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Review
Synthesis and characterization of cage octa(cyclohexylsilsesquioxane)

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The compound of cage octa(cyclohexylsilsesquioxane)$(c\text{-}C_6H_{11})_8Si_8O_{12}$ was prepared in higher yield by the hydrolysis and polycondensation of trifunctional monomer $(c\text{-}C_6H_{11})Si(OC_2H_5)_3$ in the mixtures of solvents of methyl isobutyl ketone and anhydrous ethanol with the concentration hydrochloric acid acting as the catalyst. The effects of reaction conditions, such as monomer concentration, the contents of water and catalyst were investigated. The results show that the better values of these reactive factors were 0.45 mol/L, $H_2O/XSiY_3 = 3/1$(molar ratio), $Et_4NOH/XSiY_3 = 3$ (molar ratio), respectively. The existence of the higher boiling MIBK favours the higher reaction temperature, which accelerates the formation of octamer, reduces the reaction time and eventually increases the yield. The FTIR spectrum and ^1H, ^{13}C, and ^{29}Si NMR spectra show that the compound has the formula of $(c\text{-}C_6H_{11})_8Si_8O_{12}$ and the cage structure. The TG curve shows that the cage compound has a higher decomposition temperature, higher primary decomposition temperature and higher thermal residue and that the inorganic Si—O—Si composition does not change during the thermal processing. *© 2005 Springer Science + Business Media, Inc.*

1. Introduction

Polyhedral oligomeric silsesquioxanes (POSS) are an interesting class of three-dimensional oligomeric organosilicon compounds with the general formula $[RSiO_{3/2}]n$, where R can be hydrogen or any alkyl, alkylene, aryl, arylene, or organo-functional derivatives of alkyl, alkylene, aryl or arylene group [1]. POSS was initiated in 1985 as part of an effort to develop functional solution state models for silica surfaces and silica-supported transition-metal catalysts by Frank J. Feher and his co-workers. Since its discovery, a variety of useful functionalized polyhedral silsesquioxane frameworks have been reported, including a number of frameworks with useful functional groups [2–5]. Interest in polyhedral silsesquioxanes has increased greatly in recent years. New methods to prepare useful frameworks have been developed and a number of frameworks have been employed in new and potentially valuable applications such as medicine [6], electrics [7, 8], air and aerospace [9] etc.

POSS has many excellent properties such as high thermal stability, good low dielectric constant (<3), releasing no VOCs and producing no odour or air [10]. They can be used both as direct replacements for hydrocarbon based materials or as low-density performance additives to traditional plastics [11]. In its structure, an inorganic Si_8O_{12} core is surrounded by seven or eight organic hydrocarbon groups (see Fig. 1), the inorganic core gives it high thermal stability, while the eight organic groups yield good solubility in common organic solvents and good compatibility or miscibility with organic matrices. Furthermore, the functional group in the cage can undergo graft, polymerization or co-polymerization with the polymer, which ensure favorable specific interactions existing between the POSS monomer and the polymer matrix [12].

No industrial methods for the synthesis of oligosilsesquioxanes have so far been described in the literature. However, a great number of reactions leading to the formation of polyhedral silsesquioxanea are known [12]. Depending on the nature of the starting materials, all these reactions may be divided into two large groups. The first group includes the reactions giving rise to new Si—O—Si bonds with subsequent formation of

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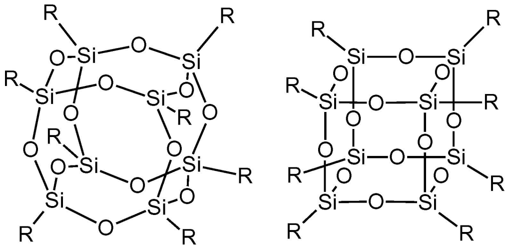


Figure 1 Structure of cage hexahedral silsesquioxane (R = organic groups).

the polyhedral framework. The second group of reactions covers the processes involving only variations in the structure and composition of substituents at the silicon atom without affecting the silicon-oxygen skeleton of the molecule. As the interest in POSS derivatives has increased, efforts to synthesize POSS with a variety of both reactive and inert substituents have increased.

The polyhedral silicon-oxygen skeleton oligosilsesquioxanes can be formed by the hydrolytic condensation of trifunctional monomers $XSiY_3$, the condensation of Si-functional oligoorganylcyclosiloxanes [XYSiO]m, the co-condensation of organosilicon monomers and/or oligomers of different structure and composition, and the thermolysis of polyorganylsilsesquioxanes [13]. In some cases, the above reactions can be combined in order to obtain certain oligosilsesquioxanes or to increase the yield.

Among the above synthesis methods, the hydrolytic condensation of $XSiY_3$ is the most universal and traditional synthetic route to oligolsilsesquioxanes and their homo derivatives. Most polyhedral compounds of this type known at present have been synthesized by this method, the corresponding organyltrichlorosilanes, less often organyltrialkoxysilanes, as well as trichlorosilane and trimethoxysilane being used as the starting monomers.

$$n\mathrm{XSiY}_3 + 1.5n\mathrm{H_2O} \rightarrow (\mathrm{XSiO}_{1.5})_n + 3n\mathrm{HY} \quad (1)$$

(X = a chemically stable substituent, such
as methyl, phenyl, or vinyl)
(Y = a highly reactive substituent,

such as Cl, OH or OR)

The hydrolytic condensation of $XSiY_3$ is a complex and time-consuming multistep processes leading to polymers and oligomers which 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 concentration of initial monomer in the solution, nature of solvent, character of substituent X in the initial monomer, nature of functional group Y in the initial monomer, type of catalyst, temperature of the reaction and addition of water. 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. This may be explained by the complicated character of the polycondensation process and the strong mutual effect of the above factors.

Cyclohexylsilsesquioxane is most interesting compound for its homo derivative cyclohexyl-trisilanol is the precursor for many functional silsesquioxane monomers [14]. It was synthesized by the hydrolytic condensation of cyclohexyltrichlorosilane in aqueous acetone and with acid or base as catalyst over a period of several weeks. Attempts to shorten the reaction time, such as performing the reaction on a large scale and filtering at early reaction time, proved largely unsuccessful [15].

In this work, the cyclohexylsilsesquioxane was synthesized in mixtures of solvents of methyl isobutyl ketone (MIBK) and anhydrous ethanol with hydrochloric acid as the catalyst. The reaction time was shortened to 3–7 days and at the same time the yield was increased to 44%. The effects of the reaction conditions on the yield are discussed in detail and the structural characterization of the products are investigated by FTIR, MS, ^{1}H, ^{13}C and ^{29}Si NMR spectra.

2. Experimental

2.1. Materials

Cyclohexyltriethoxylsilane (c-$C_6H_{11})Si(OC_2H_5)_3$, a colourless clear liquid, was synthesized in our laboratory having a purity of 90%. Methyl isobutyl ketone $(CH_3)_2CH_2CH_2COCH_3$was supported by Tianjin BoDi Chemical Corporation. Concentration hydrochloric acid was obtained from Xi'an Fine Chemical Plant. Anhydrous ethanol and methanol were obtained from Tianjin Baishi Chemical Plant. Hexane was supported by Tianjin New Fine Chemical Center. Dichloromethane was obtained from Tianjin Fine Chemical Reagent Plant. All of the above reagents are of analytical purity and were used without further treatment.

2.2. Octa(cyclohexylsilsesquioxane) (c-$C_6H_{11})_8Si_8O_{12}$ synthesis

The mixture of methyl isobutyl ketone and anhydrous enthanol with the volume ratio of 50/50 were added to the flask. Then cyclohexyltriethoxylsilane and three equivalents of deionized water were added to the solution. Concentrated hydrochloric acid HCl was used as catalyst. The reaction solution was stirred at room temperature and the solution became turbid. With longer stirring times the solution turns transparent again. At this temperature, the reaction was kept for almost 3–7 days until the formation of white microcrystals. The crude produce was obtained after filtering the solvent and wished with methanol several times. The crude white produce was recrystallised from hexane/dichloromethane and the pure compound was obtained.

2.3. Characterization of octa(cyclohexylsilsesquioxane) (c-$C_6H_{11})_8Si_8O_{12}$

The characterization of the octa(cyclohexylsilsesquioxane) (c-$C_6H_{11})_8Si_8O_{12}$ was investigated by fourier transform infrared spectroscopy (FTIR), mass spectrum (MS), element analysis and ^{1}H, ^{13}C, ^{29}Si NMR spectra.

2.4. Fourier transform infrared spectroscopy (FTIR)

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

2.5. Mass spectrum (MS)

The MS spectrum was obtained using a GC6970–MASS5973 Gas-Mass hyphenated instrument at a heating rate 10 K/min and a voltage of 70 eV.

2.6. Nuclear magnetic resonance (NMR) analyses

^{1}H, ^{13}C and ^{29}Si NMR spectra were performed with INOVA-400 "NWU400" spectrometer at 399.8 MHz (^{1}H), 100.5 MHz (^{13}C) 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 $(CH_3)_4Si$ (TMS) as the standard substance.

2.7. Element analyses

The element C and H were analysed using a Carlo Erba 1106.

2.8. Thermal gravimetric (TG) analysis

Thermal stabilities of materials under nitrogen or air were tested using a 2960 simultaneous DTA-TGA Instrument (TA Instruments, Inc., New Castle, DE). Samples (15–25 mg) were loaded in platinum pans and ramped to 800°C (5 K/min/N_2). The N_2 or air flow rate was 60 ml/min.

3. Results and discussion

3.1. Effects of the reaction conditions

3.1.1. Monomer concentration

Fig. 2 shows the relationship between monomer concentration and the yield. It is clear that the yield increases as the monomer concentration increases to 0.45 mol/L, and drops at the higher monomer concentration. The maximum value of the yield is 42.0% at a monomer concentration of 0.45 mol/L, and the yield decreases to 15.6% as the monomer concentration increases to 1.0 mol/L. This behaviour can most likely be attributed to whether the intra-molecule cyclization or inter-molecule polymerization reaction predominates during processing. The reaction processing can be divided into the formations of silanols and condensation to form the Si—O—Si framework. In the condensation processing there are two different reactions, one is intra-molecule cyclization forming the oligomer, and the other is the inter-molecule polymerization reaction forming the linear polysiloxane. These two different condensation reactions co-exist during processing and compete with each other based on the concentration of the solution. When dilute solutions are used and the monomer concentration is lower, intra-molecule cyclization predominates leading to formation of polyhedral oligomers, and the yield of which will increase with the increasing of the monomer concentration. Whereas, further increasing of the monomer concentration will cause the following effects, such as the more chances of the silanol molecules colliding with each other. All of the above factors are disadvantageous to the cage structure formation, and as a result decrease the oligomeric silsesquioxane yield.

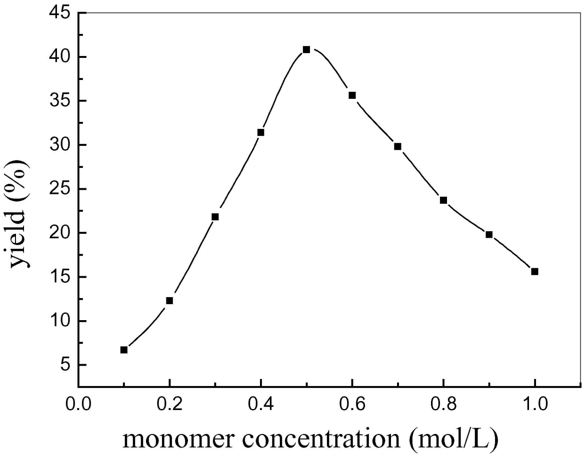
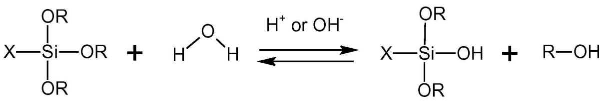


Figure 2 Effect of monomer concentration on the yield of silsesquioxane (Reaction condensations: MIBK/EtOH;$H_2O/XSiY_3 = 3$;$HCl/XSiY_3 = 2.5–3$;Boiling).

3.1.2. Addition of water

Table I shows the effects of water on the yield. From the data in table I, the yield is only 9.1% without the addition of water, while the yield increases with the water concentration. The yield reaches its highest value (42.7%) when water and monomer are in the molar ratio 3/1. The further addition of water makes the yield decrease. These behaviors 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 as the following:

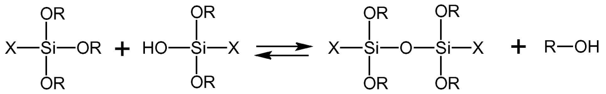
(1) Hydrolysis reaction



$$X\text{—}\overset{OR}{\underset{OR}{Si}}\text{—}OR + H_2O \underset{}{\xrightleftharpoons{H^+ \text{ or } OH^-}} X\text{—}\overset{OR}{\underset{OR}{Si}}\text{—}OH + R\text{—}OH$$

(2) Condensation reactions

1) Alcohol condensation



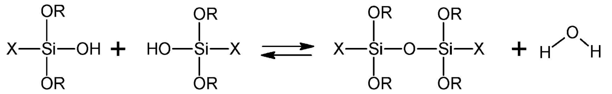
$$X\text{—}\overset{OR}{\underset{OR}{Si}}\text{—}OR + HO\text{—}\overset{OR}{\underset{OR}{Si}}\text{—}X \rightleftharpoons X\text{—}\overset{OR}{\underset{OR}{Si}}\text{—}O\text{—}\overset{OR}{\underset{OR}{Si}}\text{—}X + R\text{—}OH$$

TABLE I Addition of water and it effects on the yield

$H_2O/XSiY_3$ (molar ratio)	0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
Yield (%)	9.1	11.2	15.7	23.4	31.8	37.9	42.7	40.3	36.5	32.5	27.6

Reaction condensations: MIBK/EtOH, Monomer concentration 0.45 mol/L, $HCl/XSiY_3 = 2.5–3$, Boiling.

2) 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 to carry out the condensation reaction. While too much water also will restrict the water condensation and eventually decrease the yield of the silsesquioxane. The appropriate addition of water will not only ensure complete hydrolysis and produce enough silanols but the silanols produced condense and produce amounts of water. The latter can undergo further hydrolysis and finally make the reaction continue and obtain the higher product yields.

3.1.3. Nature of the solvent

The trifunctional organosilicon monomers $XSiY_3$ have high reactivity, especially organotrichlorosilanes, in order to form the cage structure of silsesquioxane, the hydrolytic polycondensation must hold and release its reaction rate. 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. Research shows that both polar and nonpolar solvents, such as alcohol, benzene, toluene, cyclohexane and ether, can all act as solvents for the reaction. Different solvents affect product yields, along with the initial concentration chosen, and the type of catalyst can also influence the choice of solvent. Among these solvents, alcohol is one of the most common solvent [16]. The reason is that the silanol is the first product of hydrolytic condensation and the reaction rate can be well restricted by the presence of alcohol in the solution and eventually favours the cage structure formation. On the other hand, the existence of alcohol restricts to the number of silanol units in the intermediates, thus decreasing the degree of intermolecular association via hydrogen bonds and, consequently, preventing the polycondensation processes. So the amount of alcohol must be carefully controlled.

We use solvent mixtures of methyl isobutyl ketone and anhydrous ethanol instead of a single solvent commonly used to facilitate hydrolytic condensation. These two different solvents have different functions in the processing reaction. The MIBK with a high boiling point favours the increasing rate of the reaction and reduces the reaction time, and eventually increases the yield. While the existence of alcohol efficiently restricts the hydrolysis and reduces the reaction rate, which facilitates the formation of the cage structure.

3.1.4. Content of the catalyst

The formation of polyhedral oligomeric silsesquioxanes from the hydrolytic polycondensation of trifunctional monomers, $XSiY_3$, occurs only in the presence of either acid or base catalyst. When using acid as catalyst, HCl is the most efficient acid catalyst, and the high HCl concentration accelerates the synthesis of octa(alkylsilsesquioxane). Fig. 3 shows the relationship between the yield with the content of the concentrated HCl. It is obvious that the yield increase as the molar ratio of catalyst to monomer increases to 3.0, at which the maximum yield 44.5% is obtained, after that the yield drops to 27.8% as the molar ratio increases to 4.5, which shows that the yield increases with HCl content increaseing and high HCl content favours the silsesquioxane formation, but too much higher HCl content reduces the yield. This behavior can be attributed to pH value change based on HCl content and its influence in the processing reaction. The content of acid influences the pH value of the medium and the higher HCl content, the lower pH value of the medium, which favours crystallization and oligomer formation, and as a result the yield increases with HCl content increasing. However, the further increasing of HCl content results in the too lower pH values of the medium and is disadvantageous to the formation of silanols, which are acidic in nature, and as a result the difficult formation of oligomer and the decreasing of the yields.

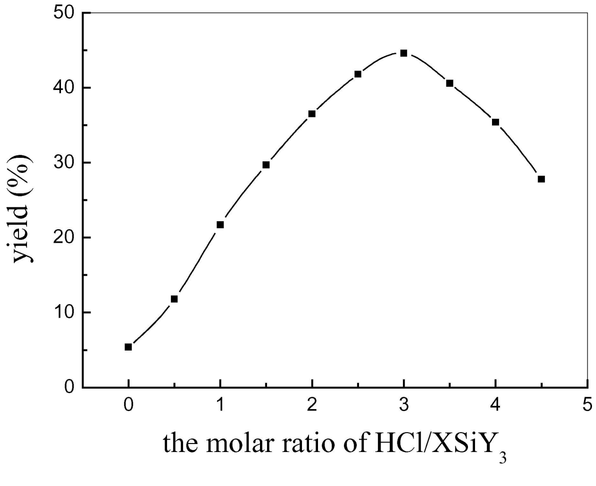


Figure 3 Effect of the catalyst on the yield of silsesquioxane (Reaction condensations: MIBK/EtOH, Monomer concentration 0.45 mol/L, $H_2O/XSiY_3 = 3$, Boiling).

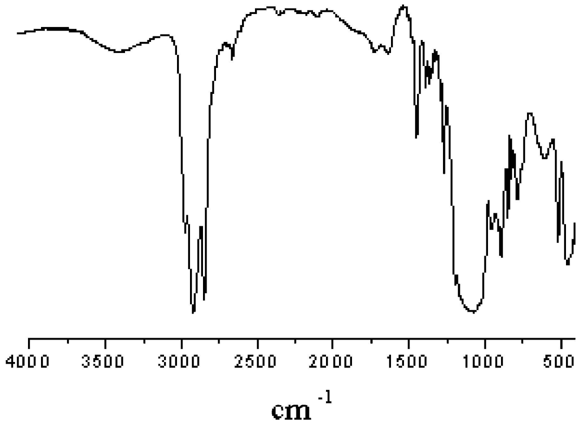


Figure 4 FTIR of the octa(cyclohexylsilsesquioxane).

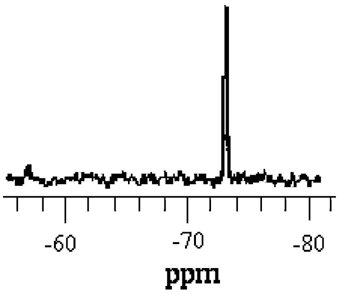


Figure 5 ^{29}Si NMR spectrum of octa(cyclohexylsilsesquioxane) (50 MHz, $CDCl_3$, 20°C).

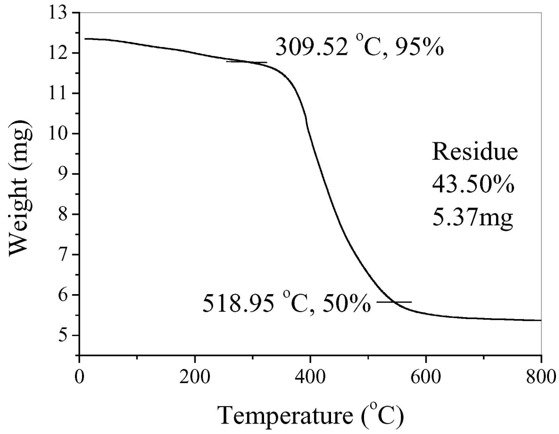


Figure 6 TG curve of octa(cyclohexylsilsesquioxane).

3.2. The structure characterization

3.2.1. FTIR spectrum

Fig. 4 is the FTIR spectrum of cyclohexylsilsesquioxane $(c\text{-}C_6H_{11})_8Si_8O_{12}$. In the region of 1200–1000 cm^{-1}, there is a very intensive and wide absorption band and the normal coordinate for this peak is a mixture of Si—O stretching, and Si—O—H, Si—O—Si, O—Si—O bending vibrations. Here it should be the characteristic absorption peak of the silsesquioxane cage Si—O—Si framework [17]. The peaks in the 2930–2860 cm^{-1} region correspond to the C—H stretching of the CH_2 groups in the cyclohexane rings. The peaks at 1265 and 760 cm^{-1} are the stretching and bending vibration of Si—C bond in Si—CH_2. The absorption at 895 cm^{-1} should be the stretching vibration of Si—C.

3.2.2. Spectra data analysis

MS (70 eV): m/z = 1081 (M + 1, 3%), 997 (M-(C_6H_{11}),100%), 915 (M-2(C_6H_{11}), 30%), 832 (M-3(C_6H_{11}),10%)$_\circ$.

^{1}**H NMR** (399.8 MHz, $CDCl_3$, 20°C): $\delta = 0.75$ (m, 8H), 1.25 (m, 40H), 1.74 (m, 40H). The eight ^{1}H nuclei attached to the silicon atom are chemically equivalent and thus have the same chemical shift of 0.75. The other ten ^{1}H nuclei in the cyclohexyl group display two different peaks, the chemical shifts for which are 1.25 and 1.74, respectively. The reason is likely to be related to the steric hindrance of the cage structure. The steric hindrance reduces the speed of the circlar motion of the cyclohexyl group and eventually make ^{1}H nucleus with different steric location in cyclohexyl group has different chemical shifts.

^{13}**C NMR** (100.5 MHz, $CDCl_3$, 25°C): $\delta = 23.10(CH,c\text{-}C_6H_{11})$, 26.68, 26.90, 27.46$(CH_2,c\text{-}C_6H_{11})$.

Fig. 5 shows ^{29}Si NMR spectrum of octa(cyclohexylsilsesquioxane) in $CDCl_3$ at 20°C. It is clear that there is only one peak in the spectrum, having the chemical shift $\delta = -71.53$ ppm, which indicates that there is only one structural conformation of silicon atom in the compound. Moreover, the value of the chemical shift is near to the that of the silicon atom in the cage structure of $(RSiO_{1.5})_8$ [18, 19]. From this we can confirm that the synthetic compound octa(cyclohexylsilsesquioxane) has the cage structure and its formula should be $[(c\text{-}C_6H_{11})SiO_{1.5}]_8$.

Anal. Calcd for $(c\text{-}C_6H_{11})_8Si_8O_{12}$: C 53.33%, H 8.15%; found C 53.01%, H 8.21%, which indicates the consistency of the experiment and the theoretical calculation.

3.3. Thermal analysis

The thermal stabilities (N_2) of octa(cyclohexylsilsesquioxane) are given in Fig. 6. The decomposition temperature (T_{dec}), the primary decomposition temperature and the char residue obtained from the TG curve can reflect the thermal stability of the material.

The decomposition temperature (T_{dec}) is the temperature at which the weight loss is about 5%. The 5% mass loss temperatures for octa(cyclohexylsilsesquioxane) is 309°C. However, the primary decomposition temperature (half mass loss point) for it is about 519°C. The char residue (N_2) of it is about 43.5% as expected because of the high silica content.

The magnitude of T_{dec} for a material is mainly determined by its chemical structure, such as the bond energy, defects inside the molecule and reactivity of the bonds. Generally speaking, the higher bond energy the higher the thermal stability. Three main covalent bonds existing in silsesquioxane molecule are Si—O, C—C, and Si—C, which have different bond energy, the values are 422.5 kJ/mol, 347 kJ/mol, and 334.7–242.7 kJ/mol, respectively. The degradation of octasilsesquioxane should start from initial cleavage of the C—C and Si—C bonds in the corner groups for their low bond energy. Moreover, the C—C and Si—C bond energies on the silsesquioxane cage vary with the chemistry of the corner groups. The more stable the corner groups on the silsesquioxane cage, the higher the T_{dec} of silsesquioxane monomer. The corner group of cyclohexyl is the stereo structure and has higher stability than the group has the plane structure. So octa(cyclohexylsilsesquioxane) has the decomposition temperature as high as 309°C

The primary decomposition temperatures may be construed as an effect of creating a hybrid material at a molecule level. One might argue that, in the hybrid material, such as octa(cyclohexylsilsesquioxane), the molecule thermal motion tether is restricted for the existing of chemical bond between inorganic and organic groups, and especially the steric effects from the silsesquioxane cage structure in the molecule chain. Thereby the organic decomposition pathway accessible to the tether was reduced. It is likely that the inorganic component provides additional heat capacity thereby stabilizing the bulk material against thermal decomposition.

The char residues are taken as the weight percentage of the sample remains after the TG test, which for octa(cyclohexylsilsesquioxane) is about 43.5%. The char residue of a material is decided by the content of organic elements and inorganic elements in the molecules, and if there are more stable molecules formed during the decomposition pathway as a result of a chemical reaction. The large the mass of the inorganic groups in the material, the higher its char residue yield. This principle also applies to silsesquioxane and the stability of the corner group should also take into according. The weight percentage of the inorganic Si—O cage in octa(cyclohexylsilsesquioxane) is 38.52% in theory, while the weight percentage of organic compound is 61.48%. The char residue from the TG curve is about 43.5%, which is higher than the theoretical value of the inorganic weight percentage. This behavior can be likely attribute to the thermal stable of cyclohexyl corner group. The large the mass of the corner groups on the silsesquioxane cage, the higher their yield. These data indicate that the organic compound decomposes and the inorganic Si—O—Si composition has no or little change at the temperature of 800°C.

4. Conclusion

Octa(cyclohexylsilsesquioxane) ($(c\text{-}C_6H_{11})_8Si_8O_{12}$) was prepared by the hydrolysis and polycondensation of trifunctional monomer $(c\text{-}C_6H_{11})Si(OC_2H_5)_3$ in the mixtures of solvents of methyl isobutyl ketone and anhydrous ethanol instead of a single solvent. The high boiling point solvent MIBK can increase the reaction temperature and favor silsesquioxane formation, and eventually shorten the reaction time and increase the yield. When keeping the solution boiling, the higher yield can be obtained at monomer concentration of 0.45 mol/L, $H_2O/XSiY_3 = 3/1$ (molar ratio), $Et_4NOH/XSiY_3 = 3$ (molar ratio). The structure characterization was investigated by FTIR spectrum, ^1H, ^{13}C and ^{29}Si NMR spectra. The results indicated the cage structure of the synthetic compound and its formula of $(c\text{-}C_6H_{11})_8Si_8O_{12}$. Thermal gravimetric analysis shown that the cage compound had a higher decomposition temperature 309°C, higher primary decomposition temperature 519°C and high char residue 43.5% in nitrogen atmosphere at 800°C for the thermal stability of the cyclohexyl corner groups and the higher weight percentage of the inorganic Si—O—Si structure.

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References

1. R. H. BANEY, M. ITOH, A. SAKAKIBARA and T. SUZUKI, *Chem. Rev.* **95**(5) (1995) 1409.
2. H. XU, P. XIE and R. ZHANG, *Eur. Polym. J.* **37**(12) (2001) 2397.
3. V. LORENZ, M. SPOIDA, A. FISCHER and F. T. EDELMANN, *J. Organomet. Chem.* **625** (2001) 1.
4. V. LORENZ, A. FISCHER and F. T. EDELMANN, *Inorg. Chem. Commun.* **3** (2000) 292.
5. V. LORENZ, A. FISCHER, K. JACOB and F. T. EDELMANN, *ibid.* **6** (2003) 795.
6. C. J. STEPHANSON and G. P. FLANAGAN, *Int. J. Hydrogen. Energy.* **28**(11) (2003) 1243.
7. S. XIAO, M. NGUYEN, X. GONG, Y. CAO, H. B. WU, D. MOSES and A. J. HEEGER, *Adv. Funct. Mater.* **13**(1) (2003) 25.
8. Z. BAO, V. KUCK, J. A. ROGERS and M. A. PACZKOWSKI, *ibid.* **12**(8) (2002) 526.
9. R. I. GONZALEZ, "Synthesis and In-Situ Atomic Erosion Studies of Space-Survivable Hybrid Organic/Inorganic Polyhedral Oligomeric Silsesquioxane Polymers," Ph.D Thesis, University of Florida, 2002.
10. Y. X. ZENG, S. W. RUSSELL, A. J. MCKERROW, P. CHEN and T. L. ALFORD, *Thin Solid Films* **360** (2000) 283.
11. S.-Y. LU and I. HAMERTON, *Prog. Polym. Sci.* **27** (2002) 1661 and references 172–184 cited therein.
12. G. KICKELBICK, *ibid.* **28**(1) (2003) 83.
13. G. LI, L. WANG, H. NI and C. U. PITTMAN, Jr. *J. Inorg Organome Polym.* **11**(3) (2001) 123.
14. M. G. VORONKOV and V. I. LAVRENT'YEV, *Top. Curr. Chem.* **102** (1982) 199.
15. J. D. LICHTENHAN, (PALMDALE CA), J. W. GILMAN, (LANDCASTER CA), F. J. FEHER and (COSTA M. CA), U. S. Patent 5,484,867, January, 16 (1996).
16. F. J. FEHER, D. A. NEWMAN and J. F. WALZER *J. Am. Chem. Soc.* **111**(5) (1989) 1741.
17. D. A. LOY, B. M. BAUGHER, C. R. BAUGHER, D. A. SCHNEIDER and K. RAHIMIAN, *Chem. Mater.* **12** (2000) 3624.
18. I. E. DAVIDOVA, L. A. GRIBOV, I. V. MASLOV, V. DUFAUD, G. P. NICCOLAI, F. BAYARD and J. M. BASSET, *J. Mol. Struct.* **443** (1998) 89.
19. A. PROVATAS, M. LUFT, J. C. MU, A. H. WHITE, J. G. MATISONS and B. W. SKELTON, *J. Organomet. Chem.* **565** (1998) 159.
20. E. RIKOWSKI and H. C. MARSMANN, *Polyhedron.* **16**(19) (1997) 3357.

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