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14. ABSTRACT High performance polyimides are utilized in a number of aerospace and microelectronic applications requiring thin films, wire coatings, adhesives, and matrices for fiber reinforced composites. ¹⁻³ In general, thermoplastic polyimides are produced from reactions between aromatic diamines and dianhydrides to form polyamic acids which in turn are thermally imidized to yield desired polymers. ¹ Due to inter-chain interactions and polymer chain rigidity, such materials are often intractable exhibiting viscosities prohibitive to the fabrication of components via melt processing. Limiting molecular weight through reactive endcapping promotes processability by improving solubility in solvents and reducing melt viscosity. ³ This approach also facilitates the precise design of thermosetting oligomers to deliver target properties once they are cured to form polymer networks.					
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SYNTHESIS AND PROPERTIES OF BIS(ANILINE, METHYL)SILOXY-OCTAPHENYLSILSESQUIOXANE MODIFIED THERMOSETTING POLYIMIDE OLIGOMERS

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Introduction

High performance polyimides are utilized in a number of aerospace and microelectronic applications requiring thin films, wire coatings, adhesives, and matrices for fiber reinforced composites.¹⁻³ In general, thermoplastic polyimides are produced from reactions between aromatic diamines and dianhydrides to form polyamic acids which in turn are thermally imidized to yield desired polymers.¹ Due to inter-chain interactions and polymer chain rigidity, such materials are often intractable exhibiting viscosities prohibitive to the fabrication of components via melt processing. Limiting molecular weight through reactive endcapping promotes processability by improving solubility in solvents and reducing melt viscosity.³ This approach also facilitates the precise design of thermosetting oligomers to deliver target properties once they are cured to form polymer networks.

Due to the inherent electronic polarity of the monomers used to synthesize most polyimides, resultant polymers suffer from property degradation due to exposure to humid conditions, especially at elevated temperatures, often compromising their capabilities in such environments. The use of monomers with less susceptibility to hydrogen bonding with water molecules without sacrificing crucial mechanical properties and thermo-oxidative stability would afford new polyimide materials for applications currently inaccessible by the state-of-the-art. Recent work by Kakimoto et. al. demonstrated that copolymerization of polyhedral oligomeric silsesquioxane (POSS) diamines into thermoplastic pyromellitic dianhydride-oxydiphenylene aniline (KaptonTM) reduced its moisture uptake by 83% concurrently improving mechanical properties.⁴ The objective of this work is to examine the effects of incorporating similar silsesquioxane anilines into the backbones of thermosetting polyimides, particularly elucidating influences on melt processing, curing kinetics, and delivered properties in the cured state. In particular, polymers synthesized from 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) and 4,4'-oxydianiline have been shown to exhibit relatively high moisture uptake in comparison with other polyimides,⁵⁻⁶ therefore, these monomers have been selected to construct the backbone of the oligomers used in this study. The amic acid route to the formation of phenylethynyl-terminated imide oligomers similarly used by Chen et. al.⁷ has been adopted in this work due to the insolubility of the chosen POSS monomers in alcohol.

Experimental

Materials. PhenylPOSS-tetrol was purchased from Hybrid Plastics. 4-[Bis(N, N-trimethylsilyl)phenylamino]methylchlorosilane was acquired from Gelest, Inc. Triethyl amine (NEt₃), tetrahydrofuran (THF), diethyl ether, methyl alcohol (MeOH), toluene, 4,4'-oxydianiline (ODA, m.p. 84°C), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA, m.p. 246°C) and N-methyl-2-pyrrolidone (NMP) were purchased from the Aldrich Chemical Co. 4,4'-ODA was recrystallized from ethanol prior to use. 6FDA was dried under vacuum at 150°C for 24 hrs prior to use. 4-phenylethynyl amine (PEA, m.p. 130°C) was synthesized in our laboratory.

Instrumentation. ¹H, ¹³C, and ²⁹Si nuclear magnetic resonance spectra were obtained on a Bruker 300 MHz spectrometer using 5 mm o.d. tubes. CDCl₃ and Me₄Si were used as internal and external reference standards, respectively.

Synthesis of Bis(aniline, methyl)siloxy-octaphenylsilsesquioxane. Under a nitrogen atmosphere, in a 50 mL round-bottomed flask, phenylPOSS-tetrol, Phenyl₈Si₈O₁₀(OH)₄, (2.00g, 1.87 mmol) was suspended in 10 mL of anhydrous THF. To this stirred suspension, a solution of 4-[Bis(N, N-trimethylsilyl)phenylamino]methylchlorosilane (1.376 g, 3.93 mmol) and NEt₃ (0.776 g, 7.67 mmol) in THF (10 mL) was slowly added in a drop-wise manner. After 30 minutes, the solution was filtered to remove NEt₃HCl (974 mg, 7.08 mmol, 95 % theoretical) and the solvent was removed under vacuum. Approximately 1 mL of diethylether was added to the product

followed by 20 mL of MeOH to make a well-stirred suspension of white-colored intermediate. The trimethylsilyl groups were hydrolyzed by the addition of 1 drop of concentrated acetic acid and 1 hour of stirring. The product was isolated by filtration and dried under a nitrogen stream to give a white powder in 77 % yield (1.922 g, 1.44 mmol), consisting of a mixture of cis and trans POSS isomers. ¹H NMR (CDCl₃, δ) 7.83-7.10 ppm (m, 44H), 6.60. ppm (m, 4H), 3.3 ppm (broad s, 4H, NH₂), 0.11 ppm (s, 6H). ²⁹Si NMR (CDCl₃) -29.7, -78.2, -79.1, -79.3, -79.4 ppm. The reaction scheme for this POSS monomer is depicted in **Figure 1**.

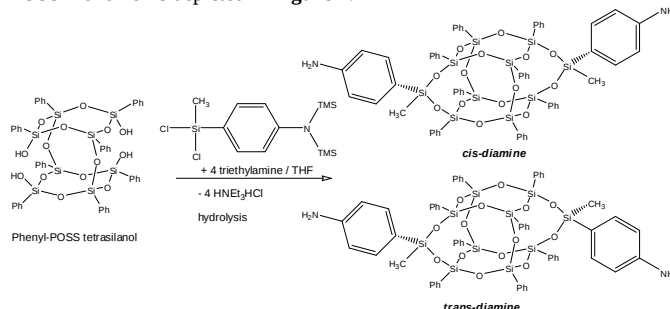


Figure 1. Reaction schematic for Bis(aniline, methyl)siloxy-octaphenylsilsesquioxane resulting in a mixture of cis and trans isomers.

Synthesis of Phenylethynyl-Endcapped Polyimide and POSS-Polyimide Oligomers. To a dried three-neck 100 mL flask configured with a Dean-Stark trap, a condenser, a nitrogen inlet and outlet, and a mechanical stirrer, 4,4'-ODA (2.41 g, 12.52 mmol), 4-PEA (1.21 g, 6.26 mmol), and NMP (10 mL) were added. The mixture was stirred at room temperature for approximately 1 hr until a homogeneous solution was obtained. A slurry of 6FDA (6.95 g, 15.65 mmol) in 8 mL of NMP was added slowly during stirring. 6 mL of additional NMP was used to rinse the slurry-containing vessel to ensure complete addition of the dianhydride. The resulting solute concentration was 30% by weight. After the addition of the slurry, the reaction temperature was increased to 80°C and was stirred for 6 hrs. Toluene (5 mL) was subsequently added. The resultant mixture was heated to 185°C and refluxed for 10 hrs during which time toluene was removed after which the solution was cooled to 120°C. The warm solution was poured into agitated hot water to precipitate the solid. The particles were isolated by filtration and washed with warm water three times. The filtrate was then dried in air at room temperature for 4 hours and then dried under vacuum at 130°C for 10 hours to give oligomer **1** which was a yellow powder in appearance, the yield of which was determined to be ~95% (~10 g). The imide oligomers **2-5** were prepared by similar procedures in comparison with that outlined for **1**. For **2-4**, the POSS dianiline was solubilized with 4,4'-ODA and 4-PEA in NMP in the initial step. The monomer ratios used to synthesize the imide oligomers are shown in **Table 1** and the reaction scheme is depicted in **Figure 2**. Each successive oligomer **2-5** contains a higher weight concentration of silsesquioxane cage (11.6%, 18.4%, 22.8%, and 26%, respectively), comprised of 8 T and 2 D silicon atoms.

ID	Monomer	mmol	Weight (g)	ID	Monomer	mmol	Weight (g)
1	6FDA	15.65	6.95	2	6FDA	11.53	5.12
	4,4'-ODA	12.52	2.41		4,4'-ODA	6.92	1.33
	POSS	0	0		POSS	2.31	3.08
	4-PEA	6.26	1.21		4-PEA	4.61	0.89
3	6FDA	9.13	4.05	4	6FDA	7.55	3.35
	4,4'-ODA	3.65	0.70		4,4'-ODA	1.51	0.29
	POSS	3.65	4.87		POSS	4.53	6.05
	4-PEA	3.65	0.71		4-PEA	3.02	0.58

ID	Monomer	mmol	Weight (g)
5	6FDA	6.44	2.86
	4,4'-ODA	0	0
	POSS	5.15	6.88
	4-PEA	2.58	0.50

Table 1. Monomer ratios used to synthesize imide oligomers **1-5** containing progressively increasing POSS.

Thermal Cure of Imide Oligomers. Imide oligomer powder was placed into a steel mold containing a 2×2" square cavity on top of a layer of Kapton™ film to facilitate demolding. After placement of the top male half of the mold, the assembly was placed into a hot press preheated to 300°C. The temperature was then increased to 370°C and held at a pressure of 1 MPa for 1 hr. The mold was then cooled to ~200°C and the pressure was released. The resultant cured neat polyimide resin plaque was finally removed from the mold assembly after being cooled to ambient temperature.

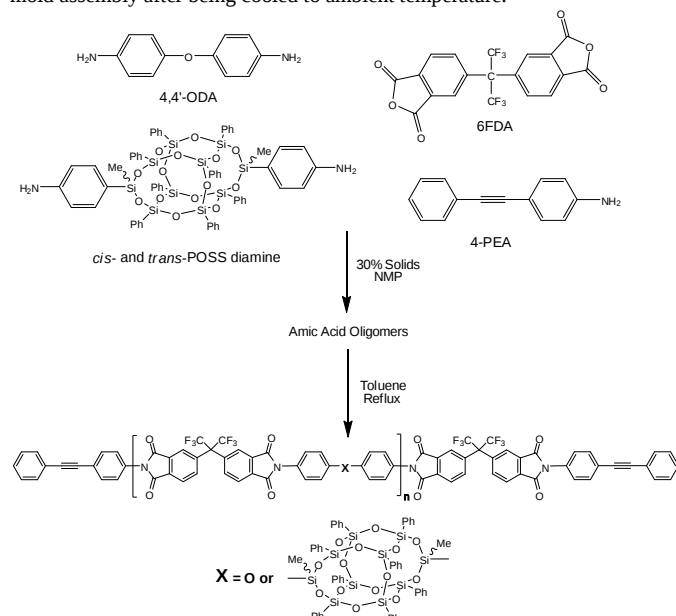


Figure 2. Synthesis scheme for phenylethynyl-endcapped imide oligomers from 6FDA, 4-PEA, and various ratios of 4,4'-ODA and POSS dianilines.

Results and Discussion

Synthesis of Bis(aniline, methyl)siloxy-octaphenylsilsesquioxane.

The synthesis of the POSS dianiline beginning with a silsesquioxane tetrol resulted in a mixture of *cis*- and *trans*-isomers about the two D silicon which can be separated via crystallization. The ^{29}Si NMR spectra for the dichlorosilane, de-protected amine isomers, end product isomer mixture, and separated isomers are shown in **Figure 3 (a-e)**. Hydrolysis of the trimethylsilyl groups causes a slight downfield shift of the signal corresponding to the peaks assigned to the two D silicon atoms. In the final products, three peaks assigned to the T silicon atoms of the silsesquioxane cage are prevalent for the *cis*-isomer, while only two signals are detected for the *trans*-isomer.

Synthesis of Phenylethynyl-endcapped Imide Oligomers. Synthesis of imide oligomers 1-5 proceeded via the polyamic acid route, in which a diamine mixture consisting of 4-PEA and various ratios of POSS and 4,4'-ODA were first dissolved in NMP. Subsequently, a 6FDA slurry also in NMP was added to the diamine solution. The temperature was raised to 80°C for 6 hrs and then to 185°C. Water resulting from imidization was removed by azeotropic distillation. The solid product was filtered and washed after precipitation using water and ultimately dried. The theoretical molecular weights of oligomers 1-5 increased with POSS content, ranging from 3194 to 7762 g mol^{-1} .

Conclusions

Thermosetting imide oligomers have been synthesized in high yield via a polyamic acid route. The oligomers contain various ratios of the dianilines 4,4'-ODA and bis(aniline, methyl)siloxy-octaphenylsilsesquioxane. The incorporation of silsesquioxane is expected to affect polyimide packing and the architecture of crosslinked polymer thus altering processability, cure kinetics, and end-use properties including those thermal, mechanical, and electrical in nature. Since the POSS monomer is intrinsically hydrophobic, its incorporation is also expected to influence moisture affinity. Full characterization of the oligomers and cured polymers is underway and will be reported in the future.

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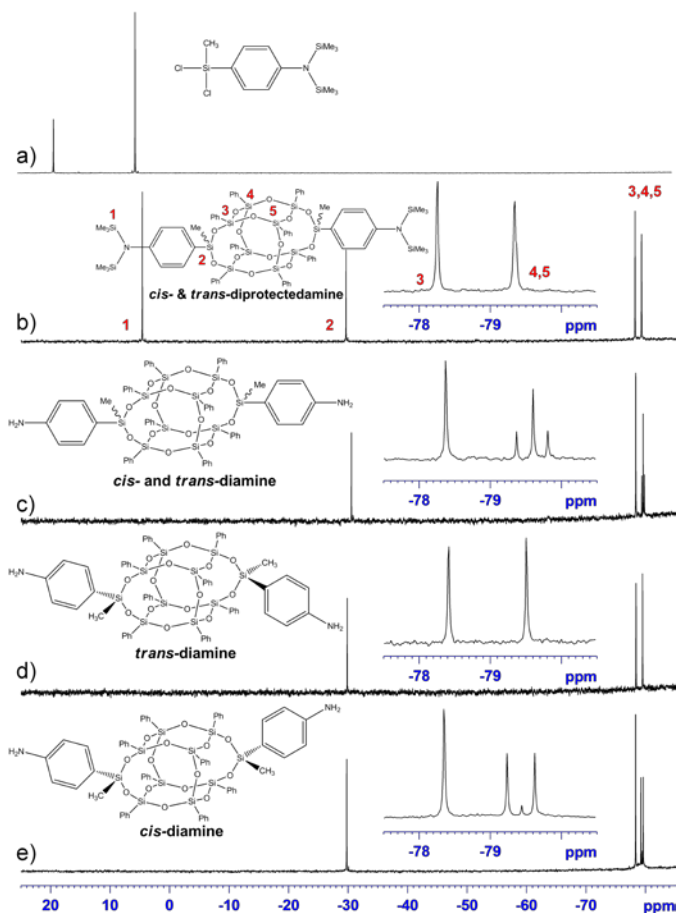


Figure 3. ^{29}Si NMR spectra of (a) 4-[bis(N, N-trimethylsilyl)phenylamino]-methylchlorosilane, (b) *cis*- and *trans*-deprotected amines, (c) mixture of *cis*- and *trans*-diamine end product, (d) *trans*-diamine, and (e) *cis*-diamine.