

Thermal Transitions and Reaction Kinetics of Polyhederal Silsesquioxane containing Phenylethynylphthalimides

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ABSTRACT: Thermal transitions and reaction kinetics of polyhedral oligomeric silsesquioxane (POSS) with phenylethynylphthalimide (PEPI) moieties were investigated. Specifically, this study was designed to probe the influence of the POSS peripheries, types of spacer group in between the PEPI and the SiO_{1.5} core, the architecture of the PEPI arrangement with respect to the SiO_{1.5} core, and the number of PEPI groups per cage on the thermal transitions and the cross-linking reaction of phenylethynyl. PEPI-POSS compounds with isobutyl peripheries exhibited lower melting temperatures as compared to those with phenyl periphery, consequently these isobutyl PEPI-POSS derivatives have a higher phenylethynyl reaction rate, although the onset of reaction temperature was not significantly affected. Changing the spacer group from propyl to phenyl causes an increase in the melting transition temperature along with a higher heat of fusion at melting; however, the more rigid phenyl spacer enables the PEPI-POSS to form a higher degree of crystallinity upon cooling. The more rigid phenyl spacer also initiates the polyene reactions at lower temperatures. For POSS with PEPI attached to either side of the cage, there are two isomers with respect to the $SiO_{1.5}$ core. This mixture of two isomers inhibits the formation of crystallinity as compared with the "pendent" derivative where both PEPI groups come off from the same corner of POSS cage. Finally, it was found that these PEPI-POSS molecules have reaction kinetics and onset temperatures on par with organic hexafluorophenylethynyl oligoimides, which make these PEPI-POSS molecules excellent candidates as nanocomposite additives in high performance composite applications.

Introduction

Chemical and physical interactions of reacting monomers can affect the kinetics of polymerization, which ultimately influences the performance of the resultant polymer. Recent advancements in the synthesis of nanostructured inorganic/organic hybrid materials with reactive moieties have prompted a surge of efforts to incorporate these hybrids into organic polymers.^{1–14} However, the performance of these copolymers depends on the molecular arrangement between the nanostructured hybrids and the organics. Hence, a systematic study that explores the kinetics of the reactive moiety on the hybrids, as influenced by the chemical and physical characteristics of nanostructures, is needed.

Polyhedral oligomeric silsesquioxanes (POSS) are a class of inorganic–organic hybrids with reactive moieties.^{1–12} POSS nanostructured chemicals consist of a geometrically well-defined silicon/oxygen, SiO_{1.5}, polyhedral core surrounded with chemically specified organic peripheral groups.^{1–13,15–21} Organic peripheral groups are covalently bonded to each silicon atom, which provides POSS molecules with specific interactions to other POSS molecules or organics in the medium.^{17–21} In addition, the relative position of reactive groups with respect to the core of POSS may also play a role during the polymerization reactions. A few examples in literature best illustrate these points. In the case of polystyrene–POSS copolymers, the POSS peripheral group was shown to affect the T_g , the modulus above T_g , and the molecular weight of the copolymers.¹⁹ This is attributed to the

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POSS–POSS interactions as well as the solubility of styrene– POSS of different peripheral groups in resultant copolymers. In the case of POSS-modified polystyrene–polybutadiene– polystyrene triblock copolymers, depending on the peripheral group of POSS used, the effects on the phase morphology and phase transition behavior differ significantly.²⁰ Hence, it is likely that other molecular variables of POSS, including the architecture, the number of functional groups, and nature of the spacer group connecting the SiO_{1.5} core of POSS to the functional group will additionally influence the properties of these copolymers.

Fundamentally, studying the reactivity of POSS compounds is best accomplished in bulk reaction conditions, thereby eliminating the effects of solvent and catalyst. Therefore, a thermally activated functional group with a high onset of reaction temperature is to be used, thereby minimizing the effects of crystallinity of POSS molecules. One possible candidate is the phenylethynylphthalimide (PEPI) functional group.²²⁻²⁶ PEPI is chemically attached to monomers via reaction of phenylethynylphthalic anhydride (PEPA) to amines. PEPI is utilized to end-cap aromatic heterocyclic oligoimides. Upon heating, phenylethynyl undergos polymerization and cross-linking reactions to form thermosets.^{22–33} The cure reaction of PEPI has been studied using solid state carbon NMR and infrared spectroscopy. These studies suggest that PEPI reactions proceed initially by polyene formation, followed by branching and cyclization reactions.²²⁻² Several kinetic studies of oligoimides end-capped with PEPI and model PEPI compounds have shown first-order kinetics for the initial polyene reactions, with a C=C conversion of under 80%.^{22,23} The kinetics deviate when the slow, diffusion controlled

Table 1. Thermal Transition of Different PEPI Compounds Investigated^a

compound	thermal transition (°C)	$\Delta H_{\rm m}$ (kJ/mol)	$\Delta H_{ m c}/\Delta H_{ m m}$
Ibu7propylPEPI-POSS	$T_{\rm m} = 157; T_{\rm c} = 87$	35.4 ± 2.0	0.608
Ibu7phenylPEPI-POSS	$T_{\rm m} = 238; T_{\rm c} = 178$	46.5 ± 1.0	0.855
Ph7phenylPEPI-POSS	no thermal transitions observed prio	r to PEPI reaction.	
Ibu7diPEPI-POSS	$T_{\rm m} = 190; T_{\rm c} = 120$	57.4 ± 6.4	0.364
Ph ₇ diPEPI-POSS	$T_{\rm m} = 296$	40.9 ± 0.9	N/O
Ph ₈ bisPEPI-POSS	$T_{g} = 100$		
HFPE-n-9	$T_{g}^{\circ} = 249$		
HFPE-n-1	$T_{\rm m} = 340$		
OctapropylPEPI-POSS	$T_{\rm m} = 234; T_{\rm c} = 190$	160 ± 4.7	0.831
OctaphenylPEPI-POSS	$T_{\rm g} = 205$		

^{*a*} Thermal transition is either the first order melt transition, T_m , or the second order glass transition, T_g . For first order transition, the corresponding heat of fusion, ΔH_m , was determined from the area of the melting peak and normalized with respect to the molar weight of specific compound. Fraction of crystallization upon cooling was determined from the ratio of heat of crystallization from the cooling curve over the heat of fusion in heating, ΔH_m . Thermal transitions were determined by a DSC with heating and cooling rate of 20 °C per minute.



Figure 1. Structures of PEPI-functionalized compounds investigated.

cyclization and cross-linking chemistries occur. It is also recognized that the transition from chemical-controlled to diffusioncontrolled reaction kinetics is influenced by the molecular weight, molecular weight distribution, molecular structure, and chain architecture of the oligoimides used. The relatively high onset of reaction temperature of phenylethynyl, i.e., above 300 °C, makes PEPI an ideal candidate to study the effects of the POSS periphery and architecture on reactivity as the thermal transitions (Table 1) of PEPI–POSS macromers are well separated from its phenylethynyl reactions.

On the basis of the above rationale, this study investigated the thermal characteristics and reaction kinetics of PEPI-functionalized POSS, as influenced by the POSS periphery, PEPI-POSS spacer group, and POSS architecture. To this, a series of PEPI-POSS were designed and synthesized by appropriate chemistries. The mono, di, and octafunctional PEPI-POSS molecules used in this study are shown in Figure 1.

Experimental Section

Materials. The compounds 1-(3-(5-(phenylethynyl)isoindolinyl-1,3-dione)propyl-3,5,7,9,11,13,15-isobutylpentacyclo-[9.5.1.1^{3,9}.1^{5.15}.1^{7,13}]octasiloxane (Ibu₇propylPEPI–POSS), 1-(3-(5-(phenylethynyl)isoindolinyl-1,3-dione)phenyl-3,5,7,9,11,13,15isobutylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (Ibu₇phenyl-PEPI–POSS), 1,3,5,7,9,11,14-hepta-phenyltricyclo[7.3.3.1^{5,11}]heptasiloxane-*endo*-3,7,14-triol (Ph₇trisilanol–POSS), 1,3,5,7,9,11,13, 15-((octa(3-(5-(phenylethynyl)isoindolinyl-1,3-dione)propyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (OctapropylPEPI–POSS), $1,3,5,7,9,11,13,15-((octa(3-(5-(phenylethynyl))isoindolinyl-1,3-dione)phenyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}] octasiloxane (Octa$ phenylPEPI-POSS), and tricyclo[7.3.3(3,7)]octasiloxane-5,11,14,17-tetraol-1,3,5,7,9,11,14,17-octaphenyl (Ph₈tetrasilanol-POSS) were obtained from Hybrid Plastics. Solvents such as toluene, tetrahydrofuran (THF), hexane, diethyl ether, and dimethylacetimide (DMAc) were obtained from Aldrich and purified prior to use. Magnesium turnings, (N-trimethylsilyl)₂-4-bromoaniline, aniline, and triethylamine were obtained from Aldrich and used as received. Phenylethynyl phthalic anhydride (PEPA) and 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (HFDA) were obtained from Chriskev Company. p-Phenylenediamine (p-PDA) was obtained from Aldrich. Trichloromethylsilane, from Gelest, and tetrachlorosilane, from United Chemical Technologies, were distilled prior to use. The protected-aminochlorosilanes were synthesized by the literature methods.³⁴ For completeness, short synthesis descriptions were provided in the Suppoorting Information. Oligoimides of n moles of HFDA, n + 1 mol of p-PDA, and 2 mol of PEPA as the end functionality, where n = 1 (HFPE-*n*-1) or 9 (HFPE-n-9), were synthesized using the PMR method.³¹

Synthetic Methods. Synthesis of Phenyl₈bisaniline–POSS (*Ph₈bisaniline-POSS*). Under a nitrogen atmosphere in a drybox, a solution of ((N-trimethylsilyl)2-aniline4(dichloromethylsilane) (2.953 g, 8.42 mmol), triethylamine (1.857 g, 18.4 mmol) and THF (10 mL) was added dropwise via an addition funnel into a well-stirred solution of Ph₈tetraol-POSS (4.455 g, 4.17 mmol) and THF (40 mL) in a 100 mL round-bottom flask. The POSS solution became cloudy after the addition of a few drops of the dichloromethylsilane/triethylamine solution, indicating formation of insoluble HNEt₃Cl salt. After 30 min of stirring, this salt was separated by filtration and the solvent was removed under vacuum. Addition of diethyl ether (2 mL) followed by a solution of acidified methanol (50 mL) gave a white suspension of product that was stirred at room temperature for 1 h. The product (3.90 g, 70% yield) was isolated by filtration and dried in a vacuum oven overnight at 60 °C. NMR resonances (ppm) follow. ²⁹Si NMR, δ: -29.7 (4 Si), -78.2 (8 Si), -79.1 (2 Si), -79.3 (4 Si), -79.4(2 Si). ¹³C NMR, δ: 148.27, 135.13, 134.39, 134.35, 134.30, 134.22, 132.29, 131.40, 131.19, 130.98, 130.52, 130.47, 130.38, 130.24, 127.93, 127.88, 127.69, 127.52, 124.64, 114.56, -0.10. ¹H NMR, δ : 7.8–7.1 (44 H's, overlapping multiplets), 6.6 (4 H's, doublet), 3.6 (4 H's, NH₂, broad singlet), 0.58 (6 H's, CH₃, singlet).

Synthesis of Phenyl₈bis(phenylethynylphthalimide)–POSS (**Ph₈bisPEPI–POSS**). Under a nitrogen atmosphere, a wellstirred solution of Ph₈bisaniline–POSS (0.248 g, 0.186 mmol) and PEPA (0.095 g, 0.38 mmol) in anhydrous THF (2 mL) and anhydrous toluene (2 mL) was heated to 60 °C for 2 h and then to 105 °C for 20 h. Most of the solvent was removed under vacuum, and the product (0.30 g, 90% yield) was precipitated into methanol, filtered, and dried in a vacuum oven at 125 °C for 24 h. NMR resonances (ppm) follow. ²⁹Si NMR, δ : -31.2, -77.9, -78.9, -79.1, -79.3. ¹³C NMR, δ : 166.4, 166.3, 137.1, 136.1, 134.0, 133.9, 133.2, 132.0, 131.8, 131.6, 130.9, 130.5, 130.4, 130.3, 130.0, 129.2, 128.5, 127.8, 127.7, 127.6, 126.5, 125.5, 123.7, 121.0, 94.2, 87.7, -0.4. ¹H NMR, δ : 8.2–7.2 (64 H's, overlapping multiplets), 0.71 (6 H's).

Synthesis of Phenyl₇monohydroxyl–POSS ($Ph_7OH-POSS$). Under a nitrogen atmosphere, a solution of silicon tetrachloride (1.903 g, 11.2 mmol) and triethylamine (3.572 g, 35.3 mmol) in THF (20 mL) was added dropwise to a well-stirred THF (70 mL) solution of Ph₇trisilanol–POSS (9.965 g, 10.7 mmol) in a 100 mL round-bottom flask. After being stirred overnight at room temperature, the suspension was filtered, collecting both Ph₇Cl–POSS product and NEt₃HCl salt byproduct. After these solids were dissolved in THF (5 mL) and chloroform (15 mL), the silicon–chlorine bond was hydrolyzed with water (15 mL) and dilute HCl (2 mL) over a 90 min period. The aqueous layer was removed and extracted twice with chloroform. The combined organic layers were extracted with water, dilute HCl, water, and saturated brine and then dried with magnesium sulfate. After filtration, most of the solvent was removed under vacuum, and the product (9.37 g, 90% yield) was precipitated into methanol, filtered, and dried at 40 °C in a vacuum oven overnight. NMR resonances (ppm) follow. ²⁹Si NMR, δ : -77.9 (3 Si), -78.2 (3 Si), -78.3 (1 Si), -100.4 (1 Si). ¹³C NMR, δ : 134.45, 134.39, 131.11, 131.05, 130.22, 130.10, 128.11, 128.10. ¹H NMR, δ : 7.87 (14 H's, multiplet), 7.51 (7 H's, multiplet), 7.45 (14 H's, multiplet), 3.9 (1 H, broad singlet).

Synthesis of Ph- and Ibu-monosiloxymethyldianiline-POSS (Ph7 or Ibu7-da-POSS). Under a nitrogen atmosphere, a diethyl ether (5 mL) solution of triethylamine (0.314 g, 3.1 mmol) and (di((N-trimethylsilyl)₂-aniline)-4,4'-(chloromethylsilane) (1.701 g, 3.08 mmol) was added, dropwise, to a POSS solution of either Ibu7OH-POSS (2.50 g, 3.00 mmol) or Ph7OH-POSS (2.92 g, 3.00 mmol) dissolved in a mixture of diethyl ether (15 mL) and THF (2 mL), and stirred overnight at room temperature. The solution was filtered to remove HNEt₃Cl, and most of the solvent was removed under vacuum. Addition of acidified methanol (50 mL) and stirring the suspension for an hour at room temperature produced the free amine. The product (\sim 60% yield) was isolated by filtration, and dried in a vacuum oven overnight at 60 °C. NMR resonances (ppm) follow. **Ph₇da**-**POSS.** ²⁹Si NMR, δ : -8.0 (1 Si), -78.1 (3 Si), -78.2 (4 Si), -109.4 (1 Si). ¹³C NMR, δ: 147.75, 135.63, 134.53, 134.41, 130.96, 130.88, 130.38, 130.32, 128.06, 127.99, 125.63, 114.57, -0.38. ¹H NMR, δ: 7.83 (14 H's, multiplet), 7.80 (4 H's, multiplet), 7.52 (7 H's, multiplet), 7.44 (14 H's, multiplet), 6.56 (4 H's, multiplet), 3.82 (4 H's, broad singlet), 0.62 (3 H's, singlet). Ibu₇da–POSS. ²⁹Si NMR, δ : -9.4 (1 Si), -67.0 (3 Si), -67.9 (4 Si), -109.9 (1 Si). ¹³C NMR, δ: 147.54, 135.60, 126.39, 114.63, 25.91, 24.06, 23.97, 22.72, 22.67, 22.54, -0.32. ¹H NMR, δ: 7.40 (4 H's, multiplet), 6.67 (4 H's, multiplet), 3.79 (4 H's, broad singlet), 1.88 (7 H's, multiplet), 0.97 (42 H's, multiplet), 0.60 (17 H's, multiplet).

Synthesis of Ph- or Ibu-monosiloxymethyldi(phenylethynylphthalimide)-POSS (Ph₇ or Ibu₇diPEPI-POSS). Under a nitrogen atmosphere, a well-stirred solution of either Ph₇da-POSS (0.250 g, 2.06 mmol) or Ibu₇da-POSS (0.249 g, 2.36 mmol) and PEPA (2.03 equiv) in anhydrous THF (2 mL) and anhydrous toluene (2 mL) was heated to 60 °C for 2 h, and then to 105 °C for 20 h. Most of the solvent was removed under vacuum, and the product (~90% yield) was precipitated into methanol, filtered, and dried in a vacuum oven at 125 °C for 24 h. Both products show a small impurity by silicon NMR. NMR resonances (ppm) follow. **Ph₇diPEPI–POSS.** ²⁹Si NMR, δ : -8.7 (1 Si), -77.8 (3 Si), -78.2 (4 Si), -109.3 (1 Si). ¹³C NMR, δ : 166.4, 166.3, 137.1, 136.3, 134.7, 134.2, 134.1, 133.0, 132.0, 131.8, 131.7, 130.8, 130.3, 130.1, 130.0, 129.8, 129.3, 128.5, 127.9, 127.8, 126.5, 125.4, 123.7, 122.0, 94.3, 87.7, -0.9. ¹H NMR, δ: 8.1-7.2 (59 H's), 0.61 (3 H's). Ibu₇diPEPI-POSS. ²⁹Si NMR, δ: -10.2 (1 Si), -66.7 (3 Si), -67.8 (4 Si), -109.6 (1 Si). ¹³C NMR, δ: 166.5, 166.4, 137.1, 136.8, 134.7, 132.9, 132.0, 131.8, 131.5, 130.3, 130.0, 129.2, 129.1, 128.5, 128.1, 126.5, 126.4, 125.4, 123.7, 123.6, 122.0, 94.2, 87.7, 25.7, 25.6, 23.8, 23.7, 22.4, 22.3, -0.9. ¹H NMR, δ: 8.1-7.2 (24 H's), 1.9 (7 H's), 1.0 (42 H's), 0.67 (17 H's).

Synthesis of Phenyl₇aniline–POSS (Ph_7 aniline–POSS). In a drybox, under a nitrogen atmosphere, a THF (5 mL) solution of ((*N*-trimethlsilyl)₂-aniline-4-(trichlorosilane) (0.871 g, 2.35 mmol) and triethylamine (0.680 g, 6.72 mmol) was slowly added in a dropwise manner to a well-stirred THF (10 mL) solution of Ph₇trisilanol–POSS (2.015 g, 2.16 mmol) in a 100 mL round-bottom flask. This solution became cloudy after the addition of a few drops, indicating formation of HNEt₃Cl salt. After stirring at room-temperature overnight, filtration was used to separate product from salt, and the solvent was removed under vacuum. The free-amine was produced by addition of diethyl ether (2 mL) followed by a solution of a acidified methanol (20 mL) and





stirring for 1 h at room temperature. The product (1.36 g, 60% yield) was collected by filtration and dried in a vacuum oven overnight. NMR resonances (ppm) follow. $CD_2Cl_2^{-29}Si$ NMR, δ : -77.0 (1 Si), -78.3 (4 Si), -78.5 (3 Si). ¹H NMR, δ : 8.0–6.8 (37 H's, multiplet), 6.7 (2 H's, doublet), 3.6 (2 H's, broad singlet).

Synthesis of Ph₇(phenylethynylphthalimide) – POSS (**Ph₇PEPI**– **POSS**). A solution of (1.049 g, 1.00 mmol) of Ph₇aniline–POSS in toluene (25 mL) and (0.250 g, 1.01 mmol) of PEPA in DMAc (3 mL) were mixed in a 100 mL round-bottom flask equipped with a 20 mL Dean–Stark apparatus. The solution was heated to 110 °C (oil bath at 150 °C) for 5 h. After cooling, the product (1.23 g, 95% yield) was precipitated into methanol, filtered, and dried in a vacuum oven at 120 °C for 24 h. NMR resonances (ppm) follow. ²⁹Si NMR, δ : –78.1 (3 Si), –78.2 (4 Si), –78.7 (1 Si). ¹³C NMR, δ : 166.7, 166.6, 137.5, 135.3, 134.3, 134.1, 132.2, 132.1, 131.1, 131.0, 130.5, 130.5, 130.3, 130.2, 129.5, 128.8, 128.2, 128.1, 126.8, 125.8, 124.0, 122.2, 94.6, 87.9. ¹H NMR, δ : 8.2–6.7 (overlapping multiplets).

Characterization. Nuclear magnetic resonance spectroscopy was performed on a Bruker 300 spectrometer, using CDCl₃ solvent (unless otherwise noted), for ¹H (300 MHz), ¹³C (75 MHz), and ²⁹Si (60 MHz). NMR spectroscopy was also performed using a Varian Unity 500 spectrometer, for ¹H (500 MHz), ¹³C (125 MHz), and ²⁹Si (99 MHz). Spectra are referenced to internal CDCl₃ at 7.26 ppm (¹H) and 77.23 ppm (^{13}C) . ²⁹Si spectra are referenced to external Me₄Si at 0 ppm. Thermal characteristics and cross-link reactions were studied using Differential scanning calorimetry (DSC). DSC studies were performed using a Mettler-Toledo DSC-1 equipped with a mechanical cooling system. Samples were placed in a 40 μ L aluminum pan and sealed with a punctured lid. Melting and melt recrystallization behavior of various PEPI-POSS were studied by heating the sample from 25 °C to a temperature about 30 °C above the melting temperature with a rate of 20 °C/min, and held for 1 min, then cool back to 25 °C at 20 °C/min. All experiments were conducted in a nitrogen atmosphere. For phenylethynyl reaction studies, samples were heated from 100





to 500 °C with heating rates of 2, 5, 10, and 20 °C/min under a nitrogen atmosphere. To isolate the thermal characteristics of the phenylethynyl reactions from the thermal characteristics of POSS moiety itself, all DSC experiments on mono- and difunctional PEPI–POSSI were analyzed using DSC trace of Phenyl₈-Si₈O₁₂ or iBu₈Si₈O₁₂ as baseline. Fourier Transform-Infrared spectroscopy (FT-IR) data was obtained using a Varian-Digilab FTS3000 equipped with a liquid nitrogen cooled mercury cadmium telluride detector. Samples were prepared by mixing ~2 mg of sample with ~80 mg of KBr, and pressed into 7 mm diameter disks.

Results and Discussion

Synthesis. The methods devised to synthesize the three difunctional PEPI–POSS materials illustrated in Figure 1 are shown in Scheme 1 ($Ph_8bisPEPI-POSS$) and Scheme 2 ($Ph_7diPEPI-POSS$ and $Ibu_7diPEPI-POSS$).

To make Ph₈bisPEPI–POSS, which has an architecture that can put a POSS cage directly into the backbone of a cross-linked network, a dichlorosilane with a protected aniline group was required for reaction with the relatively new phenylPOSS tetra silanol.³⁵ (*N*-trimethylsilyl)₂-aniline-4-(dichloromethylsilane) was synthesized in high yield from (*N*-trimethylsilyl)₂-4-bromoaniline by generating a Grignard reagent that was subsequently metathesized with methyltrichlorosilane. Figure 2a shows the ²⁹Si NMR spectrum of this compound: as expected there are just two peaks at +18.9 and +5.2 ppm in a ratio of 1:2 for the dichloromethylaniline and the trimethylsilyl silicons. Figure 3a displays the ¹³C NMR spectrum. There are the expected 4 aromatic and two silyl methyl peaks.

This dichlorosilane is cleanly reacted with Ph₈tetrasilanol-POSS in the presence of a small excess of triethylamine to



Figure 2. ²⁹Si NMR of (a) (*n*-trimethylsilyl)₂-aniline-4-dichloromethylsilane, (b) cis/trans mixture of Ph₈bisaniline–POSS, (c)mostly *trans*-Ph₈bisaniline–POSS, (d) mostly *cis*-Ph₈bisaniline–POSS, and (e) Ph₈bisPEPI–POSS (both isomers). The insets show the effect of the symmetry differences on the T-silicon resonances.

promote the formation of a POSS with two protected amines. This molecule is deprotected with acid to generate equal amounts of cis- and trans-Ph₈bisaniline-POSS; their structures and ²⁹Si NMR spectra are shown in Figure 2b-d. Because of differences in solubility, it is possible to get reasonable separation of these isomers by crystallization. The higher symmetry trans-isomer (Figure 2c) shows an expected three ²⁹Si resonances at -29.9, -78.4, and -79.5ppm in a ratio of 2:4:4. The lower symmetry cis-isomer (Figure 2d) shows an expected four ²⁹Si resonances at -29.9, -78.4, -79.3, and -79.7 ppm in a ratio of 2:4:2:2. Theoretically, one would expect to see seven resonances displayed in spectrum 2b, but because of the very similar chemical environments for these two isomers, some of the cis- and trans-isomer resonances are isochronus (overlapping). This overlapping of similar chemical environment signals has been reported for other derivatives made from the POSS tetrol.³⁵ On the basis of symmetry arguments, the peak assignments are as follows: at -29.9 ppm (2 Si) are the aniline D-silicon atoms;³⁶ at -78.4 (4 Si) are the cage silicon atoms closest to the aniline-bearing silicon; at -79.5 (4 Si) are the trans-isomer's central silicon atoms; and at -79.3 (2 Si) and -79.7 (2 Si) are the cis-isomer's central silicon atoms. The ¹³C NMR spectrum of the isomeric mixture is displayed in Figure 3b. While it is not possible to assign all the

overlapping aromatic resonances, the single methyl carbon peak at 0.3 ppm is a clear indication of purity and that the amines are fully deprotected (SiMe₃ groups are absent).

The isomeric cis/trans mixture of Ph₈bisaniline-POSS was reacted with PEPA to generate the desired Ph₈bisPEPI-POSS. The ²⁹Si NMR spectrum is displayed in Figure 2e. A small upfield shift of the D-silicon is observed (Figure 2e), but the other silicon resonances remain approximately the same. The ¹³C NMR (Figure 3c) shows several peaks indicative of the addition of PEPA, including two overlapping carbonyl resonances at 166.4 and 166.3 ppm, as well as two alkyne resonances at 87.7 and 94.2 ppm. In addition, the aromatic carbon alpha to the nitrogen also shows a significant upfield shift, as the primary amine converts to a tertiary imide. Along with the NMR data, FT-IR studies confirm the structure. The IR spectrum of Ph₈bisPEPI-POSS shows imide carbonyl absorption peaks at 1727 and 1779 cm⁻ Other important peaks include an absorbance at 2213 cm⁻ which corresponds to an alkyne bond stretch and an absorbance at 1367 cm^{-1} , which is attributed to an aromatic-imide carbon-nitrogen stretch.

The synthesis of the $Ph_7diPEPI-POSS$ and $Ibu_7diPEPI-POSS$ compounds is shown in Scheme 2, and ²⁹Si NMR spectra related to the synthesis of the phenyl derivative are displayed in Figure 4. To make $R_7diPEPI-POSS$ (R = Ph or



Figure 3. ¹³C NMR of (a) (*n*-trimethylsilyl)₂-aniline-4-dichloromethylsilane, (b) Ph₈bisaniline–POSS (cis and trans isomers), and (c) Ph₈bisPE-PI–POSS (cis and trans isomers).

iBu), which have an architecture that can put a POSS cage pendent to the backbone of a cross-linked network, a monochlorosilane with two protected aniline groups was required for reaction with a POSS-monosilanol. Di((*N*trimethylsilyl)₂-aniline)-4,4'-(chloromethylsilane) was synthesized in high yield from (*N*-trimethylsilyl)₂-4-bromoaniline by generating a Grignard reagent that was subsequently metathesized with half an equivalent of methyltrichlorosilane. Figure 4a shows the ²⁹Si NMR spectrum of this compound: as expected there are just two peaks at +10.7 and +4.8 ppm in a ratio of 1:4 for the chloromethyldianiline and the trimethylsilyl silicons.

The POSS monosilanol, $R_7Si_8O_{12}$ (OH) is made by reacting POSS trisilanol, $R_7Si_7O_9$ (OH)₃, with tetrachlorosilane and then hydrolyzing the remaining silicon–chloride bond. The ²⁹Si NMR spectrum of the phenyl derivative is displayed in Figure 4b. There are three resonances near -78 ppm in the expected 3:3:1 ratio for the seven T-type cage silicon atoms, in three inequivalent chemical environments. There is one silicon peak near -100 ppm for the Q-type silicon containing the silanol functionality.

The di((n-trimethylsilyl)₂-aniline)-4,4'-chloromethylsilane was grafted to the POSS monosilanol using a slight excess of NEt₃ to both catalyze the reaction and drive it to completion by removal of HCl. The T-type silicon resonances shift slightly to give two resonances in a ratio of 3:4 while the Q-type silicon resonance shifts from -100 to -109 ppm (Figure 4c). There is also an M-type silicon resonance at -8.1 ppm which displays a typical 20 ppm upfield shift for replacement of a Si–Cl bond with a Si–O bond. Upon addition of PEPA, the 29 Si NMR (Figure 4d) is similar to that of the diamines, with only a slight shift of the M–silicon to -8.7 ppm. Carbon NMR and FT-IR also confirms the addition of PEPA.

The monofunctional POSS compound, Ph7PEPI-POSS, was synthesized as outlined in the Experimental Section. This chemistry is very similar what was just discussed. A Grignard reagent made from (N-trimethylsilyl)₂-4-bromoaniline, was added to SiCl₄ to make (N-trimethlsilyl)₂aniline-4-trichlorosilane. Its ²⁹Si NMR spectrum displays 2 peaks in a ratio of 2:1 at +5.5 ppm (SiMe₃) and at -0.8 ppm (SiCl₃). This molecule is reacted with phenylPOSS trisilanol, $Ph_7Si_7O_9(OH)_3$, and the TMS groups are removed with acid, to generate Ph₇anilinePOSS. The ²⁹Si NMR spectrum has three resonances in a ratio of 1:4:3 at -77.0 ppm (aniline silicon), 78.3 and -78.5 ppm, (phenyl silicons). Once the PEPA group is attached, the silicon attached to the aniline group shifts from -77.0 to -78.7 ppm. Carbon NMR and FT-IR analysis also confirms the structure, with carbonyl and alkyne resonances and absorptions the similar as those outlined for Ph₈bisPEPI-POSS.

Thermal Characteristics of PEPI–POSS Molecules. As shown by NMR, PEPI–POSS molecules reported here were all well-defined chemicals with a known molar formula weight of PEPI. Therefore, DSC results reported were all normalized with respect to moles of PEPI for systematic comparison. In the following, we present the results of the thermal characteristics of PEPI–POSS molecules as affected by the peripheral moiety, the spacer group between the PEPI



Figure 4. ²⁹Si NMR of (a) bis((*n*-trimethylsilyl)₂-aniline)-4,4'-chloromethylsilane, (b) Ph₇OH–POSS, (c) Ph₇diamine–POSS, and (d) Ph₇diPEPI–POSS.

and the inorganic core of the POSS cage, and the architecture of the PEPI attachment to the inorganic core of the POSS cage.

POSS Molecules with Isobutyl Periphery. All POSS molecules containing the isobutyl periphery exhibited a first-order melt in heating and a recrystallization in cooling. Upon examining samples in the DSC crucible after the heating and cooling cycles, all isobutyl PEPI–POSS molecules show good melt flow characteristics in the aluminum DSC crucible.

Two monofunctional PEPI-POSS molecules with isobutyl periphery examined here, Ibu₇propylPEPI-POSS and Ibu₇phenylPEPI-POSS, showed a melting temperature of 157 and 238 °C, respectively. As a comparison, the DSC of octaisobutyl-POSS (Ibu₈-POSS) was obtained and found to exhibit the similar first-order solid-to-liquid melting transition. The onset of melting occurs at 263 °C. The lower melting points for Ibu7propylPEPI-POSS and Ibu7phenyl-PEPI-POSS as compared to Ibu₈-POSS can be attributed to the reduced POSS-POSS interactions when replacing one of the eight isobutyl groups with either a propyl- or phenyl-PEPI group. The higher melting temperature for Ibu₇phenylPEPI-POSS as compared to Ibu₇propylPEPI-POSS was hypothesized due to a more rigid phenyl group and the possible additional phenyl-phenyl interactions. This hypothesis was further supported by comparing the cooling curves. At a 20 °C/min cooling rate, an undercooling of about 70 °C was required for Ibu7propylPEPI-POSS to form crystals, while only 60 °C of undercooling was observed for Ibu₇phenylPEPI–POSS. Besides the onset temperatures of melting and recrystallization, DSC traces also provided $\Delta H_{\rm m}$ (heat of melting from the area of the endothermic melting peak) and $\Delta H_{\rm c}$ (heat of recrystallization from the area of the exothermic crystallization peak). The value of $\Delta H_{\rm c}/\Delta H_{\rm m}$ relates to the extent of crystallization in a crystalline-forming molecule at the specified cooling condition. Results show about 85% for Ibu₇phenylPEPI–POSS while only about 60% crystallization occurred for Ibu₇propylPEPI– POSS, which demonstrated the enhanced crystallization due to the additional phenyl–phenyl interactions.

For difunctional PEPI–POSS molecules with isobutyl peripheries, Ibu₇diPEPI–POSS, it shows a melting point at around 190 °C. Upon cooling at 20 °C/min, the extent of undercooling required to form crystals is similar to the Ibu₇propylPEPI–POSS. However, only about 36% was crystallized at this cooling rate. The decrease in the degree of crystallization was directly attributed to the size of di-PEPI functionality at the corner of the POSS cage.

POSS Molecules with Phenyl Periphery. The thermal transitions of POSS molecules with a phenyl periphery were different than those with the isobutyl periphery. The mono-functional Ph₇phenylPEPI–POSS, when heated from room temperature to 500 °C, shows only peaks associated with the exothermic reactions of phenylethyenyl. After curing, the sample remains in a powdery form, indicating a lack of flow

Table 2. Results of the nth order reaction kinetics model analysis^a

Temp. (°C)	Ibu ₇ p	Ibu7propyl		Ibu ₇ phenyl		Ph ₇ phenyl		Ibu7di		Ph7di		Ph ₈ bis		Octapropyl		Octaphenyl		HFPE-n-9	
	k	n	k	n	k	n	k	n	k	n	k	n	k	n	k	n	k	n	
340			0.87	1.15			1.40	1.86	0.71	1.48	1.53	1.95	1.75	1.59	1.06	1.43			
350	1.09	1.25	1.25	1.02			1.90	1.55	1.12	1.37	2.66	1.93	2.34	1.28	1.32	1.22			
360	1.67	1.18	1.92	0.95	0.14	0.63	2.69	1.35	1.79	1.29	3.93	1.82	3.27	1.00	1.64	0.98	1.03	1.66	
370	2.47	1.10	2.02	0.91	0.36	0.63	3.94	1.18	2.92	1.29	5.44	1.55	4.89	0.77	2.05	0.74	1.76	1.62	
380	3.62	1.00	4.67	0.88	0.71	0.60	6.14	1.08	4.45	1.24	8.02	1.39	8.06	0.61	2.89	0.61	2.56	1.29	
390	5.33	0.89	7.19	0.85	1.29	0.55	9.74	0.96	6.75	1.18	11.74	1.23	14.92	0.50	4.51	0.52	4.07	1.08	
400	8.13	0.77	10.84	0.81	2.39	0.49	16.58	0.85	10.33	1.67							6.77	0.96	
410	13.2	0.65	15.96	0.75	4.84	0.43											12.04	0.87	

^{*a*} Reaction rate constant, $k \pmod{1}$, of phenylethynyl and order of reaction, *n*, at different temperatures for various PEPI–POSS molecules. Analysis was performed using dynamic heating curves at four different heating rates as obtained by DSC.

in $Ph_7phenylPEPI-POSS$ upon melting at atmospheric pressure. This is similar to the octaphenyl-POSS (Ph_8-POSS) where a very strong phenyl-phenyl interaction inhibits solid-to-liquid transition in a normal atmosphere.

The difunctional PEPI-POSS molecules with phenyl peripheries, Ph7diPEPI-POSS, was the only phenyl-POSS molecule reported in this study to exhibit a melting transition, which occurs at about 296 °C. This was more than 100 °C above Ibu7diPEPI-POSS. The high melting temperature indicates the phenyl periphery provides stronger POSS-POSS interactions than the isobutyl. However, it was difficult to examine the kinetics of Ph7diPEPI-POSS to form crystals upon cooling from the melt. This was due to a partial overlapping of the melting transition with the phenylethyenyl reaction. Altering the attachment architecture of PEPI to the inorganic core of the POSS, Ph₈bisPEPI-POSS shows a T_{g} at 100 °C. The lack of crystallinity in Ph₈bisPEPI-POSS was attributed to the cis/trans isomeric mixture. A more careful investigation on the effect of isomeric states is ongoing. Results will be reported in the near future. However, more importantly for the intended composite matrix appli heating above their thermal transitions at the atmospheric pressure.

POSS Molecules with Eight Phenylethynyl Groups. To further evaluate the influence of the spacer group between the reactive PEPI and the inorganic core of the POSS, two octafunctional PEPI–POSS molecules were examined. OctapropylPEPI–POSS has a melting temperature of 234 °C, whereas octaphenylPEPI–POSS exhibits a glass transition temperature of 205 °C. Both molecules show good flow upon heating past their respective thermal transitions. This observation is important for using these molecules as matrix materials in composite applications.

OctapropylPEPI–POSS can be easily crystallized upon cooling from the melt. At a rate of 20 °C/min, only 45 °C of undercooling is needed to initiate crystallization, with 85 wt % transformed to the crystalline phase with continuous cooling. The lower undercooling and higher extent of crystallization of octapropylPEPI–POSS as compared to Ibu₇propylPEPI– POSS, Ibu₇phenylPEPI–POSS, and Ibu₇diPEPI–POSS can be attributed to the identical chemical moiety surrounding the inorganic core of the POSS.

Kinetics of PEPI–POSS Reactions. The dynamic heating method was used to investigate phenylethynyl reaction kinetics of all PEPI-functionalized POSS molecules synthesized. Four different heating rates ranging from 2 to 20 °C per minute were used. Analysis based on the *n*th order kinetics model combined with the Arrhenius assumption for the temperature function of the reaction rate constant was performed on these dynamic heating curves.³⁷ Results of this analysis were tabulated and shown in Tables 2 and 3. Typical exothermic profiles representing reactions of phenylethynyl for the different PEPI–POSS molecules were also

depicted in Figures 5–10. In the *n*th order kinetics model, the reaction rate constant and value of *n* were determined as a function of temperature. Since the value of *n* varies with temperature, the activation energy was affected by the temperature. However, the activation energy for a specific PEPI–POSS molecule, as listed in Table 3, was associated with the maximum cure rate temperature, which was the peak temperature of the exothermic reaction peak. The validity of the activation energy obtained was verified, as the extent of reaction at the peak maximum with respect to the overall reaction was found to be independent of the heating rate. Following are additional discussions regarding the effect of peripheral moiety, the spacer group between PEPI and the POSS core, and the architecture of the PEPI attachments to the POSS cage on the reaction kinetics of phenylethynyl.

POSS Peripheral Effects. In Figure 5, the reaction profile of Ibu7phenylPEPI-POSS was compared to Ph7phenylPEPI-POSS. As shown, the curing profile of Ph₇phenylPEPI-POSS was relatively broad and had at least two discernible peaks. Since the number of reactive phenylethynyl groups per POSS molecule was known, the normalized exothermic heat flow per mole of POSS was plotted versus temperature. The total heat of reaction, ΔH_{Rxn} , under different heating rates varies a little more for Ph₇phenylPE-PI-POSS, as compared to Ibu₇phenylPEPI-POSS, $107 \pm$ 35 versus 175 \pm 11 kJ/mol. Furthermore, the activation energy for the maximum curing rate was higher for Ph₇phenylPEPI-POSS as compared to Ibu₇phenylPEPI-POSS, 203 versus 105 kJ/mol, as was the peak reaction temperature at the same heating rate. The higher activation energy could be partially attributed to the thermal characteristics of Ph₇phenylPEPI-POSS prior to the phenylethynyl reaction, since it lacks any kind of flow as previously mentioned. In addition, this lack of flow may also contribute to the larger variance observed in the value of ΔH_{Rxn} at different heating rates. Nevertheless, for monofunctional PEPI-POSS molecules, the mean value of $\Delta H_{\rm Rxn}$ was found to be smaller for POSS with the phenyl periphery than that with the isobutyl. To further evaluate this observation, reaction kinetics of difunctional PEPI-POSS with phenyl and isobutyl peripheries were investigated.

The reaction profiles for difunctional PEPI–POSS molecules with phenyl and isobutyl peripheries are shown in Figure 6. Unlike monoPEPI–POSS, both Ph₇diPEPI–POSS and Ibu₇diPEPI–POSS exhibit good flow characteristics prior to any phenylethynyl reactions. Hence, no significant variance of the values of ΔH_{Rxn} at different heat rates was observed for both Ph₇diPEPI–POSS and Ibu₇diPEPI–POSS. The activation energies at maximum curing rate for both POSS molecules were also similar to each other, 149 and 146 kJ/mol, respectively. However, similar to monofunctional PEPI–POSS molecules, the reaction peak temperature of Ph₇diPEPI– POSS was higher than Ibu₇diPEPI–POSS at the same

Table 3. Characteristics of Phenylethynyl Reaction Profiles^a

compound	$T_{\rm Rxn,\ max}$ at 2, 5, 10, 20°C/min rate	$\Delta H_{\rm Rxn} ({\rm kJ/mol})$	$\Delta H_{\mathrm{partial}}/\Delta H_{\mathrm{total}}$	activation energy (kJ/mol)
Ibu7propylPEPI-POSS	355.8, 375.0, 392.1, 410.0	176 ± 9	51 ± 3	140
Ibu7phenylPEPI-POSS	359.5, 377.5, 391.3, 409.6	175 ± 11	60 ± 2	155
Ph ₇ phenylPEPI-POSS	382.4, 400.0, 405.9, 420.2	107 ± 35	52 ± 3	203
Ibu ₇ diPEPI-POSS	349.3, 368.2, 384.3, 400.4	163 ± 16	54 ± 2	146
Ph ₇ diPEPI- POSS	361.3, 378.8, 394.2, 413.7	84 ± 1	58 ± 2	149
Ph ₈ bisPEPI-POSS	343.1, 359.6, 375.6, 395.0	134 ± 13	49 ± 2	141
OctapropylPEPI-POSS	331.0, 349.3, 367.4, 382.6	143 ± 7	41 ± 4	143
OctaphenylPEPI-POSS (LTP)	326.0, 349.6, 362.0, 373.9	95 ± 7	22 ± 3	143
OctaphenylPEPI-POSS (HTP)	352.5, 372.9, 391.0, 407.3	95 ± 7	49 ± 5	137
HFPE-n-9	365.2, 385.1, 396.3, 410.7	140 ± 24	47 ± 2	175
HFPE-n-1	363.1, 382.0, 394.4, 415.3	131 ± 3		152

[Note:] ^{*a*} $T_{\text{Rxn, max}}$ is the reaction peak maximum temperatures at the specified heating rate; ΔH_{Rxn} is the average heat of reaction per mole of PEPI and its range from four different heat rates used; $\Delta H_{\text{partial}}/\Delta H_{\text{total}}$ and activation energy are the extent of reaction and energy barrier of reaction at $T_{\text{Rxn,max}}$, respectively.



Figure 5. Phenylethynyl reaction profiles of Ph₇phenylPEPI–POSS (solid line) and Ibu₇phenylPEPI–POSS (dashed line) with a heating rate of 10 °C per minute. The *y*-axis is the normalized heat flow with respect to the mole of POSS. Each POSS has one PEPI group.

heating rate. Values of ΔH_{Rxn} are also smaller for Ph₇diPE-PI–POSS as compared to Ibu₇diPEPI–POSS, 84 kJ/mol versus 163 kJ/mol. The reaction rate constant of phenylethynyl at a specific temperature was smaller for POSS with a phenyl periphery than POSS molecules with an isobutyl periphery, regardless of the functionality of the PEPI attached to the POSS core. Overall, it appears that the phenyl peripheries restrict or retard phenylethynyl reactions.

PEPI-POSS Spacer Effects. Figure 7 shows the phenylethynyl reaction profiles of Ibu7propylPEPI-POSS and Ibu₇phenylPEPI-POSS. Ibu₇phenylPEPI-POSS has a higher extent of reaction before the peak maximum, 60%, as compared to Ibu₇phenylPEPI-POSS, 51%, with both. having similar values of peak reaction temperature at the same heating rates, as shown in Table 3. Infrared spectroscopy was used to determine the extent of the loss of the alkyne group at the cure peak maximum for each of these molecules, using the 1779 cm^{-1} carbonyl stretch as an internal reference. The Ibu7phenylPEPI-POSS molecule had an 80% loss of the alkyne peak, whereas the Ibu7propylPEPI-POSS molecule had a 72% loss of the alkyne peak at the cure peak maximum. The rate constant for Ibu7phenylPEPI-POSS was higher than Ibu₇propylPEPI–POSS at temperatures below the cure peak maximum. These results suggest that it was easier to initiate the phenylethynyl, polyene reaction when the phenylethynyl group was attached to a more rigid spacer. However, these two POSS molecules were monofunctional, hence the subsequent network-like reactions were limited.



Figure 6. Phenylethynyl reaction profiles of Ph₇diPEPI–POSS (solid line) and Ibu₇diPEPI–POSS (dashed line), with a heating rate of 10 °C per minute. The *y*-axis is the normalized heat flow with respect to the moles of POSS. Each POSS molecule has two PEPI groups.

Therefore, the value for the overall ΔH_{Rxn} was the same for both molecules. To further explore the influence of spacer group on the phenylethynyl reactions, octafunctional POSS molecules were investigated.

The reaction profiles of octaphenylPEPI-POSS and octapropylPEPI-POSS are shown in Figure 8. Unlike their monofunctional counterparts, both octafunctional POSS molecules exhibit a more asymmetrical reaction profile with a much longer tail at the higher temperature region of reaction curves. This suggests that there exist multiple, complex reaction mechanisms after the initial polyene reaction, as the order of reaction changed from about 1.5 at 340 °C to about 0.5 at 390 °C. However, it appears that the octaphenylPEPI-POSS had two strongly overlapping broad peaks. The extent of the overlap becomes lesser as the heating rate increases, as shown in Figure 9. In Table 3, values of the low temperature peak, LTP, of octaphenylPEPI-POSS at different heating rates were similar to the value of reaction peak maximum of octapropylPEPI-POSS. Hence, the activation energies for both POSS molecules were also similar to each other.

However, the extent of reaction was different from each other, 22% versus 41%. Furthermore, the rate constant for octaphenylPEPI–POSS was much lower than that of octapropylPEPI–POSS and the overall reaction was smaller for octaphenylPEPI–POSS as compared to octapropylPE-PI–POSS, 95 versus 143 kJ/mol. These observations suggest that the flexibility of the spacer group between PEPI and the



Figure 7. Phenylethynyl reaction profiles of Ibu₇phenylPEPI–POSS (solid line) and Ibu₇propylPEPI–POSS (dashed line), with a heating rate of 10 °C per minute. The *y*-axis is the normalized heat flow with respect to the moles of POSS. Each POSS molecule has one PEPI group.



Figure 8. Phenylethynyl reaction profiles of octaphenylPEPI–POSS (solid line) and octapropylPEPI–POSS (dashed line), with a heating rate of 10 °C per minute. The *y*-axis is the normalized heat flow with respect to the moles of POSS. Each POSS molecule has eight PEPI groups.

POSS $SiO_{1.5}$ core affects the extent of initial phenylethynyl reactions and the extent of cure increases as the spacer group becomes more flexible.

Architectural Effects. The architecture of the PEPI attachment to the POSS SiO_{1.5} core was investigated by comparing Ph₈bisPEPI–POSS and Ph₇diPEPI–POSS, as shown in Figure 10. It was apparent that the onset of reaction temperature was lower for Ph₈bisPEPI–POSS as compared to Ph₇diPEPI–POSS, and the overall ΔH_{Rxn} was higher for Ph₈bisPEPI–POSS, 134 kJ/mol versus 84 kJ/mol. The reaction rate constants were also higher for Ph₈bisPEPI–POSS during the entire temperature range of phenylethynyl reactions. These observations suggest that the "in-chain" morphology of Ph₈bisPEPI–POSS allows for a great accessibility of phenylethynyl reactions when compared to that of the "T-shaped" Ph₇diPEPI–POSS.

Comparison to HFPE Oligoimides. Reaction kinetics of these PEPI–POSS molecules was compared to high temperature organic thermosetting oligoimides with hexafluorophenylethynyl, HFPE-*n*-9 and HFPE-*n*-1. On the basis of the results tabulated in Table 2 and 3, it was clear that the



Figure 9. Phenylethynyl reaction profiles of octaphenylPEPI–POSS, at 20 °C/min (solid line), 10 °C/min (dashed line), 5 °C/min (dotted line), and 2 °C/min (dashed–dotted line) heating rates.



Figure 10. Phenylethynyl reaction profiles of Ph₇diPEPI–POSS (solid line) and Ph₈bisPEPI–POSS (dashed line), with a heating rate of 10 °C per minute. The *y*-axis is the normalized heat flow with respect to the moles of POSS. Each POSS molecule has two PEPI groups.

phenylethynyl reaction kinetics were comparable. Therefore, these PEPI–POSS molecules can be cocured with HFPE oligoimides without any modifications on the curing temperature profile used in composite processing.

Conclusions

A series of phenylethynyl-functionalized POSS molecules were synthesized and studied to determine the effect of the peripheries, the space group between the PEPI and the core of the POSS cage, and the architecture of the PEPI attachment to the core of the POSS cage on the thermal characteristics of different PEPI-POSS molecules and the kinetics of phenylethynyl curing reaction. It was shown that these POSS modifications had an impact on activation energy, heat of fusion, and the overall reaction profile. Changing the peripheries of POSS from isobutyl to phenyl resulted in a restriction or retardation of phenylethynyl reactions. Changing the spacer group between the PEPI and the core of the POSS from a flexible propyl to a less flexible phenyl had an effect on the extent of initial curing with mono and octafunctional POSS molecules and caused a decrease in the extent of cure with octafunctional POSS molecules. Architecturally, changing the PEPI attachments from an "in-chain"

Article

structure to a "pendant" structure resulted in a decrease in the extent of curing reaction. Overall, the organic peripheries, the spacer group and the architecture of attachment have an important impact on the curing reactions of phenylethynyl. By selecting appropriate combinations, the curing kinetics of PE-PI-POSS molecules can be tuned and made comparable with organic phenylethynyl oligoimides, which enables the realization of curable hybrid inorganic–organic materials as the matrix materials in fiber reinforced composites.

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Supporting Information Available: Text giving the details of the syntheses of several protected aminochlorosilanes: ((*N*-trimethylsilyl)₂-aniline-4-(dichloromethylsilane), (di((*N*-trimethylsilyl)₂-aniline)-4,4'-(chloromethylsilane), and ((*N*-trimethylsilyl)₂-aniline)-4,4'-(chlorosilane). This material is available free of charge via the Internet at http://pubs.acs.org.

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