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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 $Si_{10}O_{14}$. 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.

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SYNTHESIS OF BIS(4-ANILINYLMETHYLSILYLOXY)-OCTAPHENYLSILSESQUIOXANE-MODIFIED THERMOSETTING IMIDE OLIGOMERS

Dana M. Pinson,[1] Gregory R. Yandek,[2] Timothy S. Haddad,[1] Joseph M. Mabry[2]

[1]ERC Incorporated, Air Force Research Laboratory
Edwards Air Force Base, CA 93524
[2]Air Force Research Laboratory, Propulsion Directorate
Edwards Air Force Base, CA 93524

Abstract
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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.[1-3] 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.[4-5] 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 (T_g) and mechanical properties were also greatly reduced. The objective of this work is to explore the effect of various amounts of bis(4-Anilinyle, Methylsilyloxy)octaphenylsilsesquioxane (POSS) on thermosetting oligoimides. The specific goal is the reduction of backbone polarity without detrimental effects on mechanical properties.

Experimental

Materials. 4,4' – Diaminodiphenylether (ODA) and 4,4' – (hexafluoroisopropylidiene)diphthalic anhydride (6-FDA) were purchased from Lancaster Synthesis Inc. Phenylethynyl phthalic anhydride (PEPA) was obtained from Maverick Coporation. The ODA, 6-FDA and PEPA were all purified by sublimation under dynamic vacuum. Bis(4-AnilinylMethylsilyloxy)octaphenylsilsesquioxane (cis and trans isomers) was synthesized using a previously reported method.[3,4] Anhydrous 1-methyl-2-pyrolidinone (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 ^{1}H or ^{13}C in the solvent used. ^{29}Si spectra were obtained using an inverse gated 30° pulse sequence with a 12 second delay between pulses, and were referenced to external $SiMe_4$ at 0 ppm.

Synthesis.

Table 1. Equivalents of monomers used in each of the oligomers.

Compound Mol. Wt. Formula	PEPA 248.23 g $C_{16}H_8O_3$	6-FDA 444.24 g $C_{19}H_6F_6O_6$	ODA 200.24 g $C_{12}H_{12}N_2O$	POSS 1355.98 g $C_{62}H_{58}N_2O_{14}Si_{10}$
Control	2	4	5	0
1 POSS	2	4	4	1
2 POSS	2	4	3	2
3 POSS	2	4	2	3
4 POSS	2	4	1	4
5 POSS	2	4	0	5

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 (^{1}H, ^{13}C, and ^{29}Si) 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.[3] The solid product was then dried under vacuum, and NMR spectra (^{1}H, ^{13}C, and ^{29}Si) were obtained.

Results and Discussion

The synthesis of the POSS containing oligomers depicted in **Figure 1**, involved the reaction of the 6-FDA dianhydride with the POSS dianiline and/or ODA. The oligomers were then endcapped with the dianhydride, 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.

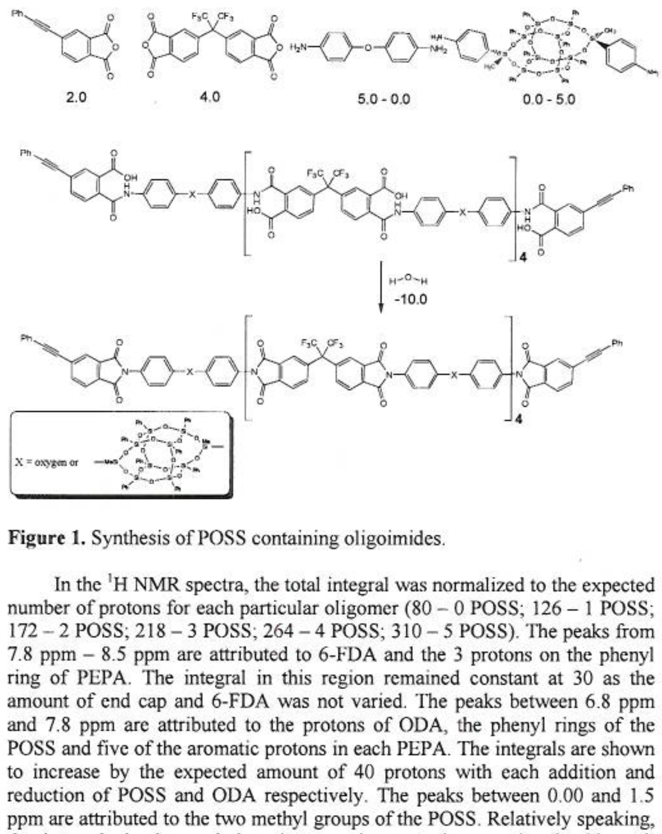

Figure 1. Synthesis of POSS containing oligoimides.

In the ^{1}H 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.

Region	0		1		2		3		4		5	
	Expected	Observed	Expected	Observed	Expected	Observed	Expected	Observed	Expected	Observed	Expected	Observed
7.8 – 8.5 ppm	30	31.08	30	29.36	30	26.70	30	27.59	30	27.45	30	32.55
7.0 – 7.8 ppm	50	56.72	90	90.97	130	133.26	170	170.91	210	216.52	250	244.41
POSS methyl region 0.0 – 1.5 ppm	0	0	6	5.67	12	12.03	18	19.5	24	20.55	30	32.04

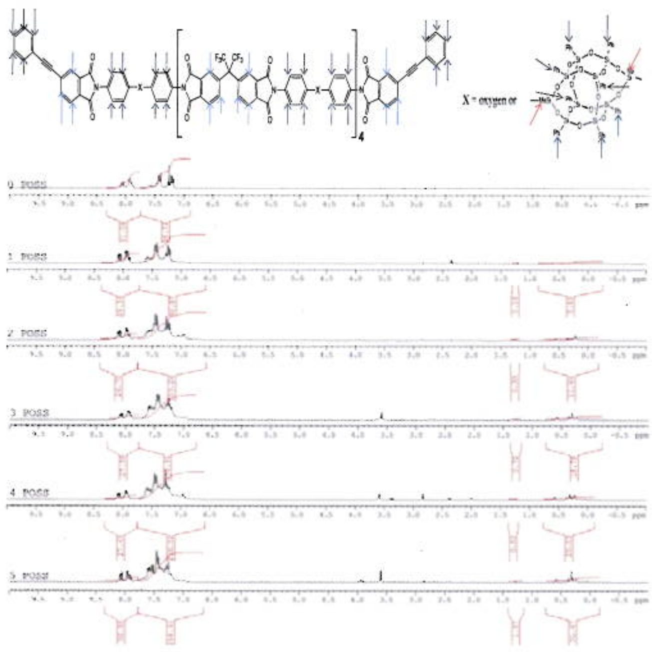

Figure 2. ^{1}H NMR spectra of oligomers containing 0 -5 equivalents of POSS respectively.

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.

Region	0		1		2		3		4		5	
	Expected	Observed	Expected	Observed	Expected	Observed	Expected	Observed	Expected	Observed	Expected	Observed
Endcap Carbonyls 166 – 167 ppm	4	4.27	4	3.59	4	3.15	4	3.23	4	3.14	4	2.73
6-FDA Carbonyls 166 – 165 ppm (all integrals calibrated to 16, except 5)	16	16	16	16	16	16	16	16	16	16	16	8.15
Acetylene carbon 94 ppm	2	1.87	2	1.92	2	2.00	2	1.86	2	1.95	2	2.00
Acetylene Carbon 87 ppm	2	1.96	2	1.98	2	1.99	2	1.88	2	1.85	2	2.15
6 – FDA septuplet 65 – 66 ppm	4	5.04	4	4.55	4	6.01	4	4.05	4	4.42	4	Can't be seen
[illegible]	0	0	2	2.51	4	8.19	6	12.48	8	14.20	10	33.70

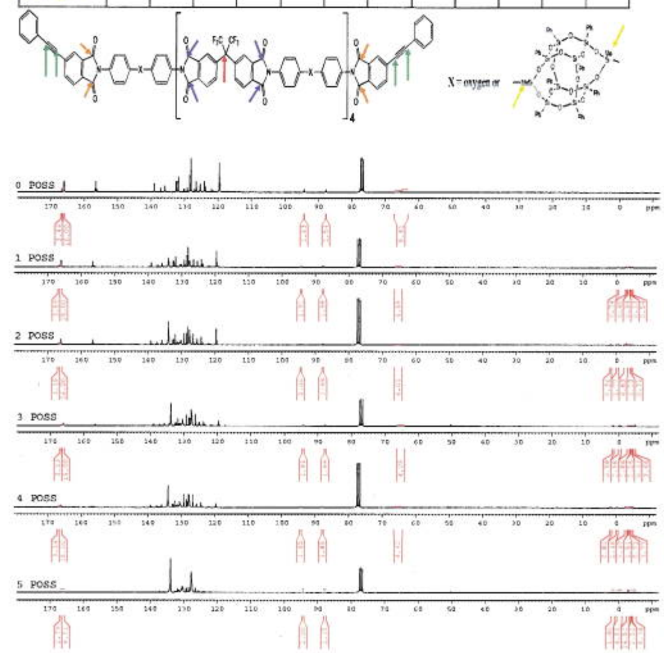

Figure 3. ^{13}C NMR spectrum and structural assignments of oligomers containing 0 -5 equivalents of POSS respectively.

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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