

Synthesis, Characterization and Thermal Properties of Silsesquioxane Organically Modified With 4,5-Diphenyl-2-Imidazolethiol

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Abstract

The present paper describes the preparation of a nanostructured silsesquioxane, the octa-(3-chloropropyl)-octasilsesquioxane (S) that was organofunctionalised with the 4,5-Diphenyl-2-imidazolethiol (DIT). The modification of silsesquioxane with DIT proposed in this paper follows two steps. The composite prepared after functionalization was ascribed as SDIT. The composite SDIT and precursors were characterized by infrared (FTIR), ¹³C and ²⁹Si Nuclear Resonance Magnetic (NMR) in solid state, Scanning Electron microscopy (SEM); X-Ray Diffraction (XRD); Energy-Dispersive X-ray spectroscopy (EDS) and Thermogravimetry. By spectroscopic analysis using above techniques, we conclude with that the SDIT synthesis was conducted with success. It was observed a cluster of particles containing cavities in an orderly fashion. The thermogravimetry analyzes performed in two different atmospheres, concluding that the materials (S, DIT and SDIT) when in air atmosphere has a slower degradation process in relation to nitrogen atmosphere. The thermogravimetry of SDIT indicate a greater thermal stability in nitrogen atmosphere.

Keywords: silsesquioxane, functionalization, 4,5-diphenyl-2-imidazolethiol

1. Introduction

In the economic and scientific context, various companies and universities are currently researching new materials from polyhedral oligosilsesquioxanes (POSS). Silsesquioxanes are materials with an empirical formula (RSiO_{1.5})_n, where R is a hydrogen atom or an organic group (Do Carmo, Bicalho, Silveira, Dias Filho, & Paim, 2013; Cordes, Lickiss, & Rataboul, 2010; Baney, Itoh, Sakakibara, & Suzukit, 1995; Kuo & Chang, 2011; Xu, Loo, & Wang, 2011; Tanaka & Chujo, 2012; Li-Chih & Shea, 2011) and n = 4, 6, 8, 10 (n ≥ 4) (Cordes, Lickiss, & Rataboul, 2010). Due to their intrinsic quality properties, and as a consequence in recent years there has been a large increase in the number of patents and publications related to these materials (Laine & Roll, 2011; Cordes, Lickiss, & Rataboul, 2010).

Such exponential increase in the number of researchers, publications, government and industrial incentive programs has resulted in these nanomaterials representing great potential in the field of nanoscience and nanotechnology (Phillips, Haddad, & Tomezak, 2004). The interest in this family of compounds has generated 14 review articles covering many ways on the synthesis, chemistry and properties of silsesquioxanes (Laine & Roll, 2011; Cordes, Lickiss, & Rataboul, 2010). However a recent literature search did not find any reports on the chemical modification of silsesquioxanes and their application to the molecules under study in this article, employing or not the proposed methodology.

In present work, we reported synthesis and characterization of a octa-(3-chloropropyl)-octasilsesquioxane (S) with 4,5-Diphenyl-2-imidazolethiol (DIT) and thermal properties of this modified silsesquioxane.

The modification of silsesquioxane with DIT proposed in this paper follows two steps. The first step includes 8 Cl reactive atoms of the nanoplateform octa-(3-chloropropyl)-octasilsesquioxane, whose structure is shown in Figure 1, which are replaced to the chloride ion form by stronger bases (shiff bases), in this case the DIT, favoring the nucleophilic substitution reaction. The DIT ligand was used due to the fact it has -NH and -NH₂ groups suitable to organofunctionalization, and also -S groups which are excellent active sites for metal ions. In this context, the organomodified silsesquioxanes (SDIT) is a potentially candidate for sorption of metal ions.

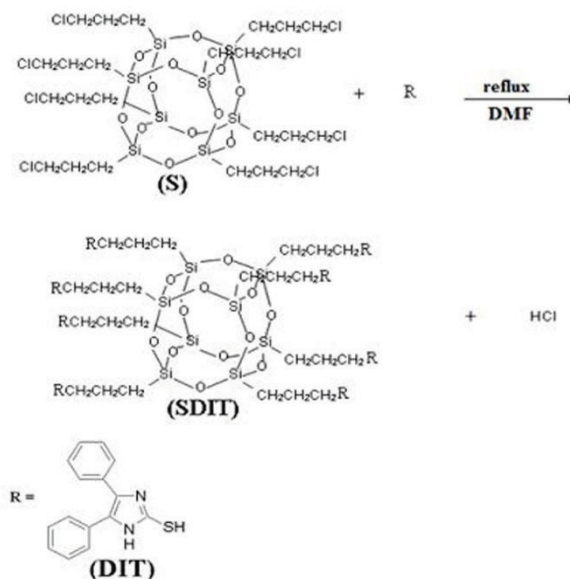


Figure 1. Organofunctionalization of octa-(3-chloropropyl)octasilsequioxane (S) with modifier 4,5-Diphenyl-2-imidazolethiol (DIT)

2. Material Studied

2.1 Reagents

All reagents and solvents were of high purity analytical grade (Vetec, Alpha Aesar, Merck or Sigma- Aldrich) and were used as purchased. Deionized water were produced with Milli-Q Gradient system from Millipore.

2.2 Techniques

2.2.1 Scanning Electronic Microscopy (SEM) and Energy-Dispersive X-Ray Spectroscopy (EDS)

The scanning electron microscopy of the any materials were obtained using a JEOL JSM T-300 microscope. The samples were adhered over aluminum holders and covered with a thin layer (20-30 nm) of gold in Sputter Coater Bal-Tec SCD-050.

2.2.2 Nuclear Magnetic Resonance Analyses (NMR)

All solid state analyses of ^{29}Si (59.5 MHz) and ^{13}C -NMR (75.4 MHz) were registred on a Varian INOVA 300 spectrometer. The samples were packed in zirconia rotors and spun at the magic angle at 4500 Hz, a relaxation delay of 10.0 and 6.0 s for ^{29}Si and ^{13}C respectively. All chemical shifts are reported in parts per million ppm (δ) with reference to external tetramethylsilane (TMS).

2.2.3 X-Ray Diffraction (XRD)

The X ray diffraction patterns (XRD) spectroscopy were obtained using a Siemens D 5000 diffractometer with $\text{CuK } \alpha$ (λ 1.5406 Å radiation), submitted to 40 kV, 30 mA, $0.05^\circ \text{ s}^{-1}$ and exposed to radiation from 5 up to 50° (2θ).

2.2.4 Thermogravimetric Analysis (TG-DTA)

The thermogravimetric analyzes of the samples were carried out using two equipments–SDT 2960 from TA Instruments and SDT Q600 from TA Instruments.

The thermogravimetric curves were obtained using approximately 6 mg samples placed in alumina crucibles and subjected to a controlled air temperature program and nitrogen flow of 100 mL min^{-1} , with a heating rate of $10^\circ \text{C min}^{-1}$. The sample analyzes were performed at the room temperature interval up to 1200°C .

3. Methods

3.1 Synthesis of Octa-(3-chloropropyl)octasilsequioxane (S)

The synthesis of octa-(3-chloropropyl)octasilsequioxane (S) was carried out as described in the literature with any modifications (Marciniec, Dutkiewicz, Marciejewski, & Kubicki, 2008): 800 mL of dry methanol, 27.0 mL

of hydrochloric acid ($\text{HCl}_{\text{conc.}}$) and 43.0 mL of 3-chloropropyltriethoxysilane were added stirred at room temperature for 5 weeks. The solid phase was separated by filtration and was then oven dried at 120 °C for 4 hours (Figure 1).

3.2 Preparation of Octa-(3-chloropropyl)octasilsesquioxane With DIT (SD)

The functionalization of octa-(3-chloropropyl)octasilsesquioxane (S) (Figure 1) was performed, as describe in the literature (Soares, Silveira, Silvestrini, Bicalho, & Do Carmo, 2013): reacting 9.70×10^{-3} mol of S, with 8.70×10^{-2} mol of ligand (DIT) in dimethylformamide (DMF). Then the solid phase was washed in a Soxhlet with solvent for two days. The prepared material was oven vacuum dried at 100 °C for 4 hours. Figure 1 illustrates (Soares, Silveira, Silvestrini, Bicalho, & Do Carmo, 2013) a scheme of this syntheses:

4. Results and Discussion

As illustrated by Figure 1, the organofunctionalization of S with 4,5-Diphenyl-2-imidazolethiol (DIT), a chlorine atom (Cl) in the structure of octa-(3-chloropropyl)octasilsesquioxane to be very reactive, is easily replaced by stronger bases, and represents a nucleophilic center susceptible to attack. Thus binding of groups 4,5-diphenyl-2-imidazolethiol (DIT) with the silsesquioxane also must occur through the nitrogen atom of position 1 (N-H), which is the position most susceptible to the formation of CN bond. The synthesized material, describe here as SDIT presented as a light yellow solid.

The vibrational spectrum of octa-(3-chloropropyl)octasilsesquioxane (S), as illustrated in Figure 2(A), showed an absorption band at about 1082 cm^{-1} which is a typical band of the material, as it regards $\text{Si-O-Si}_{(\nu\text{Si-O-Si})}$ stretching which corresponds to the cage-shaped structure of S. Two other one absorption bands were observed at around 685 cm^{-1} , attributed to deformation of the $\text{Cl}_{(\delta\text{C-Cl})}$ bond, and the other at around 2950 cm^{-1} related to the axial deformation of the $\text{C-H}_{(\delta\text{C-H})}$ (Silverstein & Webster, 1996; Do Carmo, Paim, Dias Filho, & Stradiotto, 2007).

Figures 2(B) and (C) illustrate the vibrational spectra of DIT and the functionalized materials (SDIT), respectively.

Figure 2(B) refers to the vibrational spectrum of the DIT ligand, and exhibits characteristic bands of this compound such as the bands ranging from 1300 to 1530 cm^{-1} , related to the axial deformation vibrations of the imidazole ring bonds (Silverstein & Webster, 1996). The broad and intense band at 2970 cm^{-1} was assigned to the axial deformation $\text{N-H}_{(\delta\text{N-H})}$ (Barth, 2000; Coates, 2000)

In the region between 3200 and 3500 cm^{-1} the bands observed were attributed to the axial deformation of $\text{N-H}_{(\nu\text{N-H})}$, these bands probably overlap the bands attributed to the axial deformation of $\text{C-H}_{(\nu\text{C-H})}$ ring bonds (Silverstein & Webster, 1996; Do Carmo, Paim, Dias Filho, & Stradiotto, 2007).

A decrease of the band at around 700 cm^{-1} was also observed, related to the C-Cl vibrations of S, thus evidencing its partial functionalization and suggesting that not all peripheral groups reacted with the imidazole ligand.

Additionally, the Figures 2(B) and (C), the band is related to the stretching of the C=S group ($\nu\text{C=S}$) around 768 cm^{-1} (Prado, Sales, Carvalho, Rubim, & Airoidi, 2004). The spectra of the compounds in which the C=S group is attached to a nitrogen atom (Figure 2(B)) showed an absorption band in the region of axial deformation usual $\text{C=S}_{(\delta\text{C=O})}$, and many others in the region between 1563 and 700 cm^{-1} are assigned to the axial deformation of the $\text{C=S}_{(\delta\text{C=O})}$, and $\text{CN}_{(\delta\text{C-N})}$ respectively (Evangelista, Oliveira, Castro, Zara, & Prado, 2007), but after functionalization axial deformation ($\delta\text{S-H}$) disappears and ($\delta\text{C=O}$) decreases in intensity and undergoes a slight shift to lower frequency region (Figure 2 (C)), suggesting that the binding of the aliphatic chain silsesquioxane was carried out via HS=C and/or C=NH binding. The existence of some absorptions present in S, obscure those present in the binder, damaging a better allocation of absorptions found in SDIT.

According to Figure 2(C) is not observed S-H axial deformation ($\delta\text{S-H}$) near 2579 cm^{-1} (Murti, Agnihotri, & Pathak, 2011). The justification for this is that the cyclic groups -N=C(SH) exist in the thiol form N=C(SH) and thionine -NH-C(=S) . These tautomeric forms differ in the location of the corresponding pair is H; thus the absence of a peak S-H may result from the presence of only one tautomeric thiol form.

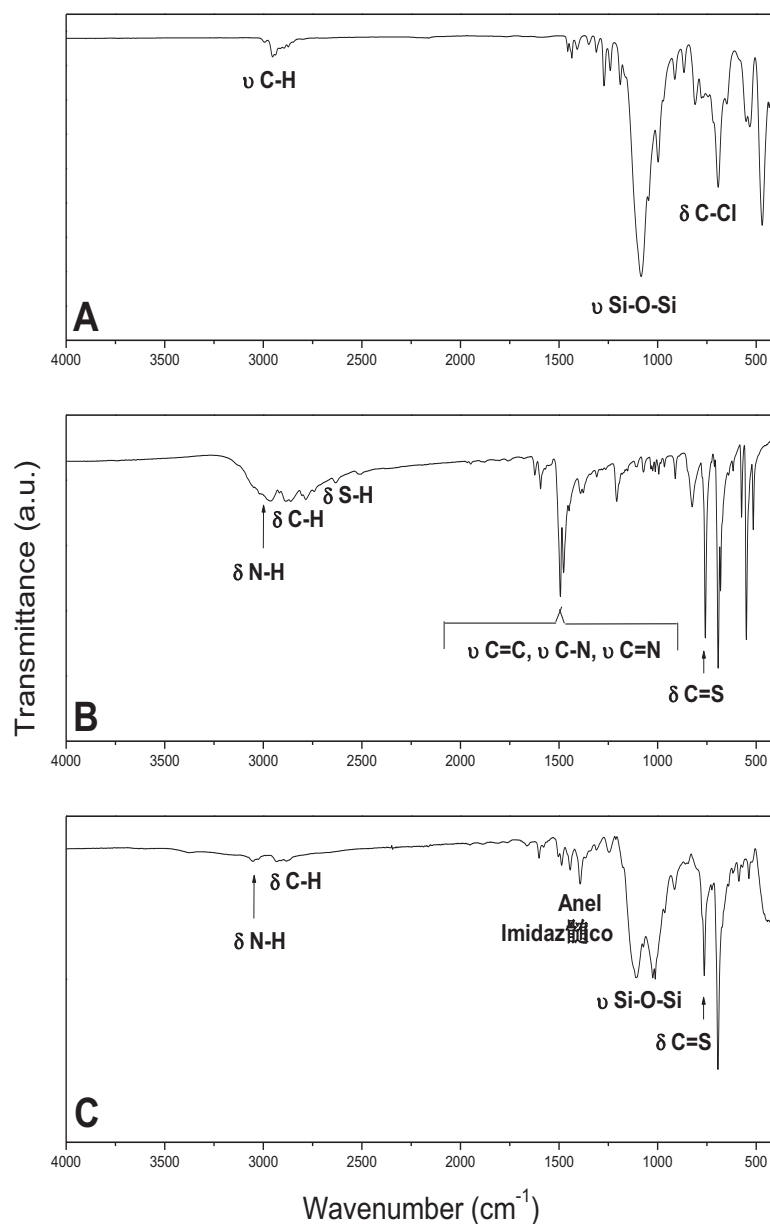


Figure 2. Vibrational spectrum of: (A) S, (B) DIT e, (C) SDIT

Figures 3 and 4 show the spectra of ^{29}Si and ^{13}C NMR of octa(3-chloropropyl)octasilsesquioxane $[\text{Cl}(\text{CH}_2)_3]_8\text{Si}_8\text{O}_{12}$ (S), respectively. The spectrum of ^{29}Si NMR (Figure 3) of $[\text{Cl}(\text{CH}_2)_3]_8\text{Si}_8\text{O}_{12}$ exhibited only a resonance at -67.42 ppm.

As illustrated by Figure 4, the ^{13}C NMR spectrum showed three resonance peaks attributed to the three carbons of the propyl groups (α -10,57, β -27,82 and γ -48,02 ppm). These carbons are determined as follows: α $\text{CH}_2\text{CH}_2\text{Si}$, β $\text{CH}_2\text{CH}_2\text{CH}_2$ and γ ClCH_2CH_2 . These results clearly show the successful synthesis of octa-(3-chloropropyl)octasilsesquioxane (Changyou & Chunye 2000; Dutkiewicz, Marciejewski, & Marciniak, 2009; Marciniak, Dutkiewicz, Marciejewski, & Kubicki, 2008). These results are in agreement with those found in the literature (Marciniak, Dutkiewicz, Marciejewski, & Kubicki, 2008) thus confirming the successful preparation of the precursor, so the product is pure and able to subsequent reactions.

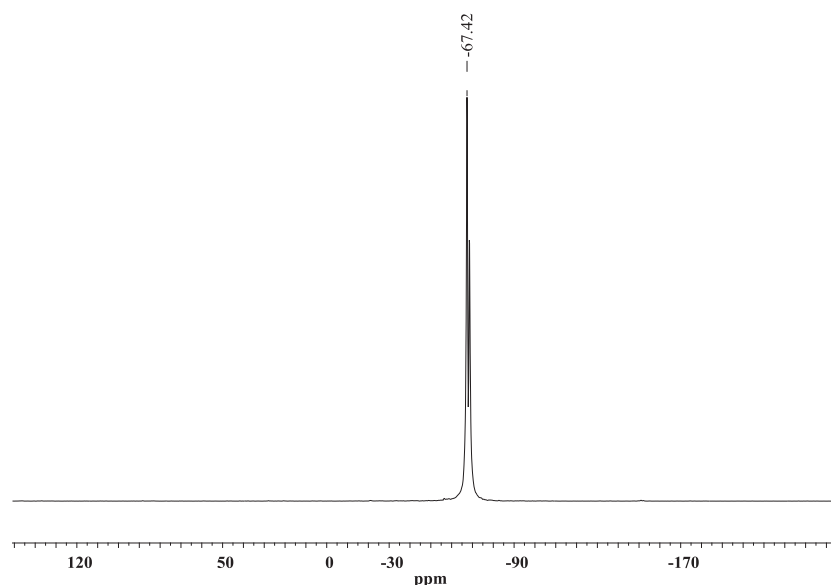
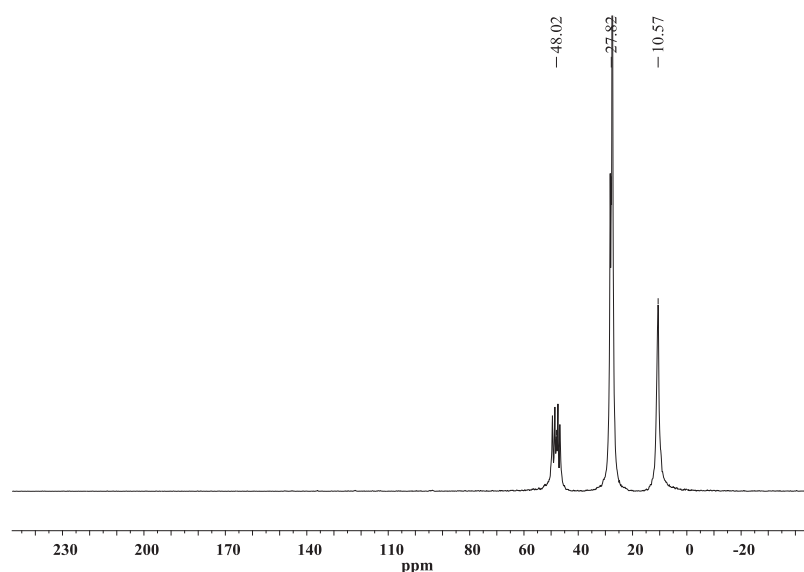
Figure 3. ^{29}Si NMR of SFigure 4. ^{13}C NMR of S

Figure 5 shows the ^{13}C NMR spectrum of the solid SDIT. Eight peaks were observed. The resonances at 10.70, 26.08 and 64.11 ppm corresponding to carbons ((CH_2Si) ; (CCH_2C); (NCH_2)) and the composite resonance peak at 47.10 ppm was assigned to the carbon γ of octa-(3-chloropropyl)octasilsesquioxano that did not react with the ligand, so it is clear that not all groups of peripheral octa-(3-chloropropyl) octasilsesquioxano been chemically modified. There was a high intensity resonance at a lower frequency at 128.6 ppm corresponding to carbons of the benzene ring (8 carbons) and the carbons bonded to the benzene ring (2 carbons). It was also found another peak at 139.25 ppm that was assigned to the imidazole thiol ring NCC. The absence of a resonance peak at 148.89 ppm (HNCS) in the composite, suggesting that the binding was conducted through the NH group present in the ligand molecule. When this occurs a new peak appears, as described above (NCH_2). These values are similar to those described in the literature (Prado, Sales, Carvalho, Rubim, & Airolidi, 2004; Alcântara et al., 2007) for analogous compounds supported on silica-based materials. For comparison purpose, Figure 6 shows the ^{13}C solid state NMR of DIT, where exactly were observed 4 resonance peaks. The carbons peak resonances at 128.89 at 148.89 ppm were assigned to 8 carbons and the benzene ring (attached) and to 2 carbon imidazol thiol rings. The peak at 157.64 was assigned to carbon HNCS.

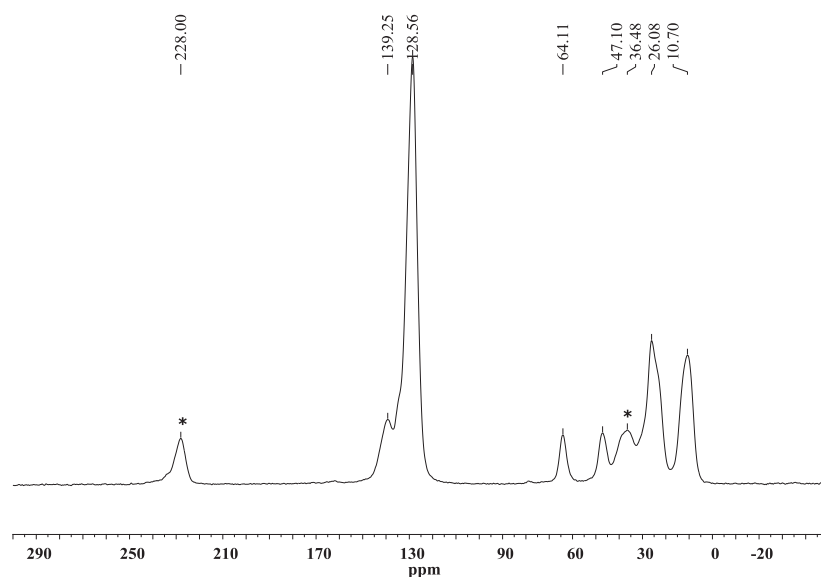
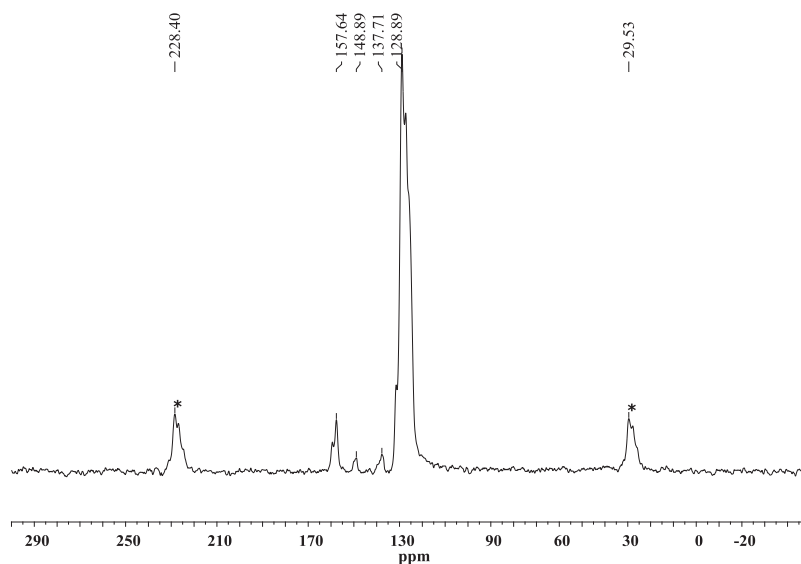
Figure 5. ^{13}C NMR of SDIT. *Side bandsFigure 6. NMR ^{13}C of DIT. *Side bands

Figure 7 shows the ^{29}Si NMR spectrum in solid state of SDIT. During the functionalization of octa-(3-chloropropyl)octasilsesquioxano with DIT new covalent Si-O-Si bonds are formed by T^3 structural units (Harrison, 1997; Urich, Cannizzaro, Langer, & Shakesheff, 1999), which corresponds to an intense and broad peak at -68.93 ppm, confirming the cubic structure containing silicon.

Figures 8(A), (B) and (C) corresponds to the XRD patterns of S, DIT and SDIT respectively. According to the XRD patterns obtained, a crystallinity quite common for octa-(3-chloropropyl)octasilsesquioxanes cubic (A) was observed (Bard & Faulkner, 2001). The S (A) showed the following characteristics $2\theta = 7.36, 9.19, 10.43, 10.93, 12, 13.33, 14.22, 19.12, 19.54, 20.55, 21.95, 22.95, 24.04, 26.48, 26.74, 27.5, 28.4, 29.4, 30.5$. The DIT (B) crystalline, had the characteristics $2\theta = 8.53, 10.23, 12.01, 14.53, 15.25, 15.97, 16.81, 17.53, 19.09, 20.63, 22.83, 23.91, 25.83, 27.54, 28.03, 28.87, 30.43, 39.22$. It was observed that after the organofunctionalization SDIT (C) showed no crystallinity their precursors (S and DIT) XRD. It was observed only two peaks (2θ), 11.05 and

20.51). This behavior is typical analogs compounds and indicated a substantial loss of crystallinity possibly due to a formed polymer network (Do Carmo, Paim, Dias Filho, & Stradiotto, 2007).

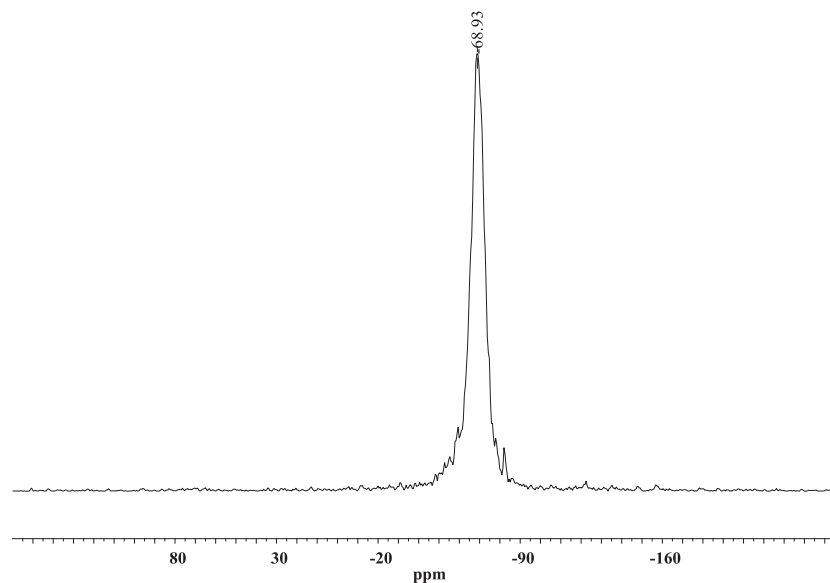


Figure 7. Espectro de RMN ^{29}Si no estado sólido do SDIT

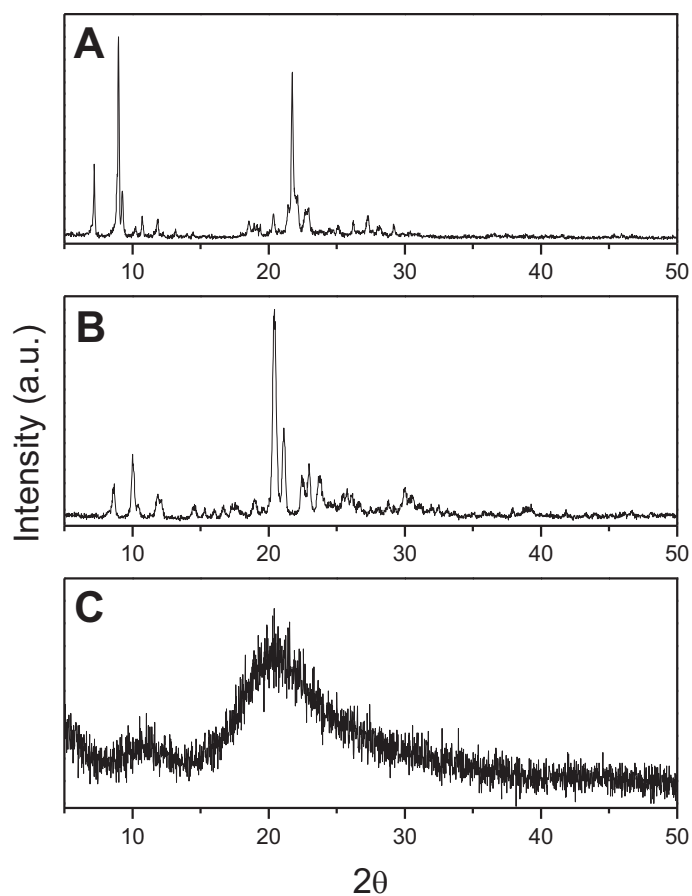


Figure 8. XRD of: (A) S, (B) DIT e, (C) SDIT

Figures 9(A), (B) and (C) show the scanning electron microscopy (SEM) of the octa-(3-chloropropyl)octasilsesquioxano (S), the DIT and SDIT with an increase of 10.000 X, respectively. Through the micrographs was possible to note the presence of cubic structural shapes with an average size of about 9 microns although they also can be observed cubic structures having size of 454 nm (Figure 9(A)). The scanning electron microscopy of 4,5-Diphenyl-2-imidazolethiol (DIT) is illustrated in Figure 9(B). It was observed the presence of dispersed microparticles with sizes of 8.5 to 10.0 micrometers. Figure 9(C) shows the micrograph of the S after their functionalization with groups 4-5-diphenyl-2-imidazolethiol (SDIT), where you can view a cluster of particles containing cavities in an orderly fashion.

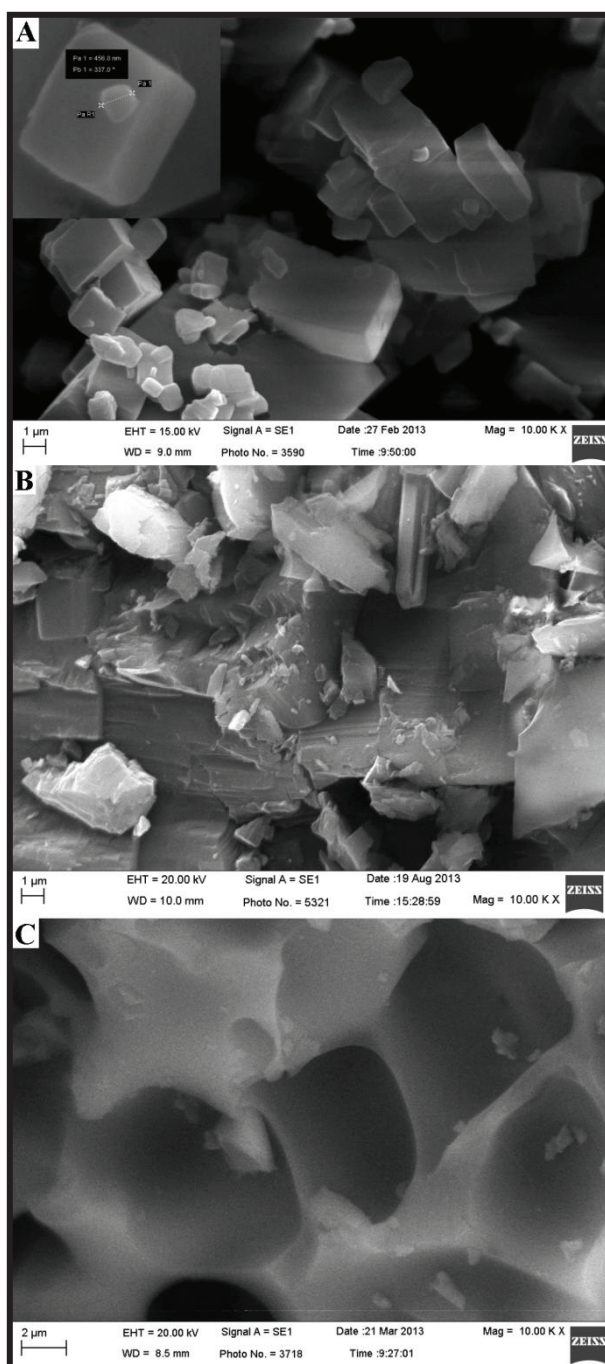


Figure 9. SEM of: (A) S, (B) DIT e, (C) SDIT

Figure 10(A), (B) and (C) show energy dispersive spectroscopy analyses (EDS) for S, DIT and SDIT samples respectively. It was observed in the EDS spectrum of S(A) the presence of Si, O, C and Cl present in octa-(3-chloropropyl)octasilsesquioxane cubic. In the EDS spectrum for 4,5-diphenyl-2-imidazoliol (DIT) (B) revealed the presence of C, N and S. For organofunctionalized materials (SDIT) (C) revealed a small Cl presence and a high concentration of S, which clearly shows the success in the preparation of SDIT.

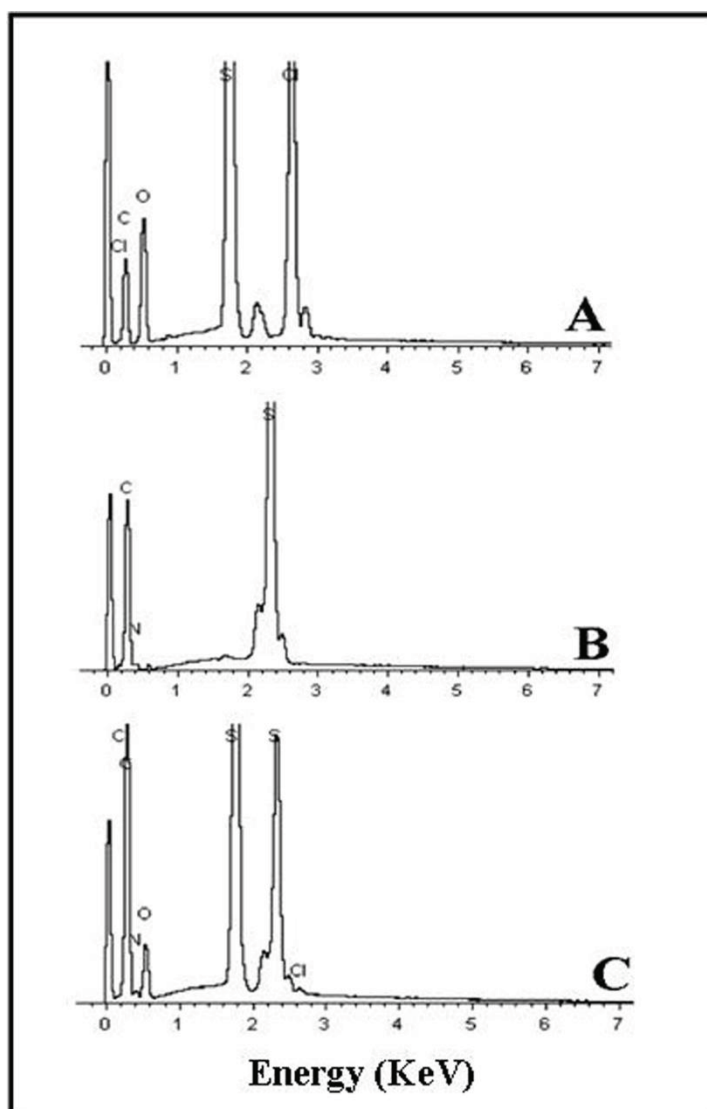


Figure 10. EDS of: (A) S, (B) DIT e, (C) SDIT

The thermogravimetric curves indicate the thermal stability of materials forward to heating with continuous and programmed temperature (Hatakeyama & Quinn, 1999) rate.

As shown in Figure 11(A) the thermogram of octa-(3-chloropropyl)octasilsesquioxano (S) in a nitrogen atmosphere, showed two stages of weight loss. In the first stage the weight loss (68% occurred from 350 to 450 °C mass loss was (68%) attributed to oxidation of organic matter (Zhang, Liang, & Lu, 2007).

It was observed that the material had a certain thermal stability up to 400 °C and in the second stage the weight loss occurred from 450 to 650 °C (7%) attributed to the decomposition of residual groups SiCH_3 (Hatakeyama & Quinn, 1999) present in the sample. The residue was 25%, and assigned to the same carbonaceous. Figures 11(B) and (C) illustrate the thermograms in nitrogen atmosphere of 4,5-diphenyl-2-imidazoliol (DIT) and functionalized materials (SDIT), respectively. In the thermogram of DIT was observed two stages of weight loss, for the first 275

to 400 °C (55%) attributed to loss of organic matter in the sample and the other occurring degradation stage was from 400 to 700 °C (45%), which can also be attributed to degradation of organic matter in the sample. The thermogram of SDIT also presented two stages of mass loss, one of 310 to 450 °C (40%), and the second event was observed from 450 to 700 °C (23%) both attributed to degradation of organic matter present in the sample, residue was 37%, being attributed to carbonaceous. Additionally, it was observed that the S and DIT materials in nitrogen atmosphere showed some thermal stability up to temperatures around 250 °C.

The thermogravimetric curves in an air atmosphere of octa-(3-chloropropyl)octasilsesquioxano (S) of 4,5-diphenyl-2-imidazoltiol (DIT) and octa-(3-chloropropyl)octasilsesquioxano functionalized (SDIT), are illustrated through Figure 11(D, E and F), respectively. The thermogram showed a stage S of weight loss from 220 to 700 °C (57%) attributed to degradation of the organic part present in the sample. The residue (43%) was silicon oxide. Figure 11(E) shows the thermogravimetric analysis of the DIT, there was two weight loss stages, the first of 250 to 350 °C (50%) and the second stage from 350 to 700 °C (50%) all of which are related to the oxidation organic part of the sample, there was no leftover residue, because all the material has degraded. In the thermogram SDIT illustrated in Figure 11(A), there are two stages of weight loss, both assigned to degradation and oxidation of organic matter present in the sample, and the first stage was from 320 to 450 °C (46%) and it was observed that the second stage occurred at the temperature range of 450 to 700 °C (30%). The residue was 24%, and assigned to silicon oxide. It was possible to compare the thermogravimetric analyzes performed in two different atmospheres, concluding that the materials (S, DIT and SDIT) when in air atmosphere has a slower degradation process in relation to nitrogen atmosphere. It was also observed that the SDIT possesses greater thermal stability in nitrogen.

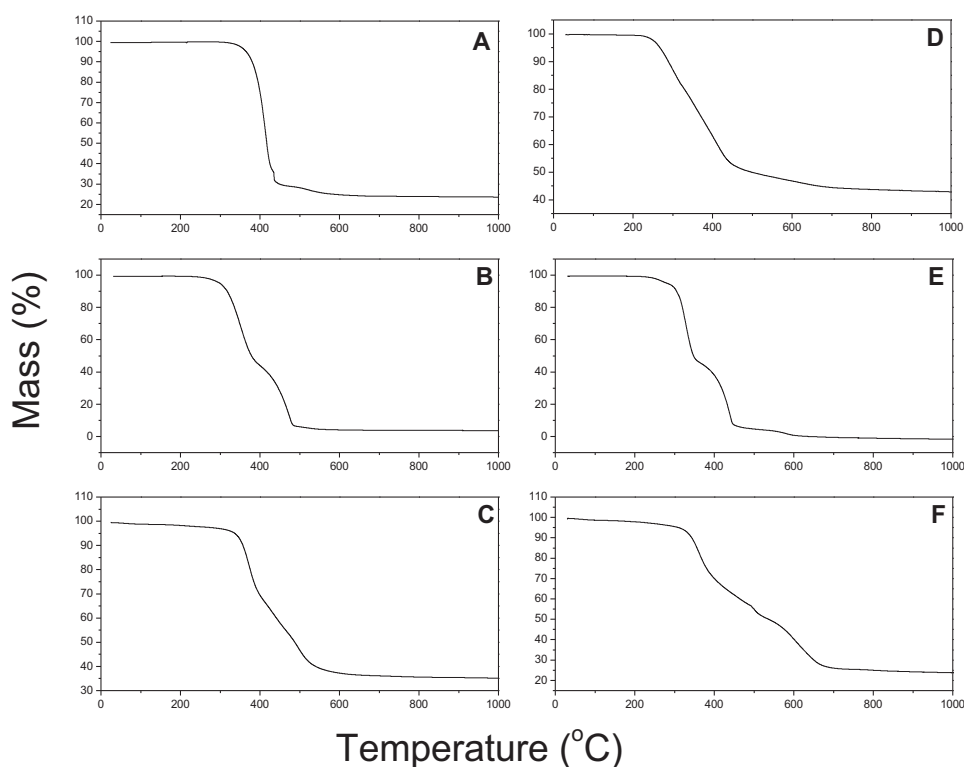


Figure 11. Thermogravimetric curves of: (A) S; (B) DIT; (C) SDIT (Nitrogen atmosphere); (D) S; (E) DIT; (F) SDIT (air atmosphere)

5. Conclusion

The organofunctionalization of octa-(3-chloropropyl)silsesquioxane with DIT (SDIT) was performed with relative success. The spectroscopic analysis (NMR, EDS and SEM) reveals that not all groups of peripheral octa-(3-chloropropyl)octasilsesquioxane been chemically modified and a loss of crystallinity after organofunctionalization. The SDIT possesses greater thermal stability in nitrogen up to 250 °C.

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