

# Selection of a Precursor of a Monofunctional Polyhedral Oligomeric Silsesquioxane Reacted with Aromatic Diamines

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**ABSTRACT:** With the aim of selecting a precursor of a polyhedral oligomeric silsesquioxane (POSS) reacted with aromatic diamines for its incorporation into an epoxy network, to generate an organic–inorganic hybrid material containing POSS, a polyhedral oligomeric silsesquioxane (glycidylisobutyl–POSS) was reacted with the diamines 4,4'-methylenebis(2,6-diethylaniline) (MDEA), 4,4'-diaminodiphenylmethane (DDM), and 4,4'-(1,3-phenylenediisopropylidene)bisaniline (BSA), at 160°C and different times, in a proportion rich in amines. The distribution of species in the reaction was followed by gel perme-

ation chromatography (GPC). From the experimental data obtained the selected precursor was POSS/BSA reacted at 160°C for 20 or 30 min, to ensure that all the POSS was reacted, that there was a maximum of the monosubstituted amines, and that there was no degradation. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1576–1583, 2004

**Key words:** nanocomposites; inorganic polymers; gel permeation chromatography (GPC); degradation; oligomers

## INTRODUCTION

Polymeric hybrid materials have generated great interest because of their advantageous performances relative to their nonhybrid counterparts. Typical hybrid materials may contain a crosslinked inorganic phase bonded with an organic phase. Recently, the polyhedral oligomeric silsesquioxanes (POSS)-based hybrid polymers<sup>1–3</sup> have received increased attention from the academic community and industries because of the unique structure of the POSS macromer.

The POSS molecules contain a polyhedral silicon–oxygen nanostructural skeleton with intermittent siloxane chains ( $\text{SiO}_{3/2}$ )<sub>n</sub>, which were first reported<sup>4</sup> in 1946. A variety of organic substituents can be incorporated on each corner silicon atom, to impart desirable functionality, with recent interest focusing on the incorporation of a polymerizable group on one of the silicon atoms, and aliphatic hydrocarbon groups on the remaining silicon atoms. These molecules, POSS monomers, can be polymerized to the corresponding POSS macromers and polymers.<sup>5</sup>

The POSS molecules have been successfully incorporated into different polymers by scientists from the Air Force Research Laboratory (AFRL).<sup>6,7</sup> Studies have shown that such organic–inorganic hybrid polymers possess improved properties such as higher  $T_g$ , increased oxygen permeability, reduced flammability, and enhanced mechanical strength.

Gel permeation chromatography (GPC) has been well recognized as a useful technique based on size exclusion in the liquid chromatographic field. Generally, the main purpose of GPC is an analysis of the molecular weight of an unknown sample by the size-exclusion technique in terms of hydrodynamic volume. The GPC technique is thus suitable to detect the composition of solute as a volume distribution, which reflects the molecular structure, aggregation state, and molecular weight.<sup>8</sup> Moreover, it is a suitable technique to follow the distribution of species at the completion of reaction,<sup>9</sup> as the sample reacts at different times at a selected temperature. For the use of GPC technique, a sample must have a good solubility for an eluent and should not have an interaction with the column used.

The aim of this work was to select an adequate precursor POSS/aromatic diamine for its incorporation into an epoxy network. This means that all the POSS ought to react, ensuring the existence of a substantial portion of the monosubstituted amines. In a second step, this precursor will be reacted with a diepoxide to generate an organic–inorganic hybrid material containing POSS.

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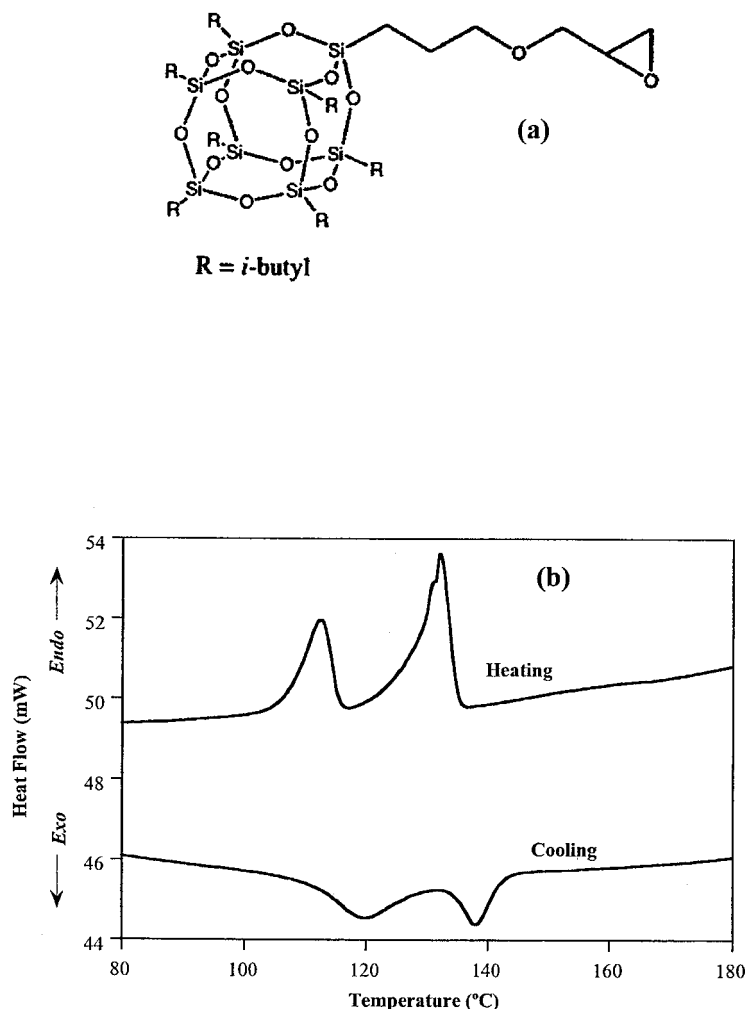


Figure 1 Characterization of the POSS: (a) molecular structure; (b) DSC scans. Heating and cooling at 10°C min<sup>-1</sup>.

EXPERIMENTAL

Materials

In this study, the selected POSS molecule (SiO<sub>3/2</sub>)<sub>n</sub> had n = 8 (cagelike), surrounded by eight organic groups, of which seven were inert, isobutyl, and just one was reactive glycidyl. This POSS was the 1-(3-glycidyl) propoxy-3,5,7,9,11,13,15-isobutylpentacyclo-[9.5.1.1(3,9).1(5,15).1(7,13)] octasiloxane, (glycidylisobutyl-POSS) (EPO418, Hybrid Plastics, Fountain Valley, CA), which allowed its incorporation into the different epoxy nets. Its molecular weight was 931.63 g mol<sup>-1</sup>. A schematic drawing of the structure of this POSS is shown in Figure 1(a). <sup>1</sup>H- and <sup>13</sup>C-NMR spectra confirmed the reported chemical structure.

The glycidylisobutyl-POSS was characterized by differential scanning calorimetry [Fig. 1(b)]. The thermogram obtained at 10°C min<sup>-1</sup> shows two well-defined melting peaks at 112.4 and 133.4°C (total melting heat of 26.1 J g<sup>-1</sup>) and two crystallization peaks in the cooling scan at 119.1 and 139.2°C at the rate of 10°C min<sup>-1</sup> (total crystallization heat of 15.1 J g<sup>-1</sup>).

These results confirm that the POSS was crystalline, as verified by atomic force microscopy.<sup>10</sup>

To complete the thermal characterization of the glycidylisobutyl-POSS, it was tested by thermogravimetry in both argon and oxygen atmospheres. A significant thermal degradation was evidenced at 220°C in the dynamic runs made at 10°C min<sup>-1</sup>. The loss weight was 42.7% in an inert atmosphere at 600°C. Isothermal runs were made at 160, 180, and 200°C. At 360 min<sup>11</sup> the chars were 99.4, 95.1, and 78.1%.

The amines were selected by considering their melting point (lower than the melting point of POSS) and their solubility in tetrahydrofuran (THF). The aromatic diamines used were 4,4'-methylenebis(2,6-diethylaniline) (MDEA; Aldrich, Milwaukee, WI), 4,4'-diaminodiphenylmethane (DDM; Fluka, Buchs, Switzerland), and 4,4'-(1,3-phenylenediisopropylidene)bisaniline (BSA; Aldrich). The molecular weights were 310.49, 198.27, and 344.50 g mol<sup>-1</sup>, with manufacturer purity values of >99, 97, and 98% according to the suppliers, and melting temperatures of 89.6, 90.9, and 110.5°C, respectively, determined by differential scanning calorimetry.

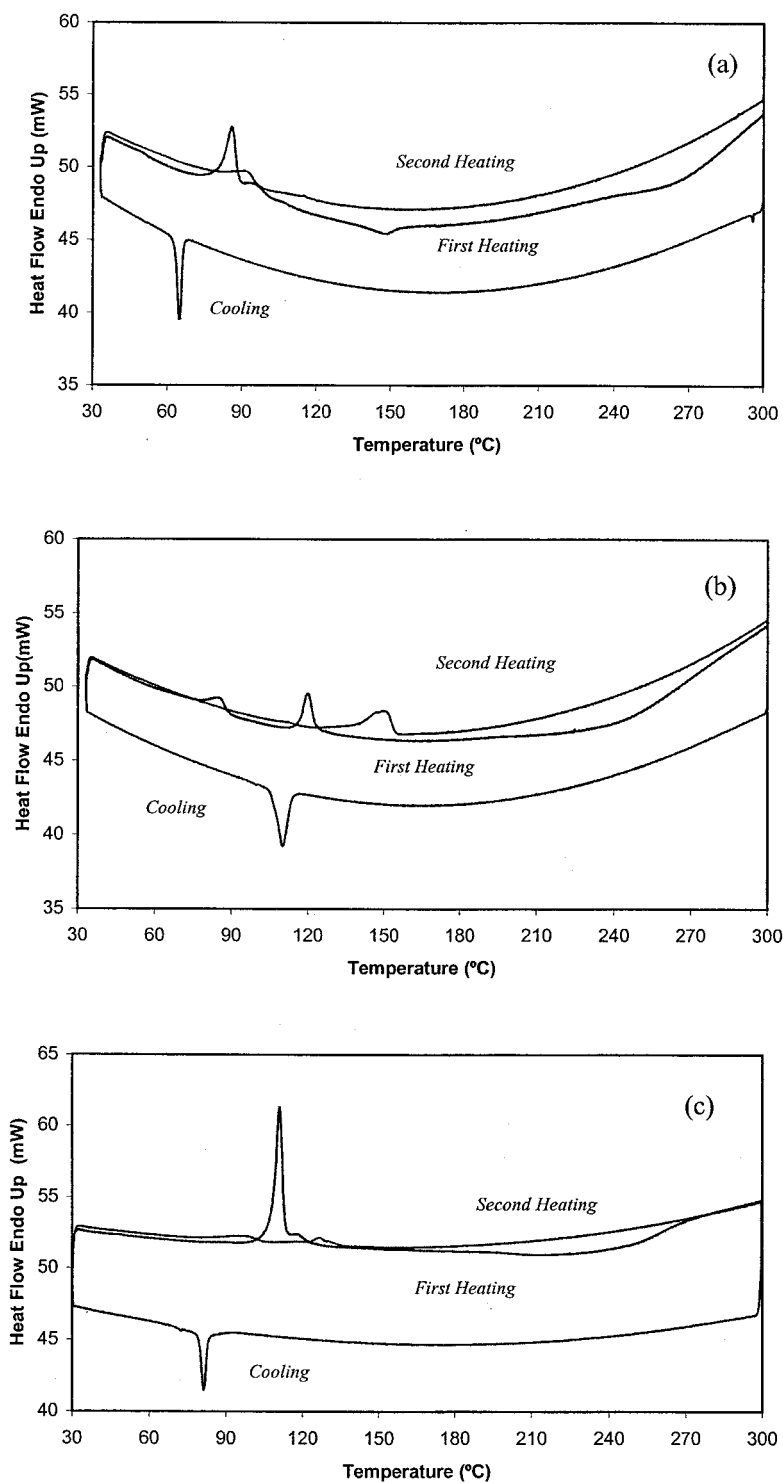


Figure 2 DSC scans of the precursors at  $10^{\circ}\text{C min}^{-1}$ : (a) POSS/MDEA; (b) POSS/DDM; (c) POSS/BSA.

### Techniques

We used a Waters 2695 separations module (Waters Chromatography Division/Millipore, Milford, MA) equipped with a quaternary bomb and an automatic injector. Detection was performed with a Waters 996 UV/VIS photodiode array detector and Millennium

software (Version 3.20) was used for the acquisition and treatment of data. The column was a Styragel HR 1 THF  $7.8 \times 300$  mm.

The chromatographic conditions used were as follows: elution in the isocratic mode with mobile-phase THF (Merck, Darmstadt, Germany),  $0.3 \text{ mL min}^{-1}$  flow rate, and injection volume of  $10 \mu\text{L}$ . Chromato-

grams were obtained at the 254-nm line. Calibrations were performed by the external standard method. The working standards were prepared by dilution of a 1000 mg L<sup>-1</sup> stock solution prepared in THF.

A Perkin-Elmer differential scanning calorimeter (model DSC-7, Perkin Elmer Cetus Instruments, Norwalk, CT) equipped with an Intracooler was used. The baseline was checked frequently, and temperature scale calibration was made at regular intervals using the melting transition of pure indium. The purge gas was dry nitrogen at a controlled flow rate.

**Procedure**

The POSS and the different amines were mixed in a proportion rich in amine, to ensure the presence of an abundant amount of monosubstituted amines. A convenient molar ratio of POSS/diamine was 1 : 1, representing a stoichiometric ratio of functionalities of 0.25. They were dissolved at room temperature with a magnetic stirrer in THF, and the solvent was evaporated at 60°C. The resulting solid was first tested in DSC to determine the optimum temperature of reaction (Fig. 2).

Several tests were performed, at temperatures from 120 to 180°C. Reactions at low temperatures in this range are not possible because not all the POSS reacted. However, at high temperatures the degradation is significant. Therefore, the selected temperature was 160°C. So, it was ensured that all POSS/diamine was completely melted and that the reaction had not yet begun, as may be seen in the first scan. The cooling

**TABLE I**  
Position of Peaks (in min) of the Unreacted Amine and Substituted Amines Obtained from Chromatograms

System	POSS/MDEA	POSS/DDM	POSS/BSA
Unreacted	26.45	27.39	25.86
Monosubstituted	22.53	22.67	22.42
Disubstituted	21.18	21.24	21.16
Trisubstituted	20.70	20.67	20.62

and second heating scans show the crystallization of the precursor.

Several vials were prepared containing known masses for each formulation. The weight of the samples was 20 mg. The glass vials with the samples were heated to 160°C in an oven and were maintained at that temperature for the time necessary to complete the reaction. At a designated time interval, one vial was withdrawn from the oven and the reaction was suddenly stopped in ice water. Subsequently, it was loaded with a premeasured volume of THF solvent to prepare 8 × 10<sup>-5</sup> g mL<sup>-1</sup> solution for the test in GPC.

**RESULTS AND DISCUSSION**

The reactions of the three precursors (POSS/diamine) at 160°C were followed by gel permeation chromatography. The chromatograms show the evolution of the distribution of species at the end of reaction as the samples are reacted at different times. Because POSS

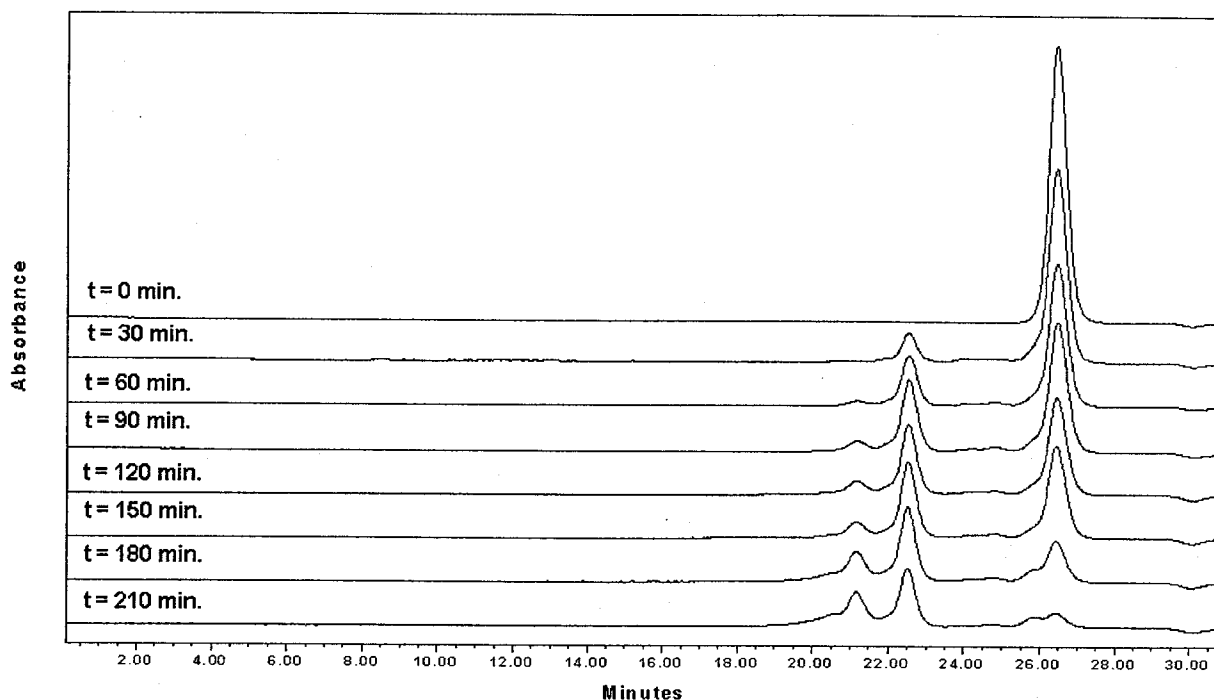


Figure 3 GPC chromatograms of the precursor POSS/MDEA obtained at different times reacted at 160°C.

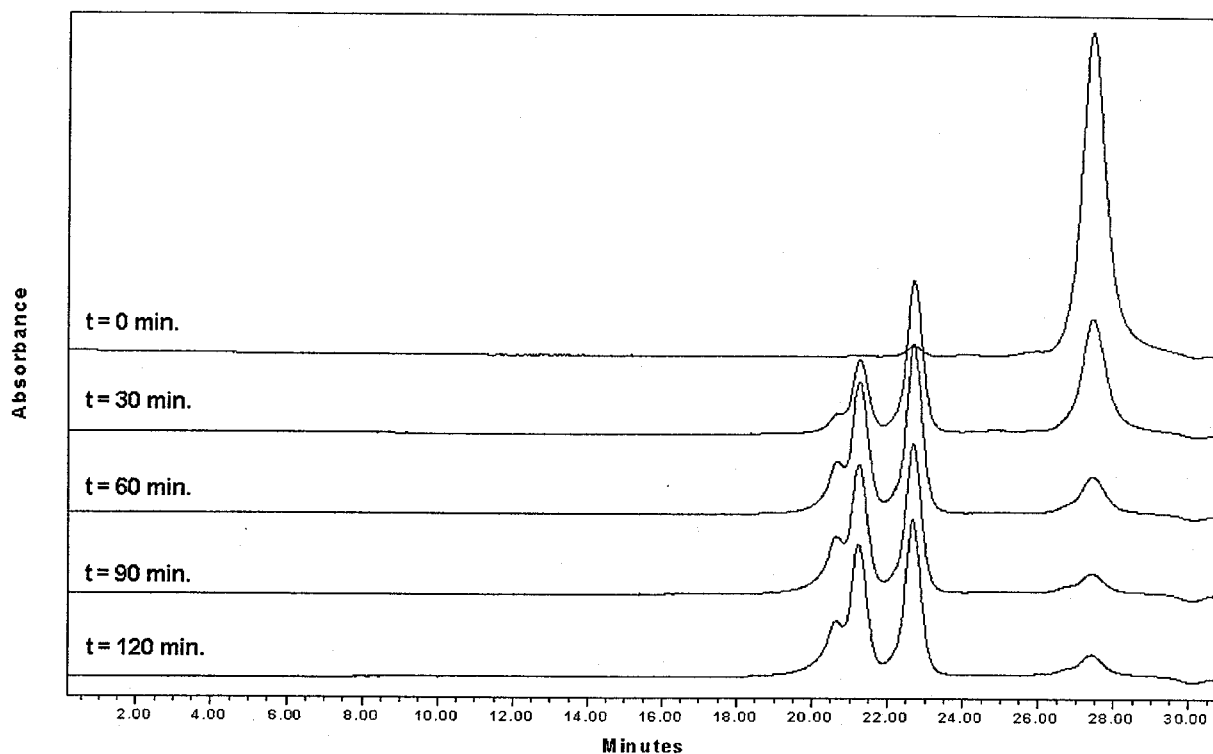


Figure 4 GPC chromatograms of the precursor POSS/DDM obtained at different times reacted at 160°C.

did not have any significant absorption at 254 nm, the signal of the UV detector was sensitive to only the amount of diamines. The peaks, corresponding to the unreacted amine, and the mono-, di-, and trisubstituted amines appeared at various time periods. The peaks of the tetrasubstituted species presented concentrations below the detection limit for all the sam-

ples. Table I shows the times at which these peaks appeared for all precursors.

The evolution of GPC chromatograms is shown in Figure 3 for the precursor POSS/MDEA. At the beginning the reaction is slow. After 30 min the peaks of the mono- and disubstituted amines appeared, and the trisubstituted appeared at 180 min. The reaction

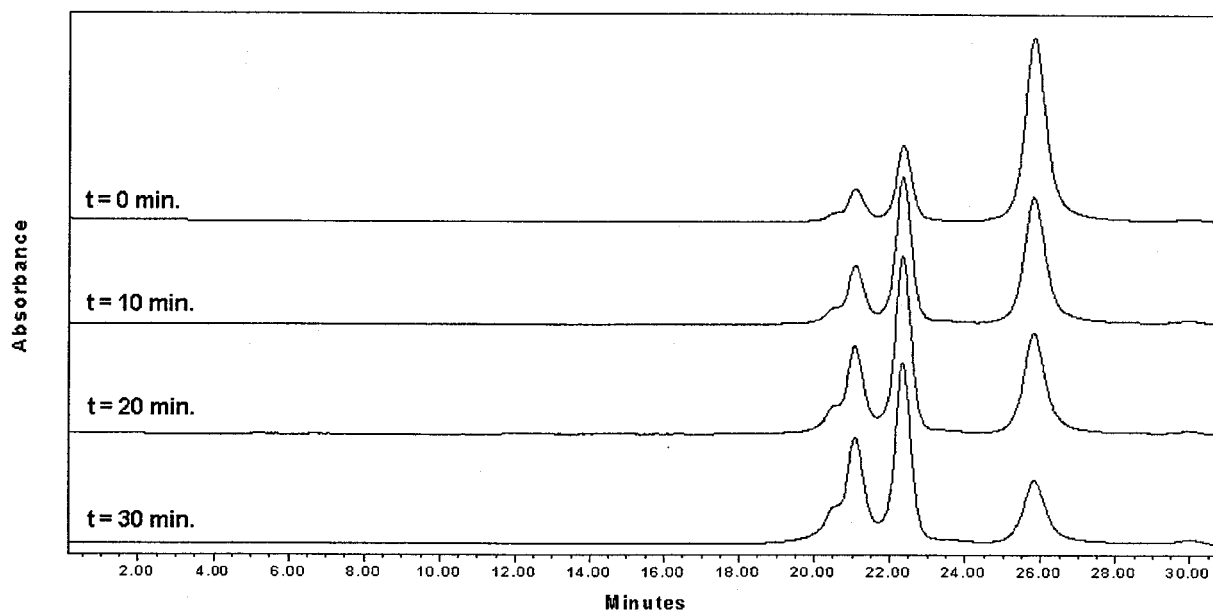


Figure 5 GPC chromatograms of the precursor POSS/BSA obtained at different times reacted at 160°C.

shows a sudden jump between 150 and 180 min, continuing on to 240 min.

The areas of the peaks corresponding to the unreacted and substituted amines in the chromatograms were integrated and the conversion was calculated as

$$\alpha = \frac{4A_4 + 3A_3 + 2A_2 + A_1}{4 \sum_{i=0}^4 A_i} \quad (1)$$

where  $A_0, A_1, A_2, A_3,$  and  $A_4$  are the integration of the areas of the peaks corresponding to the unreacted and substituted amines.

The reached conversion was 0.37 at 210 min. This value was higher than expected because the theoretical conversion ought to be 0.25, as a result of the functionality. According to these results, the possibility of amine degradation reaction was suggested. A thermal degradation assay was performed to observe the behavior of MDEA at 160°C for 120 min. An significant degradation was observed. The reached conversion was recalculated taking this supposition into account. During the reaction, the concentration of the amines, both substituted  $[c_i]$  ( $i = 1, 2, 3, 4$ ) and non-substituted  $[c_0]$ , ought to be constant at each moment:

$$[c] = \sum_{i=0}^4 [c_i] \quad (2)$$

Thus, the following equation shows the percentage of amine lost by thermal degradation at each time point:

$$\frac{[c] - \sum_{i=0}^4 [c_i]_{\text{exp}}}{[c]} \times 100 = \% \text{ Amine degraded} \quad (3)$$

where  $[c_i]_{\text{exp}}$  is the experimental value of the concentration.

According to eq. (3), the conversion can be recalculated. Now, the maximum conversion was about 0.18 at 210 min. From 90 to 180 min the value of the monosubstituted amines is maximum, although the conversion at 90 min is only 0.06 and at 180 min, is 0.15. Therefore, the precursor POSS/MDEA does not react completely at the temperature of 160°C, and the degradation is substantial.

For the second precursor, POSS/DDM, the reaction, at the curing temperature of 160°C, is fast (Fig. 4). At 30 min, there are peaks corresponding to mono-, di-, and trisubstituted amines on the chromatograms. The maximum conversion was reached between 90 and 120 min. Analysis of the reaction, similar to that for

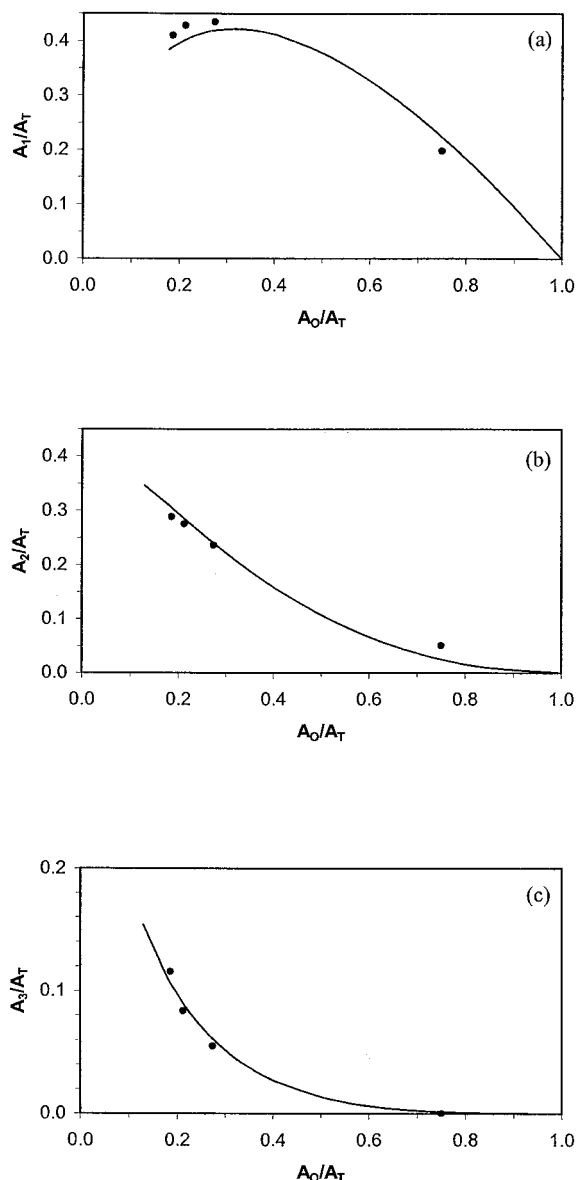


Figure 6 Theoretical and experimental data of  $A_i/A_T$  versus  $A_0/A_T$  of the precursor POSS/BSA.

POSS/MDEA, showed that the maximum conversion reached was 0.41 at 90 min.

The degradation was also studied. After removing the effect of degradation, the conversion was recalculated, which was 0.25 at 90 min; and, although the conversion was as expected, the degradation was still significant.

For the third precursor, POSS/BSA, at time zero, there was a significant reaction, produced in the course of sample preparation, as may be observed in Figure 5. The reaction is very fast and the maximum conversion is quickly reached. From  $t = 20$  min no significant changes in the peak distribution were detected within experimental error.

A time of 30 min was selected to ensure that the reaction was completed. This system did not undergo

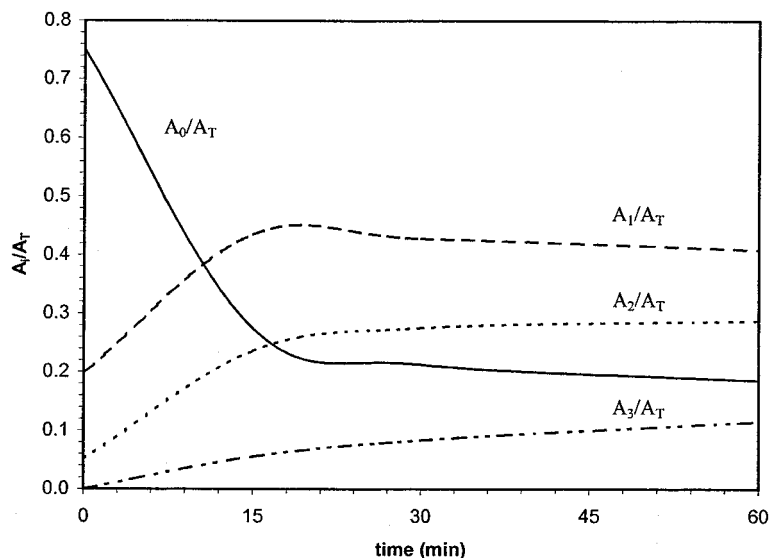


Figure 7 Evolution of species of the precursor POSS/BSA.

degradation. The thermal degradation assays show that the BSA support, without considerable degradation, endured more than 2 h at 160°C. The reached conversion of 0.30, higher than the theoretical conversion of 0.25, can be attributed to the impurities of the material.

Experimental data were compared with a theoretical model. The theoretical model to analyze the evolution of the species is a simple statistical analysis.<sup>12</sup> The concentration of unreacted monomer at any conversion  $x$  of functional groups is equal to the simultaneous probability that the four functionalities remain unreacted. If  $x$  is the probability that the amine groups have reacted,  $(1 - x)$  is the probability that it remains unreacted at a particular conversion level. Then, the simultaneous probability that four individual functionalities have not reacted is  $(1 - x)^4$ . Therefore, and for these systems, theoretically  $x$  takes the value of 0.25, and the ideal distribution of the reaction products would be

$$\begin{aligned}
 A_0/\sum A_i &= (1 - x)^4 = 0.316 \\
 A_1/\sum A_i &= 4(1 - x)^3 x = 0.422 \\
 A_2/\sum A_i &= 6(1 - x)^2 x^2 = 0.211 \\
 A_3/\sum A_i &= 4(1 - x)x^3 = 0.047 \\
 A_4/\sum A_i &= x^4 = 0.004
 \end{aligned}
 \quad (4)$$

where  $A_0/\sum A_i$  is the fraction of initial monomer that remains unreacted;  $A_1/\sum A_i$  is the fraction that arises from the simultaneous probability that one functionality has reacted, and the other three remain unreacted; and the other fractions were obtained using

similar arguments. The experimental molar fractions of reaction products, at  $t = 20$  min, were the following:

$$\begin{aligned}
 A_0/\sum A_i &= 0.33 \\
 A_1/\sum A_i &= 0.40 \\
 A_2/\sum A_i &= 0.21 \\
 A_3/\sum A_i &= 0.04 \\
 A_4/\sum A_i &= \text{undetected}
 \end{aligned}
 \quad (5)$$

These values were in a good agreement with expected values for an ideal reaction. Figure 6 shows the theoretical and experimental data of  $A_i/A_T$  against  $A_0/A_T$ .

Figure 7 shows the evolution of the species, confirming that after 30 min, the distribution of the species was constant.

Therefore, this precursor POSS/BSA seems to be the best of the three because all the POSS has reacted, the expected conversion was reached, and the precursor was not degraded.

## CONCLUSIONS

Three aromatic diamines (MDEA, DDM, and BSA) were selected to form precursors with a monofunctional polyhedral oligomeric silsesquioxane (glycidylisobutyl-POSS), for incorporation into an epoxy network. The precursors, in a proportion rich in amine, were reacted at 160°C in an oven at different times and, later, they were investigated by gel permeation chromatography.

For the precursor POSS/MDEA the reaction was slow. The apparent high conversion reached was at-

tributed to degradation, and the maximum conversion reached, after removing the effect of degradation, was 0.18. This system was not a suitable precursor because the reaction was not completed and the effect of the degradation was substantial.

For the precursor POSS/DDM the reaction was fast and the maximum conversion, after removing the effect of degradation, was reached at 90 min. This precursor shows the expected conversion of 0.25, although degradation was also significant; therefore this system does not seem to be appropriate because its incorporation into an epoxy network would be masked by degradation.

The precursor POSS/BSA reacted in the course of sample preparation and the reaction was very fast, but at 20 min no significant changes in the peak distribution were detected. The monosubstituted amines were constant and all the POSS reacted. Also, it was verified that the real distribution of species agrees with the theoretical distribution. This precursor did not degrade.

It was concluded that the presence of POSS in a cage-like conformation with a monofunctional reaction group such as epoxy does not alter the known reaction organic chemistry. The selected precursor was POSS with the diamine BSA, reacted at 160°C for 20 or 30 min, to ensure that all the POSS reacted, that there was a maximum of the monosubstituted amines, and that there was no degradation.

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