 4 | 91 |
| A₂ | 40 | 0.400 | 65.35 | ~ 6 | 93 |
| A₃ | 40 | 0.536 | 73.14 | ~ 6 | 85 |
| B₁ | 50 | 0.300 | 64.80 | ~ 5 | 87 |
| B₂ | 50 | 0.400 | 66.96 | ~ 10 | 95 |
| B₃ | 50 | 0.536 | 68.11 | ~ 8 | 90 |
| C₁ | 60 | 0.300 | 67.54 | ~ 7 | 93 |
| C₂ | 60 | 0.400 | 39.65 | ~ 11 | 96 |
| C₃ | 60 | 0.536 | 71.15 | ~ 12 | 84 |

Table 2. Yield of the as-prepared compounds with 20 μl/min monomer addition rate.

| Sample | A₁ | A₂ | A₃ | B₁ | B₂ | B₃ | C₁ | C₂ | C₂ |
|---|---|---|---|---|---|---|---|---|---|
| Yield (%) | 24 | 36 | 36 | 30 | 61 | 48 | 43 | 72 | 66 |

turbid after 2 h. The precipitates were collected after 3, 5, 10, 18, 24 h and 3 days. The compounds collected after 3 h were completely dissolved through washing with acetone which can be due to partial hydrolytic condensation and incomplete cage formation. After 5 h, the precipitates dispersed in the solution were easily separated and washed. By increasing the reaction time, precipitates were deposited and formed sticky compounds hardly separated. Figs. 4 and 5 indicate SEM and FE-SEM micrographs of samples collected after 3 days and 5 h, respectively, with different magnifications. It is obviously observed that micron size agglomerated particles without symmetrical shapes formed when reaction time is increased up to 3 days, while cubic particles were collected during 5 h. Consequently, the reaction time was considered to be 5 h for further investigations such as size reduction.

*Rate of monomer addition*
In order to investigate the effect of monomer addition period, 0.4 M VTMS was added to the mixture at various time intervals in the 15-90 min range and hydrolyzed for 5 h at 60 °C. Figs. 6 (a) and (b) show the crystallite size of the compounds synthesized through monomer addition at 15 and 90 minutes, respectively. It is obviously seen that decreasing the addition period led to decrease the crystallite size from micrometer range to < 100 nm. According to Table 2, yield of the as-prepared compound is increased significantly during 90 min (20 μl.min⁻¹ rate). This behavior can be attributed to low monomer concentration and prevalence

of cyclization and intramolecular condensation compared with polymerization and oligomerization leading to the reduction of intermediates [1].

*FTIR spectroscopy*
The FTIR spectrum of the sample prepared using 0.4 M VTMS hydrolyzed for 5 h in 60 °C is given in Fig. 7. According to the spectrum, the intense peak located at 1110.75 cm⁻¹ is related to symmetrical stretching vibration of Si-O-Si bond in silsesquioxane cage corresponding to the silsesquioxane cage structure [16, 32]. The adsorption peak at 1604.35 cm⁻¹ illustrates the stretching vibration of vinyl groups [28]. The peaks appeared at 1277.01 cm⁻¹ and 1410.35 cm⁻¹ are attributed to the bending vibration of vinyl groups [28, 33]. The intense peak at 583.14 cm⁻¹ depicts the bending vibration and deformation of Si-O-Si bond [34, 35]. The characteristic peak located at 777.76 cm⁻¹ reveals the stretching vibration of Si-C bonds [30, 34]. The low intensity peak at 3066.29 cm⁻¹ is the characteristic peak related to the stretching vibration of C-H bonds [30, 34]. Bending vibration of O-Si-C bonds, related to cage deformation, are located at 969.84 cm⁻¹ and 1005.95 cm⁻¹ [25]. The low intensity adsorption peak at 3443.34 cm⁻¹ indicates the stretching vibration of small amount of water present in the mixture [24] which can be attributed to incomplete drying and entrapment of water molecules in the porous structure.

*NMR spectroscopy*
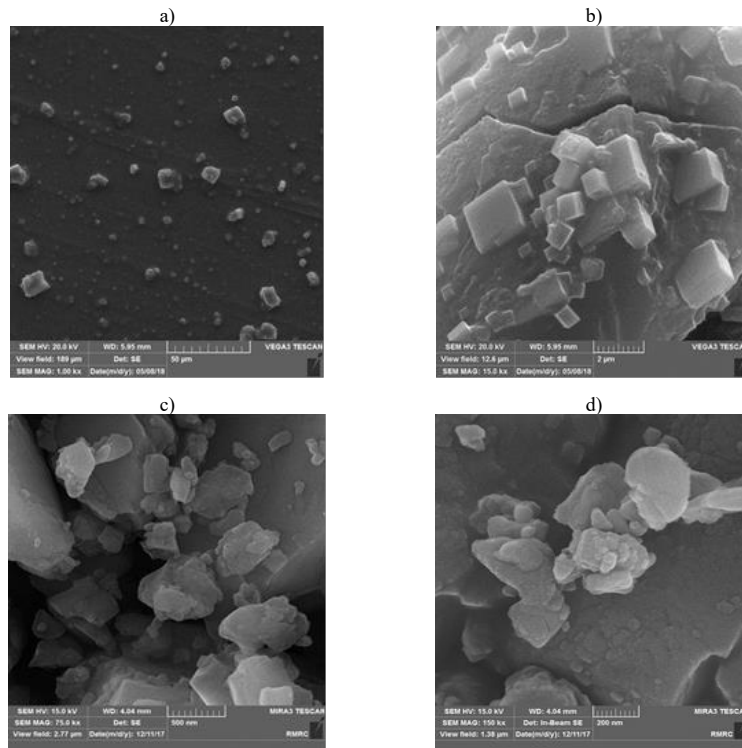¹H-NMR and ¹³C-NMR measurements were

Fig. 4. SEM and FE-SEM micrographs with (a) 1 kx, (b) 15 kx, (c) 75 kx and (d) 150 kx magnifications of the sample synthesized in 3days.
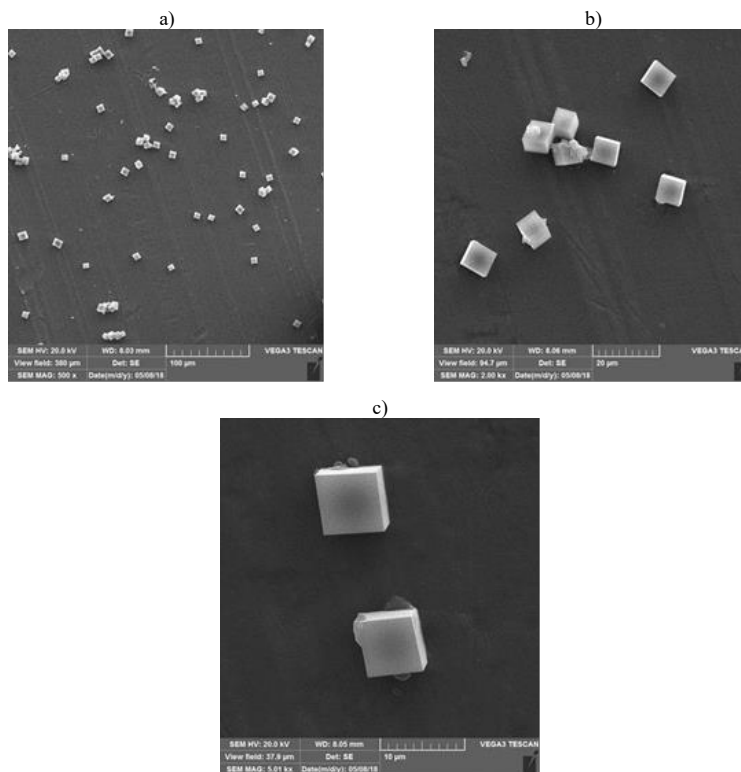


Fig. 5. SEM micrographs with (a) 500 x, (b) 2 kx and (c) 5 kx magnifications of the sample synthesized in 5 h.

a)                                                                 b)
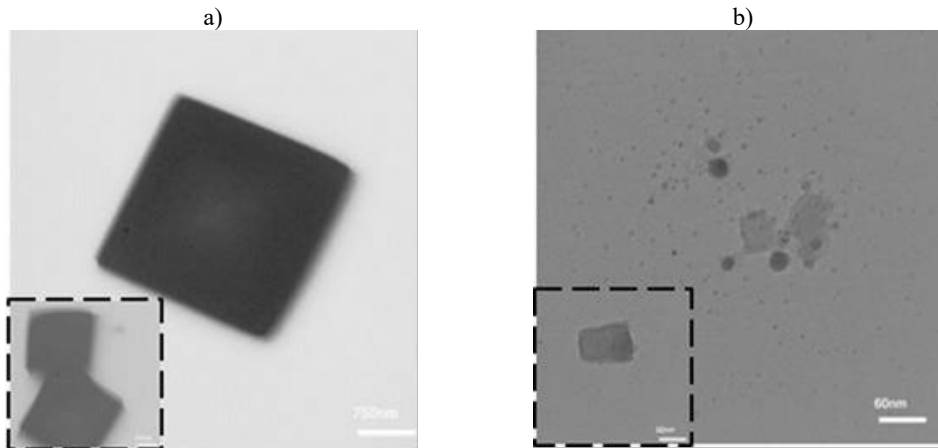


Fig. 6. TEM micrograph of sample synthesized with different monomer addition rates. Vinyl trimethoxy silane was added through (a) 15 min and (b) 90 min in 750 nm and 60 nm scale bars.
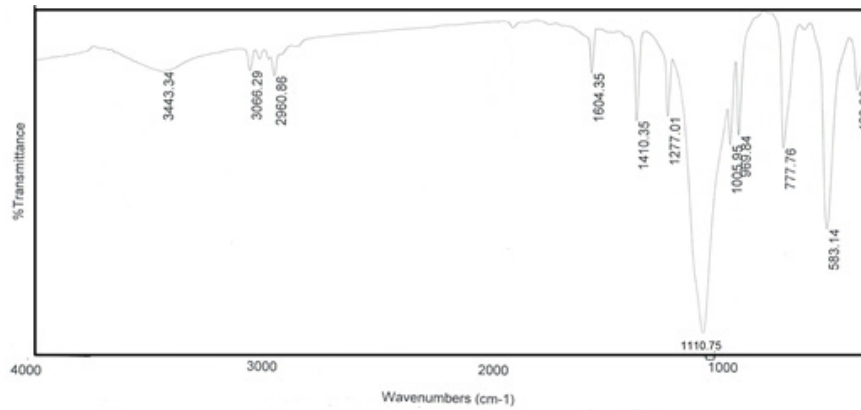


Fig. 7. FTIR spectra of the sample synthesized through 0.4 M vinyl trimethoxy silane hydrolysis for 5 h in 40 °C.
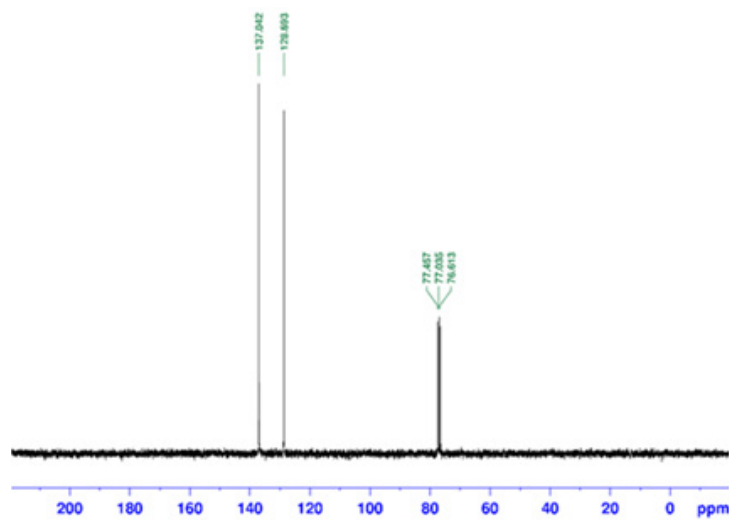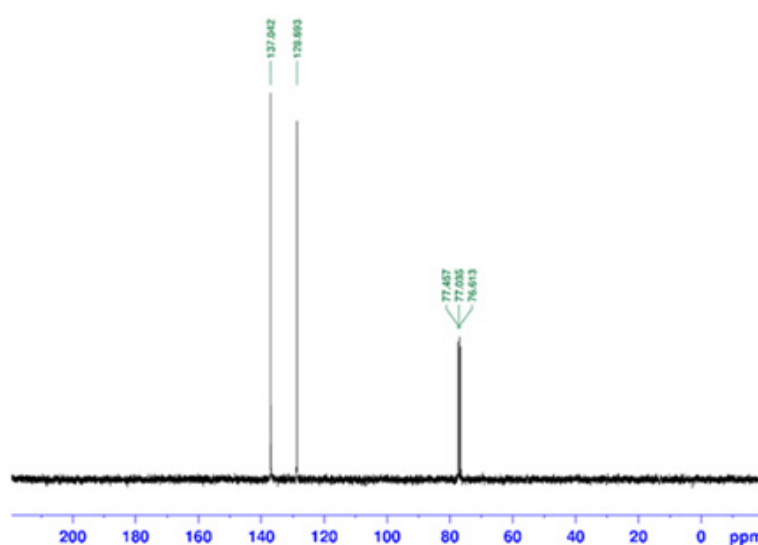


Fig. 8. ^{1}H-NMR of POSS.

Fig. 9. $^{13}$C-NMR of POSS.

performed in order to investigate the POSS structure more accurately. Figs. 8 and 9 show the $^1$H-NMR and $^{13}$C-NMR spectra of the as-prepared product, synthesized using 0.4 M monomer hydrolyzed in 5 h at 60 °C, dissolved in CDCL$_3$. According to Fig. 8, multiple resonance peaks located in the range of δ 5.903-6.183 ppm are related to vinyl proton resonance caused by coupling of hydrogen protons [27, 30, 34]. The $^{13}$C-NMR spectra of POSS are shown in Fig. 9. Peaks located at δ 128.693 ppm and 137.042 ppm are attributed to carbons in vinyl groups [30, 34]. CDCL$_3$ (deuterochloroform or deuterated chloroform) is a common solvent of POSS samples giving rise to three peaks located at 76.613, 77.035 and 77.457 ppm. In this triplet, all three peaks have approximately the same intensity of (1:1:1) [36].

**CONCLUSION**

The OV-POSS synthesis suffers from time-consuming processes. In the present study, OV-POSS building blocks were successfully synthesized through a simple hydrolytic condensation. Synthesis conditions such as monomer concentration, reaction time, synthesis temperature and monomer addition rate were considered. Monomer concentration and synthesis temperature were varied in the 0.3-0.536 M and 28-60 °C ranges. According to XRD and Scherrer Eq, it was observed that the sample synthesized using 0.4 M concentration at 60 °C showed the highest

crystallinity (96%) and the lowest crystallite size. Moreover, the reaction time was varied in the 5-72 h range and FE-SEM and SEM micrographs revealed that increasing the reaction time led to the formation of micrometric agglomerated particles without any symmetrical shape. The particles synthesized in 5 h showed micrometric cubic morphology. Furthermore, the rate of monomer addition was changed in the 15-90 min range. Interestingly, it was observed that by decreasing the addition rate the size of the as-prepared compound tended to decrease and more symmetrical particles appeared. Highly symmetrical and crystalline compounds with cubic morphology were synthesized under 20 μl.min$^{-1}$ addition rate (90 min). Consequently, fast synthesis of OV-POSS nanostructures were successfully achieved at the optimal condition of 0.4 M hydrolysis for 5 h at 60 °C with an addition rate of 20 μl.min$^{-1}$.

**CONSENT FOR PUBLICATION**

Not applicable.

**CONFLICT OF INTEREST**

The authors confirm that this article content has no conflict of interest.

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