

# Direct Synthesis and Characterization of Crosslinked Polysiloxanes via Anionic Ring-Opening Copolymerization with Octaisobutyl-Polyhedral Oligomeric Silsesquioxane and Octamethylcyclotetrasiloxane

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Received 22 November 2005; accepted 18 May 2006

DOI 10.1002/app.24876

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The crosslinked polysiloxanes were directly synthesized by anionic ring-opening copolymerization of octaisobutyl-polyhedral oligomeric silsesquioxane (POSS) as a multifunctional monomer with octamethylcyclotetrasiloxane ( $D_4$ ) under base catalysts such as potassium hydroxide (KOH) or tetramethylammonium hydroxide ( $Me_4NOH$ ) siloxanolate. The mechanism of anionic ring-opening copolymerization of octaisobutyl-POSS and  $D_4$  was discussed and the influences of the polar additive *N,N*-dimethylacetamide on gelation time at different temperatures were investigated. The results of gel content and swelling ratio, GPC, solid-state

$^{29}Si$  and  $^{13}C$  NMR, FTIR, XRD show that octaisobutyl-POSS is reacted and most of the product is crosslinked. The DSC and TG results indicate that the crosslinked polysiloxanes exhibit distinct glass transition temperatures ( $T_g$ ) and excellent thermal stability. Compared to that under KOH siloxanolate, the crosslinked polysiloxane synthesized with  $Me_4NOH$  siloxanolate has better preferable thermal stability. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3848–3856, 2006

**Key words:** POSS; mechanism; anionic; ring-opening copolymerization; crosslinked polysiloxane

## INTRODUCTION

Polysiloxanes are widely used as high temperature materials because of the superior high thermal stability and the good resistance to oxidative degradation.<sup>1–4</sup> However, as silicone materials, polysiloxanes must be crosslinked partially to prevent from flowing and to give themselves strength. Crosslinked polysiloxanes networks can be formed by numerous approaches such as condensation, transition-metal-catalyzed addition, and free radical initiation crosslinking techniques.<sup>1,5–8</sup> All of these are two-step methods to yield crosslinked polysiloxanes. Condensation crosslinking technique requires an enough high temperature and highly effective catalytic

agents to form extensively crosslinked polysiloxanes. Furthermore, considerable amount of small molecules such as water or alcohol is spilt out to form ever-larger molecules during the condensation process, leaving cracks and voids. These drawbacks affect the performance of crosslinked polysiloxanes and limit their applications. The other techniques develop very slowly due to their high cost or inconvenient use. Therefore, it is a challenge to search a novel and facile method to directly fabricate crosslinked polysiloxanes.

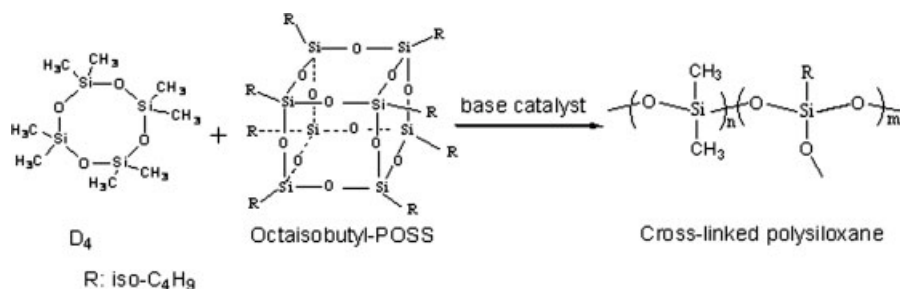
Polyhedral oligomeric silsesquioxane (POSS),<sup>9–17</sup> a cage structure with Si—O—Si framework and empirical formula  $(RSiO_{1.5})_n$ , where R is an organic substituent or a cap on the corners to improve solubility in conventional solvents and compatibility with a host polymer matrix, is a novel class of relatively large molecules containing organic and inorganic components. Because of its designable hybrid nanostructure feature, POSS has recently been developed for incorporation into synthetic polymer systems. Rikowski and Marsmann observed that the octa-silsesquioxanes were rearranged to produce the greater frameworks deca- and dodeca-silsesquioxanes under the influences of the catalysts such as sodium acetate, sodium cyanate, sodium sulfite, sodium hydroxide,

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Contract grant sponsor: China Aeronautic Industry Company.

Contract grant sponsor: Ministry of Education of China (Key Project of Science and Technology); contract grant number: 03023.

Contract grant sponsor: Committee of Natural Science Foundation of China; contract grant number: 50473041.



Scheme 1

and potassium carbonate in acetone.<sup>18</sup> This rearrangement indicates that the POSS with larger frameworks are thermodynamically more stable than those with smaller frameworks.<sup>18</sup> Feher et al. reported that the siloxane linkages of POSS frameworks could be cleaved to afford functionalized products by strong acids or strong bases.<sup>19–21</sup>

In a previous study, we reported the anionic ring-opening polymerization of dodecaphenyl-POSS (PhSiO<sub>1.5</sub>)<sub>12</sub> with octamethylcyclotetrasiloxane (D<sub>4</sub>) and octaphenylcyclotetra-siloxane (Ph<sub>8</sub>D<sub>4</sub>) under the base catalysts.<sup>22</sup> This method can directly produce crosslinked polysiloxanes of excellent thermal stability under relatively mild conditions. Because octaisobutyl-POSS (isobutylSiO<sub>1.5</sub>)<sub>8</sub> has much better solubility than dodecaphenyl-POSS in conventional solvents and is thermodynamically less stable than the POSS containing 10 or 12 silicon atoms,<sup>18</sup> the focus of this study is set on polymerization of octaisobutyl-POSS (isobutylSiO<sub>1.5</sub>)<sub>8</sub> as multifunctional monomer with D<sub>4</sub> under base catalysts such as potassium hydroxide (KOH) or tetramethylammonium hydroxide (Me<sub>4</sub>NOH) siloxanolate (Scheme 1), using the basically homogeneous polymerization process. The crosslinked polysiloxanes with isobutyl substituent obtained by the above direct polymerization process also have excellent thermal stability. In addition, the mechanism of anionic ring-opening polymerization of octaisobutyl-POSS and D<sub>4</sub> is also investigated. For convenience, in this article, D, T, and Q bondings are used to indicate the —O[(CH<sub>3</sub>)<sub>2</sub>SiO]—, —O[[C(CH<sub>3</sub>)<sub>3</sub>](O—)SiO]—, and —O[(O—)<sub>2</sub>SiO]— units, respectively.

## EXPERIMENTAL

### Materials

All reagents were commercially obtained, unless otherwise stated. D<sub>4</sub> was dried over calcium hydride (CaH<sub>2</sub>) and purified by distillation. Octaisobutyl-POSS (*M<sub>w</sub>* = 873.60 g/mol, Hybrid Plastics), KOH, *N,N*-dimethylacetamide (DMAc), and toluene were all used without further purification. Me<sub>4</sub>NOH, 10%

water solution, was concentrated by removal of the water under vacuum before use.

### Siloxanolate synthesis

KOH or Me<sub>4</sub>NOH siloxanolate were synthesized by the reaction of D<sub>4</sub> and a certain amount of base for 3 h (KOH at 130°C; Me<sub>4</sub>NOH at 90°C) with weight ratio 50:1 in a nitrogen ambient. Then trace amounts of water was removed under vacuum for 1 h<sup>23</sup> and the obtained transparent oils were stored under dry condition at a low temperature for further use.

### Crosslinked polysiloxanes polymerization

Crosslinked polysiloxanes were synthesized by anionic ring-opening copolymerization of D<sub>4</sub> (37.00 g, 0.5 mol according to the Si) and octaisobutyl-POSS (5.46 g, 0.05 mol according to the Si) in the presence of the polar additive DMAc (0.21 g, 0.5 wt % according to the total weight of D<sub>4</sub> and octaisobutyl-POSS, hereafter referred to as *W<sub>i</sub>*) with siloxanolate catalyst (0.42 g, 1 wt % according to *W<sub>i</sub>*, and KOH siloxanolate at 100–120°C; Me<sub>4</sub>NOH siloxanolate at 90–100°C) in a nitrogen ambient. Octaisobutyl-POSS was completely dissolved at above 80°C and the polymerization process was basically homogeneous. When the reaction mixture became too viscous to stir, the stirring was stopped and the reaction temperature was kept for 3 h. (After 3 h, the temperature was quickly raised to about 160°C for 0.5 h to isolate the Me<sub>4</sub>NOH, if Me<sub>4</sub>NOH siloxanolate was used as catalyst.) The resulting white solid was dried under vacuum for more than 24 h at 60°C to remove thoroughly the small molecules. The final obtained polymers were insoluble in usual organic solvents.

### Characterization

The determination of the gel content and swelling ratio

The gel content (GC) and swelling ratio (SR) of the products were measured through a 12 h Soxhlet extraction with toluene. Our experiments indicate that linear polydimethylsiloxane (PDMS) and octaisobutyl-POSS

can be removed through the extraction procedure. Therefore, it can be concluded that the extraction can remove both the uncrosslinked polysiloxanes and the unreacted monomers, and the leavings are the completely crosslinked polysiloxanes. The GC is the insoluble mass fraction and is determined by taking the ratio of the mass of the thoroughly dried gel after extraction to the mass of the starting polymer. The SR is a measure of the crosslink density and is determined by placing the extracted sample in a sealed container immediately after extraction and then taking the ratio of its mass to that of the thoroughly dried gel. GC and SR were calculated from following equations:

$$GC = \frac{W_1}{W_0} \times 100\% \quad (1)$$

$$SR = \frac{W_2}{W_1} \times 100\% \quad (2)$$

where  $W_0$  is the weight of the starting polymer,  $W_1$  is the weight of the dry gel, and  $W_2$  is the weight of swollen gel.

### Instruments

Polymer molecular weight was estimated using a Waters 515-2410 gel permeation chromatographer (GPC). Polystyrene standards were used for calibrating and tetrahydrofuran (THF) was used as an eluent at a flow rate of 1.0 mL/min. Solid-state ( $^{13}\text{C}$ ,  $^{29}\text{Si}$ ) nuclear magnetic resonance (NMR) spectra measurements were recorded on a Bruker AV300 MHz spectrometer (4 mm specimen tube). The solid-state carbon ( $^{13}\text{C}$ ) and silicon ( $^{29}\text{Si}$ ) NMR chemical shifts in parts per million (ppm) were referenced relative to tetramethylsilane (TMS). Fourier transform infrared (FTIR) spectra were performed using a Nexus 670 (FTIR) instrument. All samples were prepared as pellets using spectroscopic grade KBr. X-ray diffraction (XRD) was recorded with a D/Max 2500 VB2+/PC-based analytical diffractometer using Ni-filtered Cu  $K\alpha$  radiation. Glass transition temperature ( $T_g$ ) was determined at the inflection point of the endotherm with a Perkin-Elmer Pyris-1 differential scanning calorimeter (DSC) with a heating rate of 20°C/min under nitrogen atmosphere. Thermogravimetric analysis (TG) was performed on a Perkin-Elmer TGS-2 with a heating rate of 10°C/min under nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Polymerization mechanism

The polymerization mechanism of cyclosiloxanes (such as  $\text{D}_3$  and  $\text{D}_4$ ) under base catalysts is a typical

anionic ring-opening polymerization, which is a very important reaction in the synthesis of linear polysiloxanes and extensively used in both industry and research laboratories,<sup>24,25</sup> but no work has been yet reported on ring-opening polymerization of POSS or copolymerization with other monomers. Our experiment results indicate that octaisobutyl-POSS can not homopolymerize under the base catalysts (KOH siloxanolate at 100–120°C;  $\text{Me}_4\text{NOH}$  siloxanolate at 90–100°C) for even more than 24 h. However, it can quickly copolymerize with cyclosiloxanes under the similar conditions. Thus, it can be concluded that octaisobutyl-POSS and cyclosiloxanes incline to form random copolymer, rather than block copolymer. The mechanism of random copolymerization is common in accordance with homopolymerization mechanism of monomers and difficult to change; therefore, the copolymerization mechanism of octaisobutyl-POSS and cyclosiloxanes under the base catalysts is the same as the homopolymerization of cyclosiloxanes, which is anionic ring-opening polymerization. In this article, the mechanism of anionic ring-opening copolymerization of octaisobutyl-POSS and  $\text{D}_4$  was discussed in detail.

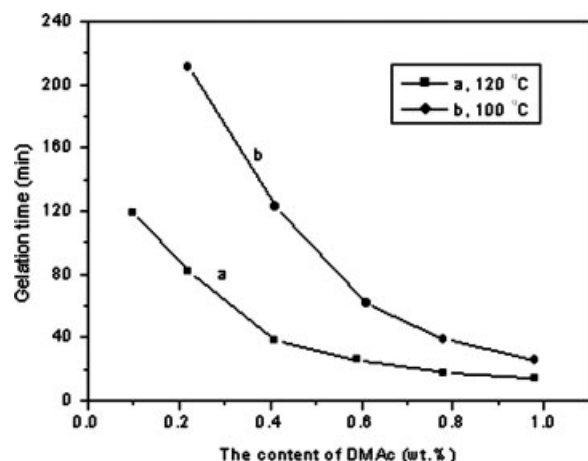
The base such as  $\text{Me}_4\text{NOH}$  or KOH generates the corresponding siloxanolate catalyst, which initiates  $\text{D}_4$  to yield the base-catalyzed (or anionic) active species. The chain propagation is believed to proceed first with the nucleophilic attachment of the anionic active species on the silicon atom of siloxane linkage and subsequently the redistribution of electron cloud density, and then the siloxane linkage is dissociated upon heating to yield new anionic active centers, which continue to react and stepwise propagate. Finally, the random crosslinked copolysiloxane is formed due to the octaisobutyl-POSS containing the  $-\text{O}[\text{C}(\text{CH}_3)_3](\text{O}-)\text{SiO}-$  units (i.e., T bonding).

The analysis is somewhat complicated. There are two distinct types of anionic active species intermediated, each of which can respectively, attack the silicon atom of siloxane linkage in  $\text{D}_4$ , octaisobutyl-POSS or the formed intermediate by nucleophilic attachment, and there are six different kinds of reactions through the chain propagation process of anionic ring-opening copolymerization with octaisobutyl-POSS and  $\text{D}_4$  (Fig. 1). However, because of more stable cage structure of octaisobutyl-POSS and bulkier effect of isobutyl, anionic active species are easier to attach on the silicon atom of  $\text{D}_4$  than that of octaisobutyl-POSS or the formed intermediate, leading to the prediction that the rate of reaction a is faster than reactions c and e, and the rate of reaction b is faster than reactions d and f. This is also the main reason for octaisobutyl-POSS and  $\text{D}_4$  inclining to form random copolymer, rather than block copolymer.









**Figure 2** The influence of the polar additive DMAc on gelation time at different temperatures; the Si mole ratio of D<sub>4</sub> and octaisobutyl-POSS is 95 : 5, KOH siloxanolate catalyst (1 wt % according to  $W_i$ ), reaction temperature: curve a, 120°C; curve b, 100°C.

to control the equilibrium reaction and reduce the content of cyclosiloxane if the GC of the products would be improved. However, with the octaisobutyl-POSS reactant increasing, the  $-\text{O}[\text{C}(\text{CH}_3)_3(\text{O}-)\text{SiO}]-$  units in polysiloxane chain also increase. As a result, the crosslinking density of polysiloxane increases, embodying that the SR decreases.

The GPC analysis of the soluble part of the polymers shows that the soluble polysiloxanes are mainly composed of the oligomers with lower molecular weight of several hundreds to thousands, and few polymers with higher molecular weight of more than ten thousands. Therefore, it is believed that the polysiloxanes with higher molecular weight are almost crosslinked.

### The characterization of crosslinked polysiloxanes

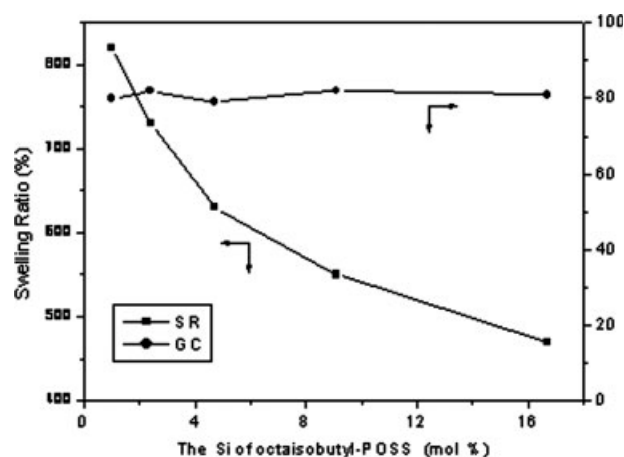
The solid-state  $^{29}\text{Si}$  NMR spectrum of the extracted crosslinked polysiloxane synthesized with  $\text{Me}_4\text{NOH}$  siloxanolate (Fig. 4) shows the detailed information about Si units present in the polymer chain. The signals at  $-20.4$  and  $-22.7$  ppm with a relatively high intensity are assigned to the silicon in the  $-\text{O}[(\text{CH}_3)_2\text{SiO}]-$  units (D bonding), and the two remained distinct signals at  $-67.9$  and  $-69.3$  ppm to the silicon in the  $-\text{O}[\text{C}(\text{CH}_3)_3(\text{O}-)\text{SiO}]-$  units (T bonding). The ratio of the two main types of resonances is 1.00:0.094, basically in accordance with the designed value of 10:1, indicating that not only the polymer chains have T bondings and the product is crosslinked polysiloxanes; but also octaisobutyl-POSS is concerned with anionic ring-opening copolymerization nearly in accordance with to the designed value. It is noted that there are multi-signals of the

silicon in the  $-\text{O}[(\text{CH}_3)_2\text{SiO}]-$  and  $-\text{O}[\text{C}(\text{CH}_3)_3(\text{O}-)\text{SiO}]-$  units because of the influence of different adjacent units. In addition, a relatively weak signal at  $-106.3$  ppm is appointed to the silicon in the  $-\text{O}[(\text{O}-)_2\text{SiO}]-$  units (Q bonding), which can be explained via the cleavage of octaisobutyl-POSS in base condition<sup>19–21</sup> and the subsequent condensation between the resulting Si—OH linkages.

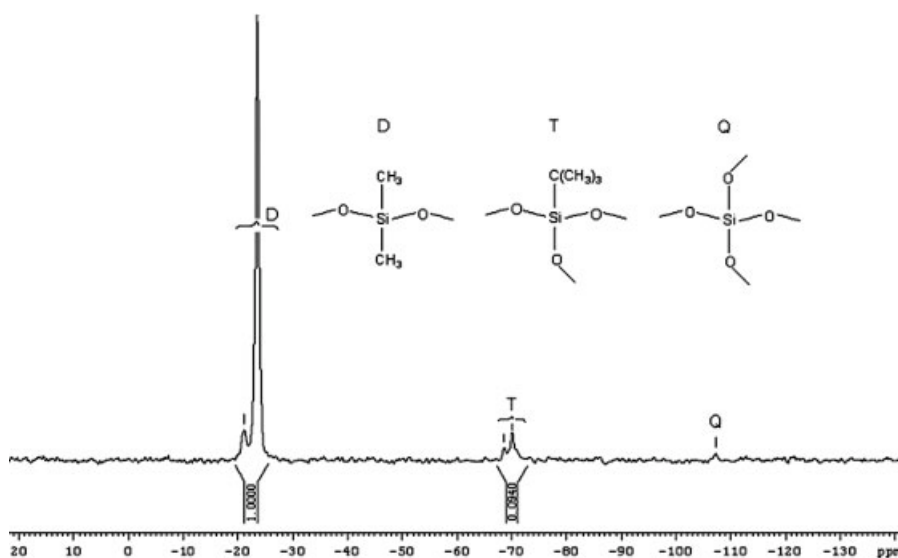
The solid-state  $^{13}\text{C}$  NMR spectrum of the extracted crosslinked polysiloxane synthesized with  $\text{Me}_4\text{NOH}$  siloxanolate is shown in Figure 5, indicating that the principal signals at 0.96 and 0.18 ppm are appointed to the carbon in the methyl of  $-\text{O}[(\text{CH}_3)_2\text{SiO}]-$  units and the other signals at 24.9 and 26.0 ppm to the carbon of methyl in the isobutyl of  $-\text{O}[\text{C}(\text{CH}_3)_3(\text{O}-)\text{SiO}]-$  units. This also indicates that octaisobutyl-POSS monomers were reacted and the crosslinked polysiloxane was formed. However, the signal of the third carbon is too weak to be affirmed due to no hydrogen coupling.

Figure 6 is the FTIR spectrum of the extracted crosslinked polysiloxane synthesized with KOH siloxanolate. The absorbances at  $1096.64$  and  $1025.72$   $\text{cm}^{-1}$  with relatively high intensity are the characteristic of Si—O—Si stretching, and the signals at  $2961.30$ ,  $1263.50$ , and  $804.64$   $\text{cm}^{-1}$  are the C—H characteristic absorbances in the Si—CH<sub>3</sub> units.

XRD are normally used to examine any evidence of POSS crystallization in a polymer matrix. The XRD patterns of POSS exhibit crystal reflections of POSS if any aggregations of POSS molecules are present in crosslinked polysiloxanes. Figure 7 shows the XRD profiles recorded from crosslinked polysiloxanes, the blend of octaisobutyl-POSS (5 wt %) and PDMS. Curve a, recorded from the extracted crosslinked polysiloxane synthesized with KOH



**Figure 3** The gel content and swelling ratio with different Si mole fraction of octaisobutyl-POSS: DMAc (0.5 wt % according to  $W_i$ ), KOH siloxanolate catalyst (1 wt % according to  $W_i$ ), 100°C.



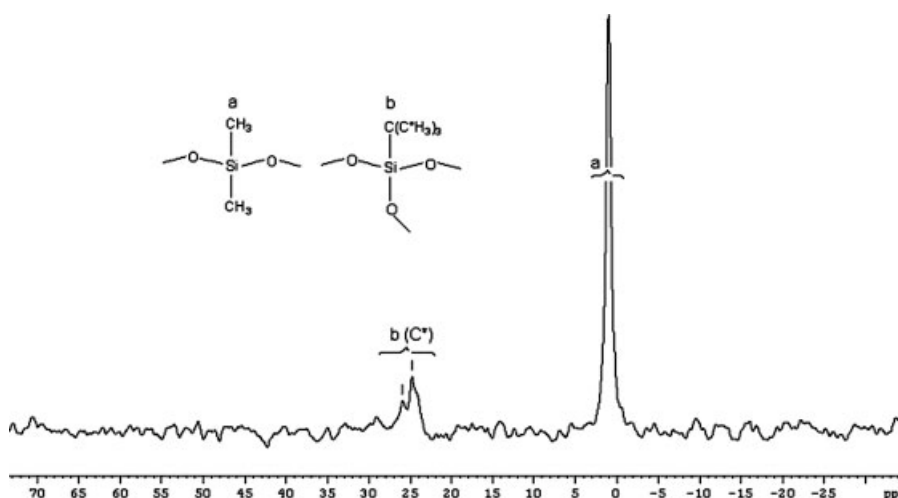
**Figure 4** Solid-state  $^{29}\text{Si}$  NMR spectrum of the extracted crosslinked polysiloxane synthesized with  $\text{Me}_4\text{NOH}$  siloxanolate.

siloxanolate, shows only a broad signal at  $2\theta = 11.2^\circ$ , indicating that the polysiloxane is not highly crystalline. Curve c was recorded from the blend of octaisobutyl-POSS (5 wt %) and PDMS, which was fabricated using the similar solution-casting method, where octaisobutyl-POSS was simply blended with PDMS in a toluene solution (0.5 wt %) and then the solvent was evaporated to form a film. It shows a few distinct narrow POSS peaks at  $2\theta = 8^\circ\text{--}9^\circ$ ,  $21.9^\circ$  and a broad PDMS signal at  $2\theta = 12.3^\circ$ , which indicates that the octaisobutyl-POSS reprecipitated back into crystals in the polysiloxane upon solvent evaporation. However, curve b was recorded from the unextracted crosslinked polysiloxane synthesized with KOH siloxanolate, which had about 9 wt % octaisobutyl-POSS before the reaction. If octaisobu-

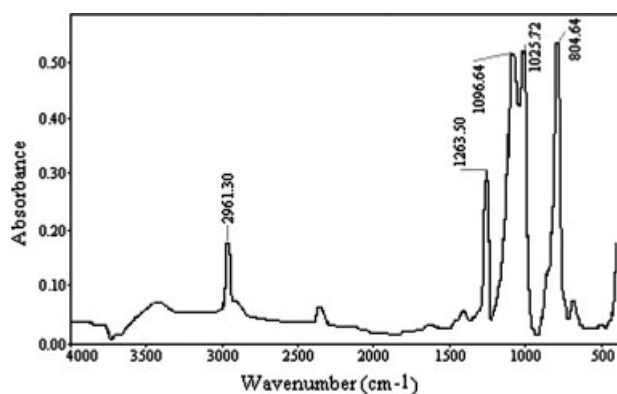
tyl-POSS would not be reacted, it should reprecipitate back into crystals in the polymer. Therefore, corresponding XRD curve, would be similar to curve c and show some evident narrow peaks at  $2\theta = 8^\circ\text{--}9^\circ$ ,  $21.9^\circ$ . However, the strong similarity between the curve b and curve a, both only having a broad signal ( $2\theta = 11.1^\circ$ ), indicates that the polymer has few octaisobutyl-POSS aggregations, thus suggesting that most of octaisobutyl-POSS monomer has reacted.

#### The thermal analysis of crosslinked polysiloxanes

Figure 8 is the DSC thermograms from the unextracted (a) and the extracted crosslinked polysiloxanes (b) synthesized with KOH siloxanolate. The DSC curves show that both crosslinked polysiloxanes

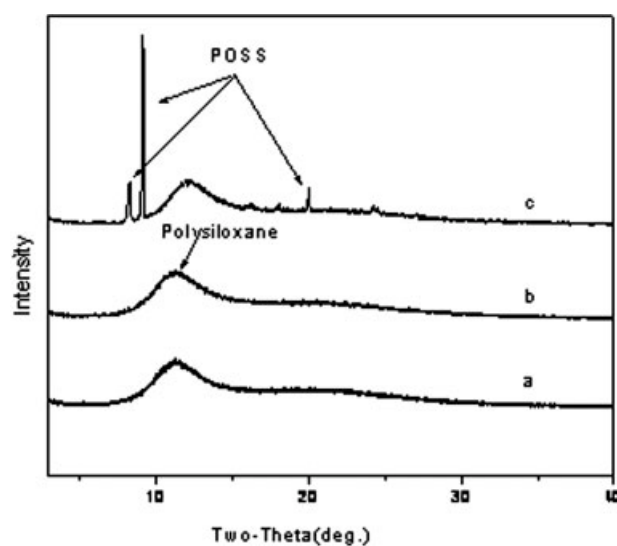


**Figure 5** Solid-state  $^{13}\text{C}$  NMR spectrum of the extracted crosslinked polysiloxane synthesized with  $\text{Me}_4\text{NOH}$  siloxanolate.

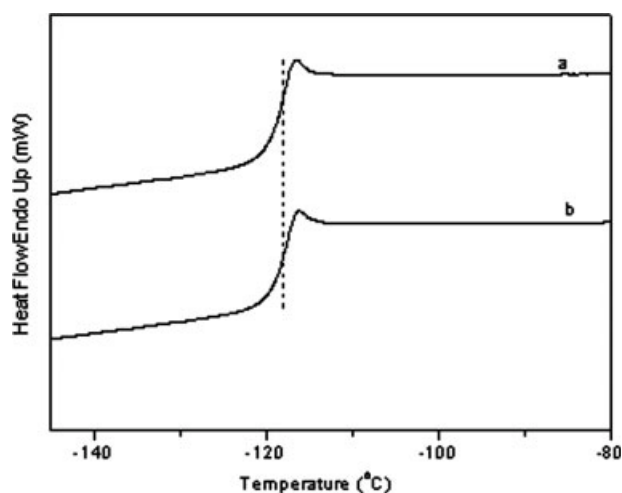


**Figure 6** The FTIR spectrum of the extracted crosslinked polysiloxane synthesized with KOH siloxanolate.

have distinct glass transition temperatures ( $T_g$ ) at about  $-119^\circ\text{C}$  (Onset Temperature), but there is no obvious difference, indicating that the uncrosslinked polysiloxanes and the unreacted monomers in the polymer have no distinct influence on  $T_g$ . The main reason is that the isobutyl, as flexible lateral group, is much bulkier than methyl, which results in an increase of molecular distances and weakens the interactions, equivalent to the effect of inner plasticizer. As a result, the influence of the uncrosslinked polysiloxanes and the unreacted monomers (equivalent to the effect of outer plasticizer) on  $T_g$  is, to a large degree, weakened. In addition, it is noted that the DSC thermograms of the crosslinked polysiloxanes have a distinct absorbed heat peak, which can be explained via the theory of macromolecular chain



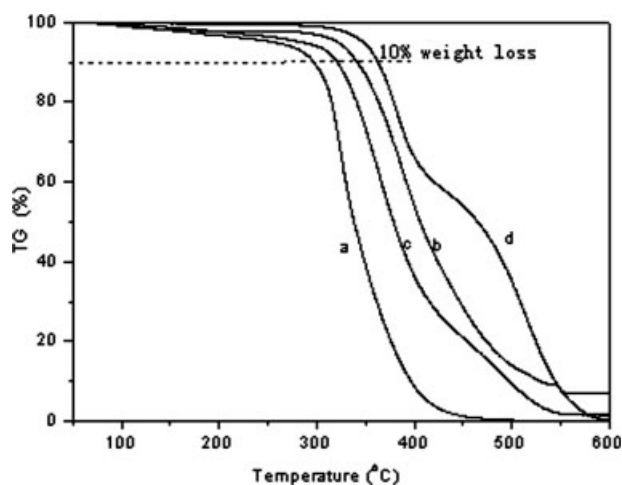
**Figure 7** The XRD patterns: (a) the extracted crosslinked polysiloxane synthesized with KOH siloxanolate; (b) the unextracted crosslinked polysiloxane synthesized with KOH siloxanolate; (c) the blend of octaisobutyl-POSS (5 wt %) and PDMS.



**Figure 8** The DSC thermograms of the unextracted (a) and the extracted crosslinked polysiloxanes (b) synthesized with KOH siloxanolate.

coil interpenetration in polymer condensed state, i.e., the absorbed heat peak opening the macromolecular chain coil interpenetration.<sup>28,29</sup>

The TG curves of crosslinked polysiloxanes under nitrogen atmosphere are shown in Figure 9. Curves a and b were respectively, recorded from the unextracted and extracted crosslinked polysiloxane synthesized with KOH siloxanolate; Curves c and d were respectively, recorded from the unextracted and extracted crosslinked polysiloxane synthesized with  $\text{Me}_4\text{NOH}$  siloxanolate. All the curves exhibit that the 10% weight loss temperatures ( $T_{10d}$ ) are 296,



**Figure 9** The TG curves of the crosslinked polysiloxanes: (a) the crosslinked polysiloxane synthesized with KOH siloxanolate; (b) the extracted crosslinked polysiloxane synthesized with KOH siloxanolate; (c) the crosslinked polysiloxane synthesized with  $\text{Me}_4\text{NOH}$  siloxanolate; (d) the extracted crosslinked polysiloxane synthesized with  $\text{Me}_4\text{NOH}$  siloxanolate.



341, 321, 362°C, respectively, illustrating that all the crosslinked polysiloxane have very good thermal stability. The crosslinked polysiloxanes with Me<sub>4</sub>NOH siloxanolate catalyst have better thermal stability than those with KOH siloxanolate catalyst, because Me<sub>4</sub>NOH siloxanolate catalyst decomposes thoroughly and easily loses its catalyst reactivity under high temperature at above 130°C, but KOH does not. Additionally, anionic ring-opening polymerization of cyclosiloxane with most strong bases is an equilibrium reaction, so the bases are not only its catalyst also its decomposer. Trace amount of KOH can dramatically accelerate polysiloxanes decomposing, which seriously affects the thermal stability of polysiloxanes. The extracted crosslinked polysiloxanes have much better thermal stability than those without extraction due to the thorough removal of the uncrosslinked polysiloxanes and the unreacted monomers, which can decompose easily at lower temperature. The easy decomposition of uncrosslinked polysiloxanes and unreacted monomers in the crosslinked polysiloxanes without extraction also contributes to the higher weight loss of curves a and c under lower temperature.

### CONCLUSIONS

The crosslinked polysiloxanes were directly synthesized by anionic ring-opening copolymerization of D<sub>4</sub> via adding multifunctional monomer octaisobutyl-POSS under KOH or Me<sub>4</sub>NOH siloxanolate. A series of crosslinked polysiloxanes with different SRs have been successfully obtained by adjusting the content of octaisobutyl-POSS monomer. The reaction mechanism of octaisobutyl-POSS and D<sub>4</sub> under base catalysts accords with the law of anionic ring-opening copolymerization. Gelation time decreases obviously with the addition of the polar additive DMAc in the bulk polymerization. In addition, compared to at 100°C, the gelation time shortens and the polymerization rate increases at 120°C. The crosslinked polysiloxanes are not highly crystalline and most of octaisobutyl-POSS monomer has reacted. The crosslinked polysiloxanes have distinct glass transition temperatures ( $T_g$ ) and excellent thermal stability. The crosslinked polysiloxane synthesized with Me<sub>4</sub>NOH

siloxanolate has better thermal stability than that under KOH siloxanolate.

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