# Synthesis and Thermal Curing of Aryl-Ethynyl-Terminated *co*POSS Imide Oligomers: New Inorganic/Organic Hybrid Resins

Michael E. Wright,*[†] Derek A. Schorzman,[†] Frank J. Feher,*[‡] and Ren-Zhi Jin[‡]

*Department of Chemistry, Virginia Commonwealth University,*
*Richmond, Virginia 23284-2006, and Department of Chemistry, University of California,*
*Irvine, California 92697-2025*

*Received March 19, 2002. Revised Manuscript Received October 14, 2002*

A new bis(amino)-functionalized POSS monomer was prepared and characterized with the formula *diexo*-($c$-$C_5H_9$)$_8$$Si_8O_{11}$($p$-$C_6H_4NH_2$)$_2$ . The new POSS monomer (1−10 mol %) along with diamines 1,3-bis(3-aminophenoxy)benzene (APB) and 3,4′-oxydianiline (ODA) and were copolymerized with 4,4′-oxydiphthalic anhydride (ODPA) and two reactive end-caps, 4-(aryl-ethynyl)phthalic anhydride {where aryl = phenyl and 9-anthracenyl} to afford a series of new inorganic/organic imide oligomers. The oligomers containing 1% and 10% POSS gave similar $T_g$ data (≈191 and 203 °C) as the pure organic imide oligomers and were shown to thermally cure to afford solvent-resistant and high $T_g$ resins. The thermal curing kinetic data for the 10%-POSS-containing imide was obtained. The kinetic data showed the rate of thermal curing to be unaffected (within experimental deviation) by the addition of the POSS units.

## Introduction

Polyhedral oligomeric silsesquioxanes (POSS), a family of nanoscale inorganic cage structures consisting of a silicon and oxygen framework, have attracted significant attention due to their unique physical and chemical properties.[1−6] Such POSS structures can be synthesized bearing organic substituents to afford an organic/inorganic hybrid material with an inorganic core and organic periphery. POSS structures are well-suited for the synthesis of hybrid organic/inorganic materials with a variety of potential applications.[5−12] The desirable properties of POSS such as abrasion resistance, thermal stability, and increased oxidative and ultraviolet stability will contribute to the bulk properties of such hybrid materials. The use of POSS-bearing polymerizable substituents in the synthesis of organic polymers has afforded hybrid materials consisting of an organic backbone with pendent POSS cages.[5−11] Other potential methods to hybrid materials include blending of POSS with existing polymers.[12] However, simple methods of incorporating POSS cages into useful materials remain relatively sparse.

We have determined that the incorporation of POSS structures into the well-established and high-performance thermally cured resins of phenyl-ethynyl-terminated imide (PETI) oligomers[13−36]will likely enhance the properties and utility of the existing resins. Such resins

---

* To whom correspondence should be addressed.

[†] Virginia Commonwealth University.

[‡] University of California.

(1) Murugavel, R.; Chandrasekhar, V.; Roesky, H. W *Acc. Chem. Res.* **1996**, *29*, 183−189.

(2) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205−2236.

(3) Feher, F. J.; Budzichowski, T. A *Polyhedron* **1995**, *14*, 3239−3253.

(4) Haddad, T. S.; Lichtenhan, J. D. *Macromolecules* **1996**, *29*, 7302−7304. Gilman, J. W.; Schlitzere, D. S.; Lichtenhan, J. D. *J. Appl. Polym. Sci.* **1996**, *60*, 591, and references therein.

(5) Tsuchida, A.; Bolln, C.; Sernetz, F. G.; Frey, H.; Mülhaupt, R. *Macromolecules* **1997**, *30*, 2818−2824.

(6) Costa, R. O. R.; Vasconcelos, W. L.; Tamaki, R.; Laine, R. M. *Macromolecules* **2001**, *34*, 5398−5407. Laine, R. M.; Choi, J.; Lee, I. *Adv. Mater.* **2001**, *13*, 800−803. Choi, J.; Harcup, J.; Yee, A. F.; Zhu, Q.; Laine, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 11420−11430, and references therein. Octa(aminophenyl)silsesquioxane is mentioned to form “imide resins.” The only characterization of the material mentioned was TGA analysis. See: Tamaki, R.; Tanaka, Y.; Asuncion, M. Z.; Choi, J.; Laine, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 12416−12417.

(7) Shokey, E.; Bolf, A. G.; Lichtenhan, J. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*, 515−516. Blanski, R. L.; Phillips, S. H.; Chaffee, K.; Lichtenhan, J.; Lee, A.; Geng, H. P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41*, 585−586. Fu, B. X.; Zhang, W.; Hsiao, B. S.; Johansson, G.; Sauer, B. B.; Phillips, S.; Balnski, R.; Rafailovich, M.; Sokolov, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41*, 587−588.

(8) For an example of polyacrylates functionalized with silsesquioxanes see: Kim, K.-M.; Chujo, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 4035.

(9) Gao, F.; Culbertson, B. M.; Tong, Y.; Schricker, S. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41*, 580−581.

(10) Haddad, T. S.; Lee, A.; Mather, P. T.; Phillips, S. H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41*, 584.

(11) Mather, P. T.; Chun, S. B.; Pyun, J.; Matyjaszewski, K.; Jeon, H. G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41*, 582−583.

(12) For a recent compilation of papers in the area see: *Organic/Inorganic Hybrid Materials*; Klein, L.; De Guire, M, Lorraine, F., Mark, J., Eds.; MRS Symposium Series 576; Materials Research Society: Warrendale, PA, 1999.

(13) Wright, M. E.; Schorzman, D. A. *Macromolecules* **2001**, *34*, 4768−4773.

(14) Ayambem, A.; Mecham, S. J.; Sun, Y.; Glass, T. E.; McGrath, J. E. *Polymer* **2000**, *41*, 5109−5124.

(15) Chang, A. C.; Jensen, B. J. *J. Adhes.* **2000**, *72*, 209−217.

(16) Cho, D.; Drzal, L. T. *J. Appl. Polym. Sci.* **2000**, *76*, 190−200.

(17) Connell, J. W.; Smith, J. G., Jr.; Hergenrother, P. M. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **2000**, *C40*, 207−230.

(18) Connell, J. W.; Smith, J. G., Jr.; Hergenrother, P. M.; Rommel, M. L. *High Perform. Polym.* **2000**, *12*, 323−333.

(19) Fang, X.; Xie, X. Q.; Simone, C. D.; Stevens, M. P.; Scola, D. A. *Macromolecules* **2000**, *33*, 1671−1681.

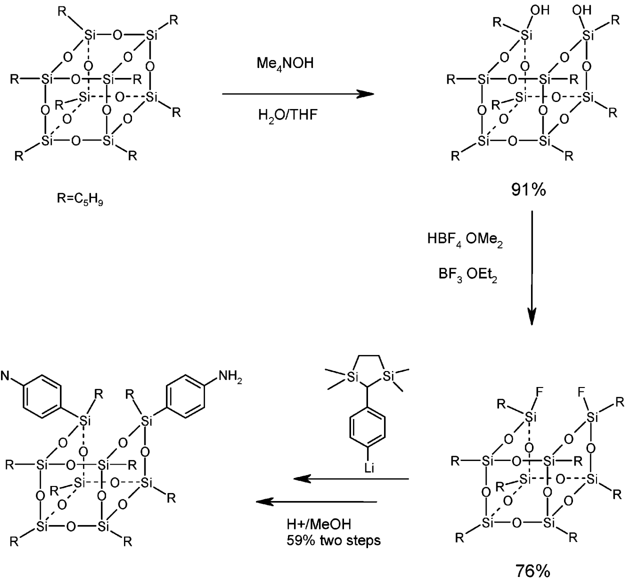
10.1021/cm020238h CCC: $25.00

should incorporate the desirable properties of PETI and POSS into a high-performance organic/inorganic hybrid resin. Additionally, recent studies of end-cap model compounds, new end-capping reagents, and new aryl-ethynyl end-capped oligomeric analogues of NASA's PETI-5 conducted in our laboratory have resulted in the development of a new class of aryl-ethynyl end-caps.[13,25,27] The substitution of the terminal phenyl unit with various polycyclic aromatics drastically modifies the thermal curing kinetics (i.e., anthracenyl-ethynyl cures much faster than phenyl-ethynyl) while the desirable properties of the cured resin appear to be retained. This simple modification method should further enhance the versatility of imide/POSS hybrid materials. Herein, we report the synthetic incorporation of POSS into aryl-ethynyl end-capped imide oligomers as well as physical and kinetic characterization of the oligomers and cured resins therefrom.

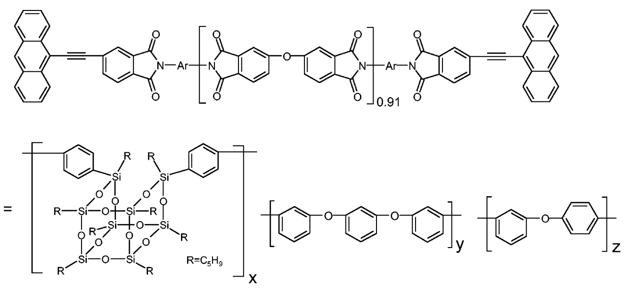
## Results and Discussion

**Synthesis of *diexo*-($c$-$C_5H_9$)$_8Si_8O_{11}$($p$-$C_6H_4NH_2$)$_2$ and the Aryl-Ethynyl-Terminated *co*POSS Imide Oligomers.** A POSS framework with two anilino pendant groups was prepared in good overall yield as outlined in Scheme 1. Several aspects of the synthesis are worth noting. First, the formation of the intermediate difluorosilsesquioxane from ($c$-$C_5H_9$)$_8Si_8O_{12}$ is best accomplished in two steps (i.e., base-mediated hydrolysis[37] and fluoridation[38] rather than the direct reaction of ($c$-$C_5H_9$)$_8Si_8O_{12}$ with $HBF_4{\cdot}OMe_2/BF_3$,[39] which is difficult to achieve with high conversion. Second, all steps in the scheme can be accomplished with multigram quantities (>40 g) and with strict stereochemical control at Si to produce a pure monomer with two aniline groups located in *exo* positions. Finally, the $p$-$C_6H_4NH_2$ groups attached to Si appear to be relatively resistant to protodesilylation, and there is no evidence for cleavage of Si-aryl bonds during the final deprotection step.

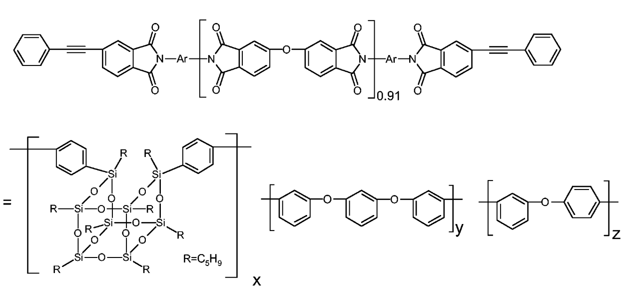
**Scheme 1**



coPOSS-AnETI-5-ODPA



coPOSS-PETI-5-ODPA



The oligomers used in this study are synthesized using procedures analogous to those reported for PETI-5-ODPA.[13,32] The bis(amino)-functionalized POSS monomer (POSS) was incorporated into the oligomers at 1% and 10%, and molar equivalents of the remaining diamine monomers, 1,3-bis(3-aminophenoxy)benzene (APB) and 3,4′-oxydianiline (ODA), were adjusted accordingly to retain the appropriate stoichiometry of PETI-5−ODPA (Table 1). End-capping of *co*POSS−AnETI-5−ODPA oligomers is carried out using our new end-capping reagent, 4-(9-anthracenylethynyl)phthalic anhydride (AnEPA), and end-capping of *co*POSS−PETI-5−ODPA oligomers is achieved using the commercially available end-capping reagent 4-(phenylethynyl)phthalic anhydride (PEPA). Hence, the oligomers 1%-POSS−

---

(20) Hergenrother, P. M.; Connell, J. W.; Smith, J. G., Jr. *Polymer* **2000**, *41*, 5073−5081.
(21) Hinkley, J. A.; Proctor, D. A. *J. Adv. Mater.* **2000**, *32*, 35−41.
(22) Holland, T. V.; Glass, T. E.; McGrath, J. E. *Polymer* **2000**, *41*, 4965−4990.
(23) Smith, J. G., Jr.; Connell, J. W. *High Perform. Polym.* **2000**, *12*, 213−223.
(24) Smith, J. G., Jr.; Connell, J. W.; Hergenrother, P. M. *J. Compos. Mater.* **2000**, *34*, 614−627.
(25) Wright, M. E.; Schorzman, D. A.; Pence. L. E. *Macromolecules* **2000**, *33*, 8611−8617.
(26) Preston, C. M. L.; Jill, D. J. T.; Pomery, P. J.; Whittaker, A. K.; Jensen, B. J. *High Perform. Polym.* **1999**, *11*, 453−465.
(27) Wright, M. E.; Schorzman, D. A. *Macromolecules* **1999**, *32*, 8693−8694.
(28) Connell, J. W.; Smith, J. G., Jr.; Hergenrother, P. M. *High Perform. Polym.* **1998**, *10*, 273−283.
(29) Fang, X.; Rogers, D. F.; Scola, D. A.; Stevens, M. P. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 461−470.
(30) Jayaraman, S.; Srinivasan, R.; McGrath, J. E. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 1551−1563.
(31) Hergenrother, P. M.; Bryant, R. G.; Jensen, B. J.; Havens, S. J *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 3061−3067.
(32) Hergenrother, P. M.; Smith, J. G., Jr. *Polymer* **1994**, *35*, 4857−4864.
(33) Hinkley, J. A. *J. Adv. Mater.* **1994**, *27*, 55−59.
(34) Johnston, J. A.; Li, F. M.; Harris, F. W.; Takekoshi, T. *Polymer* **1994**, *35*, 4865−4874.
(35) Takekoshi, T.; Terry, J. M *Polymer* **1994**, *35*, 4874−4880.
(36) Douglas, W. E.; Overend, A. S. *Eur. Polym. J.* **1993**, *29*, 1513−1519.
(37) Feher, F. J.; Terroba, R.; Ziller, J. W. *Chem. Commun.* **1999**, 2309−2310.
(38) Feher, F. J.; Phillips, S. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 3397−3398.
(39) Feher, F. J.; Soulivong, D.; Eklund, A. G. *Chem. Commun.* **1998**, 399−400.

**Table 1. Mole Fractions of Monomers Used in Synthesis of Oligomers, Based on 1.00 Mole Fraction of Diamine**[a]

| | AnEPA | PEPA | ODPA | POSS *x* | APB *y* | ODA *z* | theoretical Mn |
|---|---|---|---|---|---|---|---|
| PETI-5–ODPA | 0.00 | 0.18 | 0.91 | 0.00 | 0.15 | 0.85 | 5851 |
| AnETI-5–ODPA | 0.18 | 0.00 | 0.91 | 0.00 | 0.15 | 0.85 | 5887 |
| 1%-POSS–PETI-5–ODPA | 0.00 | 0.18 | 0.91 | 0.01 | 0.15 | 0.84 | 5972 |
| 1%-POSS–AnETI-5–ODPA | 0.18 | 0.00 | 0.91 | 0.01 | 0.15 | 0.84 | 6008 |
| 10%-POSS–AnETI-5–ODPA | 0.18 | 0.00 | 0.91 | 0.10 | 0.14 | 0.77 | 7098 |

[a] The variables *x*, *y*, and *z* are defined in the illustrations shown above. The calculated theoretical Mw is included.

**Table 2. Analysis of Oligomers Using SEC and DSC.**

| sample | PETI-5–ODPA[13] | AnETI-5–ODPA[13] | 1%-POSS–PETI-5–ODPA | 1%-POSS–AnETI-5–ODPA | 10%-POSS–AnETI-5–ODPA |
|---|---|---|---|---|---|
| $M_n$ | 2607 | 3212 | 2625 | 2592 | 5787 |
| $M_w$ | 4119 | 5166 | 4275 | 4225 | 10520 |
| PD | 1.58 | 1.61 | 1.63 | 1.63 | 1.82 |
| $T_m$ (°C) | 263 | 218 | | | |
| $T_{gu}$ (°C) | 190.3 | 198.5 | 192.7 | 189.5[a] | 203.0 |
| $T_{gc}$ (°C) | 233.5 | 234.7 | 237.4 | 226.0 | 226.7 |

[a] $T_{gu}$ revealed in first DSC scan.

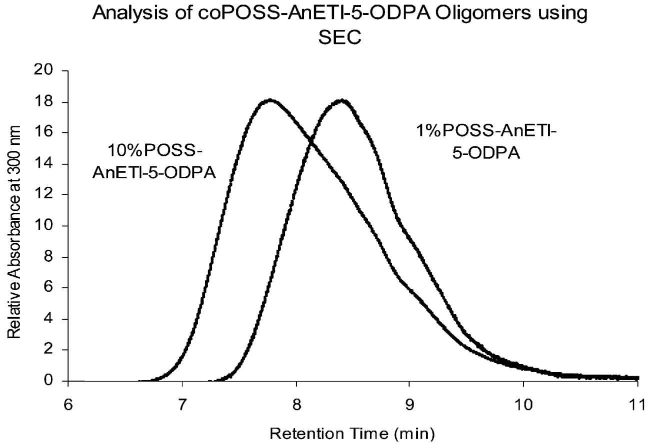


**Figure 1.** SEC traces of *co*POSS–AnETI-5–ODPA oligomers. Unreacted POSS monomer (FW = 1134), by comparison to polystyrene standards, would correspond to a retention time of 8.84 min.

PETI-5–ODPA, 1%-POSS–AnETI-5–ODPA, and 10%-POSS–AnETI-5–ODPA are synthesized and reported herein. The oligomers PETI-5–ODPA and AnETI-5–ODPA have been previously synthesized and the curing kinetics studied.[13]

For each of the POSS-containing oligomers, proton NMR spectroscopy was used as a means of verifying POSS incorporation. In general, we used the integration ratios of the aromatic region to that of the very distinctive aliphatic peaks (due to the $C_5H_{11}$ rings) for confirmation that the feed ratio of POSS is maintained in the isolated *co*POSS imide oligomer.

**Oligomer Analysis.** Analysis of oligomers using SEC and comparison to polystyrene standards revealed oligomeric product with little or no remaining monomers. Incorporation of 1 mol % POSS into the oligomers has little effect on the Mn, Mw, and polydispersity (PD) values for 1%-POSS–AnETI-5–ODPA and 1%-POSS–PETI-5–ODPA compared to those for AnETI-5–ODPA and PETI-5–ODPA (Table 2). The 10%-POSS–AnETI-5–ODPA oligomer does correspond to a larger polymer (Figure 1), with little or no unreacted POSS monomer present, in accordance with the calculated theoretical Mw values (Table 1).

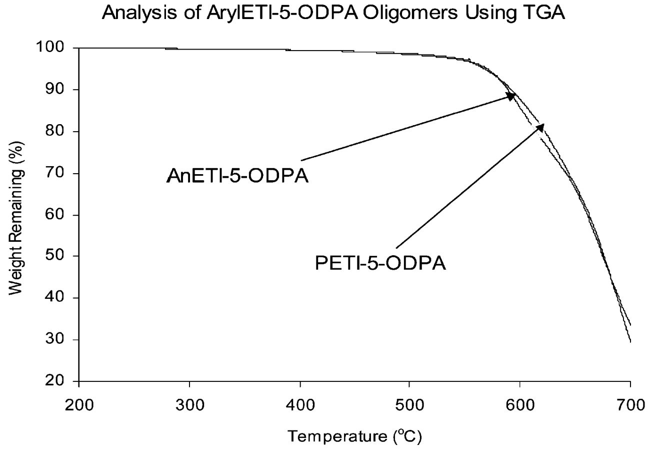


**Figure 2.** TGA traces of arylETI-5 oligomers as collected under a nitrogen atmosphere.

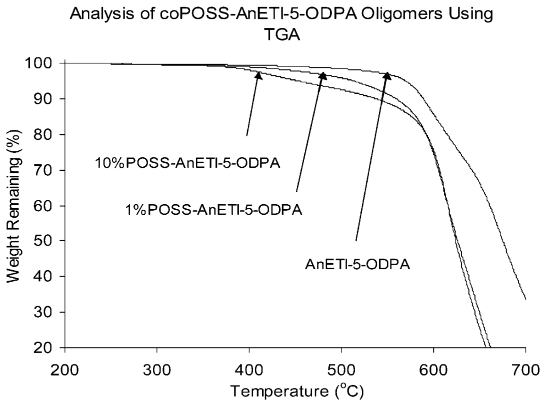


**Figure 3.** TGA traces of *co*POSS–AnETI-5–ODPA oligomers as collected under a nitrogen atmosphere.

Analysis of the cured oligomers using TGA was performed to determine thermal stability. Each sample was first heated to 250 °C to ensure standardized removal of residual water and solvents. The sample was cooled and data was collected to 700 °C. PETI-5–ODPA and AnETI-5–ODPA were analyzed to ensure thermal stability of the anthracenyl end cap. Indeed, the two systems demonstrate nearly identical thermal stability, demonstrated by the onset of rapid weight loss at approximately 500 °C (Figure 2). The onset of a slow and steady thermal degradation process of 10%-POSS–AnETI-5–ODPA at approximately 400 °C was found to occur until rapid decomposition begins at approximately 550 °C (Figure 3). The rapid decomposition of 10%-POSS–AnETI-5–ODPA is steeper, thus more rapid than AnETI-5–ODPA. 1%-POSS–AnETI-5–ODPA also demonstrates the slow and steady degradation process, although slightly less pronounced. The final degradation process of 1%-POSS–AnETI-5–ODPA at approximately 550 °C nearly identically matches the final degradation of 10%-POSS–AnETI-5–ODPA.

Oligomer samples were analyzed using DSC and compared to previous systems. The uncured oligomers were analyzed using two scans. The first scan of 1%-POSS−PETI-5−ODPA and 10%-POSS−AnETI-5−ODPA revealed no distinct melting peaks ($T_m$) or glass transitions ($T_g$) as indicated in Table 1. This is in contrast to PETI-5−ODPA, AnETI-5−ODPA,[13] and other analogous oligomers[25] that demonstrate a distinct $T_m$ in the first scan and a distinct $T_g$ in the second scan. The second scan of 1%-POSS−PETI-5−ODPA and 10%-POSS−AnETI-5−ODPA revealed distinct uncured $T_g$s ($T_{gu}$), with nearly the same values as the non-POSS analogues, PETI-5−ODPA and AnETI-5−ODPA. The 1%-POSS−AnETI-5−ODPA did not exhibit a $T_m$; however, it did reveal a distinct $T_{gu}$ in the first DSC scan. Each sample was then fully cured (380 °C for 1 h). The hardened, glassy resins were then analyzed by a third DSC scan to measure a fully cured $T_g$s ($T_{gc}$) at temperatures similar to non-POSS-containing oligomers. The $T_{gu}$ and $T_{gc}$ data show that very little effect is occurring from the incorporation of POSS and this appears to be true for both the cured and uncured materials. Very interestingly, the POSS units decrease the crystallinity of the uncured oligomers as indicated by an absence of a $T_m$ in the DSC data (Table 1).

**Analysis of Oligomer Thermal Curing.** Samples of 10%-POSS−AnETI-5−ODPA were sealed under nitrogen in a Pyrex reaction vessel and cured at selected temperatures in a calibrated aluminum heating block, as previously described.[13,25,27] Samples were removed at certain times via suction, the reaction vessel was opened, and the sample was removed. Analysis of the thermal curing of the oligomer samples was performed by monitoring the change in $T_g$ as a function of time using the DiBenedetto equation,[40−43] modified for highly cross-linked networks,

$$(T_g - T_{gu})/(T_{gc} - T_{gu}) = \lambda x/(1 - (1 - \lambda)x)$$

where $T_g$, $T_{gu}$, $T_{gc}$, $\lambda$, and $x$ represent the glass transition temperature of the sample, the glass transition temperature of the uncured material, the glass transition temperature of the fully cured material, the ratio of the isobaric heat capacity of a fully cured model compound to that of an uncured model compound, and the reaction extent (i.e., $C_t/C_0 = 1 - x$), respectively. The experimental values of $T_{gu}$ and $T_{gc}$ listed in Table 2 were used in the calculation of reaction extent. The value of $\lambda$ determined by Scola and co-workers ($\lambda = 0.69$),[29] which has been successfully applied to other end-capped arylETI-5 systems,[13,25] was again used in the calculations.

Analysis of the experimental data of 10%-POSS−AnETI-5−ODPA using a first-order rate law (i.e., time vs $\ln[C_t/C_0]$) provided the best fit, in accordance with previous oligomer analysis.[13,25] The rate data from each temperature were further used in Arrhenius (Figure 4) and Eyring plots and the Arrhenius and thermodynamic parameters, respectively, were calculated from the resulting linear regression values and compared to previous data.[13] The kinetic parameters reveal reasonably similar $E_a$ values of 10%-POSS−AnETI-5−ODPA, PETI-5−ODPA, and AnETI-5−ODPA (Table 3). The rate acceleration provided by the anthracenyl-ethynyl end cap is still very evident in that 10%-POSS−AnETI-5−ODPA cures only slightly slower than AnETI-5−ODPA and much faster than PETI-5−ODPA at all temperatures studied. The slight decrease in rate can be attributed to dilution of end caps due to the significantly larger Mw of 10%-POSS−AnETI-5−ODPA.

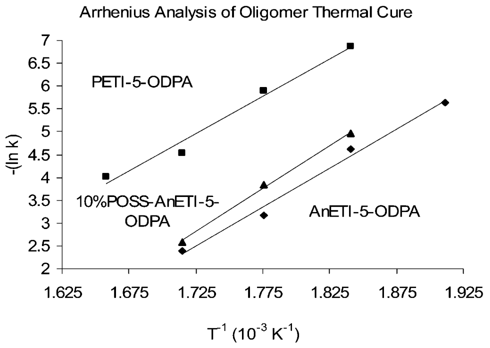


**Figure 4.** Arrhenius analysis of thermal curing of 10%-POSS−AnETI-5−ODPA (▲) with linear regression. For comparison purposes, previous PETI-5−ODPA (■) and AnETI-5−ODPA (♦) data is shown.

**Table 3. Calculated Arrhenius and Eyring Parameters of Oligomer Thermal Curing[a]**

| | PETI-5−ODPA[b] | AnETI-5−ODPA[13] | 10%-POSS−AnETI-5−ODPA |
|---|---|---|---|
| Arrhenius $R^2$ | 0.979679 | 0.990643 | 0.997685 |
| $E_a$ (kJ/mol) | 136(14) | 142(10) | 156(8) |
| $A$ (min$^{-1}$) | $1.3 \times 10^{10}$ | $5.1 \times 10^{11}$ | $6.1 \times 10^{12}$ |
| Eyring $R^2$ | 0.978139 | 0.990003 | 0.997571 |
| •$H_{act}$ (kJ/mol) | 132(14) | 137(10) | 151(7) |
| •$S_{act}$ (J/kmol) | −65 | −34 | −14 |

[a] For comparison purposes, previous PETI-5−ODPA and AnETI-5−ODPA data are included. Numbers in parentheses represent the error for the last digit(s). [b] New data were collected for heating block calibration purposes and resulting kinetic parameters are in agreement with previous data.[13]

## Concluding Remarks

The simple and successful synthesis of an organic/inorganic hybrid imide oligomer with backbone POSS units is reported. The POSS units disrupt the crystallinity of the uncured oligomer and serve as the limiting factor in the thermal stability of the resin. The thermal curing kinetics of the hybrid oligomer to form a high-performance hybrid resin was found to be relatively unaffected by the presence of up to 10 mol % POSS units. The hybrid materials can also be synthesized using new end-capping reagents to modify the kinetics of the thermal curing. This system is therefore a simple and versatile method for creating high-performance organic/inorganic hybrid resins.

## Experimental Section

**General Methods.** All manipulations of compounds and solvents were done under nitrogen using standard Schlenk line techniques. THF was purified by distillation under nitrogen from Na$^0$. The compound 1-(9-anthracenyl)ethynylphthalic

---

(40) Hale, A.; Macosko, C. W.; Bair, H. E. *Macromolecules* **1991**, *24*, 2610−2621.

(41) Pascault, J. P.; Williams, R. J. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 25.

(42) Couchman, P. R. *Macromolecules* **1987**, *20*, 1712−1717.

(43) DiBenedetto, A. T. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 1949−1969.

anhydride (AnEPA) was prepared according to a literature technique.[13] The *N*-methylpyrrolidinone (99.9%, anhydrous) was purchased from Aldrich Chemical Co. The compounds 1,3-bis(3-aminophenoxy)benzene (APB), 4,4′-oxydiphthalic anhydride (ODPA), and 4,4′-oxydiphthalic anhydride (ODA) were purchased from TCI America. The 4-PEPA was obtained from NASA. SEC analyses were performed by dilution in THF (2 mg/mL) and then injection onto a Hewlett-Packard 1100 HPLC (column: PL 300 × 7.5 mm, 5-$\mu$m particle size). Molecular weights are calculated relative to polystyrene standards. TGA analyses were performed on a 5−10-mg sample using a Perkin-Elmer TGA-7 at a heating rate of 20 °C/min under a nitrogen flow of 20 $cm^3$/min. DSC analyses were performed on ≈5-mg samples using a Perkin-Elmer DSC-7 at a heating rate of 20 °C/min under a nitrogen flow of 40 $cm^3$/min.

**Preparation of *diendo*-($c$-$C_5H_9)_8Si_8O_{11}(OH)_2$.** A methanol solution of $Me_4NOH$ (25%, 41.3 mL, 98.0 mmol) was added to a suspension of ($c$-$C_5H_9)_8Si_8O_{12}$ (100 g, 103 mmol) in THF (1.70 L) at room temperature. The resulting mixture was stirred for 2 h, neutralized with 1 N HCl solution, and extracted with diethyl ether. The ether extracts were washed with brine, dried over $MgSO_4$, and evaporated to afford ***diendo*-($c$-$C_5H_9)_8Si_8O_{11}(OH)_2$** (93.0 g, 92.6 mmol) as a white solid in 91% yield. The product obtained in this fashion is both spectroscopically ($^1$H, $^{13}$C, $^{29}$Si) and analytically pure, and it was used without further purification. $^1$H NMR ($CDCl_3$): $\delta$ 0.97 (m, 8H), 1.50 (m, 48H), 1.74 (m, 16H), 4.43 (s, 2H). $^{13}$C NMR ($CDCl_3$): $\delta$ 22.17, 22.67, 22.83, 27.01, 27.04, 27.07, 27.22, 27.38, 27.41. $^{29}$Si NMR ($CDCl_3$): $\delta$ −67.99, −65.56, −58.51 (4:2:2). m.p. 188 °C (by DSC). Anal. Calcd for $C_{40}H_{74}O_{13}Si_8$: C, 48.64; H, 7.55. Found: C, 48.37; H, 7.52.

**Preparation of *diexo*-($c$-$C_5H_9)_8Si_8O_{11}F_2$.** A $CH_2Cl_2$ (1.00 L) solution of *diendo*-($c$-$C_5H_9)_8Si_8O_{11}(OH)_2$ (91.0 g, 92.1 mmol) was added to a solution of $HBF_4{\cdot}OMe_2$ (28.0 mL, 0.23 mol) and $BF_3{\cdot}OEt_2$ (70.0 mL, 0.56 mol) in $CH_2Cl_2$ (100 mL) at 0 °C. The solution was warmed to room temperature and stirred for 2 h before washing with water. The $CH_2Cl_2$ layer was separated and saved. The aqueous layer was extracted with ether, and then the ether extract was washed with saturated brine. The $CH_2Cl_2$ layer and ether extract were combined, dried over $Na_2SO_4$, and evaporated to afford *diexo*-($c$-$C_5H_9)_8Si_8O_{11}F_2$ (69.0 g, 69.6 mmol) as a white solid in 76% yield. The product obtained in this fashion is spectroscopically ($^1$H, $^{13}$C, $^{29}$Si) pure and suitable for use without further purification. Analytical samples were prepared by crystallization from hexane/acetonitrile. $^1$H NMR ($CDCl_3$): $\delta$ 0.95−1.15 (m, 8H), 1.41−1.70 (m, 48H), 1.70−1.89 (m, 16H). $^{13}$C NMR ($CDCl_3$): $\delta$ 21.16 (d, $^2J_{C-F} = 25.0$ Hz), 22.01, 22.55, 26.76, 27.03, 27.05, 27.16, 27.22. $^{29}$Si NMR ($CDCl_3$): $\delta$ −66.22, −65.07, −61.58 (d, $^1J_{Si-F} = 268.70$ Hz). $^{19}$F NMR ($CDCl_3$): $\delta$ −137.50. Anal. Calcd for $C_{40}H_{72}F_2O_{11}Si_8$: C, 48.45; H, 7.32. Found: C, 48.33; H, 7.42.

**Preparation of *diexo*-($c$-$C_5H_9)_8Si_8O_{11}$($p$-$C_6H_4NH_2)_2$.** *N*-*p*-Lithiophenyl-*N*-1,1,4,4,-tetramethyldisilylazacyclopentane was prepared by the halogen−metal exchange reaction of *N*-*p*-bromophenyl-*N*-1,1,4,4,-tetramethyldisilylazacyclopentane (68.8 g, 219 mmol)[44] and *n*-BuLi (125 mL, 1.60 M, 200 mmol) in $Et_2O$ (150 mL) at room temperature for 2 h. This solution was added dropwise to a solution of *diexo*-($c$-$C_5H_9)_8Si_8O_{11}F_2$ (62.1 g, 62.6 mmol) in $Et_2O$ (250 mL) at 0 °C. After the addition was complete, the resulting mixture was allowed to warm to room temperature and stirred overnight before it was hydrolyzed and extracted with $Et_2O$. The combine ether extracts were washed with brine, dried over $Na_2SO_4$, and evaporated to give a white solid, which was solvolyzed by stirring with THF/MeOH (600 mL/30 mL) and pyridinium *p*-toluenesulfonate (PPTS) (0.95 g, 3.78 mmol) for 30 min at room temperature. The resulting mixture was concentrated in vacuo, diluted with water, and extracted with ether. Washing with brine, drying over $Na_2SO_4$, and evaporating in vacuo afforded a white solid. Analytically pure *diexo*-($c$-$C_5H_9)_8Si_8O_{11}$($p$-$C_6H_4NH_2)_2$ (42.2 g, 37.1 mmol) was obtained in 59% yield by precipitating the compound from hexane with methanol. m.p: >300 °C (dec). $^1$H NMR ($CDCl_3$): $\delta$ 0.82−1.01 (m, 8H), 1.20−1.86 (m, 64H), 3.84 (s br, 4H), 6.67 (d, $^3J = 8.2$ Hz, 4H), 7.40 (d, $^3J = 8.2$ Hz, 4H). $^{13}$C NMR ($CDCl_3$): $\delta$ 22.21, 23.18, 25.24, 25.50, 26.87, 27.01, 27.06, 27.17, 27.41, 114.07, 124.11, 135.38, 147.54. $^{29}$Si NMR ($CDCl_3$): $\delta$ −66.56, −64.77, −32.27. Anal. Calcd for $C_{52}H_{84}N_2O_{11}Si_8$: C, 54.89; H, 7.44; N, 2.46. Found: C, 54.98; H, 7.52, N, 2.47.

**Synthesis of 1%-POSS−PETI-5−ODPA.** A solution of 1,3-bis(3-aminophenoxy)benzene (0.096 g, 0.33 mmol), 3,4′-oxydianiline (0.372 g, 1.86 mmol), and POSS (0.025 g, 0.02 mmol) in *N*-methylpyrollidinone (18 mL) was treated with 4-phenylethynylphthalic anhydride (0.099 g, 0.40 mmol) and 4,4′-oxydiphthalic anhydride (0.624 g, 2.01 mmol) and the solution was allowed to react for 15 h under nitrogen at ambient temperature. The solution was diluted with toluene (50 mL), the reaction vessel was equipped with a dean-stark trap, and the mixture was heated at reflux for 15 h. The cooled solution was added to $H_2O$ (50 mL), stirred vigorously for 30 min, and filtered. The filtrate was washed successively with $H_2O$ (3 × 15 mL) and warm methanol (3 × 15 mL) and was dried under reduced pressure at 85 °C for 15 h to afford 1%POSS−PETI-5−ODPA (1.01 g, 88.6%); $M_n = 2625$; PD = 1.63.

**Synthesis of 1%-POSS−AnETI-5−ODPA.** A solution of 1,3-bis(3-aminophenoxy)benzene (0.096 g, 0.33 mmol), 3,4′-oxydianiline (0.372 g, 1.86 mmol), and POSS (0.025 g, 0.02 mmol) in *N*-methylpyrollidinone (18 mL) was treated with 4-(9-anthracenylethynyl)phthalic anhydride (0.139 g, 0.40 mmol) and 4,4′-oxydiphthalic anhydride (0.624 g, 2.01 mmol) and the solution was allowed to react for 15 h under nitrogen at ambient temperature. The solution was diluted with toluene (50 mL), the reaction vessel was equipped with a dean-stark trap, and the mixture was heated at reflux for 15 h. The cooled solution was added to $H_2O$ (50 mL), stirred vigorously for 30 min, and filtered. The filtrate was washed successively with $H_2O$ (3 × 15 mL) and warm methanol (3 × 15 mL) and was dried under reduced pressure at 85 °C for 15 h to afford 1%-POSS−AnETI-5−ODPA (1.04 g, 88.8%); $M_n = 2592$; PD = 1.63.

**Synthesis of 10%-POSS−AnETI-5−ODPA.** A solution of 1,3-bis(3-aminophenoxy)benzene (0.087 g, 0.30 mmol), 3,4′-oxydianiline (0.339 g, 1.69 mmol), and POSS (0.252 g, 0.22 mmol) in *N*-methylpyrollidinone (18 mL) was treated with 4-(9-anthracenylethynyl)phthalic anhydride (0.139 g, 0.40 mmol) and 4,4′-oxydiphthalic anhydride (0.624 g, 2.01 mmol) and the solution was allowed to react for 15 h under nitrogen at ambient temperature. The solution was diluted with toluene (50 mL), the reaction vessel was equipped with a dean-stark trap, and the mixture was heated at reflux for 15 h. The cooled solution was added to $H_2O$ (50 mL), stirred vigorously for 30 min, and filtered. The filtrate was washed successively with $H_2O$ (3 × 15 mL) and warm methanol (3 × 15 mL) and was dried under reduced pressure at 85 °C for 15 h to afford 10%POSS−PETI-5−ODPA (0.79 g, 57.9%); $M_n = 5787$; PD = 1.82.

**Acknowledgment.** We thank NASA, Langley, VA, for a generous donation of 4-phenylethynylphthalic anhydride (PEPA). M.E.W. wishes to thank the ONR for partial funding of this work. D.A.S. was supported in part from VCU on a Graduate Fellowship from the VCU School of Graduate Studies. F.J.F. wishes to thank Dr. Shawn Phillips for a generous gift of ($c$-$C_5H_9)_8Si_8O_{12}$ (purchased from Hydrid Plastics, Inc.) and the National Science Foundation for support of this research.

CM020238H

---

(44) Guggenheim, T. L. *Tetrahedron Lett.* **1984**, *25*, 1253.