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Chemical Modification of Fluorinated Polyimides:
New Thermally Curing Hybrid-Polymers with POSS (Preprint)

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Keywords: Polymer modification, POSS, polyhedral oligomeric silsesquioxanes, polyimide, atomic oxygen, LEO, lower Earth orbit.

Abstract: A series of four new end-capped and hydroxymethyl-functionalized polyimides were prepared. Through a two-step chemical modification process 3-aminopropylisobutyl-POSS was covalently attached to the polymer backbone. POSS loading levels as high as 40 wt-% could be obtained while maintaining excellent processability and optical clarity of thin films. Concurrent attachment of either a cyanate ester or hydroxyethyl methacrylate (HEMA) group afforded processable POSS-polyimides that underwent thermal curing to yield solvent resistant films, both having

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Introduction:

Polyhedral oligomeric silsesquioxanes (POSS) are a family of nanoscale inorganic cage structures containing a silicon/oxygen framework that are an intermediate ($RSiO_{1.5}$) between silica (SiO_2) and silicone (R_2SiO).[1,2] A vast majority of commercially available POSS compounds consist of a Si_8O_{12} cage functionalized at one corner (i.e. Si-atom) with an organic substituent that provides a point for synthetic elaboration (Figure 1).[3] It is this combination of an inorganic core and a hydrocarbon periphery that imparts unique physical and chemical properties to POSS compounds.

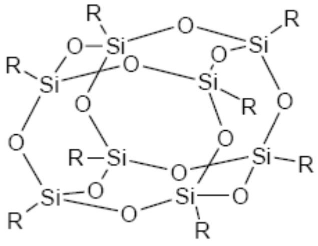


Figure 1. Structural representation of POSS nanoparticle Si_8O_{12} cage where R = alkyl, aryl, etc.

Over the past decade there has been a steadily increasing interest in the creation of POSS-polyimide nanocomposites for a variety of applications that include: low dielectric constant materials,[4-8] thermally curable aryl-ethynyl endcapped hybrid composite resins,[9] polyimides with improved thermal and mechanical properties,[10,11] and thermally stable hyperbranched-polyimides.[12]

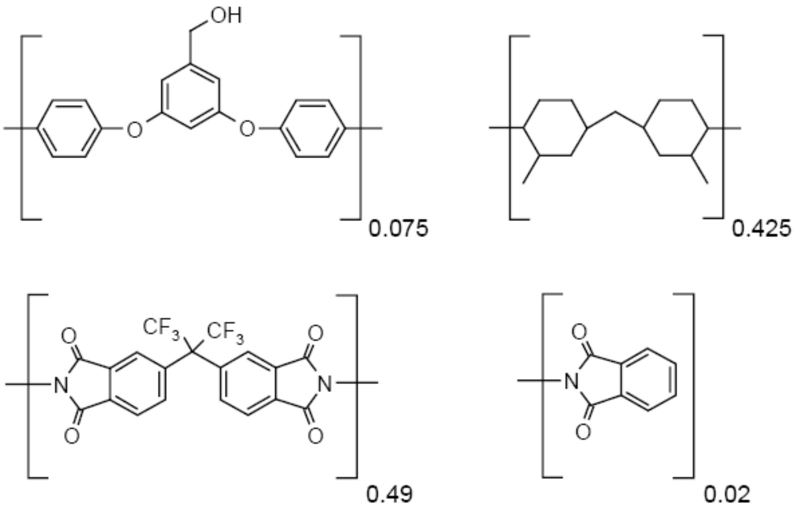
One area in particular that POSS has shown outstanding performance is the ability to impart resistance towards chemical degradation by atomic oxygen (AO).[13] Atomic oxygen comprises up to 90% of the low earth orbit (LEO) environment and is known to promote rapid chemical degradation of all organic polymeric coatings that include Kapton®.[13] Exposure of a variety of POSS-containing polymers to simulated LEO environmental conditions[13-17] has established that these materials possess dramatically improved resistance to chemical degradation by the highly reactive AO. This type of adaptive feature is attributed to an oxidative degradation of the POSS-cage to create a protective layer of silica {i.e. $(SiO_2)_n$} that minimizes further degradation by AO. Thus, POSS-containing polymers hold great promise for extending the lifetime of organic materials that must function for long periods of time in the LEO environment.

As part of an ongoing examination into new space survivable materials we present herein a method of covalently attaching POSS at very high wt-% loadings to a variety of polyimide backbone structures. The new POSS modified polyimides are easily processed into optically clear films by spin-casting, doctorblading, or aerosol spray techniques. Furthermore, we demonstrate that by incorporation of a cross-linking moiety the films can be thermally cured into solvent resistant coatings that retain their optical clarity. Lastly, we present exposure data for one polyimide coating that contained ~31 wt-% of POSS. The material exhibits excellent resistance (~0% degradation relative to Kapton®)

to atomic oxygen (simulated LEO) and that these new polyimides are much more transparent in the visible region than Kapton®.

Results & Discussion:

Hydroxymethyl-functionalized polyimide synthesis. Recently we reported the synthesis of a new benzyl alcohol diamine, 3,5-*bis*(4-aminophenoxy) 1-hydroxymethyl benzene (BHB) (Figure 2) that can be readily copolymerized with 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6-FDA) to afford a new hydroxymethyl functionalized polyimide.[18] Our initial work included 2,2-*bis*(4-aminophenyl)hexafluoropropane (6-F diamine) as a comonomer to dilute the hydroxymethyl sites in the polymer backbone. We have now extended this work to include two hydrocarbon alkyl diamines, cadaverine and 2,2'-dimethyl-4,4'-methylene-*bis*(cyclohexylamine) (RF-24) (Figure 2, Table 1). In each case the copolymers appear to be random and display a T_g that reflects the structural stiffness of the co-diamine. In order to control molecular weight of the hydroxylfunctionalized polyimides we added phthalic anhydride or 4-*t*-butylaniline as end-caps. We have characterized polyimides **1**-**5** by ^{1}H and ^{13}C NMR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and size exclusion chromatography (SEC).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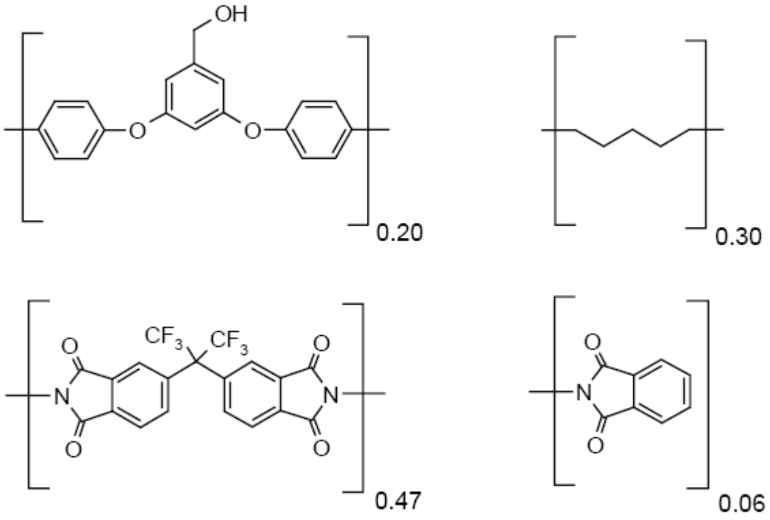
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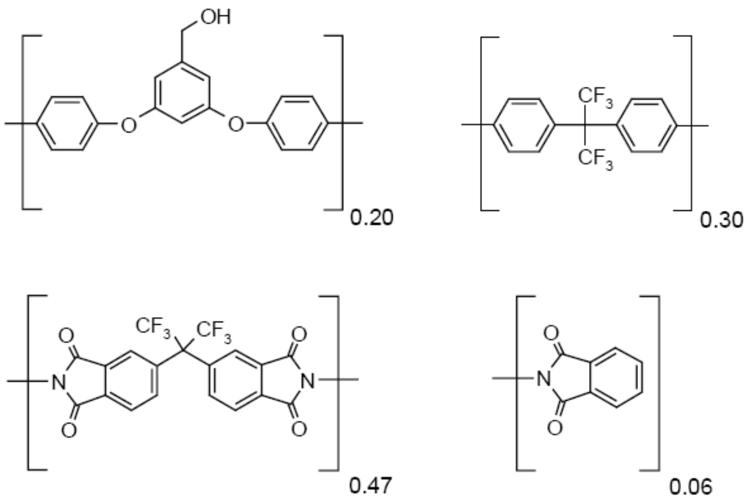

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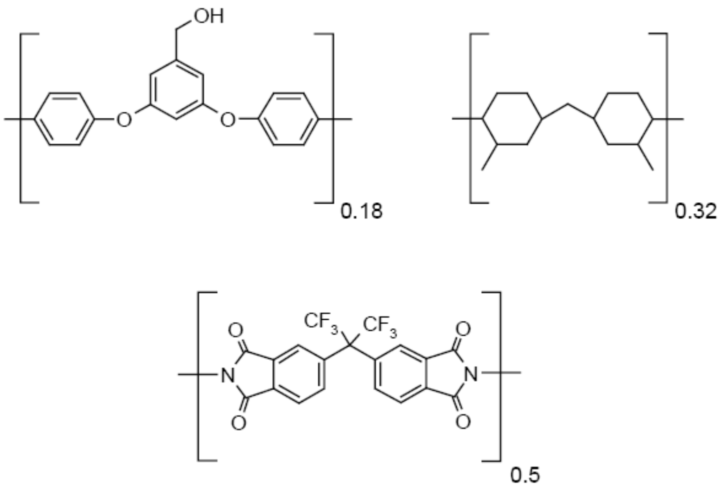

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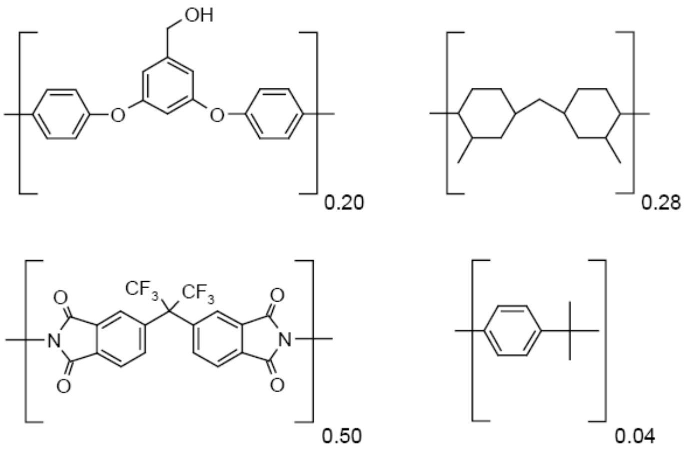

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Figure 2. Chemical Structures of polyimides **1-5** containing the reacted BHB subunit.

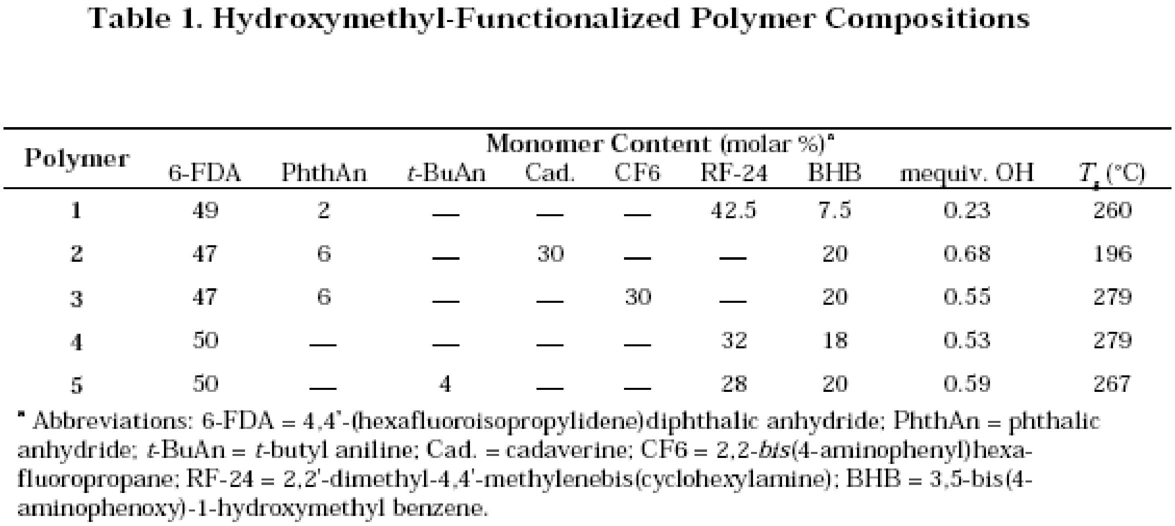


Table 1. Hydroxymethyl-Functionalized Polymer Compositions

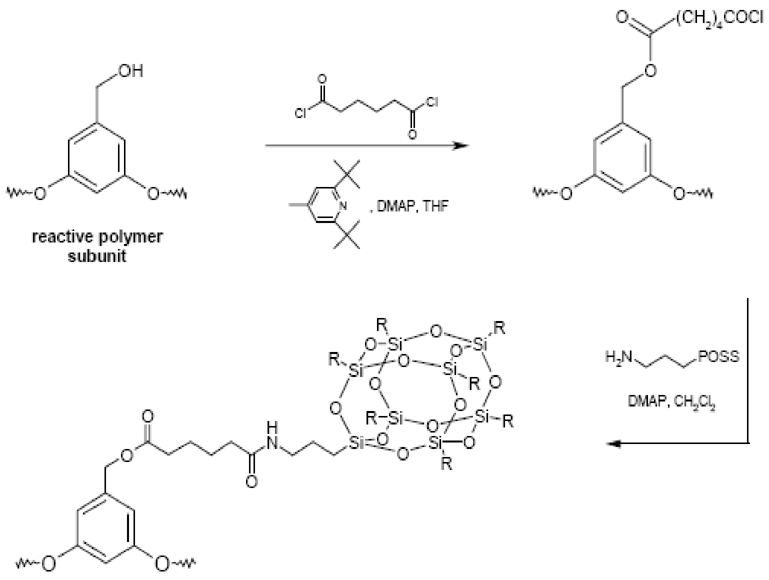
Polymer	**Monomer Content** (molar %)[a]								
	6-FDA	PhthAn	*t*-BuAn	Cad.	CF6	RF-24	BHB	mequiv. OH	T_g (°C)
1	49	2	—	—	—	42.5	7.5	0.23	260
2	47	6	—	30	—	—	20	0.68	196
3	47	6	—	—	30	—	20	0.55	279
4	50	—	—	—	—	32	18	0.53	279
5	50	—	4	—	—	28	20	0.59	267

[a] Abbreviations: 6-FDA = 4,4'-(hexafluoroisopropylidene)diphthalic anhydride; PhthAn = phthalic anhydride; *t*-BuAn = *t*-butyl aniline; Cad. = cadaverine; CF6 = 2,2-*bis*(4-aminophenyl)hexafluoropropane; RF-24 = 2,2'-dimethyl-4,4'-methylenebis(cyclohexylamine); BHB = 3,5-bis(4-aminophenoxy)-1-hydroxymethyl benzene.

The presence of the hydroxymethyl moiety as a reactive subunit within the polymer backbone can be introduced at a variety of stoichiometric levels. All work to date indicates that the feed ratio of BHB matches that found in the polyimide and that all the hydroxymethyl-sites are available for attachment chemistry. Table 1 also includes a listing for the equivalents of hydroxymethyl sites available per gram of each functionalized polyimide.

Polymer Modification. The reactive –CH_2OH subunits of polyimides **1**-**4** are first functionalized by treatment with excess adipoyl chloride in the presence of 2,6-di-*t*-butyl-4-methylpyridine and 4-dimethylaminopyridine (DMAP). This polymer is isolated by precipitation into ether, collected, washed and briefly dried under reduced pressure to afford a new polyimide with a highly reactive pendant acid chloride functional group (Scheme 1). Redissolving the latter polymers in dichloromethane followed by treatment with 3-aminopropylisobutyl-POSS in the presence of DMAP affords the POSS-modified polymers **6**-**9** (from polymers **1**-**4**, respectively). Isolation is accomplished by precipitation into methanol, followed by collection of the polymer on a glass-frit, and then drying at reduced pressure. Analysis of the materials by $_1$H NMR spectroscopy is consistent with a high efficiency (>95%) attachment of the POSS moiety in each example. More specifically, we find in the $_1$H NMR spectra a 1:1 integration ratio for the benzylic-CH_2 and the C_3 methylene (i.e. CH_2NHCO) POSS propyl signals. This latter result is consistent with complete side chain attachment. Furthermore, the C_3 methylene of the POSS propyl chain displays an expected downfield shift of ~ ™ 0.5 ppm as a consequence in going from an amino group to the chemically attached amide. Based on the spectroscopic data then the calculated Si_8O_{12} content of the POSS-modified polymers **6**, **7**, **8**, and **9** are 8, 17, 15, and 15 wt%, respectively.

Scheme 1



Polymers 6 – 9; POSS-modified polymers 1-4 respectively.

Analysis of the functionalized polyimides **6-9** by SEC is consistent with attachment of the POSS molecule and there appears to be no evidence of crosslinking in the attachment chemistry. A typical set of SEC data is shown for polyimides **3** and **8** in Figure 3. The POSS-containing polyimide **8**, after two chemical reaction steps and two precipitations, shows by SEC essentially the same polydispersity as the starting polyimide **3**. Notably, the POSS-modified polymers show very good solubility in THF, chloroform, and dichloromethane; however, we were quite surprised when they showed solubility in diethyl ether.

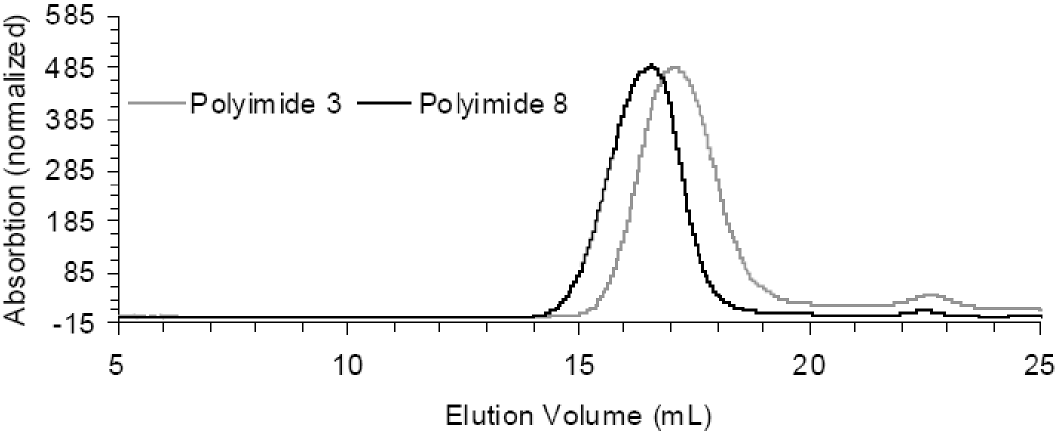
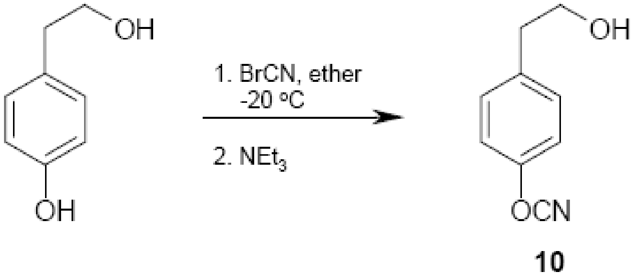


Figure 3. SEC trace showing shorter retention time (i.e. higher molecular weight) of POSS functionalized polyimide **8** compared to retention of the corresponding non-functionalized polyimide **3**.

In addition to the pendant POSS examples shown above, it is desirable to have a multi-component system that integrates a thermally curable side-chain in addition to POSS. We selected two very different types of cross-linking groups to explore the merit of this approach with the new pendant POSS-polyimides. A cyanate ester group is selected on the basis of excellent thermal stability of the triazine that is formed upon reaction and methyl methacrylate on the basis of the wide array of curing reactions and initiators available.

Selective functionalization of the phenolic group in the commercially available 2-(4-hydroxyphenyl)ethanol is achieved in high yield and thus produced the hydroxyl-functionalized cyanate ester **10** (eq 1). The solvent choice is critical for minimizing formation of diethyl cyanamide, which is a by-product that accompanies cyanate ester formation when performed in solvents such as THF, acetone, and dichloromethane (via the von Braun reaction). We find diethyl ether is the solvent of choice when synthesizing cyanate esters.

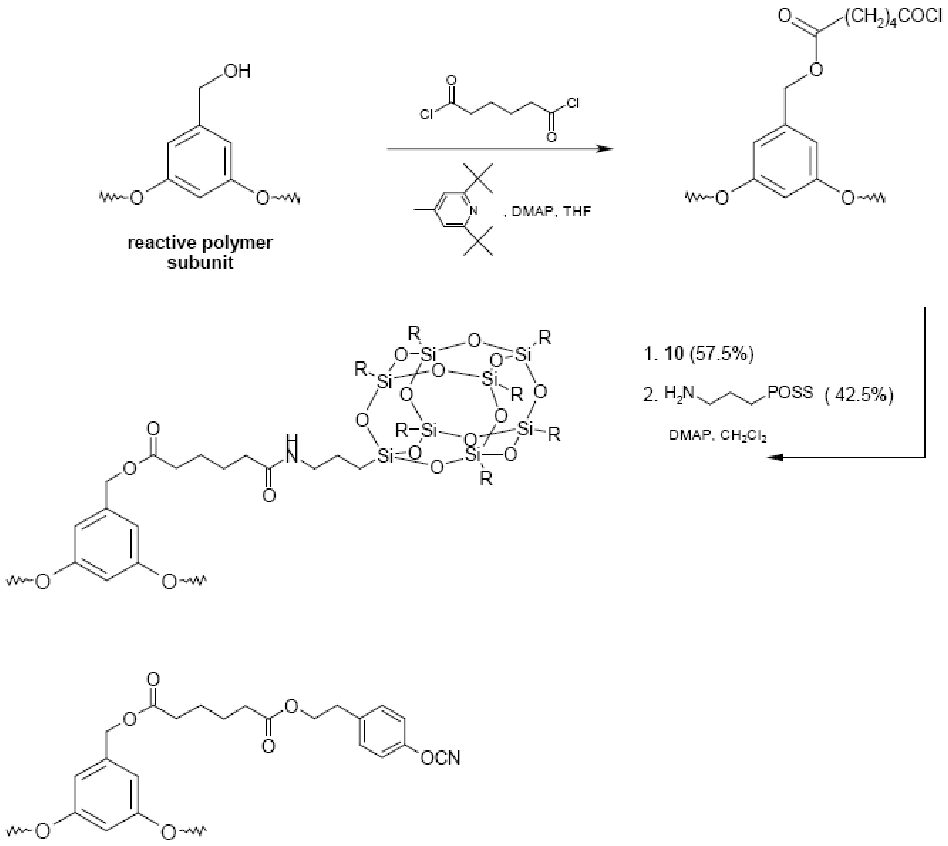
eq 1



10

Employing the same polymer modification/attachment chemistry described above we find treatment of the pendant acid chloride intermediate polymer (Scheme 3) with a dichloromethane solution containing cyanate ester **10** and 3-aminopropylisobutyl-POSS is successful in generating a multifunctional material from polymer 4 with a final Si_8O_{12} content of 8 wt-%.

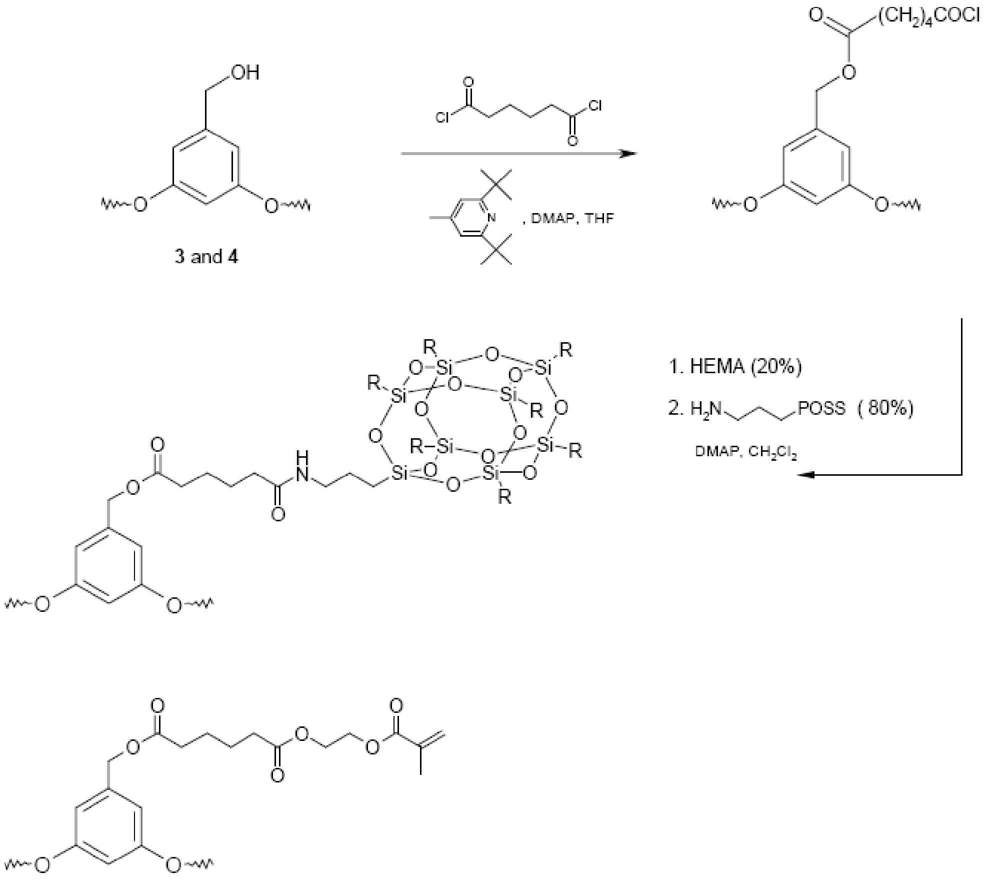
Scheme 3



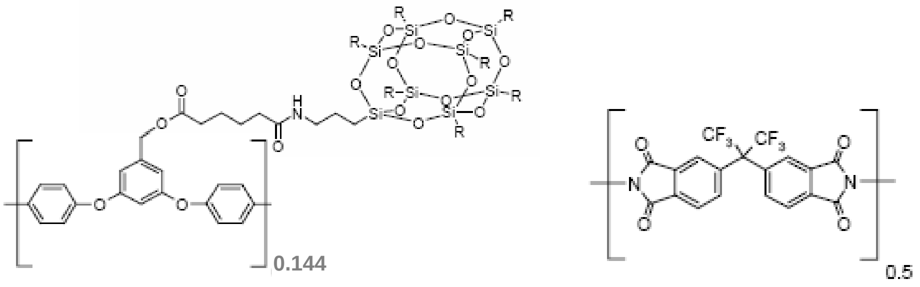
11

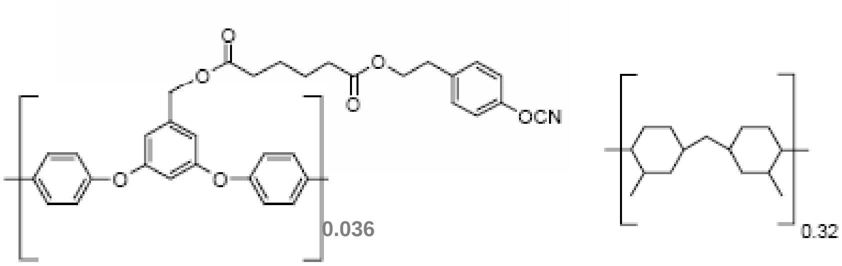
Analogous to the example utilizing a cyanate ester functionalized alcohol **10** we can introduce a controlled amount of 2-hydroxyethyl methacrylate (HEMA) and POSS to polyimides **3** and **4** (Scheme 4) to afford the multifunctional polyimides **12** and **13,** respectively. A POSS to HEMA molar ratio of 4:1 is used yielding a final Si_8O_{12} content of ~12.5 wt-% for both polymers **12** and **13**.

Scheme 4



Polymer 13 (modified polymer 4):





Analysis of the multifunctional POSS-polymers by ^{1}H NMR spectroscopy indicates that the pendant functional groups are present in the appropriate ratios. Thermally cured films of polyimide **12** were too brittle to warrant further analysis. On the other hand polyimide **13**, made with the non-fluorinated alkyl diamine RF-24, does produce high quality free-standing films. We find that thin films (~25 microns) of polymers **6-9** and **11-13** can be aerosol sprayed on to Kapton® with good adhesion. This ability to coat and adhere to other polymeric materials is useful for a number of future potential applications.

Thermal Analysis and curing kinetics for the POSS-polyimides. In Figure 4 we show in graphical terms the change in T_g as a function of POSS loading (as wt-%) for polyimides **6-9**. The POSS cage occupies a significant volume as a side group and additionally should demonstrate a relative ease of rotational motion based on the flexible connections of the POSS-cages to the polyimide backbones. Although the POSS cage itself is quite a rigid structure, the seven isobutyl groups provide a large number of degrees of conformational freedom. These factors increase the overall free volume in the bulk, thereby decreasing the ability of the polyimide chains to pack in an efficient manner. The reduction in T_g upon POSS modification is likely explained by a combination of these structural characteristics. Polyimide **6**, containing the least amount of POSS after modification (~8 wt-% Si_8O_{12}), exhibits the lowest reduction in glass transition temperature. The relatively low T_g of polyimide **7** most likely results from the inclusion of the flexible group cadaverine within the polymer backbone. Lastly, polyimides **8** and **9** exhibit nearly identical and relatively high T_g's due to the same level of POSS attachment and the rigid nature of their polymer backbones.

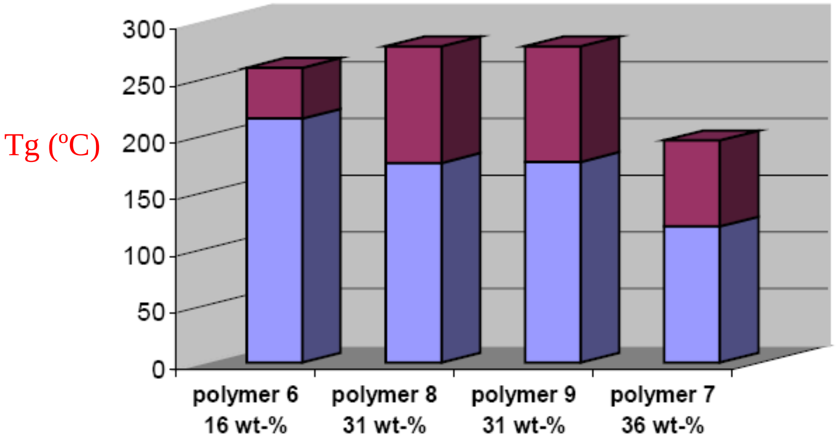


Figure 4. Comparison of pre- and post-modification T_g's for polymers **1-4** (total bar height, pre-modified) and **6-9** (lightly shaded bar, post modified).

Qualitative observations of the mechanical properties of the fabricated films revealed that the ability to cross-link the polyimide chains during the baking process resulted in dramatic improvements in fracture resistance in comparison with those polyimides devoid of reactive functionalities. With this realization in mind, it is useful to characterize the reaction kinetics of the curable polyimides. Typically thermal curing of these types of materials does not generate sufficient energy quantities for detection by DSC. Hence, it is necessary to execute kinetic analyses through an alternative method.

The application of the DiBenedetto equation,[19-23] modified for highly cross-linked networks, provides a means of relating observed Tg's to extent of reaction:

$$\frac{T_g - T_{g_0}}{T_{g_\infty} - T_{g_0}} = \frac{\lambda x}{1-(1-\lambda)x}$$

Where T_g, T_{go}, $T_{g\infty}$, λ, and x represent the glass transition temperature of the sample, the glass transition temperature of fresh 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 extent of reaction (*i.e.*, $C_t/C_0 = 1 - x$), respectively. The value of λ (= 0.69) used in the present study was taken from the work of Scola and coworkers.[24]

For both **11** and **13,** elevating the cure temperature results in an increase for the observed ultimate glass transition temperature achievable. Hence, the ultimate glass transition temperatures achieved by curing at 290 °C are used in the calculations for $T_{g\infty}$(251ºC for **11** and **13**). Pre-cure Tg's of 196 ºC and 190 ºC for **11** and **13**, respectively, are applied as T_{go} in the DiBenedetto equation. Thermal cycling of polyimides **11** and **13** after segmental isothermal cure (30 min blocks) rendered Tg data as a function of total cure time. Thus, a series of experiments were run for isothermal aging at temperatures between 230-290 ºC. The acquired Tg's were then utilized in the Dibenedetto equation to afford a calculated extent of reaction as a function of curing time. The rate plots at the various temperatures were then analyzed using a first order kinetic rate law. This analysis produced reaction rate constants for the cross-linking reaction at each temperature. These data are presented in the Arrhenius plot shown in Figure 5 and the kinetic parameters are summarized in Table 2.

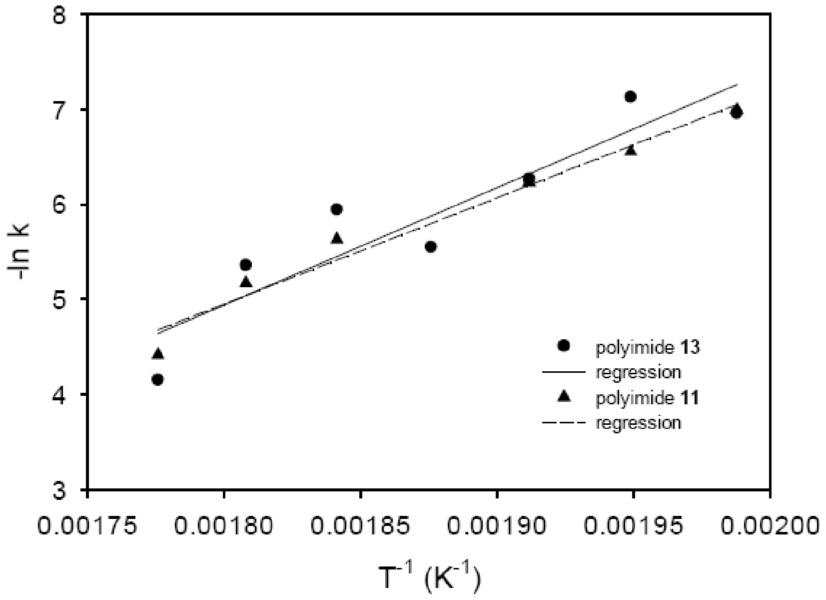


Figure 5. Arrhenius plot for the thermal curing of polyimides **11** and **13** with linear regression.

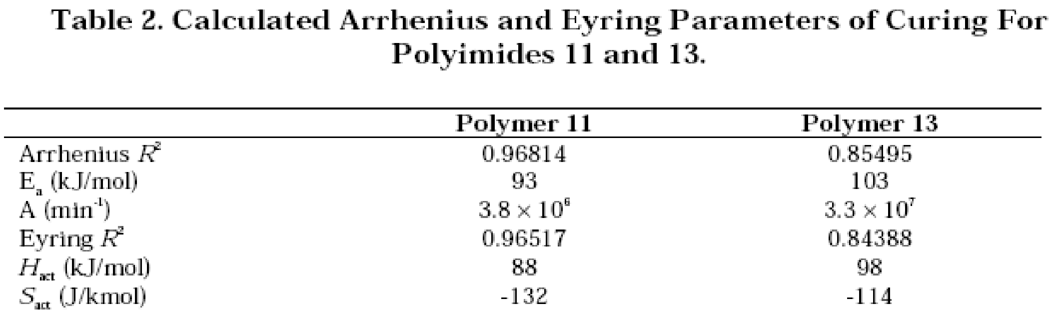


Table 2. Calculated Arrhenius and Eyring Parameters of Curing For Polyimides 11 and 13.

	Polymer 11	Polymer 13
Arrhenius R^2	0.96814	0.85495
E_a (kJ/mol)	93	103
A (min^{-1})	3.8×10^6	3.3×10^7
Eyring R^2	0.96517	0.84388
H_{act} (kJ/mol)	88	98
S_{act} (J/kmol)	-132	-114

A fairly accurate fit is obtained using the first order rate law for polyimides, however, deviations from linearity are most prominent at both low and high curing temperatures. The calculated activation energies, Ea, are statistically similar despite the difference in the type of reactive groups present in polyimide **11** over **13**. The activation energies obtained and the significant negative values for the activation entropies for both materials are consistent with a cycloadditon/polymerization reaction.

We have briefly explored the relative thermal stability for selected polymers using thermogravimetic analysis (TGA). Shown in Figure 6 are the TGA curves for polyimides **6**, **11**, and **13** (under air and nitrogen) and a summary of key aspects to the TGA plots can be found in Table 3.

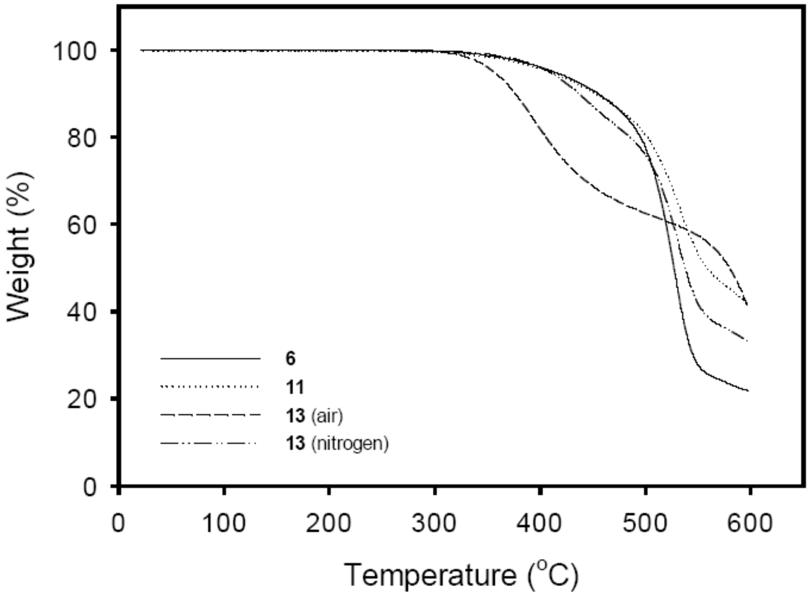


Figure 6. Graph of TGA curves for polyimides **6**, **11**, and **13** demonstrating weight loss of materials at elevated temperatures. A heating ramp rate of 10 ºC/min is employed for runs.

Table 3. Thermogravimetric Weight Loss Data for Polymers 6, 11, and 13

Sample ID	5% Weight Loss Temp. (°C)	Max. Rate Temp. 1 (°C)	Max. Rate 1 (%/min)	Max. Rate Temp. 2 (°C)	Max. Rate 2 (%/min)	Char Yield at 600 °C (%)
6	414	528	14	n/a	n/a	22
11	410	530	7	n/a	n/a	42
13 (air)	356	393	4	593	6.1	41
13 (nitrogen)	409	439	2	534	9.0	33

Polyimide **13** demonstrates a different degradation profile than the others in that two maximum weight loss rates are observed. This is an interesting observation since this particular polyimide is cross-linked via HEMA groups. In reference to the chemical architectures of the polyimide backbones, although the HEMA cross-links represent additional bonds to be cleaved during the thermal degradation process, these particular cross-links may indeed be much less stable than the remainder of the segments and may contribute to the significantly earlier weight loss events observed in the plot. Uncurable polyimide **6** performs poorly in comparison with the cross-linked materials in terms of char yield, a likely result of the high loading level of aliphatic RF-24 in the polymer backbone. Polyimide **11** exhibits the best overall thermal stability due to its slightly lower loading level of RF-24 but more importantly its greater number of cross-links, which are thermally stable triazine rings formed through the reaction of the cyanate ester groups. Polyimide **13** suffers early weight losses in an oxygen-containing environment but exhibits a relatively high char yield due to the silicon component. The materials overall demonstrate thermal stability similar to other polyimides that contain the inorganic hybrid POSS cages.

Film processing and atomic oxygen resistance studies. Typical for all POSS-functionalized polymers produced in this study, polyimide **7** shows good solubility in a number of organic solvents, most likely as a result of the presence of the seven *iso*-butyl substituents of POSS and the presence of the flexible alkyl spacer cadaverine in the polyimide backbone. Thick films (~70 microns) of this material can be cast from 20 wt-% solutions in cyclohexanone. The films appear essentially transparent and show only a slight brown coloration (Figure 7). This polymer provides an example of very high POSS loading (~36 wt-% POSS, ~17 wt-% Si_8O_{12}) while maintaining excellent film qualities.

Figure 7. A photograph of the ONR symbol (actual size 1.5” x 0.75”) taken through a thick film (~50 micron) of polymer **7** supported on a glass slide. The film was doctor-bladed from a 20 wt-% solution of cyclohexanone.

Upon solvent casting **9** (2 mil, 31 wt-% POSS, ~15 wt-% Si_8O_{12}) a thin transparent free-standing film is obtained. The sample is exposed to an atomic oxygen beam[13] using an apparatus and conditions published previously. A Kapton® film is run concurrently in the chamber to provide an accurate and instant measure for the degree of stabilization (or passivation) towards chemical degradation. In addition, a mask is placed over the samples to provide a very detailed 3-dimensional architecture and greatly assists in measuring the physical loss of material in the exposed areas. Data from the AO exposure of polymer **9** show *the new POSS-modified polyimide experiences no detectable degradation when exposed to atomic oxygen relative to Kapton® (the latter erodes ~11-12 microns for this amount of AO exposure).* Typically once the mask is removed from an AO exposed sample, a vivid pattern of the grid can be seen. *A very unique feature for polymer* ***9*** *is that no pattern is detectable after mask removal and the films remain transparent (Figure 8).*

Figure 8. Photograph of polymer **9** (left) and the Kapton® standard (right) after side-by-side AO exposure.

Concluding Remarks. We have presented a facile route for the covalent attachment of a commercially available POSS unit to a variety of polyimide backbones. Furthermore, during the attachment chemistry a reactive crosslinking group can be added concomitant with POSS and thus generate a thermally curable and easily processed coating material. The POSS-modified polyimides prepared in this study have a wide range of Tg's (120-215 ºC) and can possess a significant level of fluorine content with no apparent phase separation.

By thermal curing reactions we can prepare POSS-polyimides that remain optically clear, show good solvent resistance, and develop a final T_g of 250 ºC that is close to the T_g of the unmodified backbone. A 31 wt-% POSS (15 wt-% Si_8O_{12}) content material was tested for AO resistance and found to show exceptionally good characteristics with no detectable erosion relative to Kapton®.

Experimental:

General Synthetic Methods: All manipulations of compounds and solvents were carried out using standard Schlenk techniques. 1-Methyl-2- pyrrolidinone (NMP), dichloromethane, tetrahydrofuran (THF) and ether solvents were purchased as the anhydrous grade and inhibitor-free from Aldrich and used as received. ^{1}H and ^{13}C NMR measurements were performed using a Bruker AC 200 or Bruker 400 MHz instrument. ^{1}H and ^{13}C NMR chemical shifts are reported versus the deuterated solvent peak (Solvent, ^{1}H, ^{13}C: $CDCl_3$, ™ 7.25 ppm, ™ 77.0 ppm). Phthalic anhydride, cadaverine (1,5-pentanediamine), 4-*t*butyl aniline, adipoyl chloride, 4-dimethylaminopyridine (DMAP), 2,6-di-*t*-butyl- 4-methylpyridine, triethylamine, cyanogen bromide, 2-(4-hydroxyphenyl)ethanol and 2-hydroxyethyl methacrylate were purchased from Aldrich Chemical Co. And used as received. 4,4’-(Hexafluoroisopropylidene)diphthalic anhydride (6-FDA) and 2,2-bis(4-aminophenyl)hexafluoropropane were purchased from CHRISKEV Company and used as received. The 2,2’-Dimethyl-4,4’-methylene-*bis*-

(cyclohexylamine) (RF-24) was purchased from Resin Formulators and the 3-Aminopropylisobutyl-POSS® was purchased from Hybrid Plastics, both used as received. Elemental analyses were performed at Atlantic Microlab, Inc., Norcross, GA.

Film Preparation: Films utilized in erosion testing through atomic oxygen exposure were prepared by dissolving the desired polyimide in cyclohexanone at a solute concentration of 12.5 wt-%. The solutions were subsequently purified in a clean room environment through 5 micron syringe driven filter units. Free-standing Kapton® film substrates were coated with the resultant solutions either by conventional blade casting or spray coating using a household-spraying device at minimal gas pressures. The coated films were baked or cured under an inert nitrogen atmosphere according to the appropriate protocol (2 h at 70 ºC, 1 h at 200 º C, and then 4 h at 250 ºC). Final target film thicknesses of 25 – 50 microns for AO testing were measured vertically using a Dektak profilometer.

Thermal Analysis Measurements and Techniques. Differential scanning calorimetry (DSC): Glass transition temperature (T_g) measurements of all of the polyimides, in addition to reaction kinetics studies for the curable polyimides, were conducted on a TA Instruments Q Series 10 calorimeter. Glass transition temperatures were obtained by analysis of dynamic temperature sweeps of 3 – 5 mg samples at a heating rate of 20 °C/min slightly beyond the observed inflection, followed by cooling to 50°C and reheating again at a rate of 10 °C/min to obtain the desired T_g. Influences from sample repositioning and volatile release are eliminated through implementation of this technique. Isothermal curing data for the curable polyimides was acquired through thermal cycling and observance of T_g progression by holding the sample at the isothermal curing temperature for a 30 min period, followed by cooling to 70 °C at a rate of 5 °C/min, then heating back to the curing temperature at a rate of 10 °C/min where the progressed T_g was witnessed. This procedure was followed until cessation of T_g movement was observed. Thermogravimetric Analysis (TGA) was performed using a TA Instruments Hi-Res TGA 2950 Thermogravimetic Analyzer. The samples (2 – 3 mg) were heated in either nitrogen (30 ml/min) or air (30 ml/min) atmospheres from ambient temperature to 600 °C at a heating rate of 10 °C/min.

General Procedure for Preparation of CH_2OH-Functionalized Polyimide: A typical procedure is as follows: A Schlenk flask was charged with 3,5-*bis*(4-aminophenoxy)-1-hydroxymethylbenzene (1.000 g, 3.008 mmol), RF-24 (4.064 g, 17.045 mmol) and NMP (70 ml). When the solution had become homogenous 6-FDA (8.730 g, 19.651 mmol) and phthalic anhydride (0.119 g, 0.802 mmol, 2 mol% end-cap) were added in one portion. The mixture was stirred at ambient temperature for 16 h then fitted with a reflux condenser and immersed in an oil bath heated at 180 °C for 6 h. The reaction vessel was removed from the oil bath, allowed to spontaneously cool for 30 min and then poured into a flask containing vigorously stirred methanol (1.5 L). Vigorous stirring of the methanol was maintained during the entire precipitation process. The precipitated polyimide was collected on a 600 ml medium porosity glass-frit, washed with methanol (~1.5 L), then dried under reduced pressure for 12 h at 70 °C. This gave CH_2OH-functionalized polyimide **1** (11.85 g, 90%, M_n ~ 4,000, polydispersity 2.2, T_g 260 °C) as an off-white powder. ^1H NMR ($CDCl_3$) ™ 8.15- 7.55 (overlapping m, aromatic H's), 7.38 (d, J = 8.1 Hz, 4H), 7.14 (d, J = 8.2 Hz, 4H), 6.84 (s, 2H), 6.73 (s, 1H), 4.67, (s, 2H, CH_2OH), 4.45-4.13 (br m), 3.85-3.56 (br m), 2.65-0.50 (br overlapping m).

Selected ^{13}C NMR ($CDCl_3$) signals: ™ 167.7, 167.5, 166.4, 166.3, 158.2, 156.9, 138.9, 135.7, 132.8 (br), 128.3, 125.6 (br), 123.6 (br), 122.2, 119.6, 112.8, 109.7, 65.3 (br, CH_2OH), 57.8, 44.4 (br), 41.8 (br), 34.0 (br), 33.6 (br), 32.9 (br), 29.8, 19.4, 19.2. Anal. Calcd for **1**: C, 63.22; H, 4.64. Found: C, 61.85; H, 4.67. Polyimides **2**, **3**, **4**, and **5** were produced in a similar manner utilizing the appropriate monomers and selected data is presented below:

Polymer 2: (24.0 g, 93%, M_n ~ 10,000, polydispersity 2.1, T_g 196 °C) ^{1}H NMR ($CDCl_3$) ™ 8.15-7.65 (overlapping m, aromatic H's), 7.38 (d, *J* = 7.8 Hz, 4H), 7.13 (d, *J* = 7.5 Hz, 4H), 6.83 (s, 2H), 6.72 (s, 1H), 4.65 (s, 2H, CH_2OH), 3.69 (br s, 4H), 2.91 (br s), 1.72 (br s, 4H), 1.41 (br s, 2H). Selected ^{13}C NMR ($CDCl_3$) signals: ™ 167.4, 167.3, 166.4, 166.3, 158.3, 156.9, 145.0, 139.5, 138.9, 138.8, 136.2, 135.7, 134.7, 134.1, 133.2-132.3 (br aromatic signals), 128.3, 126.6, 125.6, 125.0, 124.3, 124.0, 123.7, 123.4, 122.2, 119.6, 112.7, 109.7, 64.6 (CH_2OH), 38.3, 28.2, 24.3. Anal. Calcd for **2**: C, 59.93; H, 3.03. Found: C, 59.32; H, 3.06.

Polymer 3: (23.6 g, 80%, M_n ~ 9,500, polydispersity 1.8, T_g 279 °C) ^{1}H NMR ($CDCl_3$) ™ 8.11-7.77 (overlapping m, aromatic H's), 7.62-7.48 (overlapping m, aromatic H's), 7.37 (br d, 4H), 7.13 (br d, 4H), 6.83 (br s, 2H), 6.71 (br s, 1H), 4.64 (br s, 2H, CH_2OH), 3.19 (br s, 1H, OH). Selected ^{13}C NMR ($CDCl_3$) signals: ™ 166.4, 166.2, 166.0, 165.8, 158.2, 156.9, 144.9, 139.6, 139.3, 136.4, 136.2, 134.9, 134.7, 133.1-132.5 (br aromatic signals), 131.4, 128.3, 126.6, 126.1, 125.7, 125.6, 125.0, 124.6, 124.4, 124.2, 124.0, 122.2, 119.6, 112.8, 109.7, 64.6. Anal. Calcd for **3**: C, 58.37; H, 2.28. Found: C, 58.19; H, 2.34.

Polymer 4: (18.3 g, 78%, M_n ~ 4,300, polydispersity 1.9, T_g 279 °C) $_{1}$H NMR ($CDCl_3$) ™ 8.02-7.65 (overlapping m, aromatic H's), 7.46-7.37 (m, 4H), 7.20- 7.13 (m, 4H), 6.84 (s, 2H), 7.67 (br s, 1H), 4.66 (s, 2H, CH_2OH), 4.37-4.15 (br m), 3.86-3.62 (br m), 2.55-0.42 (br overlapping m). Polymer **5**: (12.3 g, 87%, M_n ~ 5,500, polydispersity 1.8, T_g 267 °C) $_{1}$H NMR ($CDCl_3$) ™ 8.15-7.60 (overlapping m, aromatic H's), 7.52 (d, *J* = 7.8 Hz), 7.45- 7.29 (m, 4H), 7.21-7.04 (m, 4H), 6.84 (s, 2H), 6.72 (s, 1H), 4.65 (s, CH_2OH), 3.95-3.55 (br m), 2.65-0.50 (br overlapping m), 1.35 (s, 9H). Selected $_{13}$C NMR ($CDCl_3$) signals: ™ 167.7, 167.5, 166.44, 166.39, 166.3, 158.2, 156.9, 144.9, 139.5, 139.4, 138.8, 136.2, 135.7, 133.0-132.3 (br aromatic signals), 128.3, 126.6, 126.5, 126.2, 125.6, 125.0 (br), 124.3, 123.6 (br), 122.2, 119.6, 112.6, 109.7, 64.6 (CH_2OH), 57.8, 41.9, 34.0, 33.6, 32.9, 31.5, 29.8, 19.4, 19.2. Anal. Calcd for **5**: C, 62.95; H, 4.02.Found: C, 61.51; H, 4.06.

General Procedure for the Modification of PI-CH_2OH with a Diacid Chloride: A typical procedure is as follows: A THF solution (20 ml) containing polyimide **1** (2.0 g, 0.457 m-equivalents of OH/g), 2,6-di-*t*-butyl-4-methylpyridine (400 mg, 1.94 mmol), and DMAP (40 mg, 0.33 mmol) was treated with adipoyl chloride (2.5 ml, 17.14 mmol). Some precipitate was seen to form over the reaction period of 18 h, after which time the mixture was filtered through a plug of Celite® (1 x 2.5 cm) into a rapidly stirred solution of ether (400 ml). The polymer was collected by filtration and washed with ether (2 x 150 ml) taking care to protect the solution and polymer from air, then dried under reduced pressure (0.2 torr) for 30 min to afford 1.4 g (~68%) of acid chloride modified polyimide **1** containing ~ 5 wt-% residual ether. The polymer is used immediately for the next reaction without further purification. Polyimides **2**, **3**, **4**, and **5** were functionalized in a similar manner and were utilized immediately after formation.

General Procedure for Attachment of POSS to Acid Chloride Functionalized PI: A typical procedure is as follows: The acid chloride functionalized polyimide **1** (1.4 g) was dissolved in dichloromethane (35 ml) then treated with 3-aminopropylisobutyl-POSS (287 mg, 0.329 mmol). This mixture was stirred for 5 min and then in one portion DMAP (100 mg, 0.52 mmol) was added. The mixture was allowed to react with stirring for 2 h at ambient temperature, concentrated to ~20 ml and added to a rapidly stirred solution of methanol (400 ml). The resulting polymer was collected on a 150 ml medium porosity glass-frit, washed with methanol (2 x 150 ml) and then dried under reduced pressure at ~45 °C (~0.2 torr) for 24 h to afford POSS-functionalized polyimide **6** (1.5 g, 94%, M_n ~ 11,700, polydispersity 2.0, T_g 215 °C) as an off-white powder. ^{1}H NMR (CDCl$_3$) ™ 8.22-7.50 (overlapping m, aromatic H's), 7.40 (d, J = 8.3 Hz, 4H), 7.16 (d, J = 8.6 Hz, 4H), 6.82 (br s, 2H), 6.75 (br s, 1H), 6.69 (m), 5.51(br s), 5.07 (br s, 2H, CH$_2$OH), 4.61 (br s), 4.38-4.19 (br m), .3.92-3.73 (br m), 3.23-3.19 (m), 3.95-3.82 (br m), 2.62-0.57 (br overlapping m), 0.59 (d, J = 6.6 Hz, 14H). Anal. Calcd for **6**: C, 59.89; H, 5.24. Found: C, 59.04; H, 5.35. Polyimides **7**, **8**, and **9** were produced in a similar manner and selected data is presented below:

Polymer 7. (830 mg, 86%, M_n ~ 10,000, polydispersity 1.8, T_g 120 °C) ^{1}H NMR (CDCl$_3$) ™ 8.01-7.72 (overlapping m, aromatic H's), 7.39 (d, J = 8.5 Hz, 4H), 7.14 (d, J = 8.6 Hz, 4H), 5.51 (br s, 1H, NH), 5.05 (s, 2H, CH$_2$OH), 3.75-3.57 (br m), 3.25-3.12 (m), 2.41-1.19 (br overlapping m), 0.93 (br d, 42H), 0.58 (d, J = 7.0 Hz, 14H). Anal. Calcd for **7**: C, 54.01; H, 4.97. Found: C, 53.33; H, 4.98.

Polymer 8. (2.2 g, 85%, *Mn* ~ 9,000, polydispersity 1.8, T_g 176 °C) ^{1}H NMR ($CDCl_3$) ™ 8.13-7.72 (overlapping m, aromatic H's), 7.63-7.48 (m, aromatic H's), 7.40 (d, *J* = 8.3 Hz, 4H), 7.14 (d, *J* = 8.3 Hz, 4H), 5.51 (br s, 1H, NH), 5.06 (s, 2H, CH_2OH), 3.27-3.16 (m), 2.41-2.09 (overlapping m), 1.88-1.63 (overlapping m), 0.93 (br d, 42H), 0.58 (d, *J* = 7.0 Hz, 14H). Anal. Calcd for **8**: C, 53.73; H, 4.25. Found: C, 53.53; H, 4.33.

Polymer 9. (880 mg, 63%, *Mn* ~ 11,500, polydispersity 2.9, T_g 177 °C) ^{1}H NMR ($CDCl_3$) ™ 8.05-7.62 (overlapping m, aromatic H's), 7.40 (d, *J* = 7.5 Hz, 4H), 7.15 (d, *J* = 7.5 Hz, 4H), 6.81 (br s, 2H), 6.74 (br s, 1H), 5.51 (br s, 1H, NH), 5.06 (br s, 2H, CH_2OH), 4.35-4.19 (br m), 3.83-3.12 (m), 3.28-3.09 (m), 2.45-0.79 (br overlapping m), 0.58 (d, *J* = 6.9 Hz, 14H).

Preparation of 2-(4-cyanatophenyl)ethanol (10): A chilled (-20 °C) ether (55 mL) solution containing 2-(4-hydroxyphenyl)ethanol (1.50 g, 10.9 mmol) and cyanogen bromide (1.49 g, 14.1 mmol) was treated dropwise with triethylamine (1.51 mL, 10.9 mmol). A white precipitate was seen to form immediately and after 30 min the solid was removed by filtration on a medium porosity glass-frit and washed with ether (150 mL). The filtrate was washed with water (2 x 100 ml), dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield **10** (1.4 g, 79%) as a clear colorless viscous oil. ^{1}H NMR ($CDCl_3$)™ 7.34-7.20 (m, 4H), 3.86 (appt. q, *J* = ~6.5 Hz 2H), 2.88 (t, *J* = 6.5 Hz, 2H), 1.46 (t, *J* = 5.5 Hz, 1H, OH); ^{13}C NMR ($CDCl_3$) ™ 151.5 (aromatic C-O), 137.7 (aromatic C), 130.9, 115.3 (aromatic CH's), 108.8 (OCN), 63.3 (CH_2OH), 38.2 (CH_2).

Attachment of POSS and 2-(4-cyanatophenyl)ethanol (10) to Acid Chloride-functionalized PI (5): Acid chloride functionalized polyimide **5** (3.4 g) was dissolved in dichloromethane (100 ml) then treated with a 100 mg/ml dichloromethane solution of 2-

(4-cyanatophenyl)ethanol (**10**) (176 mg, 1.078 mmol, 0.438 equiv.) and 3-aminopropylisobutyl-POSS (702 mg, 0.80 mmol, 0.588equiv.). DMAP (340 mg, 2.78 mmol) was immediately added and the mixture stirred for 2 h at ambient temperature. The mixture was then concentrated to ~50 ml and added to a rapidly stirred solution of methanol (800 ml). The resulting polymer was collected on a 300 ml medium porosity glass-frit, washed with methanol (2 x 250 ml), then dried under reduced pressure at ~45 °C (~0.2 torr) for several hours to give POSS/cyanate ester-functionalized polyimide **11** (3.4 g, 81%, M_n ~ 7,000, polydispersity 1.8, pre-cure T_g 196 °C) as an off-white powder. ^{1}H NMR ($CDCl_3$) ™ 8.17-7.49 (overlapping m, aromatic H's), 7.39 (d, J = 8.2 Hz, 4H), 7.14 (d, J = 8.2 Hz, 4H), 6.80-6.65 (overlapping signals), 5.01 (br s, 1H, NH), 5.06 (br s, 2H, CH_2OH), 4.25-4.4.19 (m, 2H). 3.83-3.61 (br m), 3.23-3.15 (m), 2.99-2.73 (br m), 2.48-0.80 (br overlapping m), 0.58 (d, J = 6.8 Hz, 14H). Anal. Calcd for **11**: C, 59.92; H, 4.83. Found: C, 59.43; H, 4.88.

Attachment of POSS and HEMA to Acid Chloride-functionalized PI (3): Acid chloride functionalized polyimide **3** (2.1 g) was dissolved in dichloromethane (50 ml) then treated with HEMA (53 mg, 0.41 mmol, 0.4 equiv.) and 3-aminopropylisobutyl-POSS (710 mg, 0.81 mmol, 0.8 equiv.). DMAP (200 mg, 1.6 mmol) was immediately added and the mixture stirred for 6 h at ambient temperature. The mixture was then concentrated to ~20 ml and added to a rapidly stirred solution of methanol (400 mlL). The resulting polymer was collected on a 150 ml medium porosity glass-frit and washed with methanol (2 x 100 ml) then dried under reduced pressure at ~45 °C (~0.2 torr) for several hours to give POSS/HEMA-functionalized polyimide **12** (2.25 g, 83%, M_n ~ 6,000, polydispersity 1.5, pre-cure T_g 167 °C). ^{1}H NMR ($CDCl_3$) ™ 8.08-7.78

(overlapping m, aromatic H's), 7.61-7.50 (m, aromatic H's), 7.40 (d, *J* = 8.7 Hz, 4H), 7.14 (d, *J* = 8.7 Hz, 4H), 6.81 (br s, 2H), 6.74 (br s, 1H), 6.19 (br s, olefinic H), 5.56 (br s, 2H, olefinic H and NH), 5.06 (br s, 2H, CH_2OH), 4.35-4.28 (m), 3.34-3.12 (m, 2H), 2.46-2.29 (br m), 2.24-2.06 (br m), 1.90-1.52 (overlapping m), 0.99-0.82 (m, 42H), 0.58 (d, *J* = 7.0 Hz, 14H). Anal. Calcd for **12**: C, 54.48; H, 4.02. Found: C, 54.35; H, 4.13.

Attachment of POSS and HEMA to Acid Chloride-functionalized PI (4): Acid chloride functionalized polyimide **4** (1.9 g) was dissolved in dichloromethane (45 mL) then treated with HEMA (43.7 mg, 0.34 mmol, 0.4 equiv.) and 3-aminopropylisobutyl-POSS (587 mg, 0.67 mmol, 0.8 equiv.). DMAP (170 mg, 1.39 mmol) was immediately added and the mixture stirred for 8 h at ambient temperature. The mixture was then concentrated to ~25 ml and added to a rapidly stirred solution of methanol (400 ml). The resulting polymer was collected on a 150 ml medium porosity glass-frit and washed with methanol (2 x 150 ml) then dried under reduced pressure at ~45 °C (~0.2 torr) for several hours to give POSS/HEMA-functionalized polymer **13** (1.97 g, 87%, M_n ~ 11,000, polydispersity 2.1, pre-cure T_g 190 °C). ^{1}H NMR ($CDCl_3$) ™ 8.02-7.63 (overlapping m, aromatic H's), 7.40 (d, *J* = 7.7 Hz, 4H), 7.14 (d, *J* = 7.5 Hz, 4H), 6.92-6.75 (br overlapping s), 6.08 (br s, olefinic H), 5.52 (br s, 2H, olefinic H and NH), 5.06 (br s, 2H, CH_2OH), 4.31 (br s), 3.86-3.66 (br m), 3.28-3.12 (br m), 2. 42-0.66 (br overlapping m), 0.58 (d, *J* = 6.6 Hz, 14H). Anal. Calcd for **13**: C, 57.69; H, 5.26. Found: C, 56.37; H, 5.13.

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