Synthesis of Bis(4-Anilinylmethylsilyloxy)-Octaphenylsilsesquioxane-Modified Thermosetting IMIDE Oligomers

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A series of Bis(4-Anilinylmethylsilyloxy)-octaphenyl-sil sesquioxane-modified thermosetting imide oligomers were prepared and the structure were characterized by FTIR and NMR. Bis(4-Anilinylmethylsilyloxy)-Octaphenyl-sil sesquioxane was synthesized using a previously reported method and was reacted with 6-FDA, ODA and PEPA monomers to produce oligomers with 0.0, 11.9, 18.8, 23.3, 26.4, and 28.8 weight percent Si_{10}O_{14}. FTIR analysis was performed to ensure complete imidization. NMR spectra (^{1}H, ^{13}C and ^{29}Sil) were collected and integrated to ensure the target chain length was obtained.
SYNTHESIS OF BIS(4-ANILINYL METHYLSILYLOXY)OCTAPHENYL SILSESQUIOXANE-MODIFIED THERMOSETTING IMIDE Oligomers

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Abstract
A series of Bis(4-anilinylmethylsilyloxy)-octaphenyl-silsesquioxane-modified thermosetting imide oligomers were prepared and the structure were characterized by FTIR and NMR. Bis(4-Anilinylmethylsilyloxy)-Octaphenyl-silsesquioxane was synthesized using a previously reported method and was reacted with 6-FDA, ODA and PEPA monomers to produce oligomers with 0.0, 11.9, 18.8, 23.3, 26.4, and 28.8 weight percent Si₁₀O₄. FTIR analysis was performed to ensure complete imidization. NMR spectra (1H, 13C and 29Si) were collected and integrated to ensure the target chain length was obtained.

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SYNTHESIS OF BIS-(4-ANILINYL METHYLISILYLOXY)-OCTAPHENYLSELSIOXANEMODIFIED THERMOSETTING IMIDE OLIGOMERS

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Introduction
Polyimides have gained considerable interest in the development of high performance products. They have a combination of many desirable properties, including excellent thermal, mechanical, and dielectric properties, which have lead to their insertion into myriad applications including electrical insulation, spacecraft protection, aerospace components, and adhesives. However, more prolific use has been limited due to detrimental moisture uptake by the highest performing variants of the polyimide class. Beyond the deterioration of thermo-mechanical properties, rapid heating can trigger quick release of absorbed water causing delamination of polyimide matrix composite materials, often resulting in component failure. Barrier methods to decrease moisture uptake increase the number of interfaces and are therefore associated with risk. Therefore, it would be advantageous to reduce the polymer matrix’s affinity for water itself. In works by Kakimoto et al. the incorporation of a peripherally aromatic POSS silsesquioxane into thermoplastic polyimides was investigated. A variety of linear semi-aromatic polyimides were found to reduce moisture uptake by up to 40%. However, in all materials investigated, the glass transition temperature (Tg) and mechanical properties were also greatly reduced. The objective of this work is to explore the effect of various amounts of bis-(4-Anilinyl, Methylisilyleoxy)octaphenylsilsesquioxane (POSS) on thermosetting oligomers. The specific goal is the reduction of backbone polarity without detrimental effects on mechanical properties.

Experimental
Materials. 4,4’-Diaminodiphenyl ether (ODA) and 4,4’-(hexafluoropropyleneoxy)-diphthalic anhydride (6-FDA) were purchased from Lancaster Synthesis Inc. Phenylethynyl phthalic anhydride (PEPA) was obtained from Maverick Corporation. The ODA, 6-FDA and PEPA were all purified by sublimation under dynamic vacuum. Bis-(4-AnilinylMethylisilyleoxy)octaphenylsilsesquioxane (cis and trans isomers) was synthesized using a previously reported method. Anhydrous 1-methyl-2-pyrrolidinone (NMP) and methanol were purchased from Sigma-Aldrich and used as received. HPLC grade chloroform was purchased from Burdick and Jackson and used as received. HPLC grade toluene was purchased from J. T. Baker and used as received.

Instrumentation. NMR spectra were obtained on Bruker 300 or 400 MHz spectrometers. All spectra were referenced to residual H or 13C in the solvent used. 29Si spectra were obtained using an inverse gated 30p pulse sequence with a 12 second delay between pulses, and were referenced to external SiMe3 at 0 ppm.

Synthesis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>MO Wt.</th>
<th>POSS</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C4H4NO</td>
<td>C4H6NO</td>
<td>C4H4N2O2</td>
</tr>
<tr>
<td>248.23g</td>
<td>65-44g</td>
<td>200.24g</td>
<td>1355.98g</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
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<td>5</td>
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<tr>
<td>6-FDA monomer was added to an NMP solution of ODA and/or POSS in a dry nitrogen environment. After allowing the reaction to proceed for 60 minutes, an NMP solution of PEPA was then added to produce a total concentration of 10 wt% solids. The reaction was allowed to stir overnight in a dry nitrogen environment. At this point, a 1 – 2 mL aliquot of the amic acid material was removed. This aliquot was added dropwise to ether and allowed to stir overnight. The solid precipitate was collected by filtration and washed with ether. It was then dried under vacuum and NMR data (1H, 13C, and 29Si) was collected. To the remainder of the reaction mixture, toluene was added to produce a total concentration of 80% toluene by volume. The reaction was then heated overnight to 155 °C using the dean-stark methodology to promote imidization. The reaction was cooled to room temperature and added dropwise to methanol and allowed to stir overnight. The solid product was collected by filtration and washed with methanol. FTIR data was taken at this point to ensure complete imidization. The solid product was then dried under vacuum, and NMR spectra were obtained.</td>
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Results and Discussion

The synthesis of the POSS containing oligomers depicted in Figure 1, involved the reaction of the 6-FDA diimide with the POSS diamine and ODA. The oligomers were then endcapped with the diimide, PEPA. This reaction was expected to produce an AB oligomer with an average chain length containing 5 diamines and terminated with PEPA on both ends.

Figure 1. Synthesis of POSS containing oligomers.

In the 1H NMR spectra, the total integral was normalized to the expected number of protons for each particular oligomer (80 – 0 POSS, 126 – 1 POSS, 172 – 2 POSS, 218 – 3 POSS, 264 – 4 POSS, 310 – 5 POSS). The peaks from 7.8 ppm – 8.5 ppm are attributed to 6-FDA and the 3 protons on the phenyl ring of PEPA. The integral in this region remained constant at 30 as the amount of end cap and 6-FDA was not varied. The peaks between 6.8 ppm and 7.8 ppm are attributed to the protons of ODA, the phenyl rings of the POSS and five of the aromatic protons in each PEPA. The integrals are shown to increase by the expected amount of 40 protons with each addition and reduction of POSS and ODA respectively. The peaks between 0.00 and 1.5 ppm are attributed to the two methyl groups of the POSS. Relatively speaking the integrals in the methyl region are shown to increase by 6 with each additional POSS (Figure 2). This data is also tabulated in Table 2.
Table 2. Integrated values of normalized $^1$H NMR for each oligomer.

<table>
<thead>
<tr>
<th>Region</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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<tbody>
<tr>
<td>7.6-9.3 ppm</td>
<td>28.48</td>
<td>28.63</td>
<td>29.04</td>
<td>29.16</td>
<td>29.60</td>
<td>29.86</td>
<td>30.30</td>
<td>30.96</td>
</tr>
<tr>
<td>5.8-7.6 ppm</td>
<td>72.77</td>
<td>73.15</td>
<td>73.69</td>
<td>74.10</td>
<td>74.61</td>
<td>74.92</td>
<td>75.48</td>
<td>76.10</td>
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<td>4.0-5.8 ppm</td>
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<tr>
<td>3.8-5.0 ppm</td>
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<td>10.50</td>
<td>10.95</td>
<td>11.40</td>
<td>11.90</td>
<td>12.40</td>
<td>13.00</td>
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</table>

Figure 2. $^1$H NMR spectra of oligomers containing 0-5 equivalents of POSS respectively.

Figure 3 displays the $^{13}$C NMR spectra of oligomers containing 0-5 equivalents of POSS. In the carbonyl region (>160 ppm) of the spectra are two sets of peaks attributed to the carbonyls of the 6-FDA and the carbonyls of the PEPA endcaps. Although integration of $^{13}$C spectra is fraught with error, it is not unreasonable to compare integrals of like-structured carbons—especially quaternary carbons that receive no NOE enhancements. The set of peaks attributed to the 6-FDA carbonyls was calibrated to 16 in each spectrum. The integrals of the set of peaks due to the PEPA carbonyls was expected to be 4 and is shown to be approximately 4 in all spectra. The peaks at 87 and 94 ppm are attributed to the acetylene carbons of the PEPA endcaps. In each of the spectra, each of these integrals is approximately 2, indicating chains are end capped.

Table 3. Integrated values of calibrated $^{13}$C NMR for each oligomer.

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<tr>
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Figure 3. $^{13}$C NMR spectrum and structural assignments of oligomers containing 0-5 equivalents of POSS respectively.

Conclusions

Oligomers of varying POSS content were synthesized in high yield. $^1$H and $^{13}$C NMR analysis show the oligomers to be the expected products with the expected chain lengths. Future research will focus on optimizing the synthesis method and collecting thermal and mechanical property data, coupled with the effect of humidity on these properties.

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References.

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