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Investigation of thermal crosslinking and pyrolysis of ladderlike silsesquioxanes in vacuum by XRD measurements and weight analysis

Lei Liu[a], Yuan Hu[a,*], Xiaokai Li[c], Zuyao Chen[b], Weicheng Fan[a]

[a] *State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230027, China*
[b] *Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China*
[c] *Department of Polymer Science and Technology, University of Science and Technology of China, Hefei, Anhui 230026, China*

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Abstract

In this paper, we first synthesized ladderlike poly(vinylsilsesquioxane) (LPVS) by stepwise coupling polymerization on the basis of amido H-bonding self-assembling template from vinyltrichlorosilane (VTCS) monomers. We made the substitutional vinyl of LPVS polymerized at one same side (LPVS-SP), then put it in the vacuum conditions and let it carbonized at 500, 600, 700, 800 and 900 °C, respectively to observe its thermal behavior. In our experiment, 700 °C can be regarded as a distinct turning point of temperature from weight loss to inter-molecules thermal crosslinking, which can be observed by X-ray diffraction (XRD) measurements and Thermogravimetric analysis (TGA). At the same time, SEM and TEM photos of the carbonization products give very rigidity topography at micron scale, which are the auxiliary evidence for our conclusion. We also present one reasonable thermal carbonization and crosslinking mechanism of LPVS-SP at high temperature in vacuum by remaining products weight analysis.

Keywords: Ladderlike poly(vinylsilsesquioxanes); Carbonization; Crosslinking; Thermal stability

1. Introduction

Polymeric materials are widely used in architecture, traffic and many other areas in our everyday life. Polymer is very easy to be burned, which limits the extension of its applications. How to improve its fire resistant property and thermal stability is a very important question. Fire resistant polymer composites have been on research for a long time, especially these years [1–5]. Usually some additives are added into polymer substance in order to raise their fire protection level [6,7]. The additives in common use are halogen, phosphorus and hydrate. Each of these traditional fire resistant additives has their own limitation. Search after new route to get a novel generation of fire resistant polymer composites generated substantial interest in the materials community in the past decades [8].

Fire protection system containing organic or inorganic silicon is an important direction. It has many advantages comparing with traditional systems, such as limited smoke, none toxin, lower combustion heat release and upper burning point. Silicon polymer with silicon–oxygen bond in its main chain possesses excellent thermal stability. Bridged silsesquioxane [9], which has silicon–oxygen bond in its main double chains is one kind of essential fire protection materials [10]. Over the past decades, bridged silsesquioxanes have attracted widespread attention and concern [11,12]. They are easily accessible upon hydrolysis of bis-silane precursors, $(RO)_3Si{-}RA{-}Si(OR)_3$, which allow a controlled loading and arrangement of organic fragments in the hybrid silicate network through Si–C covalent bonds. In this way, Mr. Zhang' group developed a serials of ladderlike polysilsesquioxanes

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[*] Corresponding author. Tel.: +86 551 3601664; fax: +86 551 3601664.
E-mail address: yuanhu@ustc.edu.cn (Y. Hu).

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by stepwise coupling polymerization on the basis of amido H-bonding self-assembling template from different monomers [13–16].

Silicon polymers are one type of materials with great thermal stability. Their thermal behaviors and thermal products at high temperature are worth researching. And they are commonly used in the production of silicon carbide and silicon oxycarbides [17,18]. Dahn has experience in the pyrolysis of siloxane polymers for possible use as anode materials in Li-ion batteries [19–21,23], which showed how the capacity of the pyrolyzed polymers for lithium depends strongly on the stoichiometry of the silicon oxycarbide. And Lichtenhan has investigated the pyrolysis of four polyhedral oligomeric silsesquioxane (POSS) macromers and POSS-siloxane copolymers in argon, nitrogen, and under vacuum from 30 to 1000 °C [24]. Siloxane polymers differ in the number of oxygen atoms per silicon and in the chemical composition of the ligands. Previous studies into the thermolysis of polyhedral silsesquioxanes [25–27] and polysilsesquioxanes [28–31] have primarily focused on the preceramic nature of silsesquioxanes toward the formation of SiO_xC_y chars and SiC ceramics.

In this paper, we synthesized the ladder like poly(vinylsilsesquioxanes) with its side group polymerization by Mr. Zhang's method and study its inter-molecules thermal crosslinking and pyrolysis in vacuum circumstance at high temperature. We study the whole crosslinking course by diffraction (XRD) measurements and give one possible crosslinking mechanism on the basis of weight analysis and elemental analysis.

2. Experimental

2.1. Materials.

Vinyltrichlorosilane (VTCS) was purified by partial pressure distillation (0.02 MPa, 50 °C) prior to use. All the other reagents were commercially available and of analytical grade. Toluene and acetone were distilled prior to use.

2.2. Techniques

Infrared spectra were obtained using a Bruker EQUINOX 55 FT-IR spectrophotometer. Proton NMR spectra were acquired using a Bruker AVANCE 300 spectrometer using $CDCl_3/CHCl_3$ as a reference at 7.24 ppm downfield from TMS (0.00 ppm). Crystalline phases of the powder samples were identified by powder X-ray diffraction (XRD) using a Rigaku K/max-γA X-ray diffractometer with a Cu Kα ($\lambda = 1.5415$ Å) at the scanning rate 0.02°/s. Thermogravimetric analysis (TGA) of polymer samples was performed on a Netzsch STA-409c thermal analyzer under a 50 mL/min nitrogen flow. The samples were heated from 25 to 750 °C at a rate of 10 °C/min. SEM photos and TEM photos were obtained from AMRAY-1000B scanning electronic microscope system and TEM-H-800, respectively. The elemental analysis result were obtained by Elementar Vario EL-III elemental analyzer.

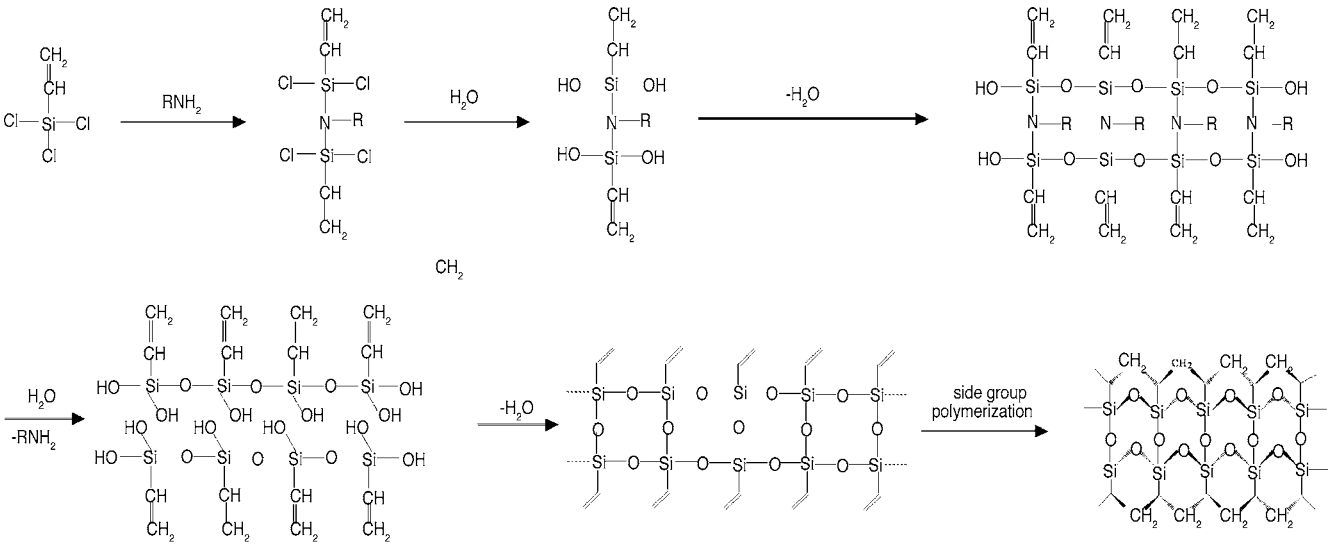
2.3. Synthesis of side vinyl polymerized LPVS by in situ polymerization

Ladderlike poly(vinylsilsesquioxane) (LPVS) was synthesized from vinyltrichlorosilane (VTCS) according to the former literature [13–16]. First 500 mL acetone was added to a three-necked flask, holding it in ice-water bath for half an hour. Then 100 mL (0.7835 mol) vinyltrichlorosilane was added into the acetone slowly and cooled for another half an hour with vigorous stirring. Forty-five millilitres butylamine was diluted with 205 mL acetone and was added dropwise into the flask. The temperature of reaction system was controlled approximately at 0 °C. With the entering of butylamine/acetone, adhesion of the system increased and hydrochloride smoke generated from the surface of the reaction solution. The solution reaction system was stirred at about 0 °C for 1 h. Twenty-five millilitres distilled water and 100 mL acetone mixture was added dropwise into it at about 0 °C. Then increased the temperature slowly and 1 h later reached 40 °C, holding the solution at this temperature for 24 h with vigorous stirring. In this way ladderlike poly(vinylsilsesquioxane) (LPVS) was obtained in acetone.

LPVS/acetone solution was transferred into extraction filler and cooled to room temperature, 250 mL toluene was added to leach LPVS. Distilled water was used to wash the LPVS/toluene solution till pH 7. After desiccated by anhydrous $NaSO_4$, about 0.1 g benzoyl peroxide (BPO) was added into the solution as initiator. Then at 100 °C with vigorous stirring and refluxing for 10 h, the vinyl of LPVS as side group began to polymerize side by side. After distilling toluene, the ladderlike polysilsesquioxane with four parallel chains in its backbone (LPVS-SP, Here we name LPVS with side vinyl polymerized as LPVS-SP) was obtained (Scheme 1). Vinylsilsesquioxane is one kind of reagent with extraordinary chemical active properties, so diluent system and low temperature will reduce the reaction rate effectively. This can guarantee the formation of LPVS structure instead of orderless structure.

2.4. Vacuum carbonization of LPVS-SP

LPVS-SP was obtained by distilling toluene away. Most of solvent was eliminated by using a rotate vaporizer. Then it was dried at 100 °C in vacuum oven for more then 10 h in order to get rid of residual toluene in the sample. Then a piece of LPVS-SP (about 0.1 g) was put into a quartz tube, charged pure nitrogen in it and then vacuumized by a vacuum pump. Repeated this step three times and sealed the tube immediately. The vacuometer showed that the pressure was less than 0.01 atm. This hermetic vacuum system was heated to 500 °C and last for 10 h. After persistent heating in vacuum, we obtained the product of LPVS-SP carbonization, which



Scheme 1. The form process of LPVS and LPVS-SP.

Table 1
The detailed experiment results of LPVS-SP carbonization at different temperature (from 200 to 900 °C)

Carbonization temperature (°C)	Sample weight before heating (g)	Sample weight after heating (g)	Percentage of residual	$2\theta_1$/d – 1(Å)	$2\theta_2$/d – 2(Å)
200	0.1188–0.1190	0.1180–0.1185	99.160–99.747	9.50/9.331	22.15/4.08
500	0.1110–0.1115	0.1046–0.1054	93.821–94.952	9.40/9.429	21.77/4.15
600	0.1197–0.1204	0.1106–0.1112	91.855–92.775	9.20/9.632	22.00/4.11
700	0.1168–0.1170	0.1048–0.1058	89.568–90.627	8.36/10.592	21.70/4.16
800	0.1120–0.1127	0.1003–0.1009	89.036–90.107	6.11/14.468	21.32/4.23
900	0.1433–0.1440	0.1286–0.1288	89.306–89.847	4.40/20.073	21.16/4.26

was mainly made up of silicon oxycarbide and silicon carbide. The same experiment proceedings were repeated at 600, 700, 800 and 900 °C, respectively. By this way, we obtained different carbonization products. The detailed experiment results were listed as following (Table 1).

3. Results and discussion

3.1. Synthesis and characteristics of LPVS and LPVS-SP

In H^{1}NMR spectrums (Figs. 1 and 2), the chemical shift at 5.93 ppm corresponds to the hydrogen of side vinyl of LPVS (Hc in Fig. 2), and the chemical shifts at 1.26 and 1.54 ppm correspond to hydrogen of the polymerized alkyl (Ha and Hb in Fig. 2), whose ratio of integral peak area is 2:1. Comparing with Figs. 1 and 2, almost all the vinyl belongs to the main double chains and has been replaced by saturated alkyl, which is the direct evidence for that vinyl, has taken part in the polymerization with each other. FTIR results of LPVS (the top curve) and LPVS-SP (the bottom curve) were shown in Fig. 3. It shows the appearance of absorbing peaks corresponding to saturated C–H ($\nu = 2958.43\ \mathrm{cm}^{-1}$) and C–C ($\nu = 1410.30\ \mathrm{cm}^{-1}$) vibration and disappearance of absorbing peaks corresponding to unsaturated C–H ($\nu = 3069.63\ \mathrm{cm}^{-1}$) and C–C ($\nu = 1602.49\ \mathrm{cm}^{-1}$) vibration. This is the second evidence to the polymerization of side vinyl. The two curves both have a strong absorbing peak between 1000 and 1150 cm^{-1}, which stands for the stretch vibration of O–Si–C system (νSi–O at 1049 cm^{-1} peak and νSi–C at 1127 cm^{-1}).

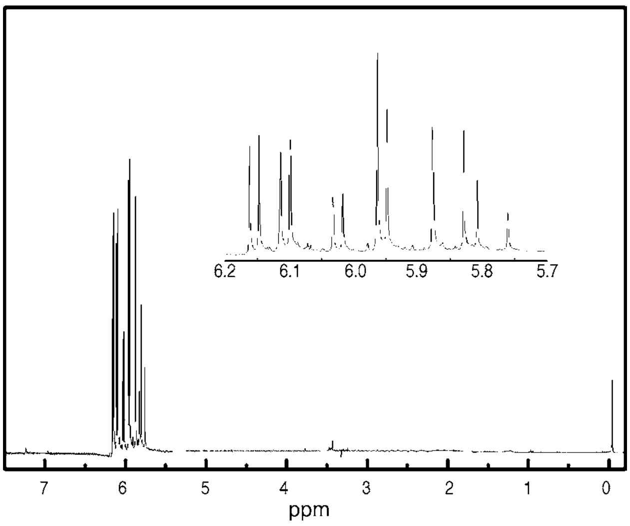


Fig. 1. ^{1}HNMR spectrum of ladderlike poly(vinylsilsesquioxanes) (LPVS).

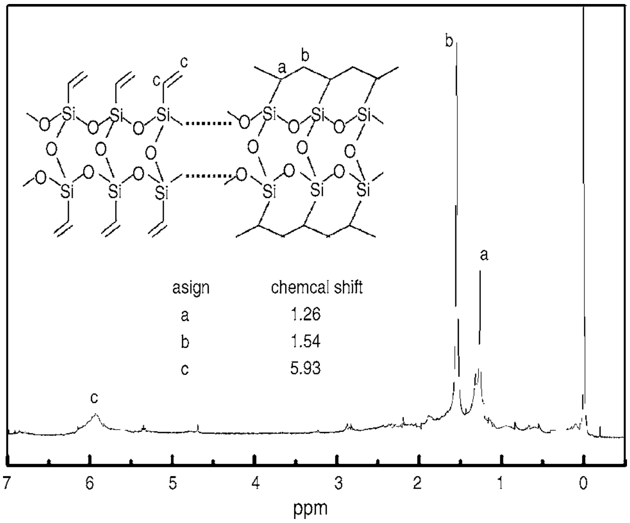


Fig. 2. ^{1}HNMR spectrum of LPVS-SP (2 days continuative side group polymerization of LPVS) and idealized structures of LPVS and LPVS-SP.

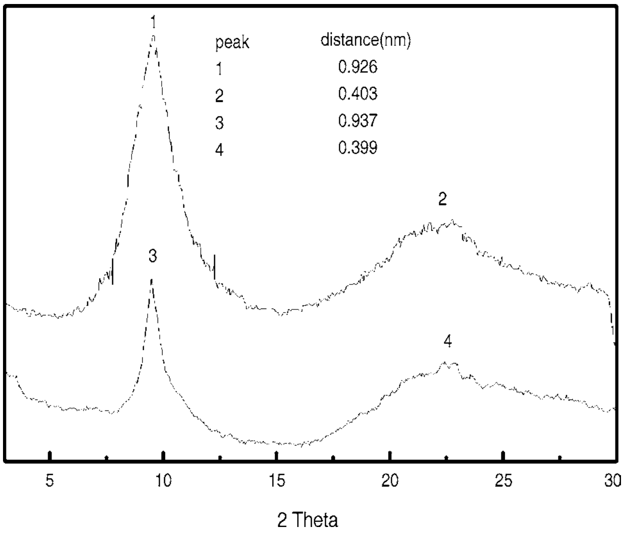


Fig. 4. XRD pattern of LPVS (top curve) and LPVS-SP (bottom curve).

Little difference was detected in X-ray diffraction measurements. The top curve and the bottom curve in XRD pattern represent LPVS and LPVS-SP, respectively. Each curve has two distinct peaks in the XRD pattern of polymer LPVS and LPVS-SP in Fig. 4. Referring to Brown [9,10], Andrianov [20,21], Zhang [13] and Shi, the first peak ($d_1 = 0.926$ nm and $d_3 = 0.937$ nm), which represents the intra molecular chain-to-chain distance (i.e., the width of ladderlike main chain) of the polymer is narrow and sharp. This implies that the polymer has a relatively regular ladderlike skeleton. This is also a very important experimental evidence of our previous expectation, which point out that vinyl polymerization mostly occurs in the same ladderlike double chains side by side. The second wide peak ($d_2 = 0.403$ nm and $d_4 = 0.399$ nm) possibly stands for the thickness of the macromolecular chain or the intermolecular spacing between the polymer molecules. Because of vinyl polymerization in the same side of one ladderlike macromolecule, there are tiny difference between d_1 and d_3, d_2 and d_4. It depends on the structure stretch difference in space between vinyl and hexacyclic ring. From a steric view, side polymerization of vinyl from one macromolecule will not change the width of the polymer greatly.

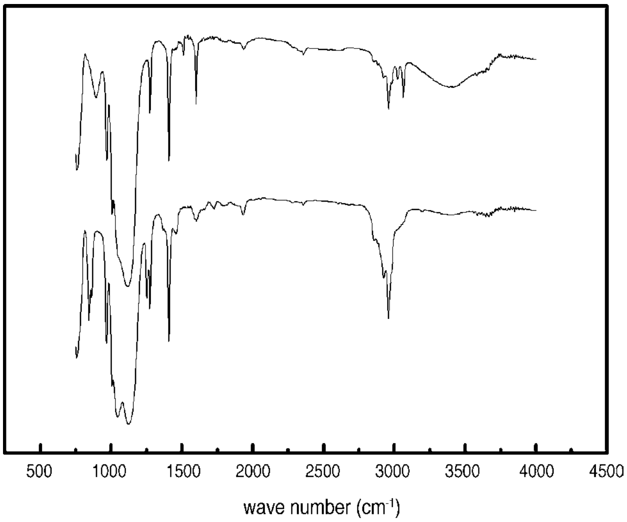


Fig. 3. FT-IR spectrum of LPVS (top curve) and LPVS-SP (bottom curve).

We regard the polymerization can mostly occur in the vinyl side by side of the same macromolecule chain because of the following analysis: (1) This kind of polymerization will be prone to take place for its special steric structure. On one hand, if the vinyl can react between different ladder chains, the whole macromolecule chain will be looked as side group of vinyl, which makes the tremendous steric hindrance in the farther reaction. So the polymerization of vinyl from two different chains is very difficult to carry out and vinyl from the third chain seems impossible to add up. On the other hand, if the polymerization takes place between the two vinyls from same chain side by side, it only needs vinyl making little rotation. That will promote the probability of polymerization greatly. (2) If the vinyl react in the way described in Scheme 1, many hexacyclic rings which are made of one oxygen atom, two silicon atoms, two carbon atoms form methylidynes (≡CH) and one carbon atom form methylidene (=CH_2) can be formed along the ladderlike macromolecule's double chains. As we know, hexacyclic ring is a kind of structure with great stability in chemical thermodynamics. Although we can convict the structure of ladderlike poly(vinylsilsesquioxanes) with side vinyl polymerized by spectrochemical and XRD characterization, we know that the frame of LPVS-SP in Scheme 1 is an idealized structure.

3.2. Carbonization and crosslinking of LPVS-SP

The whole process of LPVS-SP carbonization and crosslinking was detected by X-ray diffraction (XRD) mea-

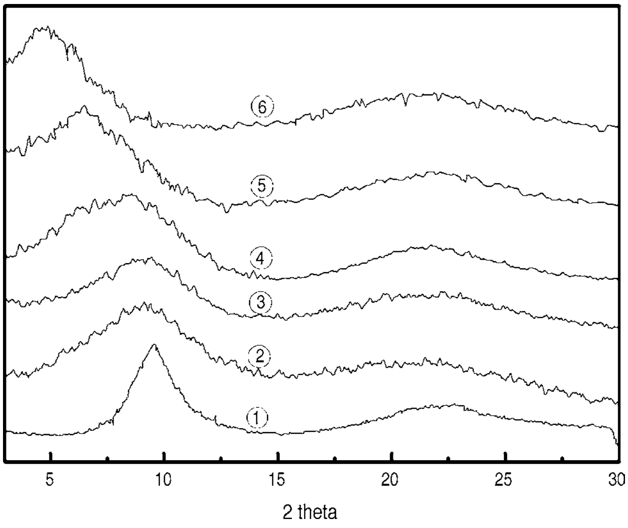


Fig. 5. XRD pattern of LPVS-SP carbonization product. (1) LPVS-SP (2) LPVS-SP at 500 °C (3) LPVS-SP at 600 °C (4) LPVS-SP at 700 °C (5) LPVS-SP at 800 °C (6) LPVS-SP at 900 °C.

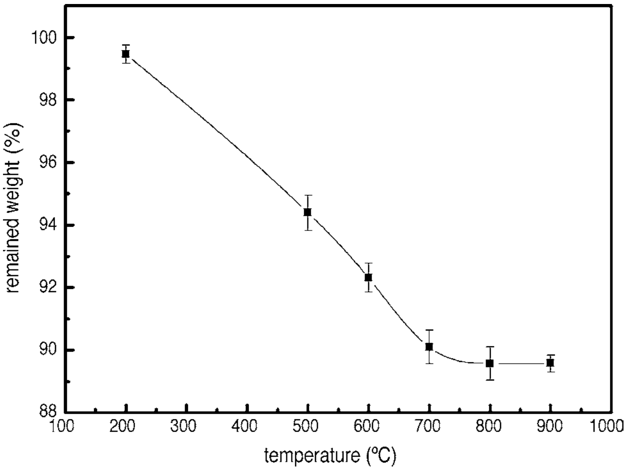


Fig. 7. The remained mass ratio (%) of LPVS-SP carbonization product with temperature.

surements and weight changing analysis. Figs. 5 and 6 show that the first diffractive peak of carbonization product of side vinyl polymerization LPVS shifts to the small angle direction monotonously, corresponding to the increasing d space. According to the front lines, we know that the first diffractive peak means the width of the ladderlike polymer, so this also indicates the average width of the macromolecules augments gradually. With the temperature rising, a number of chemical bond began to rupture, the dropped fragment from the polymer chain depart from the solid, changed into gases and deposited on the inner wall of quartz tube. This will result in the weight decrease of our sample. At farther higher temperature, the bond rupture recede to a subsidiary station, the remained molecular chain accelerated to move, some new bonds (such as C–C, C–Si, Si–Si, Si–O, C–O) formed at the same time. In our experiments, 700 °C is an important turning point temperature in the carbonization and pyrolysis process. From 500 to 700 °C in vacuum, the main behavior of LPVS-SP is losing weight (Fig. 7), the first diffractive angle in XRD pattern changes to small angle direction extraordinarily very little. But when the temperature rises to 700–900 °C period, its weight almost remains at constant level, but the first diffractive angle rises approximately linear. At 900 °C, the d space corresponding to the first diffractive angle which representing the intra molecular chain-to-chain distance is almost as twice as that of LPVS. This did not indicate that at this temperature LPVS changed into dimers, different connected molecular chains coexist in the three-dimensional space with different stretch tropism, the XRD results is only the statistical average value of the all kind of different possibility. Of course it really indicates that when the temperature rises more than 700 °C, the molecular chains get connected with each other. In the XRD pattern, we can find the peak of LPVS is much shaper than the peak of LPVS after carbonization in high temperature. Because of high temperature, part of LPVS-SP molecular chains were destroyed, the regularity of chain declines. Another possible reason is that the carbonization environment of LPVS is not critical ultra high vacuum; minim rudimental oxygen will accelerate the decomposition and destroy the molecular chains of LPVS. In the other hand, we found that the second diffractive peak of carbonization product almost remained in its position steadily. According to the literature [13], the second peak is possibly related to the thickness of the polymer, we here presume that the crosslinking process would take place in two-dimensional space instead of three-dimensional space.

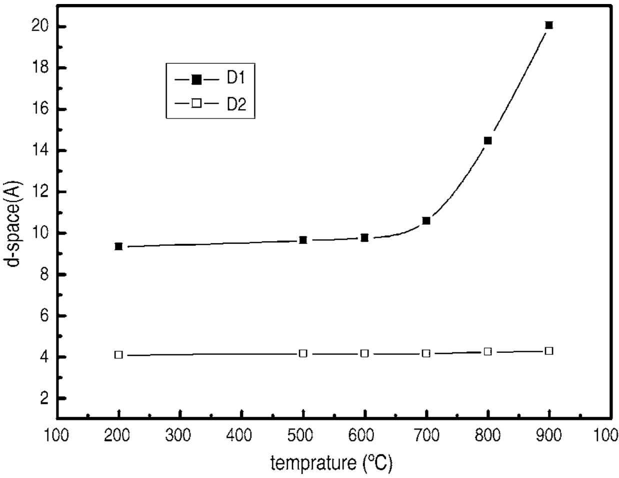
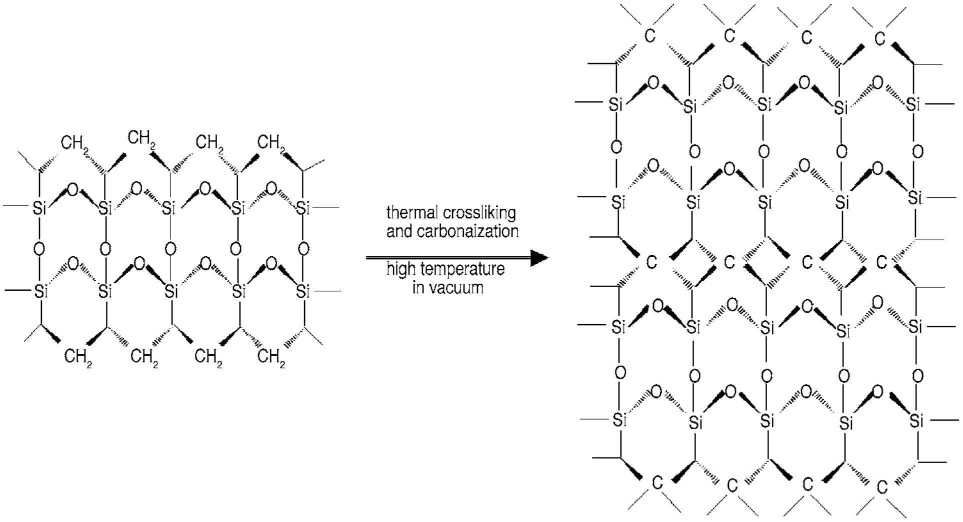


Fig. 6. The d space changes of LPVS-SP carbonization product with temperature.

The sketch course of LPVS-SP carbonization process can be described as Scheme 2. Because C–H bond energy is the lowest among all the chemical bond in LPVS-SP, the bond will rupture at the very beginning of the mass loss. With the temperature rising, outside heating system infuse energy into the sealed vacuum system, which made LPVS-SP macromolecules act more tempestuously. During the micro-



Scheme 2. The carbonization and inter-molecule crosslinking of LPVS-SP at high temperature.

cosmic movements, new chemical bonds formed by inter-macromolecules or by intro-macromolecules mode. The crosslinking and carbonization process happened simultaneously. We note that vacuum degree influence the crosslinking results obviously, a little oxygen will change it into noncrystal silicon oxide because of the high temperature. Attenuated atmosphere will help the crosslinking between macromolecules. Carbonization in inert airflow will not result in the change of d space in the powder XRD pattern.

We know that polymer LPVS-SP can be described using the simple chemical formula as $[Si_2O_3C_4H_6]_n$, its relative weight of one unit is about 160, and the carbonization and crosslinking product generated by the approach in Scheme 2 has a simple chemical formula as $[Si_2O_3C_3H_2]_n$, and its relative weight of one unit is about 144. By this we can calculate that the theory remained weight percentage is 90. Let us come back to our experiment, Fig. 7 shows that the remained weight percentage stabilized at about 89 when the temperature is more than 700 °C. This can be explained by our speculation in Scheme 2. One percentage in difference perhaps results from the trace oxygen in the vacuum system or a small quantity of impurity in our sample. On the other hand, we find that the error of remained weight percentage varies in a big range, but when the temperature reaches 900 °C, the error seems very small. The elemental analysis results of LPVS-SP at 900 °C give the 24.71% of C content and 1.349% of H content. The corresponding molar ratio of C and H is 3.05:2.00, which accords with ideal chemical formula as $[Si_2O_3C_3H_2]_n$. This indicates the product has achieved a steady structure, which can be formed by different ways.

3.3. SEM and TEM photos of vacuum carbonization products

Figs. 8 and 9 are the SEM results of LPVS-SP 900 °C carbonization product at different scale. Comparing with LPVS-SP (Fig. 10), the raw product remains in its original condensed state mostly as a piece of hard solid. The product was grinded into powders before taking SEM photos, so that we can realize the inside appearance after carbonization at high temperature. The photos showed that comparing with LPVS-SP, the carbonization products still keep comparative compact solid structure after 10 h at 900 °C, which provides evidence that most of the molecular chains were not destroyed. In the same way, we find there are very few differences between the carbonization products and the origin polymer in TEM photos. Similar inside topographies indicate that carbonization is the dominant chemical reaction in the system when compared to the oxidation (Figs. 11 and 12).

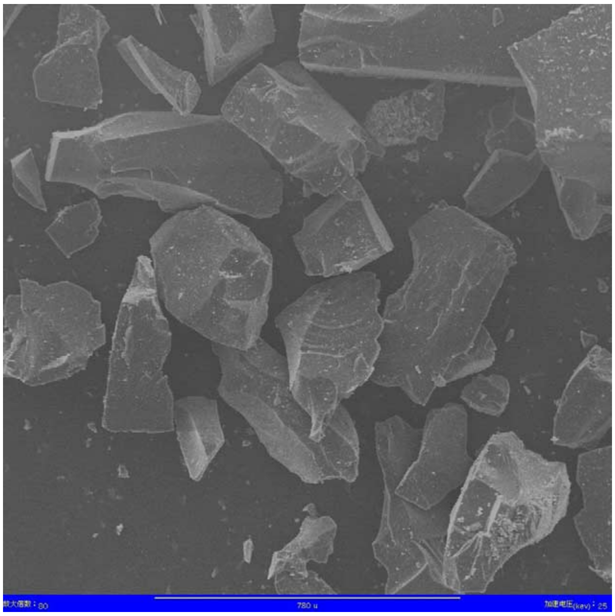


Fig. 8. SEM photo of LPVS-SP carbonization product at 900 °C (80 times).

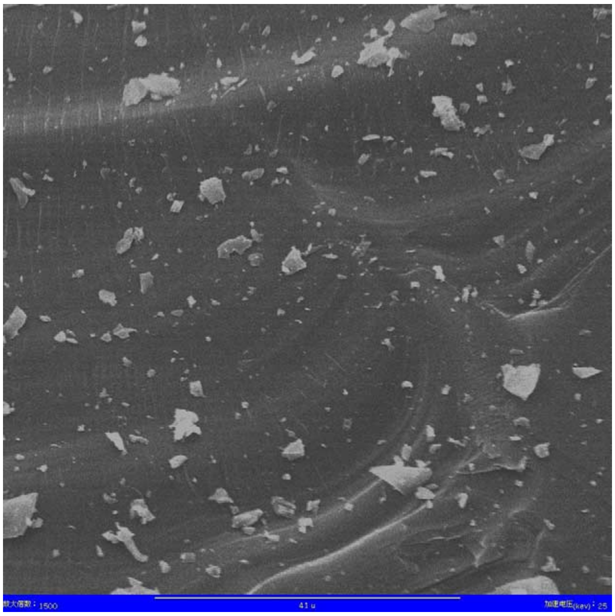


Fig. 9. SEM photo of LPVS-SP carbonization product at 900 °C (1500 times).

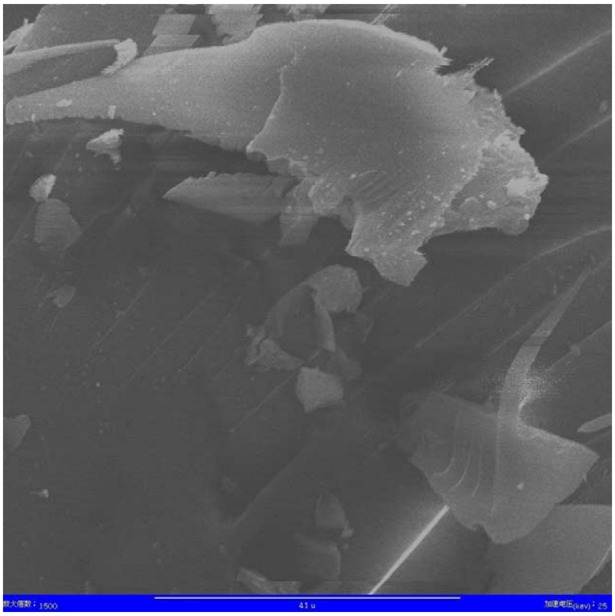


Fig. 10. SEM photo of LPVS-SP (1500 times).

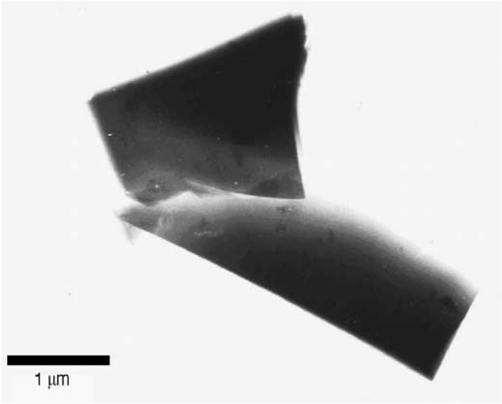


Fig. 11. TEM photo of LPVS-SP (12000 times).

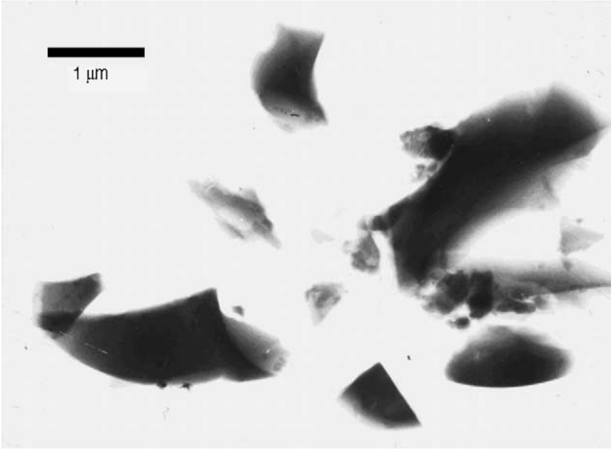


Fig. 12. TEM photo of LPVS-SP carbonization product at 900 °C (12000 times).

3.4. Thermal stability analysis

Polymer LPVS-SP and its carbonization product (at 900 °C) showed excellent thermal stability. The thermal behavior characterized by TGA is provided in Fig. 13. It is much more stable than most of other polymers. The 5% mass loss temperature for LPVS-SP is at ~630 °C, and the temperature LPVS-SP begins to decompose as high as ~500 °C. The reason why this polymer can resist such high temperature is as following: first, Si–O bond which constitutes the main double chains has a high bond energy at ~452 kJ/mol, which is more than the C–C bond (~345.6 kJ/mol), C–O bond (~357.7 kJ/mol) and Si–Si bond (~222.0 kJ/mol), so it is more difficult to make the polymer chain ruptured and decomposed. And in LPVS-SP, $(SiO)_{1.5}$ unit takes 66% in

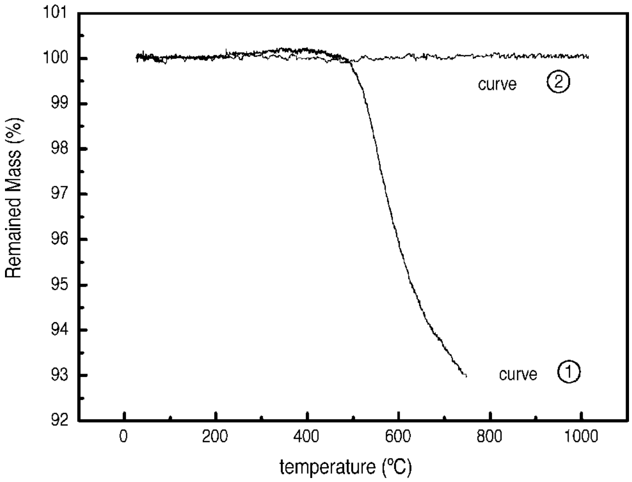


Fig. 13. The thermal stability composition between LPVS-SP (curve (1)) and its carbonization product at 900 °C (curve (2)).

mass proportion. Second, double chains of ladderlike structure is more stable than single chain structure. If one bond of single chain is destroyed, the macromolecule will divide into two molecules with much lower molecular weight. But if one bond of double chains of ladderlike structure is destroyed, there will be no influence on the molecular weight. When the condition is permitting, the destroyed bond will remedy itself. Only if the two bonds are destroyed simultaneously in the same position of the parallel chains, molecular weight of the ladder like polymer reduces. In polymer LPVS-SP, because of side group polymerization, there seems to form one extra parallel chain at each side of the primary double chains of ladderlike structure, which will reinforce the thermo-stability of the polymer by a long way.

When the polymer was carbonized in vacuum, the crosslinking between molecules formed. Several parallel molecular chains made of silicon–oxygen covalent bonds enhanced its thermal stability greatly. TGA result of the product silicon oxycarbide gives excellent thermal stability that almost no weight loss can be detected from room temperature to 1000 °C. We consider that molecules crosslinking is one possible reason of the high thermal stability of LPVS-SP.

4. Conclusion

In summary, we have succeeded in making ladder like poly(vinylsilsesquioxanes) with side vinyl polymerized (LPVS-SP) crosslinking in vacuum conditions by thermal methods. X-ray diffraction measurements and weight measurements indicate that 700 °C was the turning point temperature from weight loss to inter-molecules thermal crosslinking. The formation of silicon oxycarbides by molecular crosslinking is one possible thermal stabilization mechanism of ladderlike polysilsesquioxanes.

Acknowledgements

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References

[1] J. Giancaspro, P. Balaguru, R. Lyon, Sampel J. 40 (5) (2004) 42–49.
[2] H. Zhang, P.R. Westmoreland, R.J. Farris, et al., Polymer 43 (20) (2002) 5463–5472.
[3] Z.K. Brzozowski, D. Kijenska, W. Zatorski, Designed Monom. Polym. 5 (2-3) (2002) 183–193.
[4] S. Bourbigot, X. Flambard, M. Ferreira, F. Poutch, J. Fire Sci. 20 (1) (2002) 3–22.
[5] Y.W. Chen-Yang, H.F. Lee, C.Y. Yuan, J. Polym. Sci. Part A-Polym. Chem. 38 (6) (2000) 972–981.
[6] S. Srinivasan, L. Kagumba, D.J. Riley, et al., Macromol. Symp. 122 (1997) 95–100.
[7] D. Kumar, M. Khullar, A. Gupta, Polymer 34 (14) (1993) 3025–3029.
[8] Shui-Yu Lu, Ian Hamerton, Prog. Polym. Sci. 27 (2002) 1661–1712;
Z.K. Brzozowski, D. Zatorski, W. Kijeńska, Design. Monom. Polym. 5 (2–3) (2002) 183–193.
[9] D.A. Loy, K.J. Shea, Chem. Rev. 95 (1995) 1431–1442.
[10] Yuxiang Ou, Fire retardant polyurethane, plastics science and technology (Chinese), vol. 134, 1992, p. 12.
[11] K.J. Shea, D.A. Loy, O.W. Webster, J. Am. Chem. Soc. 114 (1992) 6700.
[12] R.J.P. Corriu, J.J.E. Moreau, P. Thépot, M. Wong Chi Man, Chem. Mater. 4 (1992) 1217.
[13] H. Tang, J. Sun, J. Jiang, X. Zhou, T. Hu, P. Xie, R. Zhang, J. Am. Chem. Soc. 124 (2002) 10482–10488.
[14] C. Liu, Z. Liu, Y. Liu, P. Xie, R. Zhang, Polym. Int. 49 (2000) 1658–1664.
[15] J. Sun, Huatang, J. Jiang, X. Zhou, P. Xie, R. Zhang, P.-F. Fu, J. Polym. Sci.: Part A: Polym. Chem. 41 (2003) 636–644.
[16] Q. Yuan, S. Ji, R. Zhang, C. He, N.T. Chung, Polym. Int. 50 (2001) 643–650.
[17] G.T. Burns, R.B. Taylor, Y. Xu, A. Zangvil, G.A. Zank, Chem. Mater. 4 (1992) 1313–1323.
[18] M.A. Abu-eid, R.B. King, A.M. Kotliar, Eur. Polym. J. 28 (1992) 315–320.
[19] A.M. Wilson, J.N. Reimers, E.W. Fuller, J.R. Dahn, Solid State Ionics 74 (1994) 249–254.
[20] A.M. Wilson, G. Zank, K. Eguchi, W. Xing, J.R. Dahn, J. Power Sources, Nagoya Proceedings 68 (1998) 195.
[21] W. Xing, A.M. Wilson, G. Zank, J.R. Dahn, Solid State Ionics 93 (1997) 239–244.
[23] A.M. Wilson, G. Zank, K. Eguchi, W. Xing, B. Yates, J.R. Dahn, Chem. Mater. 9 (1997) 1601–1606.
[24] R.A. Mantz, P.F. Jones, K.P. Chaffee, J.D. Lichtenhan, J.W. Gilman, Chem. Mater. 8 (1996) 1250–1259.
[25] F.J. Feher, K.J. Weller, Chem. Mater. 6 (1994) 7.
[26] M.M. Banaszak Holl, F. Read McFreely, Phys. Rev. Lett. 71 (1993) 2441.
[27] S. Lee, S. Makan, M.M. Banaszak Holl, F. Reed McFeely, J. Am. Chem. Soc. 116 (1994) 11819.
[28] G.T. Burns, R.B. Taylor, Y. Xu, A. Zangvil, G.A. Zank, Chem. Mater. 4 (1992) 1313.
[29] R.M. Laine, J.A. Rahn, K.A. Youngdahl, F. Babonneau, M.L. Hoppe, Z.-F. Zhang, J.F. Harrod, Chem. Mater. 2 (1990) 464.
[30] J.A. Rahn, R.M. Laine, Z.-F. Zhang, Mater. Res. Soc. Symp. Proc. 171 (1990) 31.
[31] F.I. Hurwitz, P. Heimann, S.C. Farmer, D.M. Hembree Jr., J. Mater. Sci. 28 (1993) 6622.