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The molecular structures of aminophenyl substituted silsesquioxanes, prepared by two different approaches, have been investigated using ^{29}Si NMR spectroscopy. Aminophenyl silsesquioxane prepared by nitration/reduction of octaphenyl POSS®, exhibits broad resonances in the ^{29}Si NMR spectrum, whereas aminophenyl silsesquioxanes prepared directly from aminophenyltrimethoxysilane exhibit very narrow line widths. Wide-angle X-ray diffraction of the products from the direct synthesis show a diffraction peak with a d-spacing value similar to the 101 hkl reflection peak of the rhombohedral lattice seen in several other crystalline POSS® octamers, whereas the products from the nitration/reduction exhibit no diffraction peaks. Our analysis suggests that aminophenyl silsesquioxane prepared by the nitration/reduction of octaphenyl POSS® no longer retains the Si-O structure of the starting octaphenyl POSS®, while the aminophenyl silsesquioxanes prepared by the direct synthesis have significant Si-O cage structure.

Thermogravimetric analysis on both products indicates that the aminophenyl silsesquioxanes from the direct synthesis have better thermal and thermo-oxidative stability (TOS). Furthermore, this improved thermal stability is extended to highly crosslinked resins prepared from the phenylethynyl phthalimide derivatives of the aminophenyl silsesquioxanes. The thermal analysis suggests that the discrete Si-O frameworks found in POSS® monomers play an important role in maximizing the thermal and thermal-oxidative stability of the materials in which they are incorporated.

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Molecular Structure Analysis of Aminophenyl Silsesquioxanes (Preprint)

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ABSTRACT

The molecular structures of aminophenyl substituted silsesquioxanes, prepared by two different approaches, have been investigated using ^{29}Si NMR spectroscopy. Aminophenyl silsesquioxane prepared by nitration/reduction of octaphenyl POSS®, exhibits broad resonances in the ^{29}Si NMR spectrum, whereas aminophenyl silsesquioxanes prepared directly from aminophenyltrimethoxysilane exhibit very narrow line widths. Wide-angle X-ray diffraction of the products from the direct synthesis show a diffraction peak with a d-spacing value similar to the 101 hkl reflection peak of the rhombohedral lattice seen in several other crystalline POSS® octamers, whereas the products from the nitration/reduction exhibit no diffraction peaks. Our analysis suggests that aminophenyl silsesquioxane prepared by the nitration/reduction of octaphenyl POSS® no longer retains the Si-O structure of the starting octaphenyl POSS®, while the aminophenyl silsesquioxanes prepared by the direct synthesis have significant Si-O cage structure.

Thermogravimetric analysis on both products indicates that the aminophenyl silsesquioxanes from the direct synthesis have better thermal and thermo-oxidative stability (TOS). Furthermore, this improved thermal stability is extended to highly crosslinked resins prepared from the phenylethynyl phthalimide derivatives of the aminophenyl silsesquioxanes. The thermal analysis suggests that the discrete Si-O frameworks found in POSS® monomers play an important role in maximizing the thermal and thermal-oxidative stability of the materials in which they are incorporated.

Key Words: Aminophenyl silsesquioxanes; Thermo-oxidative stability; phenylethynyl terminated oligoimides.

INTRODUCTION

The field of nanocomposite inorganic-organic polymers has historically been concerned with combining the beneficial properties of inorganic materials with those of organic materials so as to create new compositions having physical properties which are superior to either of the individual components [1-4]. Traditionally, the key to realizing success in this endeavor is linked to the ability to control the nanoscale size regime as well as the dispersion of the inorganic component. Ideal materials would have well-defined structure, be compatible with an organic matrix, and if desired have reactive functionality that could be used in exactly the same way as traditional organic monomers. Nanostructured® chemicals based on polyhedral oligomeric silsesquioxanes, POSS®, provide a particularly attractive route into nanocomposite materials [5-9]. POSS® monomers possess a precise three-dimensional, nanoscopic structure comprised of an inner silica core surrounded by an organic outer shell. The outer organic shell may be tailored to provide compatibility with almost any type of organic matrix and can have both inert and reactive functionality. These features make POSS® monomers especially well suited to a systematic, bottom-up approach to incorporate inorganic structure into traditional materials.

The use of silsesquioxane building blocks in polymeric matrix composites to provide higher thermo-oxidative stability over conventional organic matrix materials is especially attractive. Particular interest in using POSS® in high performance polymers such as polyimides, PI, has lead to development of new methods and approaches for preparing POSS® based PI and has lead to the development synthetic routes to POSS® monomers bearing reactive aromatic functionality such as aminophenyl.

Preparation of functionalized POSS® frameworks can be classified into two general synthetic approaches. In one approach, the organic groups (or functional groups) on an existing POSS® framework are simply functionalized (or transformed) using traditional organic synthesis.

A second approach involves the direct synthesis of functionalized POSS® cages from silicon based starting materials. Generally this approach involves the hydrolytic condensation of trifunctional organosilanes, i.e., R-SiX_3, and may occur under either acidic or basic conditions. In the first approach, the stability of Si-O core is generally assumed. Therefore, if one begins with a monodisperse Si-O framework (e.g. an octamer) the product will and should retain the same monodisperse Si-O framework. In the second approach, the product distribution is influenced by the choice of reaction conditions with the formation of completely and incompletely condensed Si-O structures possible. Although several different structures are possible, with the proper selection of reagents and solvents a high degree of selectivity can be achieved.

Several papers describing the synthesis and use of aminophenyl substituted POSS® monomers have recently appeared [10-13]. This body of work has dealt exclusively with synthetic procedures based on the first approach in which existing POSS® frameworks are modified using traditional organic chemistry. Typically, transformations involve aromatic nitration of phenyl bearing POSS® monomers such as octaphenyl POSS® and dodecaphenyl POSS® followed by reduction of the nitro group to an amine. Originally, Olsson and Grönwall[14] reported that a variety of reduction protocols failed to reduce the nitro group cleanly, later Laine[10] et al. claimed to overcome this difficulty. More recently, Pittman [13] et al. suggested the nitration/reduction reaction must be performed in completely water-free environment.

In the course of our work with crosslinkable POSS®-based oligoimides, we began to suspect that the aminophenyl based POSS® monomers prepared by the nitration/reduction of octaphenyl POSS® did not retain a precise SiO cage structure. This finding raises an important question about POSS® and silsesquioxane resins in general: Is the precise, three-dimensional structure of POSS® monomers necessary to obtain the desired property enhancements, or are ill-

defined silsesquioxane oligomers or resin sufficient? Additionally, since the nitration/reduction procedure is nonselective and leads to the formation of meta-, para-, and ortho- positional isomers, we were concerned that the processibility and thermo-oxidative stability of the resulting PI polymers might suffer as it is generally accepted that an isomeric distribution can affect the performance of composites.

In this paper, we report synthetic procedures for the aminophenyl substituted POSS® monomers directly from aminophenyltrialkoxysilanes and the analysis of the products by ^{29}Si NMR spectroscopy, as well as Wide-Angle X-ray Diffraction (WXRD) analysis. Analysis of the thermo-oxidative stability of the aminophenyl silsesquioxanes prepared by these two different synthetic approaches was also carried out using DSC and TGA analysis. In addition, we present data on phenylethynyl phthalimide as derived from the different aminophenyl silsesquioxanes.

EXPERIMENTAL

General information on synthesis and materials: Reaction solvents tetrahydrofuran (Gallade Chemicals) and acetone (Burdick & Jackson, HPLC-grade) were used as received. Methanol was dried by passage through activated alumina columns, Glacial acetic acid (Gallade Chemical), para-aminophenyltrimethoxysilane (90%, Gelest), meta-aminophenyltrimethoxysilane (90%, Gelest), 4-phenylethynylphthalic anhydride (4-PEPA electronics grade; provided by Performance Polymer Solutions), tetrabutylammonium hydroxide 40wt% in water (Aldrich) were used as received. Octaaminophenyloctasilsesquioxane (OAPS), $(NH_2C_6H_5)_8Si_8O_{12}$, was supplied by Mayaterials and it was prepared through nitration/reduction of octaphenylsilsesquioxane, $phenyl_8Si_8O_{12}$. All NMR spectra were collected on either a Bruker 300 or 400 MHz instrument and obtained in either d_6-DMSO or $CDCl_3$ solution. The nitrogen-

containing silsesquioxane compounds were all dissolved at a concentration of about 90 mg in 0.5 ml.

Synthesis of meta-aminophenyl-POSS® Cage Mixture: *(m-$NH_2C_6H_5[SiO_{1.5}]$)$_n$* (n = 8, 10, 12): A solution of tetrabutylammonium hydroxide (5.54 g, 7.72 mmol, 5.60 mL of a 40wt% soln in water) was added to a solution of meta-aminophenyltrimethoxysilane (32.0 g, 150 mmol) in THF (110 mL). The resulting clear brown reaction mixture was stirred for 5 days after which the reaction mixture was quenched with glacial acetic acid (0.63 g, 10.53 mmol). The solvent was removed from the reaction mixture by rotary evaporation to provide a solid foam which was collected and stirred with water (400 mL). The solid was collected by vacuum filtration and dried under vacuum. The ^{1}H NMR spectrum was obtained and indicated the presence of tetrabutylammonium acetate which was also indicated by mass of the crude product 17.4 g (Theoretical 15.84 g). The tetrabutylammonium acetate could be removed by dissolving the crude product in acetone followed by precipitation into water. In a typical procedure p-aminophenyl Cage Mixture (2.0 g) was dissolved in acetone (10 mL) and then poured into deionized water (40 mL) to give a slurry. The slurry was centrifuged and the supernatant decanted. The process was then repeated a second time after which the solid was collected and dried to provide 1.6 g of purified product.

Synthesis of p-aminophenyl-POSS® Cage Mixture: *(p-$NH_2C_6H_5[SiO_{1.5}]$)$_n$*: A solution of tetrabutylammonium hydroxide (6.83g, 10.53 mmol, 6.90 mL of a 40wt% soln in water) was added to a solution of para-aminophenyltrimethoxysilane (32.0 g, 150 mmol) in THF (150 mL). Approximately 5 hrs after the addition of the base, the initial brown color of the para-aminophenyltrimethoxysilane became a deep green. The reaction mixture was stirred for 5 days after which it was quenched with glacial acetic acid (0.63 g, 10.53 mmol). Upon quenching the reaction mixture turned purple. The solvent was removed from the reaction mixture by rotary

evaporation to provide solid foam which was stirred with water (500 mL). The solid was collected by vacuum filtration and dried under vacuum. The ^{1}H NMR spectrum was obtained and indicated the presence of tetrabutylammonium acetate which was also indicated by mass of the crude product 24.2 g (Theoretical 21.6g). The procedure for removing the tetrabutylammonium acetate is the same as for the m-aminophenyl-POSS® cage mixture.

General Synthesis of Phenylethynyl phthalimide from aminophenyl silsesquioxanes [15-17]:

A flame-dried 100 ml round-bottom flask was charged with 4-PEPA (4.0 g, 16.1 mmol), methanol (5 ml), and fitted with a condenser. The mixture was magnetically stirred at 50˚C under a nitrogen purge. After about 1.5 hours, the reaction mixture became light-yellow in color and was completely homogeneous. The reaction mixture was then stirred for additional 30 minutes, and aminophenyl silsesquioxanes, 2.335 g (16.1 mmol) were added. The reaction mixture changed to a dark brown color immediately upon addition of the aminophenyl silsesquioxanes, indicating a rapid formation of phthalic amic acid. The reaction mixture was stirred for 20 minutes and then the phthalic amic acid solution was transferred to a glass bottle and heated to reflux on a hot plate with magnetic stirring for additional 10 minutes. After cooling to room temperature the reaction mixture was placed into a mechanical-convection oven. The oven was heated from RT to 200^{o}C at a rate of 5˚C/min and held at 200˚C for 2 hours, and then heated to 240˚C at a rate of 5˚C/min and held at 240˚ C for 1 hour. A brown-colored powder was obtained. The ^{1}H, ^{13}C and ^{29}Si NMR spectra of the powder were consistent with the formation of phenylethynyl phthalimide silsesquioxane, and indicated that the silsesquioxane structure was not altered by the synthetic procedure.

X-ray Diffraction (WXRD): X-ray diffraction measurements were performed using a Scintag 2000 XRD with Cu-K_{α} target (λ=1.5416Å) radiation generated at 45 kV and 200 mA. The diffraction angle ranged from 5˚ to 30˚, with step size and scan rate of 0.05˚ and 2˚ per minute,

respectively. Aminophenyl silsesquioxane powder (about 200 mg) was mixed with gel and placed on a glass slide. A blank gel sample was used as the background and a simple background subtraction performed.

Thermal gravimetric analyses (TGA): Thermal and thermo-oxidative stability of various silsesquioxanes were evaluated using a TA Instruments Q50 thermogravimetric analyzer in dry nitrogen and dry air environment. Typical heating rates of 10˚C/min and gas flow rate of 80 ml/min. were used.

Differential Scanning Calorimetry (DSC): Crosslinking reactions of phenylethynyl moiety were examined using a TA Instruments Q1000 differential scanning calorimeter under a flow of nitrogen and with a heating rate of 10˚C/min. The onset temperature of reaction, peak temperature and overall heat of reaction were determined using the TA Universal Analysis package provided.

RESULTS AND DISCUSSIONS

Synthesis and ^{29}Si NMR Spectral Analysis: A number of different procedures exist for the assembly of POSS® monomers having precise, well-defined structures. One of the most common methods involves the hydrolysis of appropriate chloro- or alkoxysilanes and for our purposes a series of aminophenyltrialkoxysilanes, having various isomeric purities, were commercially available. To investigate effect of positional isomeric state on the thermo-oxidative performance of cage-like aminophenyl POSS®, it was necessary to verify that cage-like aminophenyl POSS® can be obtained using a direct synthetic approach. Our efforts centered on starting from a specified isomer of aminophenyltrimethoxysilane and using acid or base catalysis to assemble the SiO framework. Our initial efforts involved acid catalysis using the conditions similar to that reported for the synthesis of octa(aminopropyl)POSS®. While this approach was

successful for obtaining cage-like aminophenyl POSS®, the product was isolated as an anilinium salt which was undesirable for further transformations. This led us to examine the use of base catalysis. As opposed to the acid catalysis which in the case of the octa(aminopropyl)POSS® produces exclusively the octamer, base catalysis results in mixtures of cage sizes generally ranging in size from 8-14 silicon units, with the dodecamer often being the predominant cage size.

It is well established that the solution ^{29}Si NMR spectroscopy is an excellent tool for revealing the structural environment of silicon containing materials [18]. For silsesquioxanes, the spectra of well-defined oligomeric cages contain sharp resonances with half-peak widths on the order of 1 or 2 hertz, while the spectra of ill-defined silsesquioxane "resin" is broad and uninformative due to a myriad of chemical environments present. For example, in the top trace of Figure 1, the ^{29}Si spectrum of octaphenylsilsesquioxane, $(C_6H_5)_8Si_8O_{12}$, reveals a single sharp resonance 2 hertz wide as all eight silicons are chemically identical. The second trace in Figure 1 shows the spectrum of dodecaphenylsilsesquioxane, $(C_6H_5)_{12}Si_{12}O_{18}$, a single pure compound with two chemical environments and thus just two sharp resonances a few hertz in width shifted a few ppm from their $(C_6H_5)_8Si_8O_{12}$ cousin. The bottom trace is of ill-defined polyphenylsilsesquioxane that contains a small amount of $(C_6H_5)_{12}Si_{12}O_{18}$. The bulk of the material has so many different chemical environments for all the silicon atoms present that the spectra shows a broad hump of peaks running into each other, extending from approximately -76 to -82 ppm.

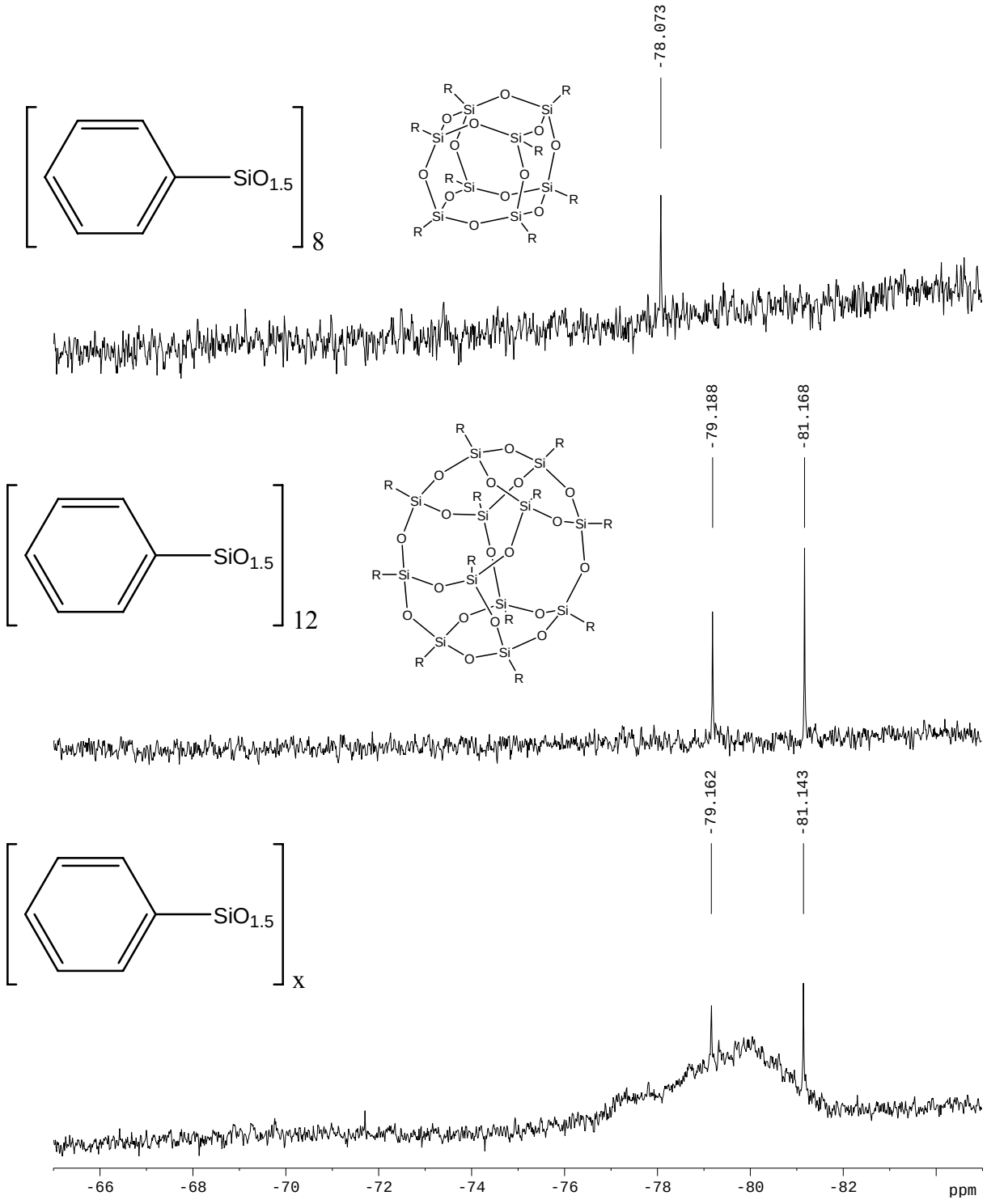

Figure 1. Comparison of the ^{29}Si NMR spectra of octaphenylsilsesquioxane (upper trace), dodecaphenylsilsesquioxane (middle trace), and ill-defined silsesquioxane resin containing a small amount of the dodecaphenylsilsesquioxane (lower trace). All spectra were obtained from $CDCl_3$ solution.

It is reported in the literature that octaphenylsilsesquioxane, $(C_6H_5)_8Si_8O_{12}$, is converted into an isomeric 60:30:10 mixture [10b] of meta- ortho- and para-substituted octanitrophenylsilsesquioxane, $(NO_2C_6H_5)_8Si_8O_{12}$, and that this compound can be reduced to an isomeric mixture of meta- ortho- and para-substituted octaaminophenylsilsesquioxane, $(NH_2 C_6H_5)_8Si_8O_{12}$. [10-12] Solution ^{29}Silicon NMR spectra of these materials are shown in Figure 2 (Top two spectra). The top trace shows the product from the nitration of octaphenylsilsesquioxane. Two main environments are clearly visible centered at -79 and -83 ppm. The ^{1}H NMR spectrum reveals that each phenyl ring has but one nitro group on it; with three isomeric positions possible on each phenyl ring, a number of structural octanitrophenylsilsesquioxane isomers are possible. This would explain the large number of sharp lines observed, and thus it is not unreasonable to assume that the compound consists of an isomeric mixture of T_8 cages. After this material is reduced to an amine, the ^{29}Si spectrum is suddenly much broader than is reasonable for just T_8 isomers to be present. It is far more likely to suggest that the octameric cage structure is no longer intact, and that under the synthesis conditions, the cage was opened and redistributed into a structurally ill-defined resin. Note that the breadth of the signals from -75 to -82 ppm is similar in size to that observed for polyphenylsilsesquioxane resin. For comparison, the bottom two spectra in Figure 2 show the ^{29}Si NMR spectrum of a meta- and para-aminophenylsilsesquioxane cage mixture, that probably also have a small amount of poorly-defined resin present. Based on similar ^{29}Si NMR spectral analysis of $(HSiO_{3/2})_n$ and $(C_2H_3)_n(SiO_{3/2})_n$ where n = 8, 10, 12, and 14 it appears that the meta- and para-aminophenylsilsesquioxane prepared by the direct method have a similar composition of POSS® cages.

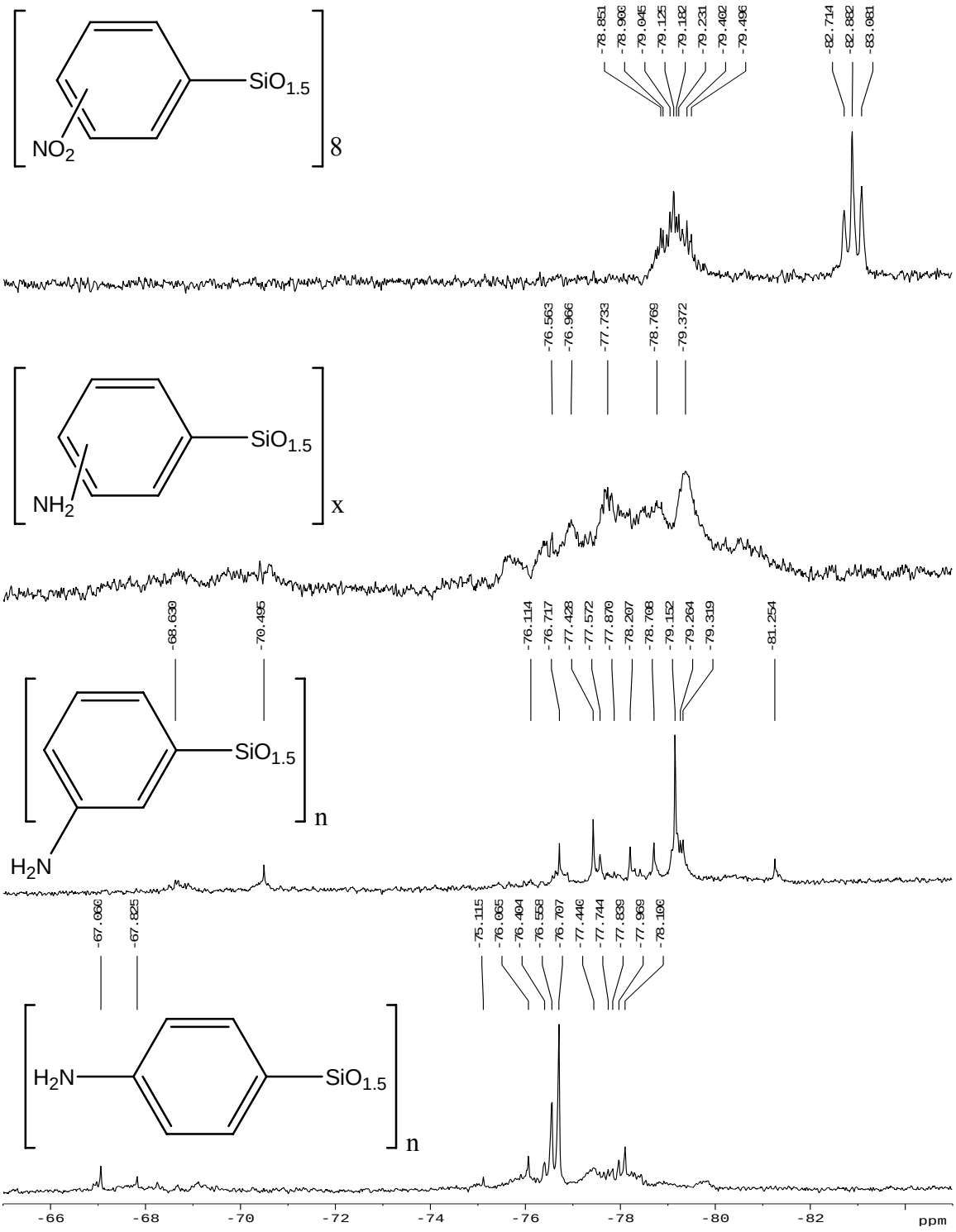

Figure 2. Comparison of the ^{29}Si NMR spectra of mixed isomers of octanitrophenylsilsesquioxane obtained by nitration of octaphenylsilsesquioxane (upper spectrum obtained from $CDCl_3$ solution), the product obtained by reduction of octanitrophenylsilsesquioxane (second spectrum), and a cage mixture of either meta- or para-aminophenylsilsesquioxane obtained by the base assisted condensation of either meta- or para-aminophenyltrimethoxy silane (lower spectra). The lower three spectra are all obtained from DMSO-d6 solutions.

Figure 3 compares the ^{29}Si NMR spectra of the phenylethynyl phthalicimide silsesquioxane resin (top trace) and cage mixture (lower trace). Since there is no significant change observed as compared to spectra shown in Figure 2, it can be concluded that the aniline/anhydride reaction has very little effect on the cage structure and its distribution. It is interesting to note that the phenylethynyl phthalicimide prepared from the meta-aminophenylsilsesquioxane by the direct method appears to have been enriched in n = 12 cage size.

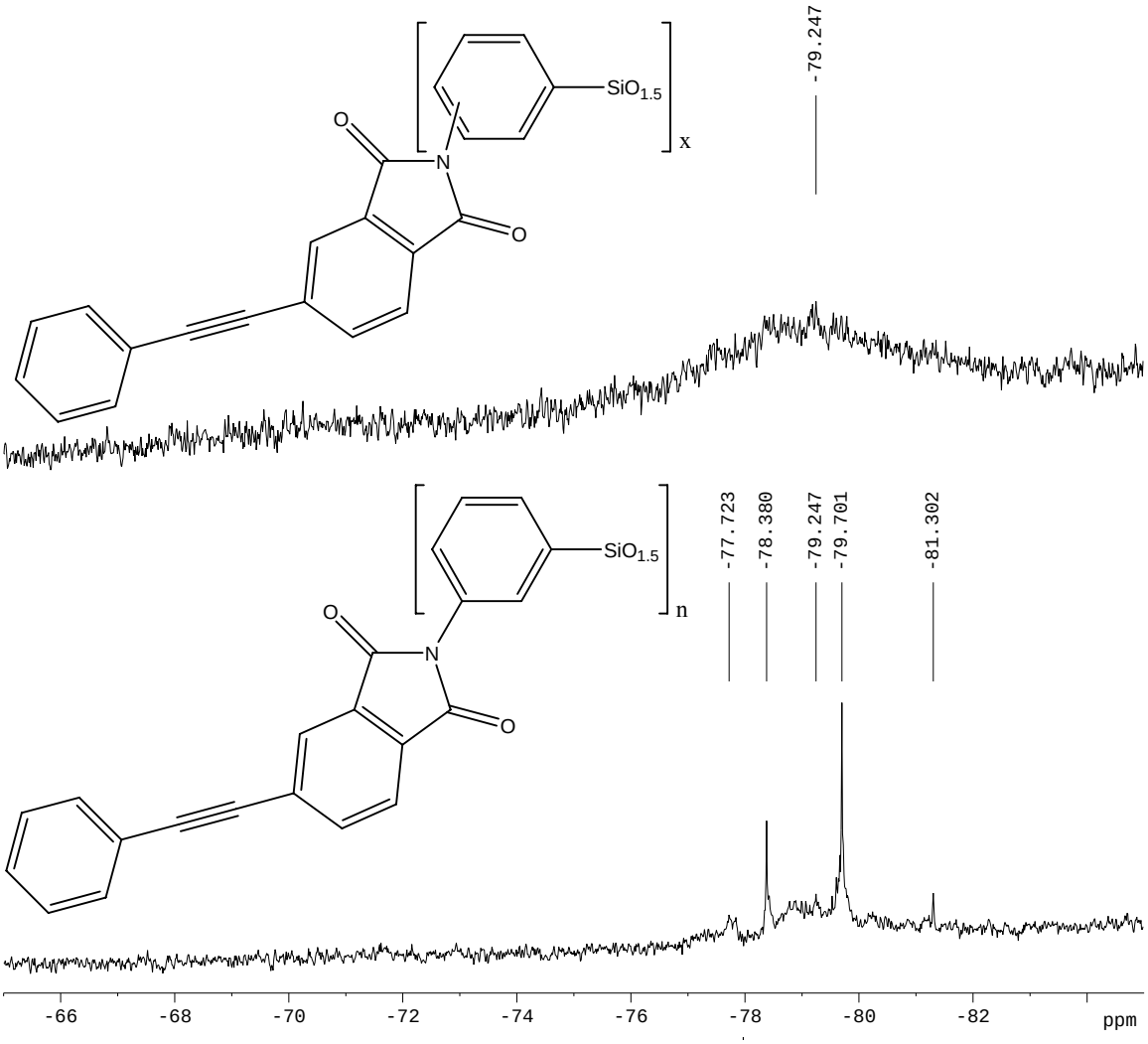

Figure 3. Comparison of the ^{29}Si NMR spectra of the imidization derivatives obtained from structurally undefined aminophenyl silsesquioxane (upper trace), and that obtained from a cage mixture of meta-aminophenylsilsesquioxane (lower trace). Both spectra were obtained from $CDCl_3$ solution.

Morphological Characterization

Figure 4 shows the wide-angle X-ray powder diffraction patterns of (a) OAPS as supplied by Mayaterials; (b) meta-aminophenylsilsesquioxane cage mixture *(m-APSC)$_n$* where n=8,10,12; and (c) para-aminophenylsilsesquioxane cage mixture *(p-APSC)$_n$*. Unlike other highly crystalline POSS® octamers, the only reflection peak observed is centered at around 2θ = 7.8° (corresponding to d-spacing of 11.26 Å) for all three aminophenylsilsesquioxanes. This d-spacing value was similar to the 101 hkl reflection of rhombohedral lattice as observed in many very crystalline octamers of POSS®. It is important to point out here that the intensity of (m-APSC)$_n$ was higher than OAPS and a much more intense reflection peak was observed for (p-APSC)$_n$. This observation further supports the conclusion from solution ^{29}Si NMR that the OAPS obtained from Mayaterials is probably a resin-like material having an isomeric mixture of aminophenyl groups. Furthermore, since there are two possible sites for *(m-APSC)$_n$*, while there is only one possible site for *(p-APSC)$_n$*, it is not too surprising that *(p-APSC)$_n$* exhibited a higher crystallinity than *(m-APSC)$_n$*.

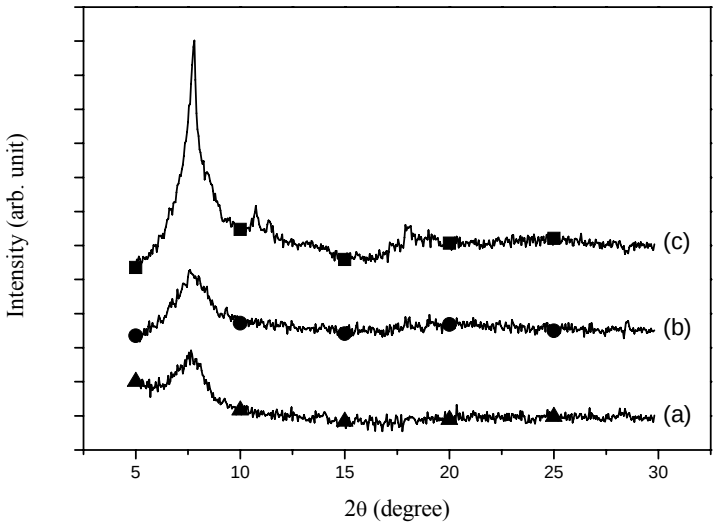

Figure 4. WXRD traces of baseline-corrected of intensity versus diffraction angle. (a)OAPS from Mayaterials; (b) meta-aminophenylsilsesquioxane cage mixture *(m-$NH_2C_6H_5[SiO_{1.5}]$)$_n$* where n=8,10,12; and (c) para-aminophenylsilsesquioxane cage mixture *(p-$NH_2C_6H_5[SiO_{1.5}]$)$_n$*. Curves are vertically shifted for clarity.

Thermal Analysis

Aminophenyl silsesquioxanes (APS's): Using thermogravimetric analysis (TGA) we compared the thermal and thermo-oxidative stability (TOS) of the different aminophenyl-POSS® materials. Analysis was carried out using constant heating-rate, under a constant flow-rate of nitrogen or air as supplied by high pressure gas cylinders. Traces of percent weight remaining (wt %) versus temperature for all three types of APS are shown in Figure 5 (a) and (b), respectively. Regardless of the gas type used, the OAPS as supplied by Mayaterials exhibited a mass loss between 100˚C and 150˚C. In a nitrogen environment, Figure 5(a), the $(m\text{-}APSC)_n$ shows an initial mass loss starting around 550˚C, while the p-APSC shows an initial mass loss starting around 500˚C. The OAPS of Mayaterials shows a second mass loss starting near 400˚C. We were somewhat surprised that $(m\text{-}APCS)_n$ demonstrated better thermal performance than $(p\text{-}APSC)_n$, however, this observation may be related to the additional isomeric flexibility attributed to the meta-functionality. As shown in Figure 5(b) the $(m\text{-}APSC)_n$ also exhibited a superior thermo-oxidative stability in air relative to the other two aminophenyl silsesquioxanes.

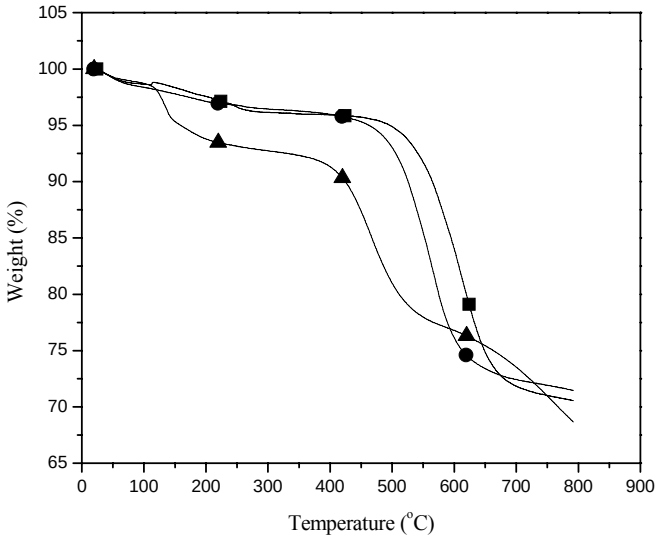

Figure 5 (a). Thermogravimetric analysis (TGA) of different aminophenyl silsesquioxanes. The heating rate was 10°C/min under constant flow of N_2. The line with ■ represents meta-aminophenylsilsesquioxane cage mixture *(m-$NH_2C_6H_5[SiO_{1.5}]$)$_n$* where n=8,10,12; the line with ● represents para-aminophenylsilsesquioxane cage mixture *(p-$NH_2C_6H_5[SiO_{1.5}]$)$_n$*; and the line with ▲represents OAPS from Mayaterials.

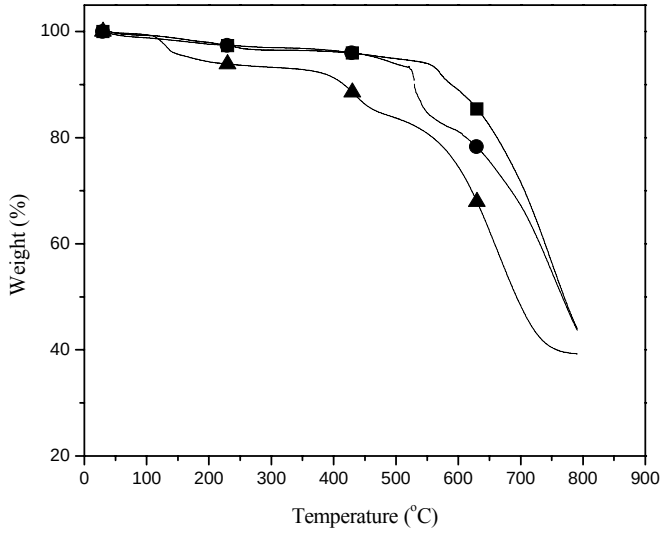

Figure 5 (b). Thermogravimetric analysis (TGA) of different aminophenyl silsesquioxanes. The heating rate was 10°C/min under constant flow of air. The line with ■ represents meta-aminophenylsilsesquioxane cage mixture *(m-$NH_2C_6H_5[SiO_{1.5}]$)$_n$* where n=8,10,12; the line with ● represents para-aminophenylsilsesquioxane cage mixture *(p-$NH_2C_6H_5[SiO_{1.5}]$)$_n$*; and the line with ▲represents OAPS from Mayaterials.

Phenylethynyl phthalimide Silsesquioxanes (PETISS): Phenylethynyl phthalimide silsesquioxanes (PETISS) derived from *(m-APSC)$_n$* (cage-PETISS) and Mayaterial's OAPS (resin-PETISS) were also analyzed by DSC analysis and are shown in Figure 6. The traces clearly demonstrate that reaction of the ethynyl group in these silsesquioxanes begins near 330˚C, with peak exotherm near 400˚C and the integrated heat of reaction of close to 270 J/g (or 96 KJ per mole of ethynyl group). These results are similar to other high temperature phenylethynyl phthalimide end-capped oligoimide resins [16, 19-20], suggesting that the Si-O core has no effect on crosslinking reactions of the ethynyl group. This suggests the phenylethynyl phthalimide POSS® monomers are excellent candidates for use as additives in existing high temperature PETI based oligoimide resins to improve their thermo-oxidative stability especially in applications involving carbon-fiber reinforced polymer matrix composites.

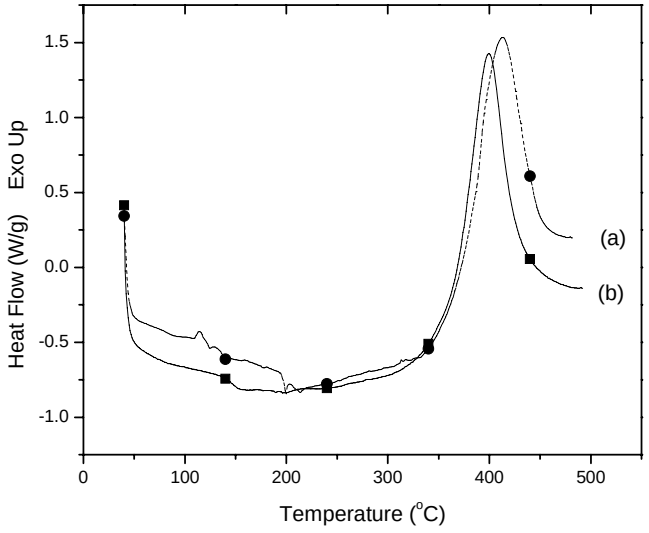

Figure 6. Differential Scanning Calorimetry (DSC) analysis of curing of Phenylethynyl phthalimide derived from (a) OAPS from Mayaterials; and (b) meta-aminophenylsilsesquioxane cage mixture *(m-$NH_2C_6H_5[SiO_{1.5}]$)$_n$* where n=8,10,12. The heat rate was 10°C/min.

Further comparison of the DSC traces for the cage-PETISS and resin-PETISS, reveal that the peak temperature for meta-PETISS is about 11˚C lower than resin-PETISS and the width of the exothermic peak for cage-PETISS is narrower than that for resin-PETISS. These observations provide further evidence that cage-PETISS has a more cage-like structure, while resin-PETISS has more resin-like structure. In addition, the cage-PETISS exhibits a clear T_g near 150˚C, while the resin-PETISS shows a T_g around 200˚C. Results for DSC are also consistent with the WXRD observation that both silsesquioxanes contains no significant degree of crystallinity. The data indicate that both materials exhibit liquid-like behavior at temperatures above T_g, prior to any significant ethynyl crosslinking.

To further evaluate these cage-PETISS and resin-PETISS as potential additives for high temperature organic PETI oligoimide resins, we examined their thermal stability by TGA using a ramp-soak cycle under a constant flow of nitrogen. Samples were first heated from 40˚C to 371˚C at a rate of 20˚C/min., and then held isothermally at 371˚C for 2.5 hours. Figure 7(a) shows plots of the normalized percentage of weight remaining versus time for cage-PETISS and resin-PETISS. From the data, it is clear that the meta-PETISS has significantly better thermal stability than the resin-PETISS (4.5% versus 11.5% weight-lost). To further evaluate the thermo-oxidative stability (TOS) of these two silsesquioxanes, we examined the weight loss behavior of cured PETI-silsesquioxanes in a constant flow of air environment, as shown in Figure 7(b). The results (presented in Figure 7(b)) show cage-PETISS has a significantly better TOS performance than resin-PETISS. We also note here that the TOS performance of resin-PETISS was already significantly better than the non-silsesquioxane organic 6-F oligoimide resins end-capped with phenylethynyl phthalimide. This result suggests that the use of cage-like nanostructure chemicals should have a significant benefit in TOS performance in the high temperature carbon-fiber reinforced PMC community.

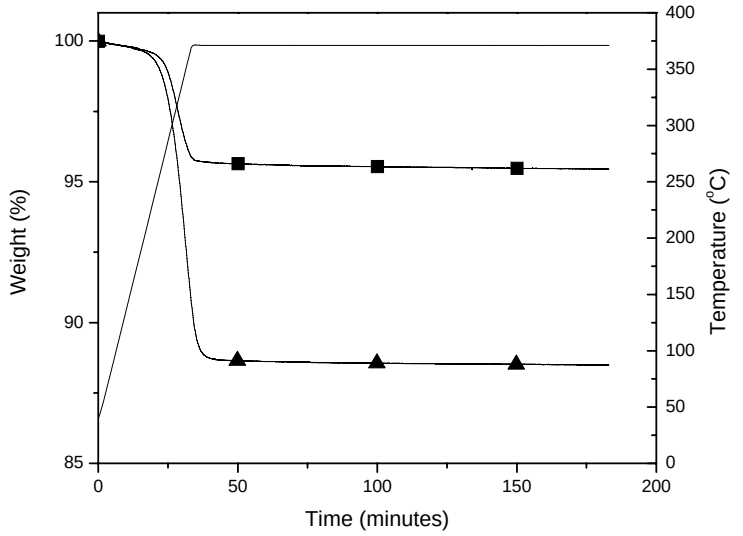

Figure 7(a). Thermogravimetric analysis (TGA) of different phenylethynyl phthalimide silsesquioxanes (PETISS)in a simulated cure cycle. The heating ramp from 40°C to 371°C with a rate of 20°C/min and held at 371°C for 150 minutes. The line with ■ represents meta-cage-PETI silsesquioxane and the line with ▲represents resin-PETI silsesquioxane.

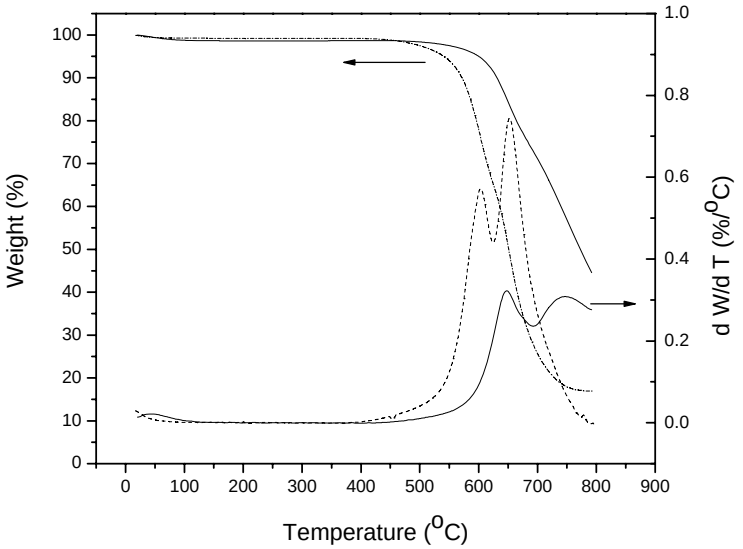

Figure 7(b). Thermogravimetric analysis (TGA) of different phenylethynyl phthalimide silsesquioxanes (PETISS) after cured at 371°C for 2.5 hours. The heating rate was 10°C/min under a constant flow of air. The solid lines represent meta-cage-PETI silsesquioxane and dotted lines represent Resin-PETI silsesquioxane. The weight change with respect to temperature was also presented to demonstrate thermo-oxidative stability of these silsesquioxanes.

CONCLUSIONS:

We have presented an analysis of structure/property relationships for aminophenyl POSS® monomers prepared by two different approaches. The first approach involved the nitration/reduction of a preformed octaphenyl-POSS® using standard organic synthesis, while the second approach involved a direct synthesis from aminophenyltrimethoxysilane. Structural analysis of the Si-O framework was carried out using ^{29}Si NMR spectroscopy. Our results indicate that the Si-O cage of aminophenyl POSS® (OAPS) synthesized using the first approach and provided by Mayaterials was no longer intact. However, using the second approach we were able to obtain a mixture of various sizes of aminophenyl POSS® cage with both meta-, and para-aminophenyltrimethoxysilane. Moreover, the cage mixture of $(p\text{-}APSC)_n$ exhibited a crystalline structure as indicated by WAXD measurements. With this cage-like nanostructure, both $(p\text{-}APSC)_n$ and $(m\text{-}APSC)_n$ show superior thermal and thermo-oxidative stability relative to the resin-like OAPS from Mayaterials. The enhanced thermal stability was also demonstrated in the crosslinked phenylethynyl phthalimide derivatives, cage-PETISS made from the cage mixture of $(m\text{-}APSC)_n$.

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