

Synthesis and Characterization of Cage Octa(aminopropylsilsesquioxane)

Zengping Zhang, Guozheng Liang, Tingli Lu

Applied Chemical Department, School of Science, Northwestern Polytechnical University, Xi'an, Shaanxi, 710072, People's Republic of China

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ABSTRACT: The compound of cage octa(aminopropylsilsesquioxane) (POSS-NH₂) was prepared in higher yield by the hydrolysis and polycondensation of trifunctional monomer H₂NCH₂CH₂CH₂Si(OC₂H₅)₃ in the mixture of solvents acetonitrile and 1-propanol, with tetraethyl ammonium hydroxide (Et₄NOH) as the catalyst. The effects of various parameters influencing the reaction, such as monomer concentration, nature of solvents, and the content of catalyst, were investigated. Results showed that the better values of these reactive factors were $n\text{H}_2\text{O}/n\text{XSiY}_3 = 8\text{--}9/1$ (molar ratio), $n\text{Et}_4\text{NOH}/n\text{XSiY}_3 = 0.0045$ (molar ratio), respectively. The use of acetonitrile as a solvent favors the deposition and formation of the product. The existence of the higher boiling

pointing 1-propanol favors the higher reaction temperature, which accelerates the formation of octamer, reduces the reaction time and eventually increases the yield. The cage structure and its formula (H₂NCH₂CH₂CH₂)₈Si₈O₁₂ of the synthetic compound were characterized by FTIR, MS, ¹H, and ²⁹Si NMR. TG curve of POSS-NH₂ shows that the cage-like compound has high decomposition temperature and higher thermal residue than the theoretical values during the thermal processing. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2608–2614, 2007

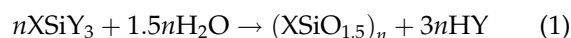
Key words: octa(aminopropylsilsesquioxane); cage structure; hydrolysis–condensation reaction

INTRODUCTION

Polyhedral oligomeric silsesquioxanes (POSS), with the general formula [RSiO_{3/2}]_n, are nanosized cage structures that can be incorporated into thermoplastic or thermosetting polymers to improve their thermal and oxidation resistance, and reduced flammability (Fig. 1).^{1–4} POSS compounds have increasing number of applications in the fields of medicine,⁵ electronics,⁶ aerospace.⁷ In POSS molecule, R can be hydrogen or any alkyl, alkylene, aryl, arylene, or organofunctional derivatives of alkyl, alkylene, aryl, or arylene group with $n = 6, 8, 10, \dots$. Octahedra ($n = 8$) are the most representative members of this family and have been described as the smallest version of colloidal silica.⁸ Depending on the reactivity of the organic group (R), POSS can be classified as nonfunctional and functional. The latter is more attractive to material researchers, since the reactive R groups permit bonding of the cages to polymers by copolymerization or grafting onto the chain backbone.⁸ Functional POSS can be different as the R groups vary. Recently, a series of thermoset organic–inorganic hybrid nanocomposites based on several types of octa-functional POSS

have been prepared and studied by Gravel and Laine.⁹ In these composites, the cubic silica cores are completely defined as hard particles with a 0.53 nm diameter and a spherical radius of 1–3 nm including peripheral organic units. As the interest in POSS derivatives has increased, efforts to synthesize POSS compounds with a variety of both reactive and inert substituents have also increased greatly.¹⁰

POSS compounds can be formed by the hydrolytic condensation of trifunctional monomers XSiY₃, the condensation of Si-functional oligoorganylcyclosiloxanes [XYSiO]_m, the cocondensation of organosilicon monomers and/or oligomers of different structure and composition, and the thermolysis of polyorganylsilsesquioxanes.¹¹ Among these methods, the hydrolytic condensation of XSiY₃ is the most universal and traditional synthetic route to oligosilsesquioxanes and their homo derivatives.



where X = a chemically stable substituent, such as methyl, phenyl, or vinyl; and Y = a highly reactive substituent, such as Cl, OH, or OR.

However, until now, no industrial methods for the synthesis of oligosilsesquioxanes have so far been described in the literature, although a great number of reactions leading to the formation of POSS are known.¹² The reason is that the hydrolytic condensation of XSiY₃ is a complex and time-consuming

Correspondence to: G. Liang (lgzheng@nwpu.edu.cn).

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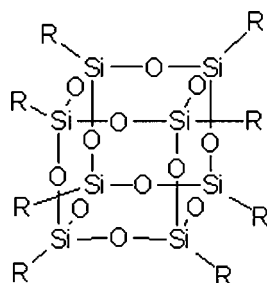


Figure 1 Structure of cage hexahedral silsesquioxane (R = organic groups).

multistep processes leading to polymers and oligomers that may include oligosilsesquioxanes and their homo derivatives. The reaction rate, the degree of oligomerization, and the yield of the polyhedral compounds formed strongly depend on the nature of the catalyst, concentration of the reagents, nature of the hydrolysable group, solvent, etc.¹³ The influence of all these factors, both individual and together, has been studied only in general, without any quantitative estimation of their effect on the reaction course.

Octa(aminopropylsilsesquioxane) POSS-NH₂ is one of the most interesting functional POSS because it can be used as the precursor for many functional POSS derivatives,¹⁴ and it also can be used as the nanometer hardener for thermosetting resins and shows great potential in nanocomposites.¹⁵ It was first synthesized by the hydrolytic condensation of γ -aminopropyltriethoxysilane in MeOH–conc.HCl over a period of 6 weeks at 25°C with the yield <30%. And, this method indeed provides access to an amine-substituted framework, but the first product obtained under the conditions reported by Wacker-Chemie is the corresponding chloride of POSS-NH₂ rather than POSS-NH₂ (i.e., the free amine).⁹ It is also surprisingly difficult to neutralize without destroying the Si/O framework, leading to the decrease of the yield of the final product POSS-NH₂.¹⁵ So, it is urgent to develop a novel way to synthesize POSS-NH₂. In addition, although much knowledge about the structures of POSS has been obtained recently by means of *in situ* FTIR, ²⁹Si NMR, UV-MALDI-TOF MS, etc, the characterization of the POSS molecular structures is still ambiguous, and the understanding of their structures are superficial owing to the complexity of these compounds.^{8,16,17}

In this work, there are two objectives: (1) to provide a practical and direct method to synthesize POSS-NH₂ in mixtures of solvents of acetonitrile and anhydrous 1-propanol with tetraethyl ammonium hydroxide (Et₄NOH) as the catalyst under basic environment and investigate the effect of reactive parameters on the synthetic reaction in detail, and (2) to fully characterize the structure of POSS-NH₂ and study the thermal property of POSS-NH₂.

EXPERIMENTAL

Materials

γ -Aminopropyltriethoxysilane H₂NCH₂CH₂CH₂Si(OC₂H₅)₃, colorless clear liquid, was supplied by Jingzhou Jiangnan Fine Chemical, China. Anhydrous Propynol CH₃CH₂CH₂COH and acetonitrile was supported by Tianjin BoDi Chemical. Cyclohexane was supported by Tianjin New Fine Chemical Center. All of the above reagents are of analytical purity and were used without further treatment. Tetraethyl ammonium hydroxide (Et₄NOH), 25% aqueous solution was obtained from Shanghai Reagent Plant, China.

Synthesis of Octa(aminopropylsilsesquioxane) POSS-NH₂

Typically, 90 g deionized water, 40 mL propyl alcohol, 10 mL acetonitrile, and 2 mL Tetraethyl ammonium hydroxide were added in consequence to a 500-mL flask and mixed to get a heterogeneous solution. Then, 221 g γ -aminopropyltriethoxysilane was added carefully to the solution while vigorous stirring within 10 min. The solution as obtained was heated to 50°C while stirring vigorously; some white crystallites formed after 12 h. The reaction ended after further 12 h when little further product formed. The crystalline precipitate was collected and treated as described earlier. The product was washed thrice with H₂O (100 mL) and twice with cyclohexane (50 mL) and dried under vacuum for 24 h at 100°C. The final product is a white powder with a melting point of 220–222°C.

Characterization of POSS-NH₂

POSS-NH₂ was characterized by using Fourier transform infrared spectroscopy (FTIR), mass spectroscopy (MS), element analysis, and ¹H, ²⁹Si-NMR spectroscopy.

Fourier transform infrared spectroscopy

FTIR spectrum of synthetic compound was obtained using a WQF-310 FTIR spectrometer (The Second Optical Instruments Plant of Beijing, China). Optical grade potassium bromide (KBr, Beijing Yixing Fine Chemical Corp.) was used as a background material.

Mass spectrum

Matrix-assisted UV-MALDI-TOF MS, was performed using an Applied Biosystems Voyager DE-STR device, equipped with a pulsed nitrogen laser ($\lambda = 337$ nm; pulse width = 3 ns). The selected matrix was 2,5-dihydroxybenzoic acid [gentisic acid (GA); Sigma]. Samples were irradiated just above the threshold laser power to obtain molecular ions.

Nuclear magnetic resonance

^1H and ^{29}Si -NMR spectra were performed with INOVA-400 "NWU400" spectrometer at 399.8 MHz (^1H) and 50 MHz (^{29}Si) at temperature of about 20°C . All the spectra were recorded in CDCl_3 medium. The chemical shift δ in the spectra uses the tetramethylsilane (CH_3) $_4\text{Si}$ as the standard substance.

Element analyses

The element C and H were analyzed using Carlo Erba 1106.

Thermal gravimetric analysis

Thermal stabilities of materials under N_2 were tested using a 2960 simultaneous DTA-TGA Instrument (TA Instruments, New Castle, DE). Samples (15–25 mg) were loaded in platinum pans and ramped to 800°C ($5^\circ\text{C}/\text{min}$ per N_2). The N_2 flow rate was 60 mL/min.

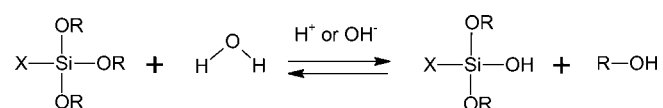
RESULTS AND DISCUSSION

Effects of the reaction conditions

Concentration of monomer

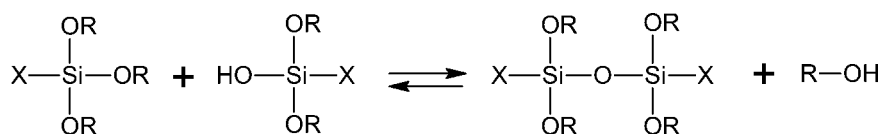
Figure 2 shows the effect of relative amount of water and XSiY_3 on the yield. XSiY_3 stands for γ -aminopropyltriethoxysilane $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$. As can be seen from Figure 2, the yield increases as the molar ratio of H_2O to XSiY_3 (R) increases to 8–9, and drops at the higher R values. The maximum value of the yield is 72% when R reaches 8, and the yield decreases to 54% as R increases to 20. This behavior can be explained by the function of water in the reaction processing. There are two type reactions in the trifunctional XSiY_3 -type hydrolysis and polycondensation, one is the hydrolysis reaction, and the other is the condensation reaction. The condensation reaction includes alcohol condensation and the water condensation. The reaction processing is listed below.

1. Hydrolysis reaction

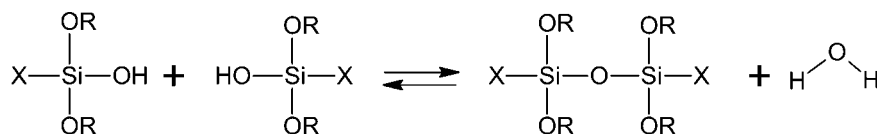


2. Condensation reactions

a Alcohol condensation



b Water condensation



The reaction processing shows that water is the reactant in the hydrolysis reaction, while it is the product in the water condensation. Too little water will render the hydrolytic reaction incomplete and as a result influence or even hinder the condensation reaction for there is not enough silanol carrying out the condensation reaction; however, too much water also will restrict the water condensation and eventually decrease the yield of the silsesquioxane. The appropriate addition of water will ensure complete hydrolysis and produce enough silanols, and the

silanols produced in turn condense and produce water. The latter can undergo further hydrolysis and finally make the reaction continue and obtain the more product yields.

Nature of the solvent

To form the cage structure of silsesquioxane, the hydrolytic polycondensation must hold and release its reaction rate, for the trifunctional organosilicon monomers XSiY_3 is highly reactive, especially for

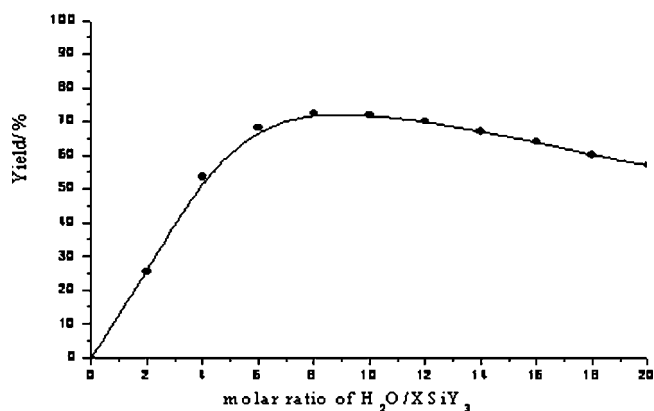


Figure 2 The relationship between the yield and the molar ratio of H₂O to XSiY₃ (reaction conditions: 1-propanol/acetonitrile; $n\text{Et}_4\text{NOH}/n\text{XSiY}_3 = 0.0045$; 50°C).

organotrichlorosilanes. So, the synthesis of the most oligomer silsesquioxanes is carried out in an organic solvent with the addition of water and in the presence of an appropriate acid or base catalyst. It is reported that alcohol, benzene, toluene, cyclohexane, and ether can be the solvents for the reaction. Different solvents affect product yields, along with the initial concentration chosen, and the type of catalyst also influences the choice of solvent. Among these solvents, alcohol is one of the most commonly used solvents.¹⁸ Feher and Wyndhamsynthesized cage POSS-NH₂ successfully using methanol or ethanol as the solvent at 25°C.¹⁴ However, this method is very complex, time-consuming, and is relatively low in yield. In this work, we use the solvent mixtures of acetonitrile and 1-propanol instead of a single solvent commonly used to facilitate hydrolytic condensation. These two different solvents have different functions in the reaction process. The 1-propanol with a high boiling point favors the increasing rate of the reaction and reduces the reaction time, and eventually increases the yield. On the other hand, the existence of acetonitrile can efficiently accelerate the precipitation of the product cage POSS-NH₂, which is also favorable to the formation of the cage structure and the increase of yield.¹⁷

Content of the catalyst

The formation of polyhedral oligomeric silsesquioxanes from the hydrolytic polycondensation of trifunctional monomers, XSiY₃, occurs only in the presence of either acid or base catalyst. When using acid as catalyst, HCl is the most efficient acid catalyst for the synthesis of many POSS. But, HCl may not be the best catalyst for the hydrolytic condensation of γ -aminopropyltriethoxysilane to synthesize POSS-NH₂, because the first product is the octa(aminopropylsilsesquioxane) chloride rather than POSS-NH₂. Further neutralization of octa(aminopropylsilsesquioxane) chloride, which may destroy the Si/O framework in part,

is needed to obtain POSS-NH₂. More synthetic steps lead to the decrease of the yield. We first use a basic catalyst Et₄NOH for this reaction, realizing the one-step synthesis of POSS-NH₂ in higher yield.

Figure 3 shows the relationship between the yield and the content of Et₄NOH. It is obvious that the yield increase as the molar ratio of catalyst to monomer increases to 0.0045, at which the maximum yield 72.5% is obtained, and after that, the yield drops to 51.0% as the molar ratio increases to 0.008, which shows that the yield increases with Et₄NOH content increasing and high Et₄NOH content favors the silsesquioxane formation, but a higher content of Et₄NOH reduces the yield. This behavior can be attributed to pH value change based on Et₄NOH content and its influence in the processing reaction. The content of base influences the pH value of the medium: the higher the Et₄NOH content, the higher the pH value of the medium; this favors crystallization and oligomer formation, and as a result, the yield increases with Et₄NOH content increasing. However, further increase in catalyst content results in too higher pH values of medium and is disadvantageous to the formation of Si—O—Si bond, leading to the difficult formation of oligomer and the decrease of the yields.

Structural characterization of POSS-NH₂

FTIR spectrum

Figure 4 is the FTIR spectrum of POSS-NH₂. The wide and intensive peak at 3350 cm⁻¹ is attributed to the characteristic absorption of —NH₂ groups. The strong double peaks at 2930 and 2873 cm⁻¹ correspond to the C—H stretching of the CH₂ groups in the organic corner groups of the cage structure. The absorption band

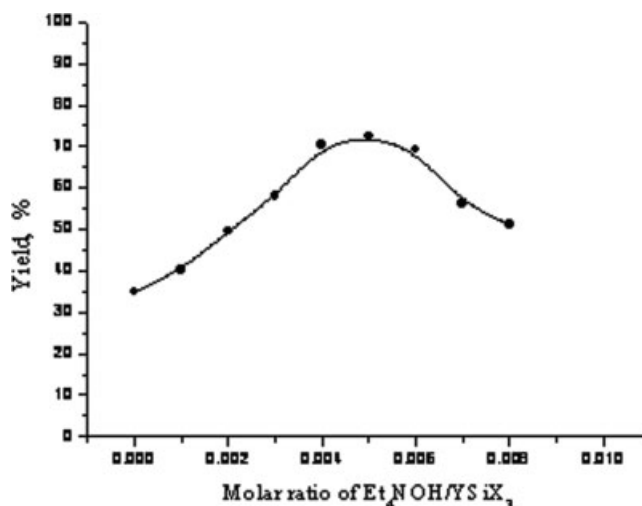


Figure 3 Effect of the catalyst on the yield of silsesquioxane (reaction conditions: 1-propanol/acetonitrile; H₂O/XSiY₃ = 8; 50°C).

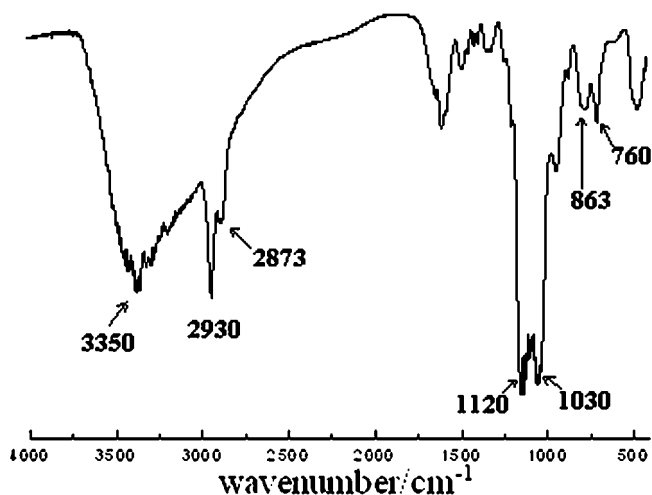


Figure 4 FTIR spectrum of the POSS-NH₂.

at 1120 cm⁻¹ is the characteristic vibration of Si—O—Si bond. The absorption peaks at 1030 and 863 cm⁻¹ are attributed to the special characteristic vibration of silsesquioxane cage Si—O—Si framework.¹⁸ The peak at 760 cm⁻¹ is the bending vibration of Si—C bond in Si—CH₂. So, the FTIR spectrum of the product gives good assignment to the structure of POSS-NH₂.

Spectra data analysis

Mass spectrum(MALDI-TOF, DHB matrix), *m/z*(relative intensity), 881.5([M+H]⁺, 100%), 863.5([M-NH₃]⁺, 49%).

¹H-NMR (399.8 MHz, CDCl₃, 20°C): δ = 0.75 (m, 8H), 1.25 (m, 40H), 1.74 (m, 40H). Figure 5 is the ¹H-NMR spectrum of POSS-NH₂ in CDCl₃ at 20°C. Four peaks with chemical shifts of 8.10 (a, 2H), 2.85 (b, 2H), 1.75 (c, 2H), and 0.72 (d, 2H) appear in the spectrum. Each of them is assigned to one type of hydrogen atoms of the same chemical environment, as described

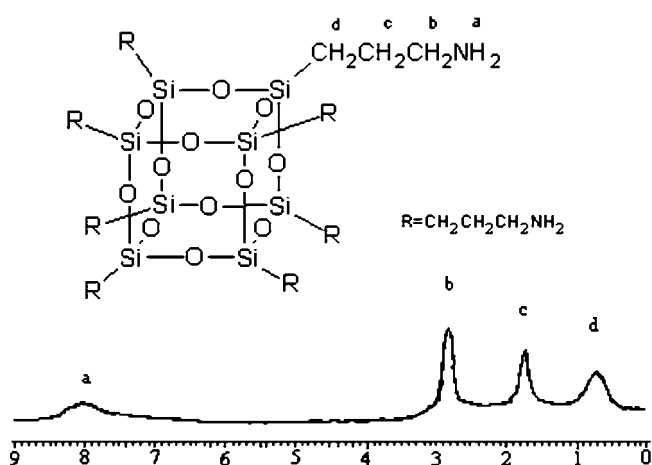


Figure 5 ¹H-NMR spectrum of POSS-NH₂.

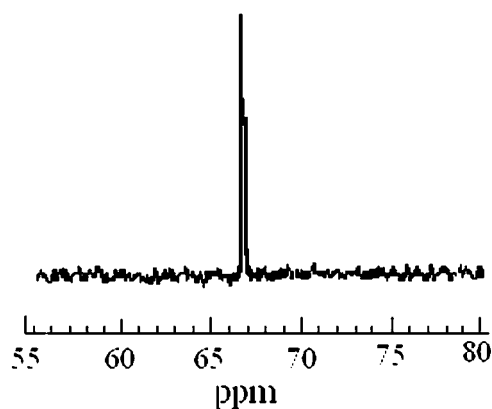


Figure 6 ²⁹Si-NMR spectrum of POSS-NH₂ (50 MHz, CDCl₃, 20°C).

in Figure 5, further supporting the cage structure of POSS-NH₂.

Figure 6 shows the ²⁹Si-NMR spectrum of POSS-NH₂ in CDCl₃ at 20°C. It is clear that there is only one peak in the spectrum, having the chemical shift δ = -66.5 ppm, indicating that there is only one structural conformation of silicon atom in the compound. It also indicates that the product is of one uniform structure and of high purity. Moreover, the value of the chemical shift is near to that of the silicon atom in the cage structure of (RSiO_{1.5})₈.¹⁹ From this, we can confirm that the synthetic compound POSS-NH₂ have the cage structure and its structural formula should be (H₂NCH₂CH₂)₈Si₈O₁₂.

Anal. Calcd. for (H₂NCH₂CH₂CH₂)₈Si₈O₁₂: C 32.73%, H 7.27%; found C 32.50%, H 7.58%, which indicates the consistency of the experiment and the theoretical calculation.

X-ray diffraction

The XRD pattern of POSS-NH₂ is shown in Figure 7. The peak in the XRD profile is attributed to the rhom-

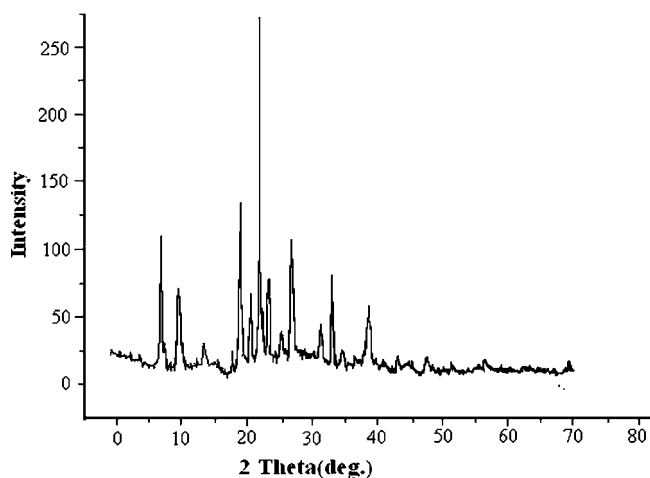


Figure 7 X-ray diffraction profile of POSS-NH₂.

bohedral unit cell formation as expected in the presence of POSS inorganic segments. XRD spectrum shows that the sample is highly crystalline evidenced by sharp peaks, only a few amorphous characters are observed. This finding may be attributed to the Si—O—Si linkages indicating that high degree of crystal character due to the rigid network caused by POSS segment.

Thermal analysis

Figure 8 shows the thermal gravimetric (TG) curve of POSS-NH₂. There are two main steps of weight loss on the TG curve. The first weight loss step at 150°C should be attributed to the loss of some crystalline water in the sample, for POSS-NH₂ is very hygroscopic, as evidenced by the DSC curve of POSS-NH₂ in Figure 9. The second one, starting from 425°C and mainly taking place at 500°C, corresponds to the degradation of octasilsesquioxane, especially for the decomposition of the organic corner groups. Char residue obtained from the TG curve is one parameter reflecting the thermal stability of one material. The char residues are taken as the weight percentage of the sample remains after TG test, which is 62.34% for POSS-NH₂.

The char residue of a material is dependent on the content of organic and inorganic components in the molecules and whether there are more stable compounds forming during the decomposition process. The higher the content of inorganic groups in the material, the higher its char residue yield. The weight percentage of the inorganic Si—O cage in POSS-NH₂ is 46.36 wt % in theory, whereas the char residue from the TG curve is about 62.34 wt %, much higher than the theoretical value. This behavior indicates that some unknown reactions may have taken place during the heating process, with the formation of certain new thermally stable compounds besides SiO₂. And,

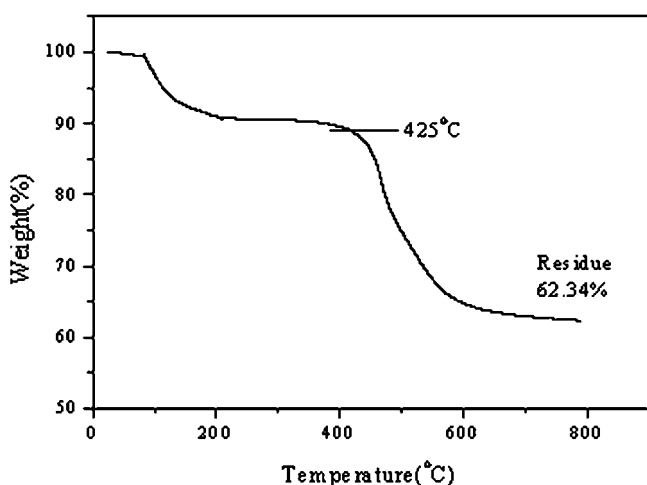


Figure 8 TG curve of POSS-NH₂.

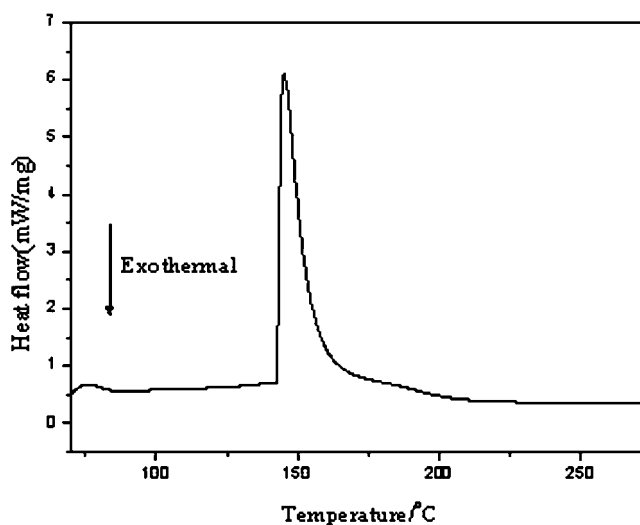


Figure 9 DSC curve of POSS-NH₂.

these compounds can endure thermal treatment as high as 800°C. Further study to identify the formation mechanism and properties of these materials is underway.

As can be observed from the TG test, POSS-NH₂ possesses superior thermal stability to common polymeric materials. Owing to its peculiar nanometer structure, it shows great potential as modifier to improve the properties of plastics, especially for thermal properties.

CONCLUSIONS

POSS-NH₂ was prepared by the hydrolysis and polycondensation of trifunctional monomer γ -aminopropyltriethoxysilane in the mixture solvents of acetonitrile and 1-propanol instead of a single solvent. Mixture solvents contributed to the increase of reaction temperature and favored the formation of the silsesquioxane, and eventually shortening the reaction time and increasing the yield. Keeping the solution at a relatively high temperature 50°C, higher yield could be obtained when H₂O/XSiY₃ = 8/1 (molar ratio) and Et₄NOH/XSiY₃ = 0.0045 (molar ratio). The cage structure of the synthetic compound and its formula (H₂NCH₂CH₂CH₂)₈Si₈O₁₂ were characterized by FTIR, MS, ¹H, and ²⁹Si NMR. Thermal gravimetric analysis showed that the cage compound had superior thermal stability to common polymeric materials.

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