



SYNTHESIS AND CHARACTERIZATION OF ORGANIC/INORGANIC HYBRID MATERIALS BASED ON POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (POSS) AND POLY(ETHYLENE GLYCOL) VIA CLICK CHEMISTRY

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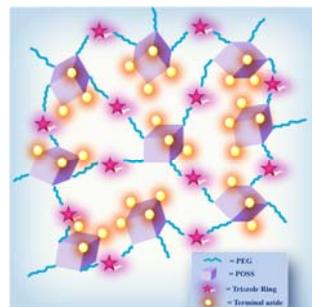
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Cu(I)-catalyzed alkyne–azide Huisgen 1,3-dipolar cycloaddition (CuAAC) was used for the creation of POSS-PEG architecture. Herein, we presented the preparation of functionalized mono and bis PEG₂₀₀₀ with maleic anhydride. Then the mono and dialkyne-terminated compounds were produced by the treatment with propargyl alcohol. Finally, click reaction occurred between azide end-functionalized polyhedral oligomeric silsesquioxane [POSS-(N₃)₈] and alkyne-terminated compounds. The resultant products were characterized by ¹H NMR, FT-IR, SEM, EDX, TGA and DTA.



INTRODUCTION

Poly(ethylene glycol) (PEG), is a biocompatible polyether with prominent applications from industrial manufacturing to medicine which have been recently reviewed.^{1,2} This hydrophilic block has been used as PEG-functionalized polymers to produce amphiphilic systems.³

Polyhedral oligomeric silsesquioxane (POSS) is a class of unique inorganic nano-components with cubic inorganic core, and the composition of R₈Si₈O₁₂ is the most studied form. This structure has some prominent properties such as well-defined, three dimensional and highly symmetric structure, low density, high temperature stability, the absence of trace metals, having size of about 1.5 nm in diameter, organic shell (eight R groups)

surrounds the inorganic core. The POSS cage could demonstrate different compatibility in the polymer matrix by the modification of R groups. This organic layer can be varied from hydrogen to alkyl (methyl, isobutyl, cyclopentyl or cyclohexyl, etc.), alkylene, or arylene. According to these mechanical and thermal properties, POSS is a perfect building block for high performance polymer nanocomposites⁴⁻⁶ and has been used in electronic devices, aerospace and biological applications.

However, inorganic–organic hybrid polymeric materials deserve to be expanded because of their combined properties of the organic and inorganic components.⁷⁻¹¹ POSS molecules can be regarded as truly inorganic/organic hybrid system, which is compatible with polymers and natural biomaterials.¹²

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There are several ways of preparing this kind of hybrid scaffold and “click chemistry” is one of the most commonly used which possesses excellent characteristics such as a short reaction time, high selectivity and mild reaction conditions.¹³

According to our previous efforts,¹⁴⁻¹⁹ we tried to investigate the synthesis of novel clickable structures, and characterization of hybrid polymer with POSS core. In this work the synthesis of an inorganic-organic hybrid polymer with POSS *via* click chemistry was investigated. In this hybrid polymer, poly(ethylene glycol) (PEG) was used as polymeric segment to be linked into POSS nano core and the click reaction was performed between azid POSS [POSS-(N₃)₈] and alkynyl PEG.

EXPERIMENTAL

Materials

3-Chloropropyltrimethoxysilane, di-*n*-butyltin dilaurate, sodium azide (NaN₃), CuSO₄, sodium ascorbate, maleic anhydride and concentrated HCl were obtained from Merck Co. Germany. PEG₂₀₀₀ with mono and bis -OH tails were purchased from Aldrich. In addition, 4-(dimethylamino) pyridine (DMAP), Propargyl alcohol and dicyclohexylcarbodiimide (DCC) were provided from Aldrich and used as received. Organic solvents, such as *N,N*-dimethylformamide (DMF), methanol and dichloromethane were of chemically pure grade, obtained from commercial sources. Before use, all solvents were purified by fractional distillation and dried.

Instrumentation

¹H NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 MHz using CDCl₃ or DMSO-*d*₆ as solvents. Infrared spectra were recorded in the wavenumbers ranging from 4000 to 400 cm⁻¹ with a FT-IR Bruker Tensor 27 instrument using a KBr wafer. Melting points were measured using the capillary tube method with an electro thermal 9200 apparatus. Scanning electron microscopic (SEM) and images, energy-dispersive X-ray (EDX) analysis instruments were used to get electronic images of nanocomposites. The morphology of the nanocomposite was investigated by a Philips XL30 scanning electron microscope. Thermal behavior of the synthesized nanocomposites was studied by Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA). TGA and DTA were conducted with a BAHR: STA 503 TGA/DTA instrument at a heating rate of 10°C min⁻¹ in air.

Synthesis of POSS-(Cl)₈

POSS-(Cl)₈ was prepared as followed:²⁰ 3-chloropropyltrimethoxysilane (15 g) was added to a mixture of concentrated HCl (5 mL) and dry methanol (150 mL) in a two-necked round-bottom flask by a dropping funnel strongly stirring in 10 min. After 2 h, the mixture was cooled to the room temperature and remained statically for 48 h. Di-*n*-butyltin dilaurate (0.15 g) was added as catalyst. The white precipitated crystals were collected, washed with methanol for several times and dried in vacuum.

Synthesis of POSS-(N₃)₈

Azidation of POSS-(Cl)₈ was carried out according to a typical procedure:^{9,21} NaN₃ (2.5 g) was added to POSS-(Cl)₈ (1 g) and dry DMF (30 mL). After stirring at 393 K for 48 h, the mixture was filtered. 100 ml distilled water was added to the filtrate and extracted with CH₂Cl₂ (4 × 20 mL). The purified product was obtained after removal of the solvent and a yellow viscous liquid was obtained.

Synthesis of M-PEG (3)

A typical esterification procedure for the divergent reaction of two kinds of PEG₂₀₀₀ (2 and 4) with the maleic anhydride (1) is as follows:²² PEG (2) (3.0 g) was dissolved in 15 mL dry CH₂Cl₂, and maleic anhydride (0.11 g, 1.5 mmol) and DMAP (0.08 g, 1 mmol) were added subsequently. Then, the reaction vessel was cooled to 0 °C and diluted solution of the DCC (0.2 g, 1 mmol) was added dropwise over 1 h. The reaction was carried out at room temperature for 24 h. The formed by-product, urea, was filtered off and the solvent removed. The resulting product was obtained by precipitation into excess methanol. The precipitation cycle was repeated twice and the brownish solid product (3) dried under vacuum at room temperature.

Synthesis of M-PEG-M (5)

Similar to above procedure, PEG (4) (3.0 g) was dissolved in 15 mL dry CH₂Cl₂, and maleic anhydride (0.22 g, 3 mmol) and DMAP (0.16 g, 2 mmol) were added subsequently. Then, the reaction vessel was cooled to 0 °C and diluted solution of the DCC (0.4 g, 2 mmol) was added dropwise over 1 h. The reaction was carried out at room temperature for 24 h. The formed by-product, urea, was filtered off and the solvent removed. The resulting product was obtained by precipitation into excess methanol. The precipitation cycle was repeated twice and the brownish solid product (5) dried under vacuum at room temperature.

Synthesis of alkyne-terminated M-PEG (7)

Another esterification reaction was performed as followed: propargyl alcohol (6) (0.5 mL, 10 mmol), DMAP (0.3 g, 3.75 mmol), and compound 3 (1.07 g, 0.5 mmol) were dissolved in dry CH₂Cl₂. Then, the reaction vessel was cooled to 0 °C and diluted solution of the DCC (0.15 g, 0.75 mmol) was added dropwise over 1 h. The reaction was carried out at room temperature for 24 h. The formed by-product, urea, was filtered off and the solvent removed. The product (7) was obtained by precipitation into excess methanol.

Synthesis of dialkyne-terminated M-PEG-M (8)

As mentioned above, in the case of compound 5, the same treatment was occurred including: propargyl alcohol (6) (1 mL, 20 mmol), DMAP (0.6 g, 7.5 mmol), and compound 5 (1 g, 0.5 mmol) were dissolved in dry CH₂Cl₂. Then, the reaction vessel was cooled to 0 °C and diluted solution of the DCC (0.3 g, 1.5 mmol) was added dropwise over 1 h. The reaction was carried out at room temperature for 24 h. The formed by-product, urea, was filtered off and the solvent removed and the desired product (8) was achieved.

Click reaction between POSS-(N₃)₈ and alkyne-terminated compounds

A solution of alkyne-terminated M-PEG (7) (0.108 g, 0.05 mmol) in water was added to strongly stirring POSS-(N₃)₈ (0.12 g, 0.11 mmol) in CH₂Cl₂. CuSO₄ and sodium ascorbate

1M (1 ml) were added to the mixture. The brownish precipitation was formed immediately and the mixture was stirred for 24 h at room temperature. The solid was separated by centrifuge and washed with dichloromethane and water and the final product (**12**) was obtained. In the same procedure, alkyne-terminated M-PEG-M (**8**) (0.1 g, 0.05 mmol) in water was added to strongly stirring POSS-(N₃)₈ (0.24 g, 0.22 mmol) in CH₂Cl₂. CuSO₄ and sodium ascorbate 1M (2 ml) were added to the mixture. After producing a brownish precipitation, the mixture was left to stir for 24 h at ambient temperature. The solid was separated by centrifuge and washed with dichloromethane and water and the final product (**13**) was obtained and all resultant materials were characterized.

RESULTS AND DISCUSSION

In this study, two organic/inorganic POSS-PEG nanocomposites were synthesized *via* “click” chemistry. The synthetic route for the amphiphilic POSS-PEG is depicted in Scheme 1 and 2. The PEG₂₀₀₀ derivatives as one of the most commonly used hydrophilic polymers were used as starting materials. First, functionalization of PEG with small organic compounds was performed (Scheme 1). For this purpose, PEG was reacted with maleic

anhydride to produce carboxylic acid terminated compounds [M-PEG (**3**) and M-PEG-M (**5**)]. Simple esterification reaction using DCC and DMAP was applied. The FT-IR spectrum (Fig. 1a) of M-PEG (**3**) showed a characteristic band for the ester at 1734 cm⁻¹ and two bands for carboxyl end group at 1730 cm⁻¹ and 2921 cm⁻¹. ¹H NMR revealed the characteristic proton signals of the methylene protons of ethylene glycol (-CH₂CH₂-) at 3.42-3.89 ppm and -CH=CH- at 6.91. The same procedure was performed for the PEG with two -OH tails (**4**) and subsequently M-PEG-M (**5**) was obtained in the first step. The FT-IR of compound **5** (Fig. 1b) had a sharp peak at 2920 cm⁻¹ which is ascribed to the stretching vibration of carboxylic groups. Monoalkyne-terminated PEG (**7**) was prepared by the reactions of propargyl alcohol (**6**) with M-PEG (**3**). Dialkyne-terminated PEG (**8**) was produced by similar treatment as mentioned above. The Ft-IR spectra of compounds **7** and **8** are illustrated in Fig. 1c and 1d respectively. In these spectra a sharp peak at 2120 cm⁻¹ which is attributed to the terminal alkynes is observed.

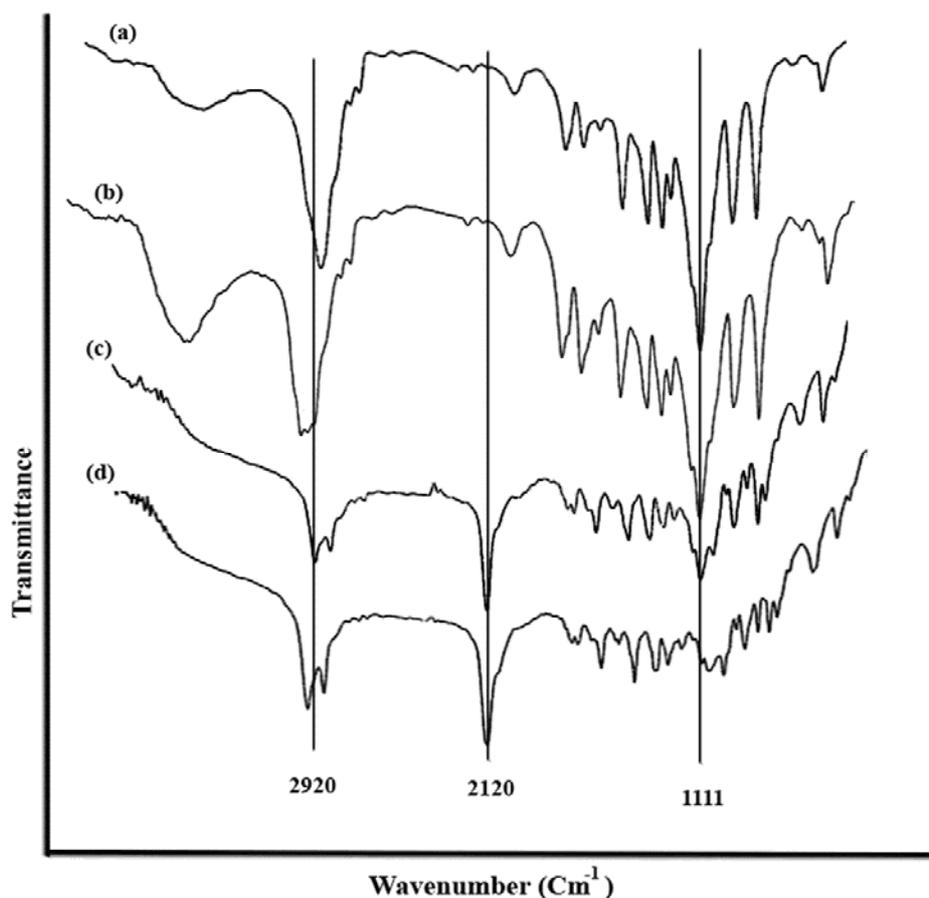
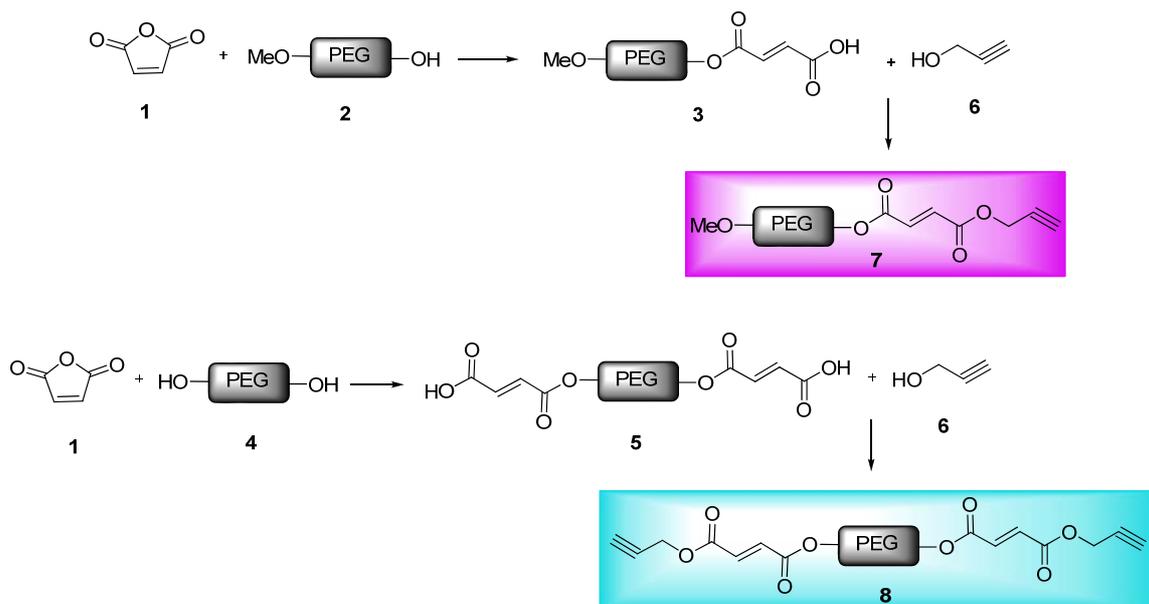


Fig. 1 – FT-IR spectra of (a) compound 3 (b) compound 5 (c) compound 7 and (d) compound 8. (The measurements were performed using dry KBr pellets).



Scheme 1 – Preparation of compounds 7 and 8 by esterification reaction.

POSS-(Cl)₈ was prepared from 3-chloropropyltrimethoxysilane as precursor. The terminal Cl functionality of POSS-(Cl)₈ was then easily converted to azide by reacting with NaN₃ at 70 °C.

The FT-IR spectrum of POSS-(Cl)₈ is shown in Fig. 2a. In this spectrum the peak at 740 cm⁻¹ could be attributed to the O–H out-of-plane vibration. The band due to the asymmetric Si–O–Si stretching vibration appears in 1100–1000 cm⁻¹. The ¹H NMR of this compound clearly showed peaks of CH₂ groups at 0.81, 1.88 and 3.54 (Fig. 3a). After azidation of POSS-(Cl)₈ by NaN₃, it can be seen that the resonance signal of proton in –CH₂Cl shifted from 3.5 ppm to 3.2 ppm, the latter was ascribed to –CH₂N₃ of POSS-(N₃)₈ (Fig. 3b). This shielding demonstrates that the –Cl group has been replaced by an electron back drawing group which decreases the density of electrons around the protons and resulted to resonance in weaker field. This suggests that the azidation reaction was completed. The FT-IR of POSS-(N₃)₈ (Fig. 2b) revealed the presence of absorbance peak at 2100 cm⁻¹, which is characteristic of the terminal azide group.

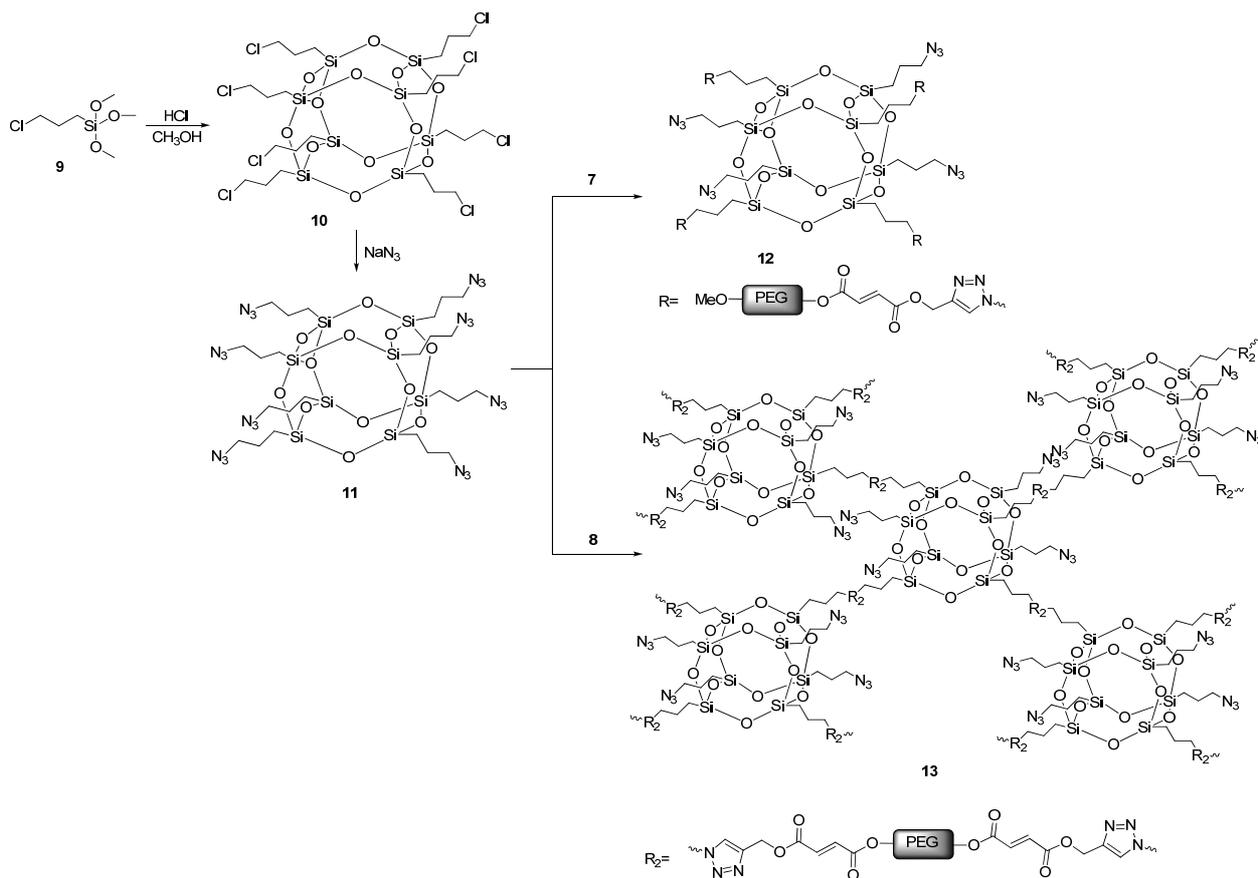
In the last step, the above mono and dialkyne-terminated PEG were reacted with POSS-(N₃)₈ to obtain organic/inorganic POSS-PEG *via* click reaction. The Huisgen 1,3-dipolar cycloaddition was carried out at room temperature, with the mixture of CuSO₄/sodium ascorbate as the catalyst (Scheme 2).

The FT-IR of the resultant click products (**13**) (Fig. 2d) showed that the absorbance peak of azide group at 2100 is not suppressed. The same result was obtained for compound **12**. It's assumed that the occurrence of click cyclization was not occurred for eight azide groups of POSS because of steric hindered of polymer segments and there were some remained azide tails. This phenomenon makes this hybrid to a clickable material which can be performed the click reaction with other smaller molecules. The protons resonance of triazole structures is observed at 7.97 ppm therefore; the ¹H NMR spectrum indicated that organic/inorganic POSS-PEG was successfully obtained (Fig. 3c).

SEM experiments were carried out to monitor the structural evolution of these materials. Fig. 4a depicts the cubic structure of POSS-(Cl)₈ with a diameter of around 10 μm which consists of numerous POSS-(Cl)₈ nanoparticles. The morphology of POSS after click reaction was illustrated in Fig. 4b.

The presence of some elements such as Cl, O and Si in POSS-(Cl)₈ was confirmed by Energy Dispersive X-ray analysis (EDX) (Fig. 5a). EDX analysis of POSS-(N₃)₈ in Fig. 5b indicates that the clean product is mostly composed of O and Si, with no other signals of Cl which shows the successful nucleophilic substitution.

The thermogravimetric analyses of the synthesized nanocomposites are displayed in Figure 6. The shown curves represent the thermal decomposition of crude PEG₂₀₀₀, compounds **12** and **13**.



Scheme 2 – Synthesis of desired compounds **12** and **13** using click reaction between POSS-(N₃)₈ and compounds **7** and **8** (CDCl₃ and TMS were used as the solvent and internal standard, respectively).

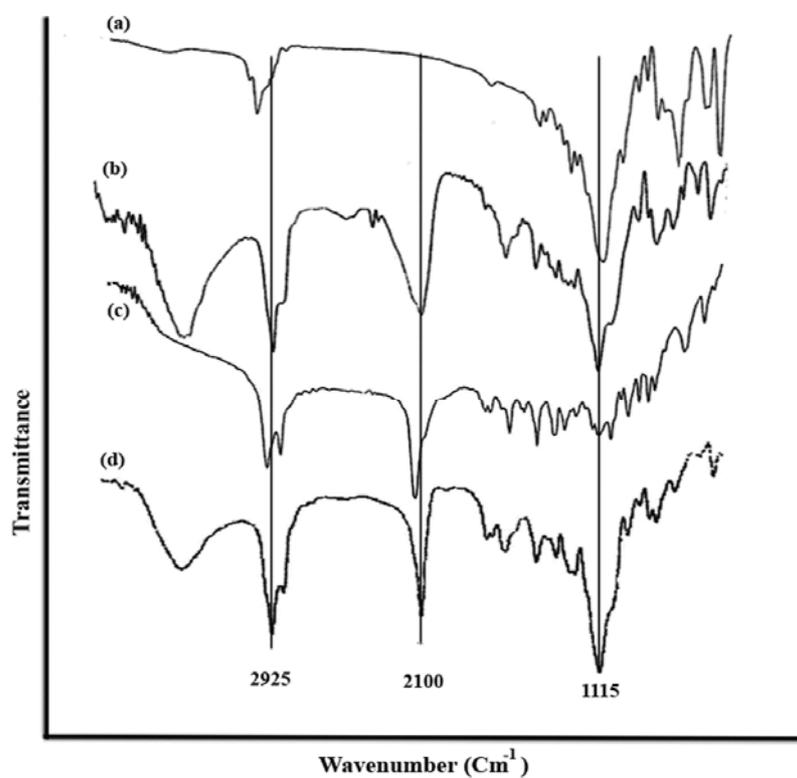


Fig. 2 – FT-IR spectra of (a) POSS-(Cl)₈ (b) POSS-(N₃)₈ (c) compound **8** and (d) compound **13**. (The measurements were performed using dry KBr pellets).

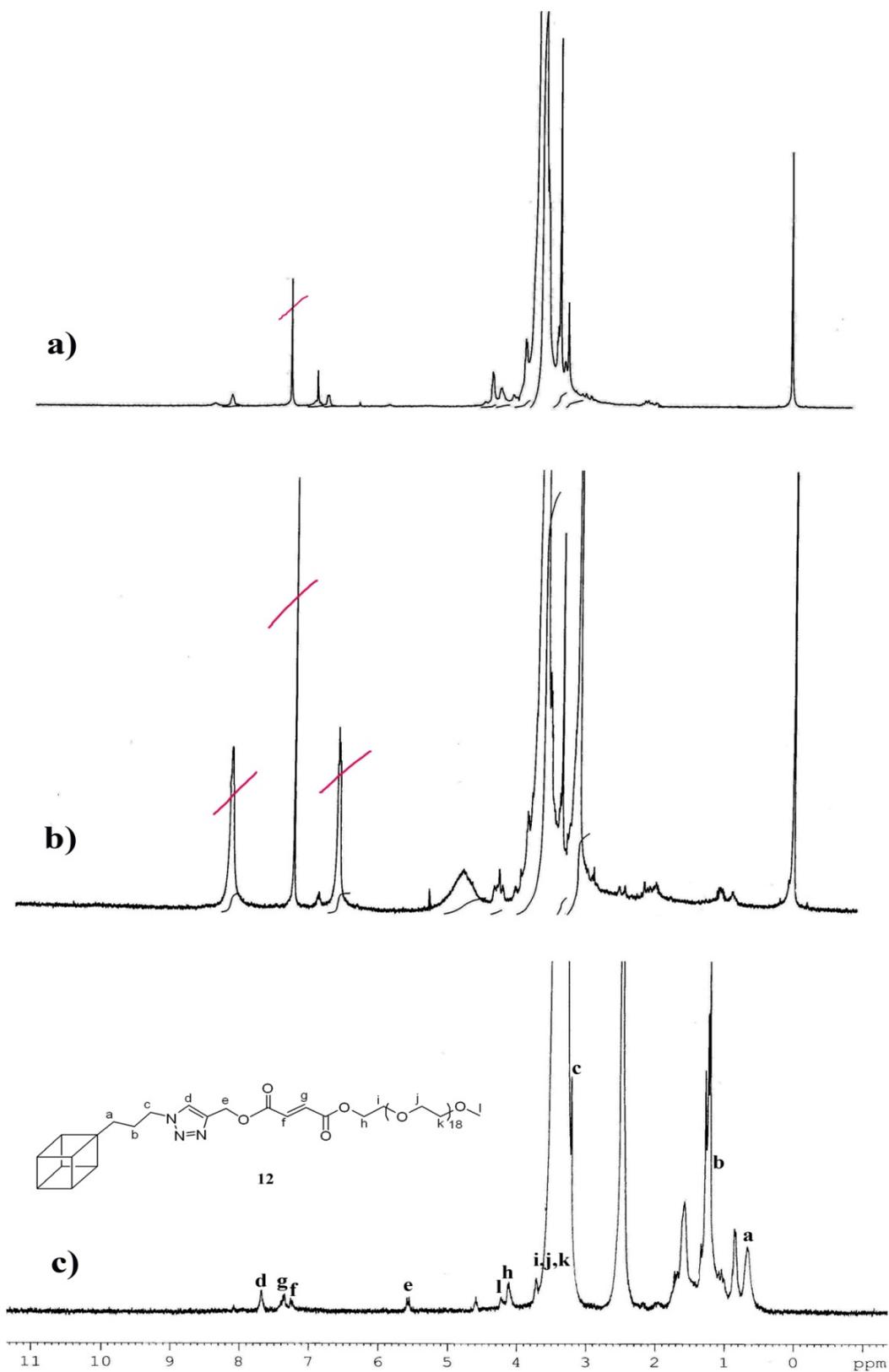


Fig. 3 – ^1H NMR spectra of (a) $\text{POSS}(\text{Cl})_8$ (b) $\text{POSS}(\text{N}_3)_8$ (c) compound **12**. (CDCl_3 and TMS were used as the solvent and internal standard, respectively).

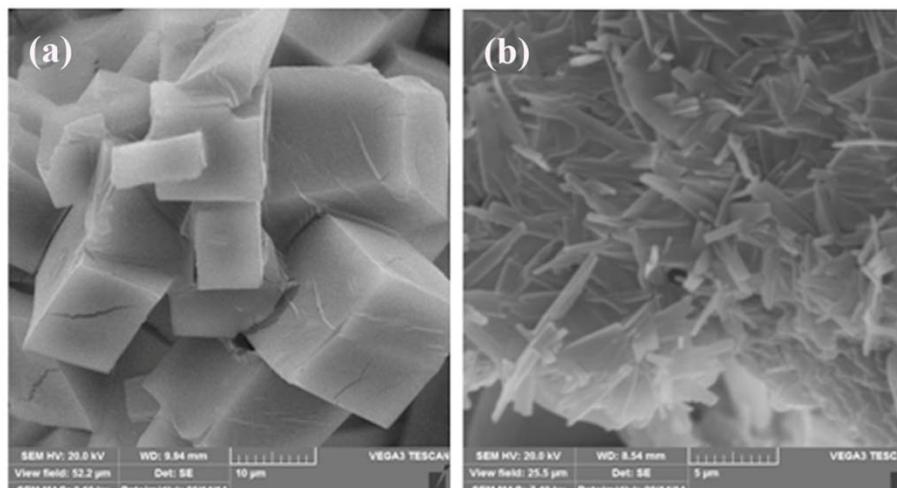


Fig. 4 – SEM of POSS-(Cl)₈ (a) and POSS-(N₃)₈ (b).

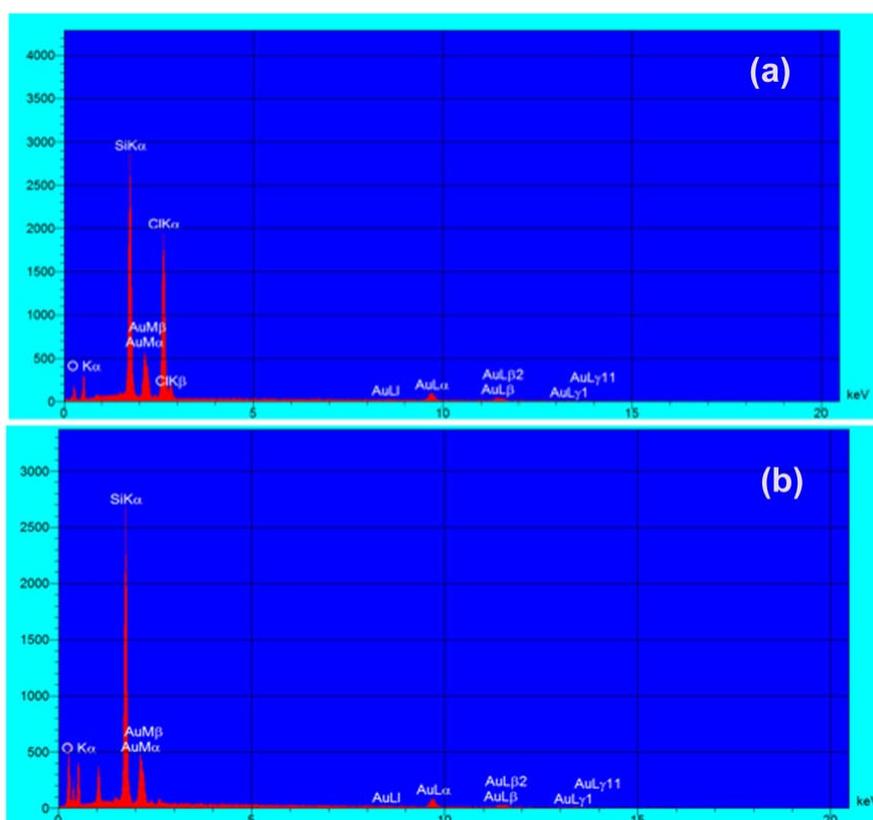


Fig. 5 – EDX analysis of (a) POSS-(Cl)₈ and (b) POSS-(N₃)₈.

In the case of PEG₂₀₀₀ a sharp weight loss was observed at 230 °C, which was related to degradation of polymeric chain. At the end of analysis, nearly 100% of PEG₂₀₀₀ was consumed that revealed the complete degradation of the main skeleton. The curve of material **12** showed three steps of weight loss. The first loss observed from 185 to 250 °C was due to the degradation of polymeric segments. The second loss occurred from 270 to 400 °C, attributed to the breaking of

organic segments from the surface, and the third loss from 405 to 623 °C was maybe due to the thermal degradation of organic segments on the surface of POSS. The 15% of residue was related to burned silicon compounds. Similarly, in the case of compound **13**, three weight loss in the ranges of 177-231, 270-384 and 400-658 °C were observed and 29% residue was left at the end of the experiment.

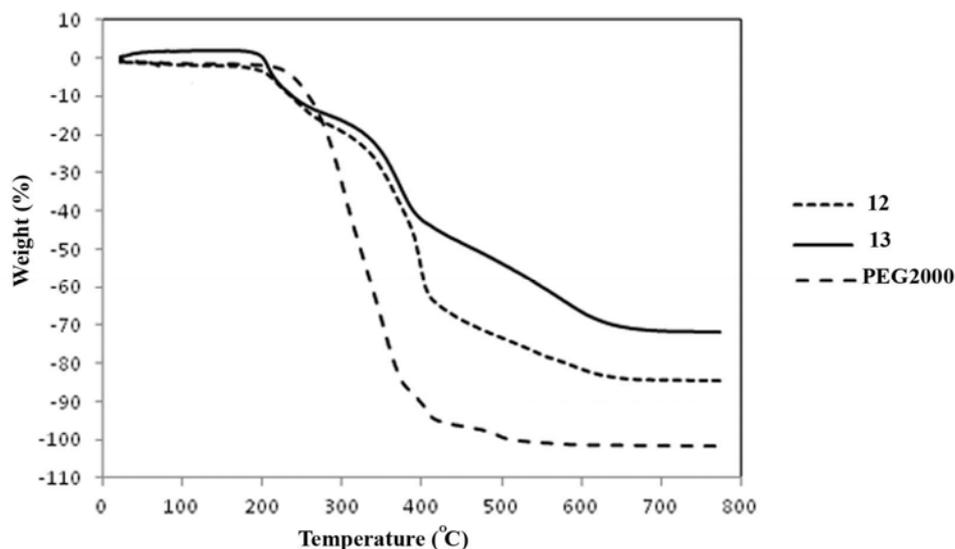


Fig. 6 – TGA analysis of crude PEG₂₀₀₀, compounds **12** and **13**.

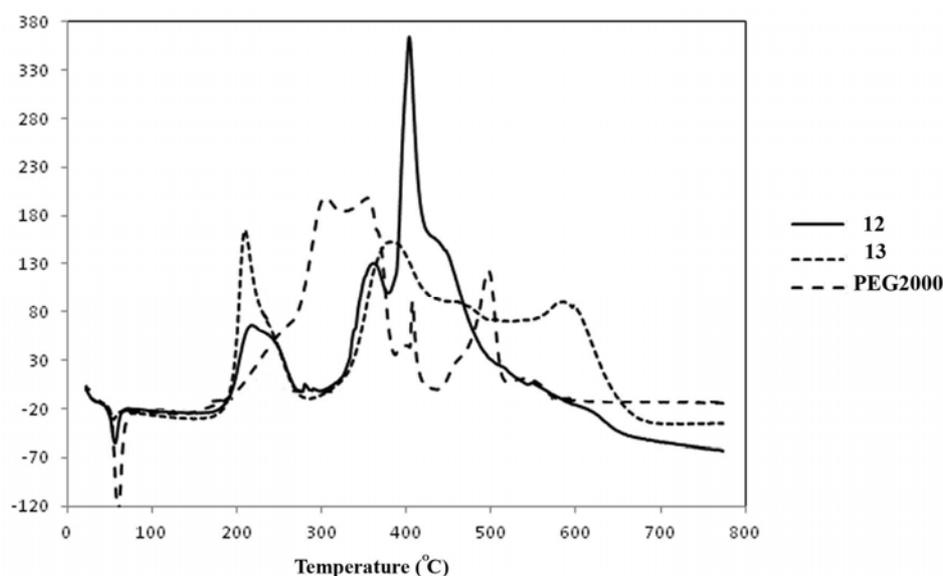


Fig. 7 – DTA analysis of crude PEG₂₀₀₀, compounds **12** and **13**.

The DTA analysis of crude PEG₂₀₀₀ and desired nanocomposites (compounds **12** and **13**) was shown in Fig. 7. As can be seen, the PEG₂₀₀₀ spectral region was deconvoluted into two endo and exo region. The first peak in endo region at 55 °C is related to loss of water. The main weight loss at 200-380 °C in TGA of PEG₂₀₀₀ was illustrated in DTA by a sharp peak in exo region. Another strong peak at 400-600 °C was attributed to aggregation of polymer chain. In DTA of compound **12** in addition to primary endo peak at 55 °C several exo peaks at 230, 363, 403 and 434 °C were observed and were related to loss of organic moieties. The exo peaks of compound **13** appeared at the range of 206, 376, 463 and 583 °C.

CONCLUSION

A novel polymeric organic-inorganic hybrid material based on POSS as nano core was successfully synthesized by click chemistry of POSS-(N₃)₈ and alkynyl terminated PEG. First, we synthesized both mono- and bis maleic acid (M)-functionalized poly(ethylene glycol) derivatives (M-PEG and M-PEG-M, respectively) through esterification reaction of maleic anhydride to PEG₂₀₀₀, using DCC and DMAP. Then, the following compounds were treated by propargyl alcohol *via* another similar esterification since the mono and dialkyne-terminated compounds were produced. In the second step, octakis(3-

chloropropyl)octasilsesquioxane [POSS-(Cl)₈] as a nano cube-like T₈ silsesquioxanes was converted to azid POSS [POSS-(N₃)₈] through nucleophilic substitution. Finally, azide end-functionalized polyhedral oligomeric silsesquioxane [POSS-(N₃)₈] was incorporated into the mono- and bis PEG-functionalized materials *via* highly efficient azide-alkyne click reaction, resulting a hydrophilic/hydrophobic system. The resultant organic/inorganic hybrid materials were characterized by means of ¹H NMR, FT-IR, SEM, EDX, TGA and DTA.

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