

RESEARCH PAPER

## Effect of Solvent properties on Crystallinity and Morphology of Octavinyl-POSS: A Comparative Study

Sahar Foorginezhad and Mohammad Mahdi Zerafat \*

Nano-chemical Engineering Department, Faculty of Advanced Technologies, Shiraz University, Shiraz, Iran

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### ABSTRACT

Polyhedral Oligomeric Silsesquioxanes (POSSs) are a class of hybrid structures synthesized through hydrolytic condensation (Sol-Gel method) of trifunctional silane monomers under specific conditions. Octavinyl silsesquioxane (OVS) nanostructures are comprised of a rigid inorganic silica core surrounded by vinyl functional groups with an under-developed synthesis procedure. Generally, POSS morphology, yield and crystallinity depend strongly on synthesis conditions such as solvent type, synthesis temperature, sequence of reagents addition, water/monomer molar ratio, etc. In this study, effect of solvent properties on the formation of OVS compounds, their morphology and crystallite size was studied under specific conditions. Finally, n-pentanol and butanol as the most efficient solvents were suggested according to solvent characteristics, theoretical background reported in previous studies and experimental results. Different characterization techniques such as XRD to investigate crystallinity and crystallite size, FE-SEM and TEM to determine the morphology, EDX to identify elemental and chemical composition, C-NMR and <sup>1</sup>H-NMR to confirm the attachment of vinyl groups and FTIR to define chemical bonds, were employed to confirm the formation of the as-prepared structure. Based on the results, butanol and n-pentanol represent the best results regarding crystallinity and size by optimizing other influential parameters.

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### INTRODUCTION

Nanostructured polyhedral oligomeric silsesquioxanes (POSS) are a class of 3D silsesquioxanes, comprising of an inorganic silica core surrounded by organic functional or non-functional groups with  $(RSiO_{1.5})_{2n}$  general formula, with R representing the organic section and n the number of repeating units. More reactive R groups can be utilized to enhance the properties of host matrices including hydrophobicity, oleophobicity, mechanical, thermal and optical properties [1]. Octavinyl silsesquioxane (OVS) polyhedrals, are a class of POSS compounds consisting of vinyl groups (Fig. 1). The unsaturated vinyl groups can be chemically modified to obtain compatibility

with corresponding host matrices. OV-POSS compounds have been used in various applications as cross-linkers [2], dielectric films [3], polymeric nanocomposites [4] and resists for electron lithographic manufacture of semiconductor microreliefs [5].

However, the synthesis chemistry of silsesquioxanes has remained underdeveloped due to the lack of straightforward methods [6]. POSS building blocks are usually synthesized through sol-gel processing of three functional silane monomers. Yield, morphology and crystallinity depend strongly on operating conditions such as monomer concentration, solvent properties, reaction temperature, catalyst type, etc. Due to

\* Corresponding Author Email: [mmzerafat@shirazu.ac.ir](mailto:mmzerafat@shirazu.ac.ir)



immiscibility of water and alkoxy silane, a mutual solvent is usually used as the homogenizing agent facilitating water-precursor contact and facile hydrolysis. So, solvent type plays a determining role in the sol-gel mechanism; thus on the characteristics of the product. But, based on the literature review and to the best of our knowledge, effect of solvent properties on POSS formation, its morphology and crystallinity is not studied in detail. Different characteristics of solvents such as polarity, availability of labile protons, viscosity, and boiling point have a significant effects on POSS properties. These properties can be further classified as follows:

#### *Polarity*

Generally, solvent-solute interactions have a significant influence on the product at the molecular level. Polar solvents comprising of electronegative atoms have much stronger interactions with polar species. So, hydrolyzed molecules solvated strongly by polar solvents maintain incomplete condensation. Dielectric constant and dipole moment of a solvent as respective macroscopic and microscopic properties determine polarity. Solvents with higher polarity are characterized by higher dielectric constants or dipole moments (DPs). The reduction of solvent dipole moment leads to enhance the recognition distance of species consequently affecting the attraction or repulsion behavior of  $H_3O^+$  and  $OH^-$  toward reaction sites [7]. In other words, solvents with low polarity exhibit loose solvation and interaction with reaction sites and charged species. So, hydrolysis and condensation can be

promoted in solvents with low polarity. On the other hand, hydrolyzed species would interact with each other without limitation in non-polar solvents. Consequently, polymerization would be enhanced by extension of hydrolytic condensation rate. In POSS synthesis, rate of hydrolysis and condensation reactions must be controlled and monomer concentration must be kept low. From a theoretical point of view, polar solvents specially alcohols have the ability to solvate siloxane intermediates and hydrolyze species through hydrogen bonding and stabilize the incompletely condensed silsesquioxanes through interaction with OH groups produced during hydrolysis. So, the hydrolysis rate would be decreased. In other words, high polarity solvents increase the degree of intermolecular condensation, favoring polymer formation [5, 6]. Extremely high polarity solvents may completely solvate hydrolyzed species and hinder condensation. On the other hand, non-polar solvent and inert media lead to extend hydrolysis and condensation reactions and favor polymerization. As a result, the polarity of synthesis medium can control hydrolytic condensation rate and lead to cyclization and POSS formation. However, POSS synthesis can be practiced in both polar and non-polar media at various optimal conditions, which clarify the necessity to find an optimum condition to obtain the favorable product. Table 1 gives a summary of properties of solvents used in this study expected to affect POSS properties.

#### *Proticity of the solvent*

Protic solvents containing hydrogen atom

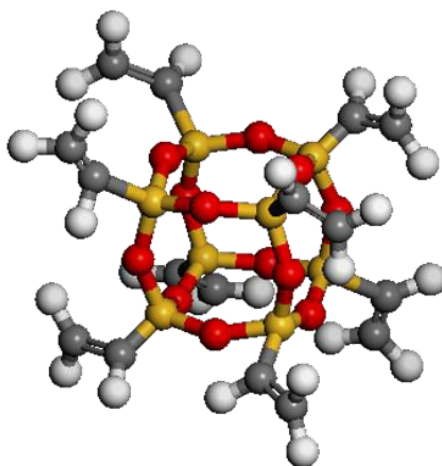












Fig. 1. Schematic of Octavinyl polyhedral silsesquioxane.

Table 1. Properties of the solvents used in this study [8].

Solvent	Mw (g/gmol)	BP (°C)	Solubility in water at 25 °C (%w/w)	Dielectric Constant	Viscosity (cP) at 25°C	Proticity	DP (D)	Molecular Structure
Ethanol	46	78	miscible	22.4	1.08	Protic	1.7	
Butanol	74	118	7.3	18.2	3	Protic	1.66	
Pentanol	88	138	1.7	13.9	4	Protic	1.7	
Hexanol	102.17	155-159	5.9	13.3	4.592	Protic	1.65	
Heptanol	116.2	175.8	1.67	10.88	7.4	Protic	1.71	
Heptane	100	98	3E-4	1.924	0.41	Aprotic	0.0	
Cyclohexane	84	81	0.0055	2.01	0.98	Aprotic	0.3	
THF	72	66	miscible	7.6	0.55	Aprotic	1.75	
Toluene	92	110.6	0.052	2.38	0.590	Aprotic	0.4	
DCM	85	40	1.30	9.1	0.44	Aprotic	1.8	

bound to oxygen or nitrogen, can participate in hydrogen bonding, donate labile  $H^+$  and serve as weak acids. Catalytic activity and rate of hydrolytic condensation would be affected by solvent in case that hydrogen bonding to  $OH^-$ ,  $H_3O^+$  precursors present in the solution. To be more precise, solvents hydrogen bonding to  $OH^-$  in basic solutions and to  $H_3O^+$  in acidic solutions results in the reduction of hydrolysis rate [7].

$OH^-$  becomes more nucleophilic in the presence of aprotic solvents. Whereas,  $H_3O^+$  becomes more

electrophilic in protic solvents. On the other hand, hydrogen bonding to solvent activates non-hydrolyzed weak groups [9, 10]. Furthermore, presence of labile  $H^+$  in protic solvents makes them capable of deprotonating the product species. This makes them more nucleophilic which increase reverse reactions such as esterification and alcoholysis; thus reducing hydrolysis and condensation promotion [7]. Protic and aprotic solvents also have a significant role in condensation reactions. Nucleophilicity of deprotonated silanols

lead to hydrogen bonding with protic solvents. On the contrary, protonated silanols hydrogen bond to aprotic solvents. Consequently, protic solvents retard base-catalyzed condensation and promote acid-catalyzed condensation and aprotic solvents behave vice versa. Reverse reactions of condensation lead to depolymerization and promote molecular networks and particle-like products. Reverse reactions such as hydrolysis of siloxane bonds occur in base-catalyzed condition and in the presence of  $\text{OH}^-$ . So, aprotic solvents not able to form hydrogen bond to  $\text{OH}^-$ , are more nucleophilic leading to enhance restructuring and depolymerization of siloxane networks [7].

#### Viscosity

Viscosity can also influence the hydrolysis rate. Rearrangement of ligands surrounding the nucleus would increase hydrolysis due to the separation of charge between the attacking and leaving groups. This reorientation would be reduced as the viscosity of the solution is increased. As a result, high viscosity solvents may prevent hydrolysis rate through the reduction of diffusion coefficients [7]. Artaki et al. [11], studied the effect of solvent viscosity on hydrolysis in the sol-gel process. According to the results, lower viscosity solvents and chemical additives give rise to faster hydrolyzation due to less steric hindrance and mobility reduction.

#### Boiling point

It is known that the kinetics of hydrolysis is strongly dependent on solvent boiling point. High kinetic energy of atoms at high temperatures leads to faster rate of hydrolysis and condensation resulting in the formation of highly condensed polymers [12]. The process temperature can be elevated in case of high boiling point solvents without much evaporation.

Generally, various solvents have been used for the synthesis of POSS such as ethanol [14-19], methanol [20-22], isopropyl alcohol [23], acetone [24-26], benzene [27,28], tetrahydrofuran [26,29] and also various solvent mixtures [19,30-32] with alcohols as the most prevalent. Frye & Collins [27], used benzene as the solvent in presence of concentrated and also fuming sulfuric acid to isolate octahydridosilsesquioxanes. Benzenesulfonic acid, serves as a polar protic solvent. Furthermore, they synthesized polyhedral silsesquioxane in cyclohexane in which acetic acid serves as a polar

agent. Also, POSS nanostructures have been synthesized using trifunctional monomers with bulky R functional groups in non-polar solvents such as benzene [28, 33]. Bulky R species perform steric hindrance and limit the rate of hydrolytic condensation consequently decreasing the rate of polymerization. Also, several studies have utilized solvent mixtures to increase the yield in addition to facilitate hydrolytic condensation. For example, Lu et al [16], used a methylisobutyl ketone (MIBK)-ethanol mixture for synthesizing multiepoxy cubic silsesquioxane. Harrison and Hall [19], hydrolyzed  $\text{HSiCl}_3$  using a mixture of methanol, hexane and toluene. Dare et al. [30], synthesized octa-hydridosilsesquioxane using a hexane-methanol mixture. Lu et al. [31], used methylisobutyl ketone (MIBK) as a high boiling point agent to improve the yield and ethanol as a hydrolytic condensation restricting agent for the synthesis of Octa(cyclohexylsilsesquioxane). In another study, Zhang et al. [32] synthesized octa(aminopropylsilsesquioxane) cages in a solvent mixture of acetonitrile as the precipitating and 1-propanol as a high boiling agent leading to increase the yield. Also, OVS polyhedrals have been synthesized in various solvent media such as ethanol [14, 15], methanol [20], acetone [25] and an alcoholic media [34].

In the present study, different solvents were used to investigate the effect of solvent characteristics on OVS morphology and crystallinity. Consequently, the best solvents were determined according to theoretical background and performed characterization techniques. In addition, some solvent selection general trends based on empirical and theoretical results were presented for POSS synthesis.

#### MATERIALS AND METHODS

Vinyltrimethoxysilane (98% purity) (VTMS), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), methanol ( $\text{CH}_3\text{OH}$ ), butanol ( $\text{C}_4\text{H}_{10}\text{O}$ ), concentrated hydrochloric acid 36% (HCl), toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), cyclohexane ( $\text{C}_6\text{H}_{12}$ ), n-heptane ( $\text{C}_7\text{H}_{16}$ ), pentanol ( $\text{C}_5\text{H}_{11}\text{OH}$ ) and tetrahydrofuran (THF) were purchased from Merck Co. and deionized water is used for preparation of all solutions. All the reagents were of analytical grade and used without further purification.

#### Characterization techniques

Different methods were used to characterize

the synthesized POSS compound. 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 and giving information of various chemical bonds. Also, used for the detection of POSS functional groups. X-Ray Diffraction (XRD) was carried out from the as-prepared powder on Panalytical Xpert PRO X-Ray Diffractometer (Holland) with Cu ( $\lambda = 0.154\text{nm}$ ) irradiation at 40kV and 30 mA in the range of  $2\theta = 5\text{--}90^\circ$  to determine crystallinity and presence of amorphous content. Also, XRD results can be used to measure the crystalline size. Transmission Electron Microscopy (TEM) were taken from the sample using Philips CM30 (Holland) apparatus to illuminate POSS morphology. Field Emission Scanning Electron Microscopy (FE-SEM) with Energy Dispersive X-Ray prob of the POSS samples were obtained using Mira3-Tescan XMU operated at 15kV to define POSS morphology and elemental analysis. Nuclear Magnetic Resonance (NMR) analyses were performed using a Bruker AVANCE III (300 MHz) spectrometer in  $\text{CDCl}_3$  as solvent to confirm the structure more accurately such as investigating silica cage structure and presence of vinyl groups attached to silicon atoms. The specific surface area was measured using the Brunauer-Emmett-Teller (BET) method. Pore width and pore

volume, meanwhile, were calculated directly from the adsorption–desorption plot (surfer, porotec, Germany).

#### Synthesis of Octavinyl-POSS

Octavinyl POSS was synthesized through modifying the procedure reported by Chen et al. [15] with ethanol, butanol, pentanol, n-heptane, toluene, tetrahydrofuran, cyclohexane, dichloromethane and mixtures of pentanol and n-heptane with various ratios as solvent. Typically, 7.29 g deionized water, 86 mL from each solvent and 7.5 mL concentrated hydrochloric acid were added in sequence to a 250-mL flask and mixed to obtain a heterogeneous/homogeneous solution depending on the solvent type. Then, 9 ml of vinyltrimethoxysilane (VTS) was added in a dropwise manner over a period of 15 min while vigorous stirring. In addition, several mixtures comprising of [heptane/pentanol] = [90/10], [80/20] and [70/30] were prepared. The solution was refluxed in an oil bath at 60 °C. The solution gradually turned turbid after several hours. The reaction mixture was maintained at 60 °C for 16 h while stirring until a white crystalline precipitate appeared. The crystallites were dissolved in acetone and recrystallized. The white product was washed twice with a solution of methanol/ethanol (1:1) and dried for 24h at 100 °C. The appearance

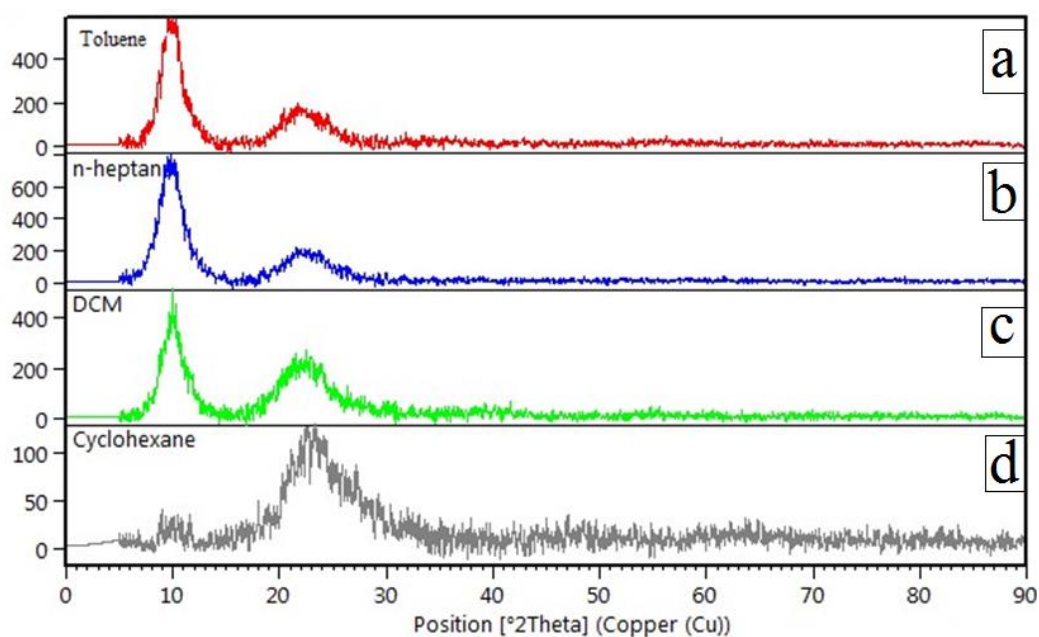


Fig. 2. X-Ray diffraction spectrums of as-prepared compounds synthesized using: (a) Toluene, (b) n-heptane, (c) Dichloromethane and (d) Cyclohexane.

of the as-synthesized powder changes drastically based on the solvent.

## RESULTS AND DISCUSSION

### XRD Patterns

Figs. 2, 3 & 4 represent the XRD spectra of POSS materials synthesized using various solvents summarized in Table 1. Figs. 2(a-d) represent the XRD pattern using toluene, n-heptane, dichloromethane, and cyclohexane as solvents, respectively. All samples exhibit a broad peak in the  $2\theta = 17-30^\circ$  range which can be attributed to amorphous silica. Among these, Dichloromethane

has the highest amorphous phase content which can be related to the lowest boiling point and highest dielectric constant and polarity. In case of heptane and toluene, boiling point temperature is approximately in the same range. But fewer amorphous phase was formed in heptane due to lower polarity and viscosity. According to XRD spectrum of the product in cyclohexane (Fig. 2(d)), the broad smooth peak in  $2\theta = 17-30^\circ$  range is related to the formation of a completely amorphous silica structure. The XRD patterns of all samples agree with the formation of amorphous silica as given in the JCPDS (International Centre

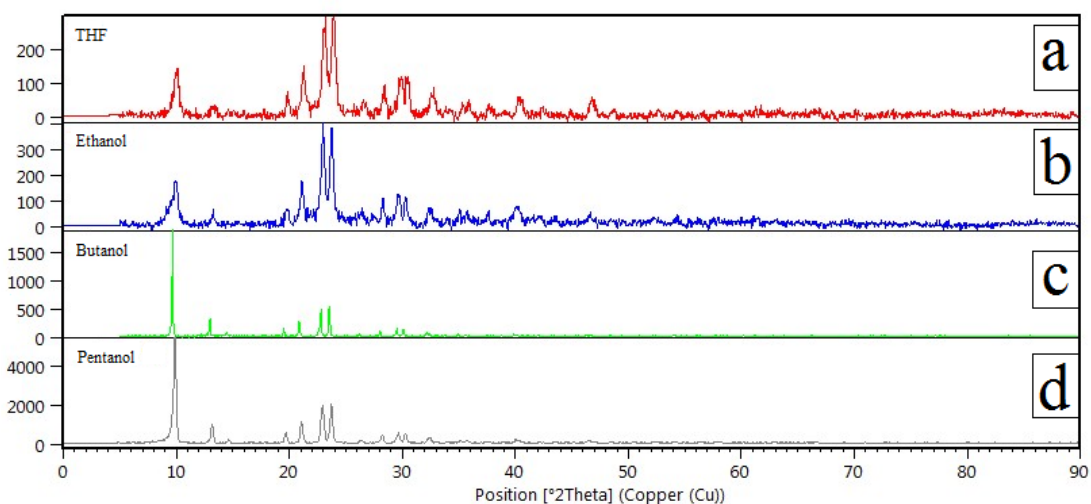


Fig. 3. X-Ray diffraction spectra of as-prepared compounds synthesized using: (a) Tetrahydrofuran, (b) Ethanol, (c) Butanol and (d) pentanol.

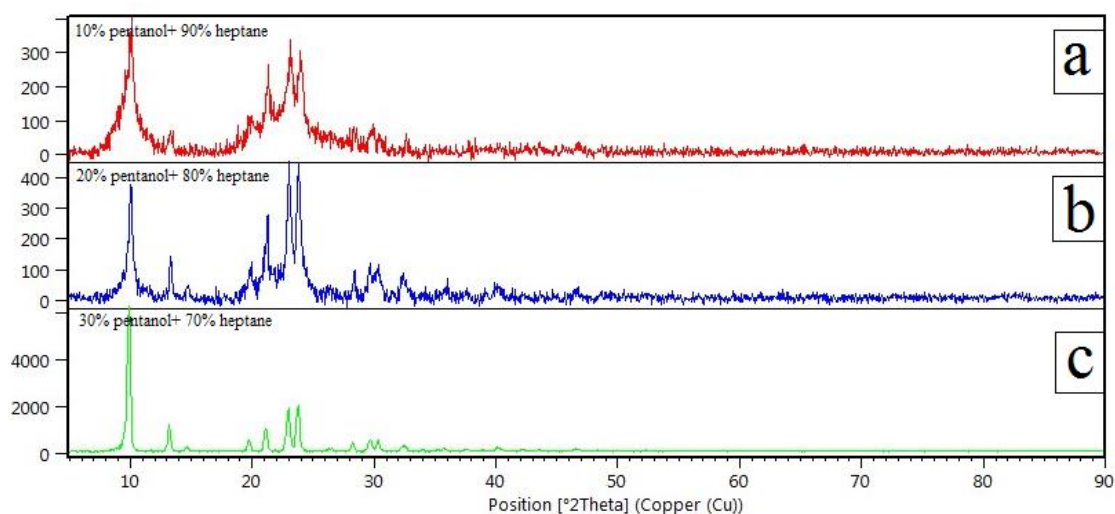


Fig. 4. X-ray diffraction curve of compounds synthesized using: (a) 90% heptane + 10% pentanol, (b) 80% heptane + 20% pentanol and (c) 70% heptane + 30% pentanol.

for Diffraction Data,  $2\theta=22^\circ$ , (101)). Figs. 2 (a-c), meanwhile, delineate the appearance of a sharp peak in the vicinity of  $2\theta=9.5^\circ$  which is attributed to the spacing of the (002) (JCPDS database No. 96-411-3638). It can be concluded that the crystalline content of the sample is enhanced while the intensity of the amorphous silica diminished.

The Diffractogram of POSS structures prepared in THF is shown in Fig. 3(a). The pattern describes the crystalline phase with several distinct sharp peaks [32]. The XRD spectrum shows the crystallinity of the sample with a trace amorphous phase. The sharp peaks could be attributed to the rhombohedral unit cell due to presence of POSS inorganic segments [32]. The peak corresponding to  $2\theta = 23.92^\circ$  (JCPDS Database No. 96-411-3638, (200)) are related to the crystalline molecular size and the others related to the crystalline structure. Dipole moment of all four samples are in the same range, but THF viscosity, boiling point and dielectric constant are the least. So, low boiling point and high viscosity can extend the degree of oligomerization.

The diffraction pattern of the synthesized POSS using ethanol is presented in Fig. 3(b). The sample shows a high crystallinity and just a small amorphous fraction. The peak at  $2\theta = 23.74^\circ$  (JCPDS Database No. 96-411-3638, (033)) determines the crystalline size of the POSS and other peaks are produced by the crystalline structure. Fig. 3(c) exhibits the XRD spectrum of the sample synthesized in butanol. The highly crystalline compound with characteristic peak located at  $2\theta = 9.67^\circ$  without any amorphous phase can be observed. Other peaks can be attributed to the rhombohedral crystallite structure [32]. Fig. 3(d) depicts the sample produced in pentanol. Several sharp peaks with high intensity illustrate the crystalline structure of the sample with no amorphous phase present. The peak located at  $2\theta = 9.63^\circ$  is caused by the size of POSS structure and other peaks are related to the rhombohedral crystalline structure [32]. Consequently, compounds isolated in butanol and pentanol display the highest crystallinity. These two solvents have higher boiling point and lower dipole moment in comparison with ethanol. Also, higher viscosity can act as a hydrolysis restricting factor.

The lowest amorphous/crystalline ratio can be seen in Fig 3(d). Moreover, the as-prepared sample synthesized in n-heptane represents the

highest yield (~57%). On the other hand, the sample synthesized in pentanol shows the lowest yield (~12%) and high crystallinity. Consequently, different amounts of pentanol were added to heptane to increase solution polarity and boiling point. Moreover, the overall structure and sharp peaks of Figs. 3 (a-c), has a crystalline structure and also match well with the sample peaks for silica as given in the JCPDS database (96-411-3638). Also, it is conspicuous that the samples synthesized using THF and ethanol comprised of amorphous content. Not only the samples synthesized using butanol and pentanol are of high crystallinity, but also the intensity of the peaks in the  $20-30^\circ$  range decrease drastically.

Figs. 4(a-c) describe the XRD pattern of samples prepared using various heptane to pentanol solvent ratios. According to the spectrums, by increasing the pentanol fraction the amorphous phase is decreased resulting in the enhancement of crystallinity. Also, the broad peak in the  $17-30^\circ$  range which is related to presence of amorphous silica tends to disappear by increasing the amount of pentanol. Finally, according to Fig. 4(c), the sample has a high crystallinity and related diffractogram was similar to the sample prepared using pure pentanol. On the other hand, increasing the amount of pentanol leads to decreasing the sample yield to ~10% which can be attributed to increasing solution viscosity due to high viscosity of pentanol.

Crystallite size of the samples synthesized in THF, ethanol, butanol and pentanol using Scherrer Eq. were ~27.52, 34.34, 71.08 and 40.50 nm, respectively. Furthermore, the yield of all four samples are ~12%. According to the XRD spectra, compounds synthesized using butanol and pentanol media represents the best crystallinity; thus selected for further characterization. As a conclusion, the amorphous content of the as-synthesized structures diminishes by increasing the amount of butanol and pentanol and  $2\theta=9.6^\circ$ ,  $22.9^\circ$ ,  $23.7^\circ$  corresponding to the spacing of (022), (200), and (033) according to the JCPDS Database (96-411-3638) would successfully form which are attributed to the characteristic peak of the OV-POSS structure [32].

#### FTIR Spectra

FTIR analysis was performed to identify the chemical bonds present in the synthesized POSS nanostructures. Figs. (5-7) represent the FTIR

spectra of the synthesized compounds. According to the spectra, strong absorption peaks located at 1123.96, 1126.43, 1122.77, 1124.52, 111.31, 1110.9, 1110.75, 1116.55, 1112.96 and 111.56

$\text{cm}^{-1}$  were related to the symmetric stretching vibration mode of Si-O-Si bonds in silsesquioxane cages, networks and cycles [15, 33, 35, 36]. The peaks appeared in the range of 1604.35-1604.87

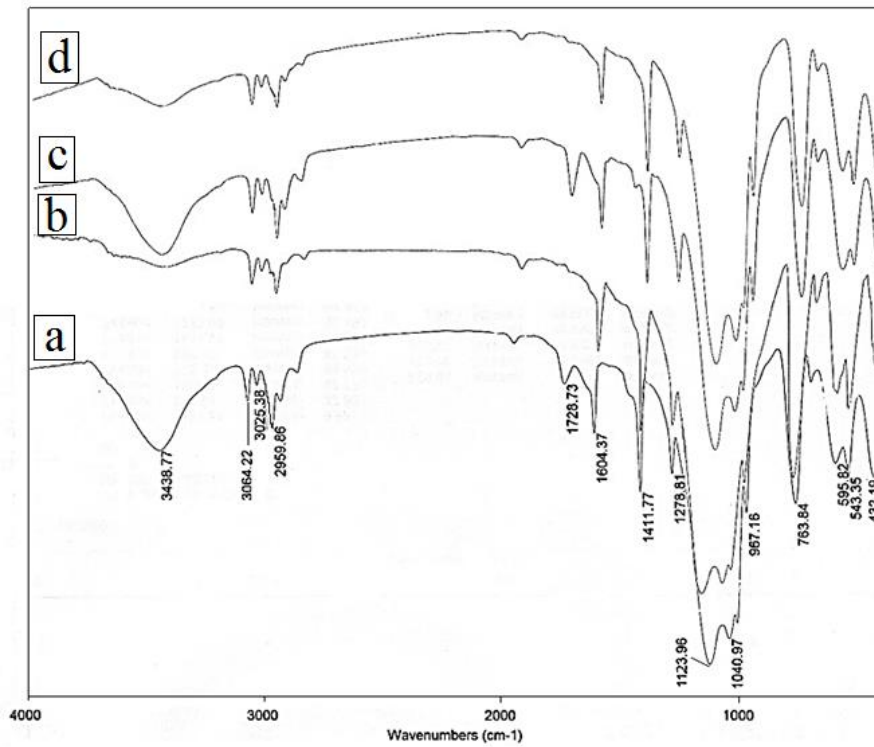


Fig. 5. FTIR spectra of (a) Toluene, (b) n-heptane, (c) Dichloromethane, (d) Cyclohexane.

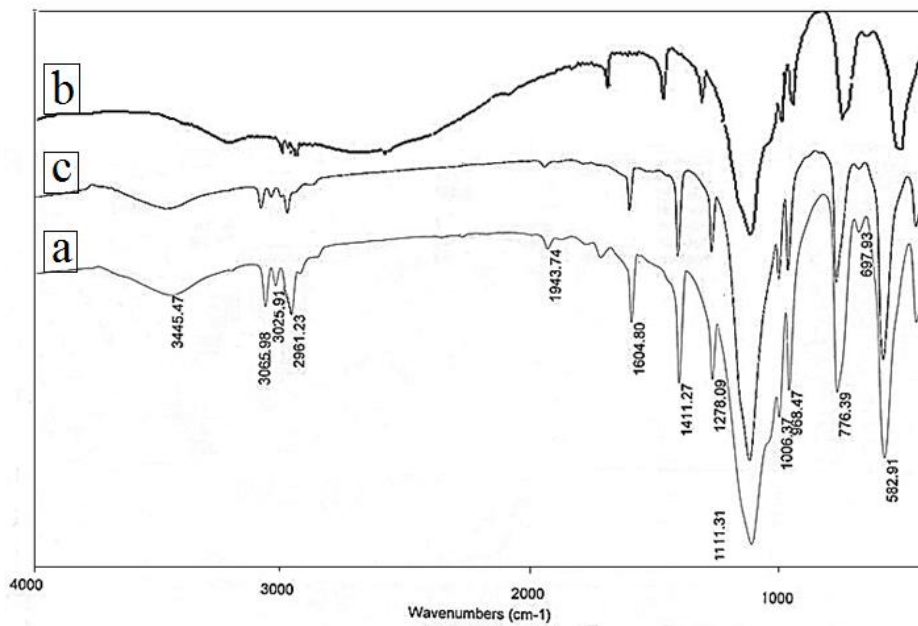


Fig. 6. FTIR spectra of (a) Tetrahydrofuran, (b) Ethanol, (c) pentanol.



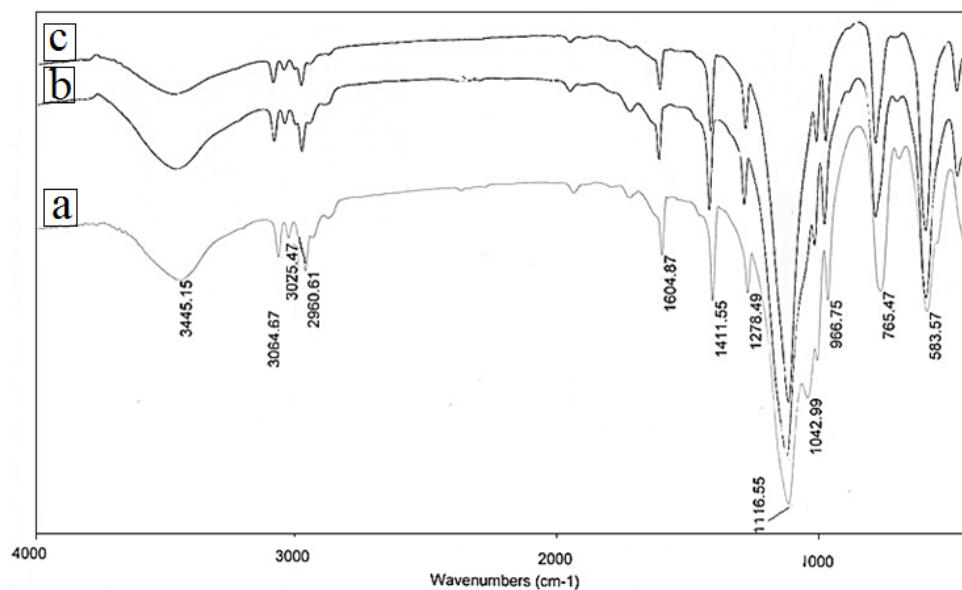


Fig. 7. FTIR spectra of (a) 90% heptane + 10% pentanol, (b) 80% heptane + 20% pentanol and (c) 70% heptane + 30% pentanol.

$\text{cm}^{-1}$  were attributed to the stretching vibration of vinyl groups [15, 21]. Absorption peaks in the range of  $1277.01\text{-}1280.6\text{ cm}^{-1}$  and  $1410.35\text{-}1412.53\text{ cm}^{-1}$  were due to bending vibration of vinyl groups [15, 20, 25]. Intense peaks in the range of  $582.89\text{-}595.82\text{ cm}^{-1}$  illustrate bending vibration and deformation of Si-O-Si bonds [24, 25]. Characteristic peaks in the range of  $762.18\text{-}779.2\text{ cm}^{-1}$  were due to stretching vibration of Si-C bonds [21, 25]. Absorption peaks located in the  $3063.82\text{-}3070.5\text{ cm}^{-1}$  and  $3024\text{-}3025.91\text{ cm}^{-1}$  ranges were characteristic peaks related to stretching vibration of C-H bonds [21, 25]. Adsorption peaks in the range of  $3437.76\text{-}3447.37\text{ cm}^{-1}$  can be related to deformation of OH groups in case of incompletely condensed silsesquioxanes, OH groups attached to  $\text{SiO}_2$  in case of amorphous samples or stretching vibration of  $\text{H}_2\text{O}$  molecules present [24, 37-39]. Furthermore, peaks appeared in the range of  $964.3\text{-}969.84\text{ cm}^{-1}$  confirmed the presence of Si-OH bond related to incompletely condensed POSS siloxanes. In addition, adsorption peaks located in the range of  $1040.66\text{-}1042.99\text{ cm}^{-1}$  illustrate the presence of incompletely condensed linear/network siloxanes [40]. According to Fig. 7 (a-c), increasing the amount of pentanol from 10 to 30% leads to the disappearance of the adsorption peak located at  $1042.99\text{ cm}^{-1}$  which is related to incompletely condensed silsesquioxanes which was also confirmed by the XRD results.

#### FE-SEM & SEM micrographs

Figs. 8 (a), (b) & (c) show the FE-SEM micrographs of OV-POSS samples synthesized using butanol with two different magnifications. According to the Figures, formation of micro and submicron clusters can be observed. Presence of some agglomerated particles in Fig. 8 (a) can be related to the self-assembly of nanostructures during synthesis or sample purification [24]. Furthermore, Figs. 8 (b) & (c) show the appearance of polyhedral crystallite and cubic structures. Meanwhile, Figs. 8 (d) and (e) delineate the SEM micrographs of the as-prepared samples. According to the figures, it is conspicuous that the as-prepared samples have almost crystalline structures. The formation of cubic structures, also, can be seen obviously. Fig. 9 represents the corresponding EDX spectra of POSS sample synthesized in butanol. The highest atomic mass of silicon atoms leads to the highest weight percent of 38.53% and the large number of carbon atoms related to attached vinyl groups lead to presence of 38.09% of sample weight. In addition, 23.38% of sample weight is attributed to oxygen atoms in silica cage. According to the spectrum, OV-POSS sample is mainly composed of Si, C and O atoms which can define the formation of silica cage with attached organic groups. Furthermore, no content of other elements and impurities are observed.

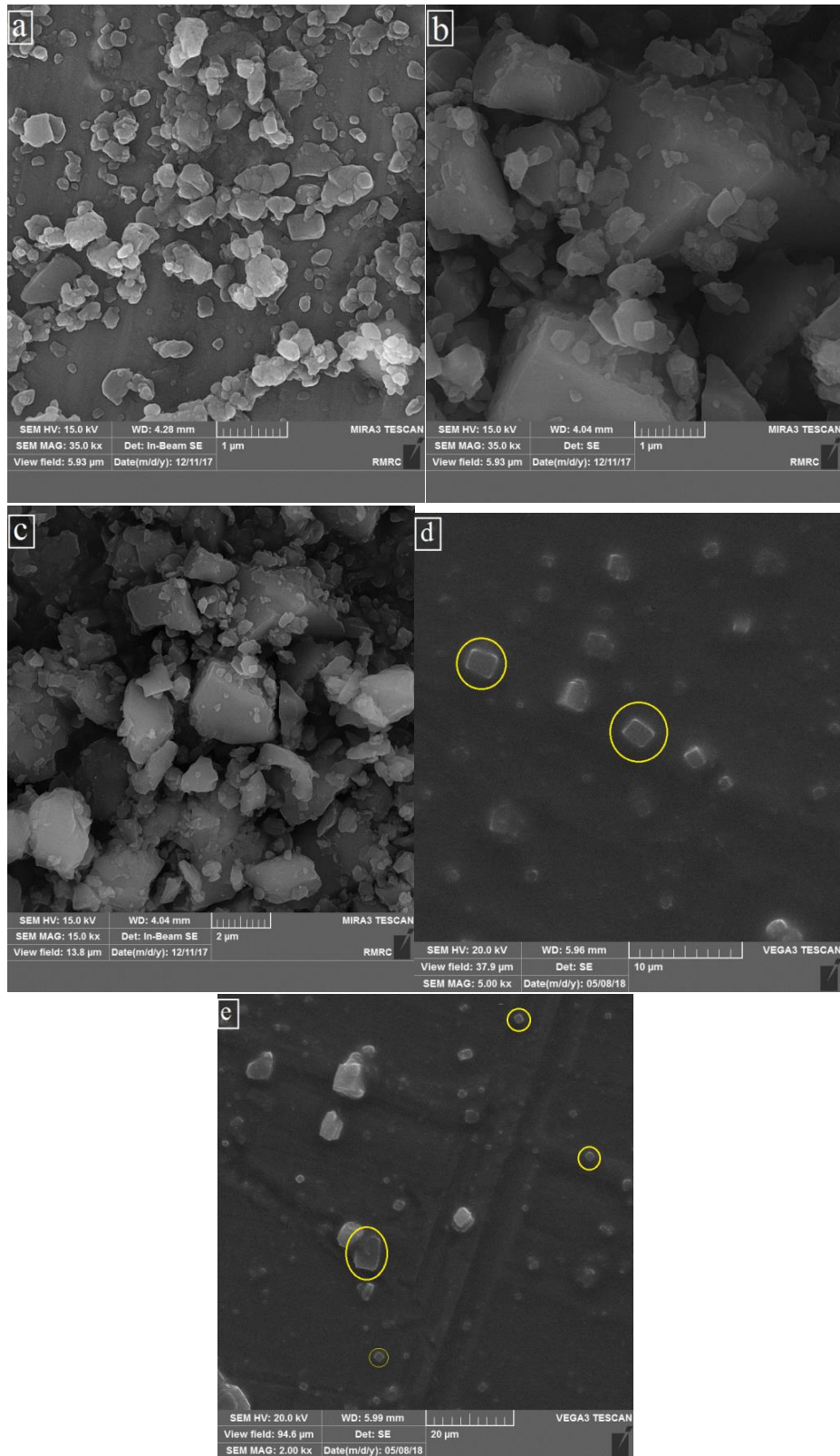


Fig. 8. FE-SEM micrographs of OV-POSS synthesized using butanol media in (a) & (b): x35000 and (c): x15000 magnifications. SEM micrographs in (d) x5000 and (e) x2000 magnifications.

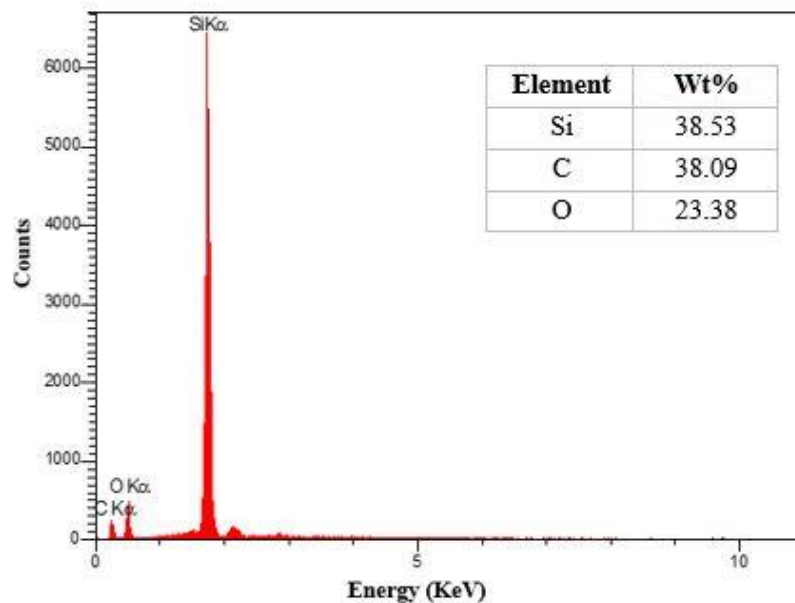


Fig. 9. Energy Dispersive X-Ray (EDX) spectrum of OV-POSS synthesized in butanol media.

#### TEM analysis

Fig. 10 (a-h) represent TEM micrographs of sample synthesized using pentanol at different scale bars. Similar morphology to those were displayed on FE-SEM micrographs can be seen in TEM analysis. As can be obviously seen, the product consists of cubic and polyhedral particles with almost regular shape which are in good agreement with FE-SEM micrographs. Furthermore, Figs. 11 (a) & (b) display particle size distribution of the as-prepared sample given in TEM micrographs in 80 nm and 100 nm scale bars using ImageJ software. According to Fig. 11 (a), ~ 62.5% of the particles show diameters in the 3.15-5.55 nm size range. Moreover, ~ 90% of particles with almost sharp size distribution in the range of 5-15.91nm can be seen from Fig. 11 (b). Furthermore, Fig. 12 (a) & (b) shows TEM micrograph of POSS sample synthesized in butanol. Also, similar morphologies to those are displayed in Fig. 11 can be observed in Fig. 12.

#### NMR spectroscopy

Nuclear magnetic resonance (NMR) is a spectroscopic method which can determine the number of magnetically distinct atoms such as hydrogen and carbon and also give information about the environment of each type [41].  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  measurements were recorded in order to illustrate POSS structure more accurately. Figs.

13 & 14 show  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of the as-prepared product dissolved in  $\text{CDCl}_3$ . According to Fig. 13, multiple resonance peaks located in the range of  $\delta$  5.903-6.183 ppm are related to vinyl proton resonance caused by coupling of hydrogen protons [20, 21, 25].  $^{13}\text{C-NMR}$  spectra of POSS is shown in Fig. 14. Peaks located at  $\delta$  128.693 ppm and 137.042 ppm are attributed to carbons of vinyl groups [21, 25].  $\text{CDCl}_3$  (deuteriochloroform or deuterated chloroform) is a common solvent of POSS samples which give 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) [41].

#### Brunauer-Emmett-Teller (BET) isotherm measurements

Figs. 15 (a) & (b) are plots concerning nitrogen sorption isotherm of OV-POSS synthesized in pentanol appeared to show type IV adsorption-desorption isotherm, which is a variation of type II with a finite multilayer formation for capillary filling completion. Also, an obvious hysteresis loop reflecting the spot of mesopores in the middle pressure area [42]. Surface area, pore size distribution, and pore volume of the as-synthesized sample, are evaluated. According to the figures provided, it can be inferred that OV-POSS possesses ~ 437.62  $\text{m}^2 \cdot \text{g}^{-1}$  surface area and a significant majority of pores are smaller than 5

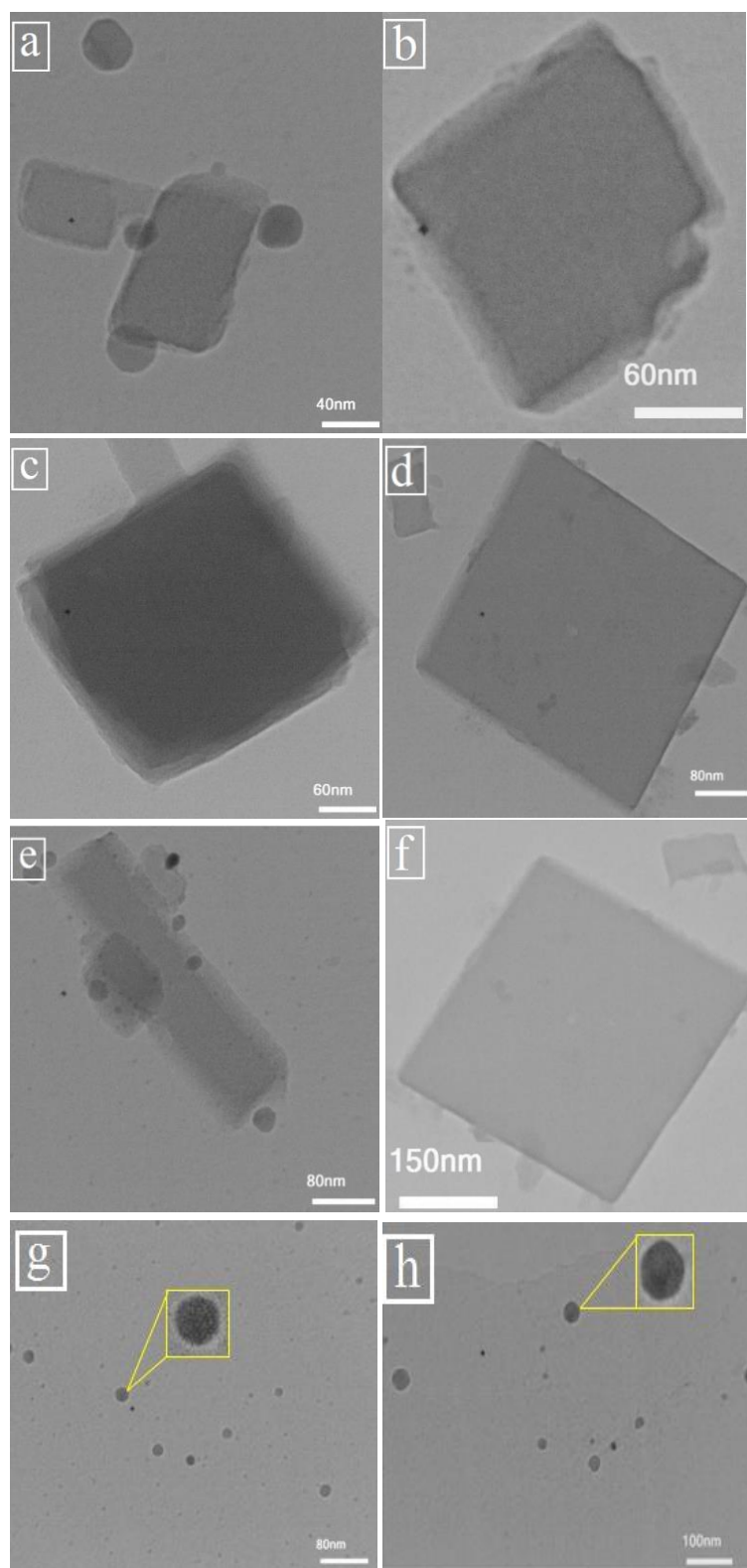


Fig. 10. TEM micrographs of OV-POSS synthesized using pentanol media in (a) 40nm, (b) & (c) 60nm, (d), (e) & (g)80nm, (f) 150nm and (h) 100nm scale bars.

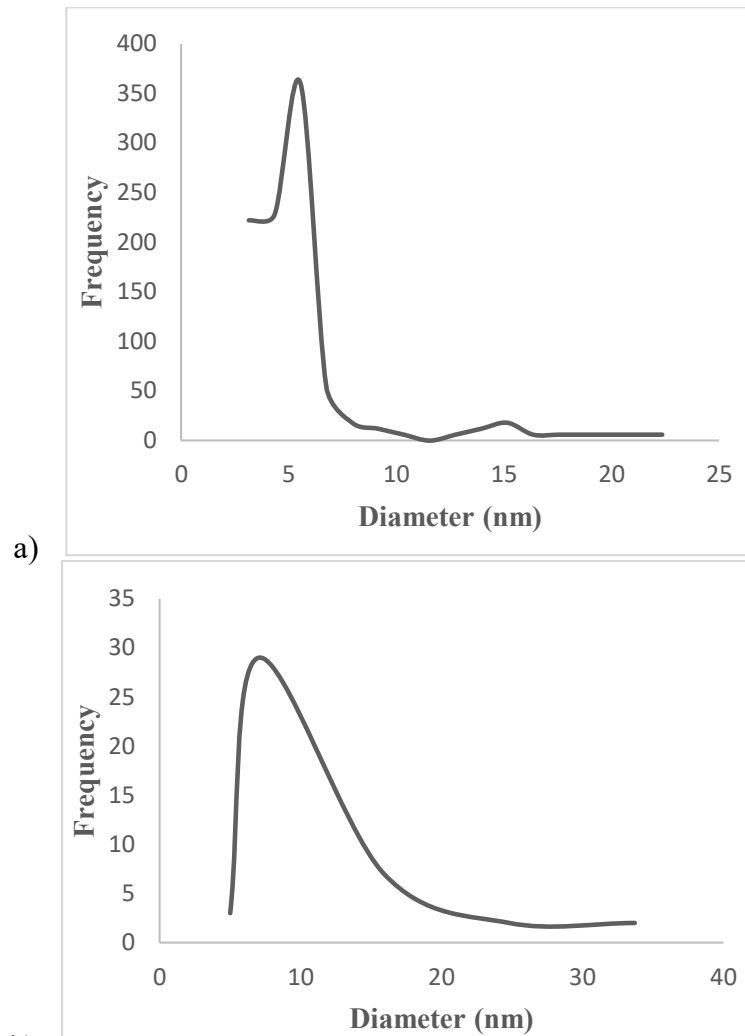


Fig. 11. Size distribution of OV-POSS sample synthesized in butanol media plotted using TEM micrographs with (a) 80nm & (b) 100nm scale bars.

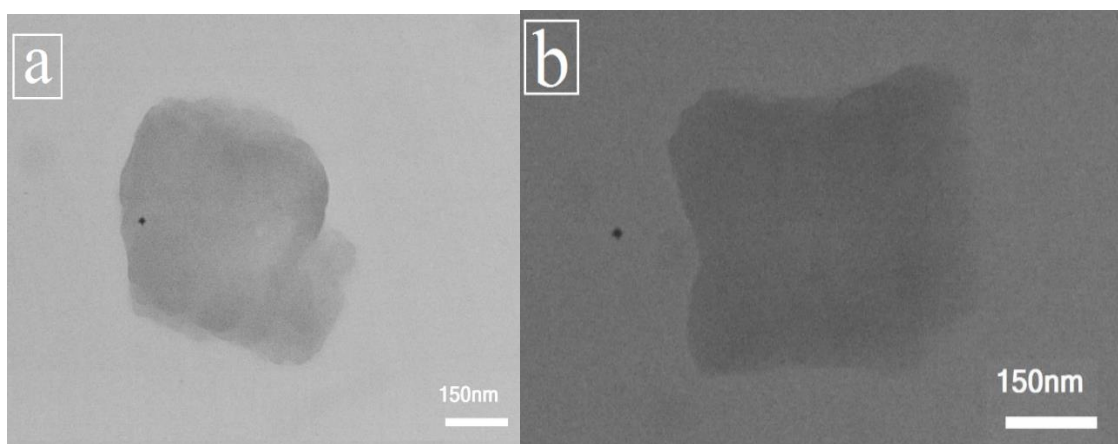


Fig. 12. TEM micrographs of OP-POSS synthesized using butanol media in (a) & (b) 150nm scale bar.

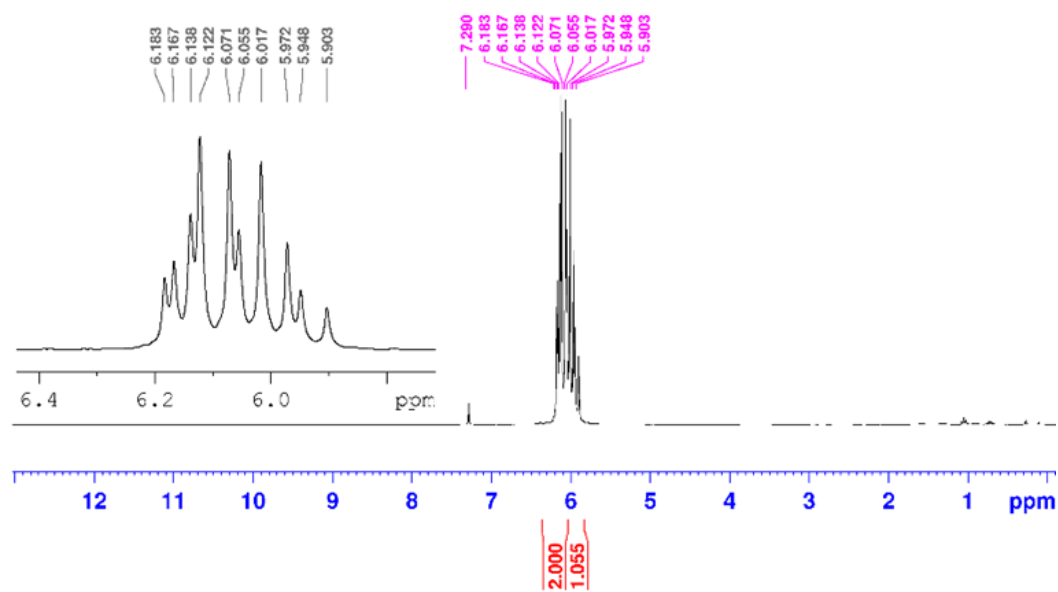


Fig. 13. <sup>1</sup>H-NMR of POSS.

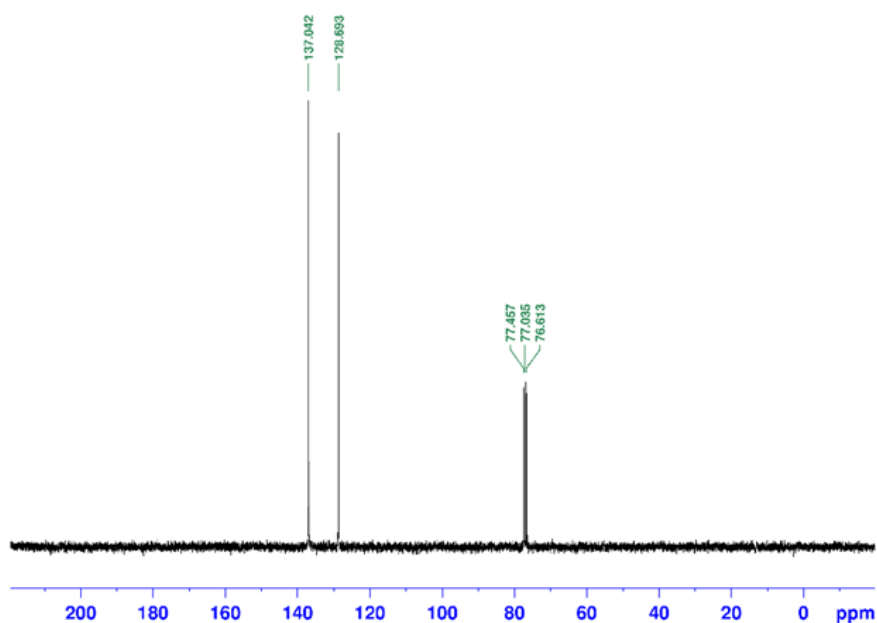


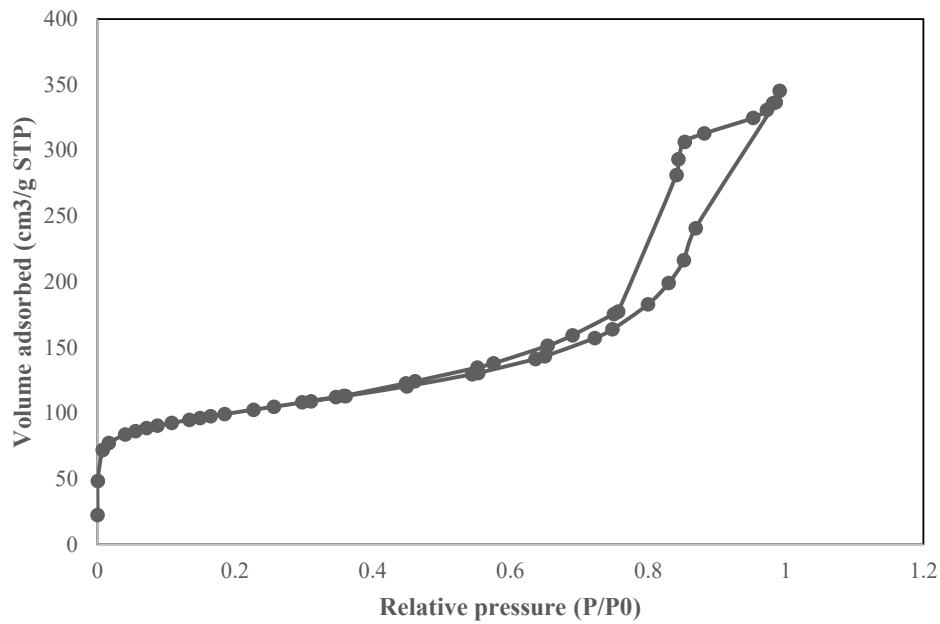
Fig. 14. <sup>13</sup>C-NMR of POSS.

nm which can be attributed to the mesoporous structure, while pores with larger diameters up to ~50 nm exist in the sample. Also, 0.56 cm<sup>3</sup>/g, is the total pore volume of the as-synthesized OV-POSS.

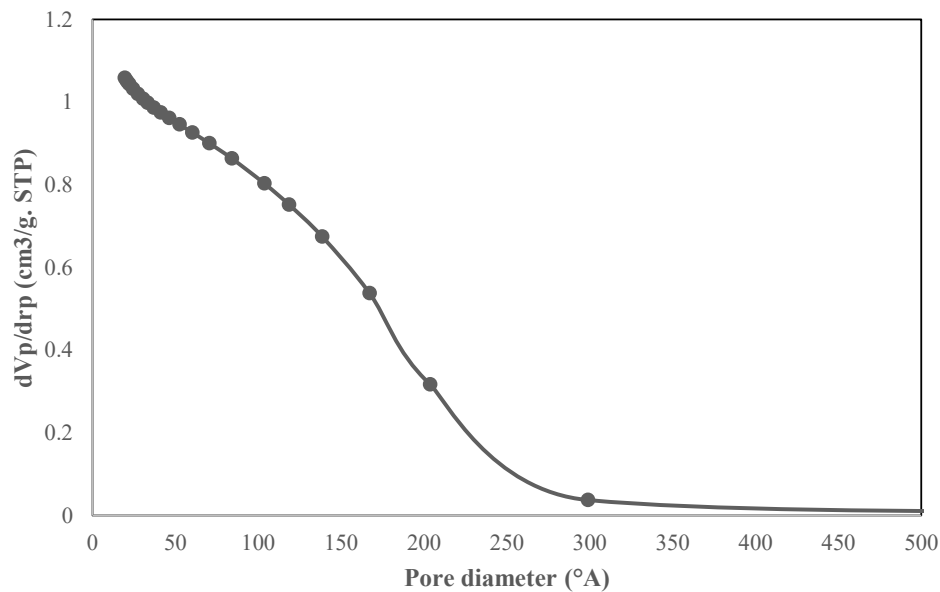
## CONCLUSIONS

The effect of solvent properties on morphology

and crystallinity of silsesquioxane compounds synthesized using hydrolytic condensation was studied. According to the theoretical background, solvation of hydrolyzed monomers and solution viscosity are of the most determining parameters which control the morphology and crystallinity. Polarity/proticity of the solvents would enhance



a)



b)

Fig. 15. (a) Nitrogen adsorption and desorption isotherms and (b) pore size distribution of OV-POSS synthesized using pentanol.

the solvation, consequently controlling the reaction rates thus reducing the polymerization. On the other hand, low viscosity solvents increase the mobility of species, reactions promotion and complete hydrolysis. XRD results show that samples synthesized in THF, ethanol, butanol and pentanol represent high crystallinity which can

approve the effect of polarity and solvation effect on morphology. FTIR spectrums illustrate the formation of silsesquioxane bonds and attached vinyl groups. FE-SEM and TEM micrographs represent formation of high crystalline polyhedral and cubic morphology of OVS compounds synthesized in butanol and pentanol, respectively.

Table 2. OV-POSS size, yield and crystallinity.

Solvent	Size (nm)		Yield (%)	Crystallinity
	XRD	TEM		
Butanol	71.08	--	~ 12	~89
Pentanol	40.50	3-16	~ 12	~76

Also, C-NMR and <sup>1</sup>H-NMR analyses confirmed the attachment of vinyl groups. Consequently, empirical results were in good accordance with theoretical backgrounds. Table 2 summarize average crystallite size using XRD, size of individual particles using TEM analyses, yield and crystallinity of OV-POSS synthesized using butanol and pentanol as the best result.

In summary, the most important suggestions for solvent selection for POSS synthesis according to the literature review performed on solvent type and solution conditions and also the experiments performed can be summarized as follow:

1. Due to solvation effect of polar solvents, alcohols are good alternatives in most cases to control the hydrolytic condensation.
2. In solvent mixtures, an alcoholic solvent should be among the constituents.
3. Polar solvents are preferred in case of non-alcoholic solutions.
4. Different additives are accompanied with non-polar solvents to increase the polarity or chemically modify the solvent to become compatible with the species present.
5. Low viscosity solvents are used due to steric hinderance prevention and hydrolytic condensation promotion.
6. Mixture of solvents can be used to take advantage of each solvent such as low viscosity, high polarity and/or high boiling point.
7. Protic solvents give better results in acidic medium while basic media is more appropriate for aprotic solvents.

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#### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper.

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