REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
26-03-2009

2. REPORT TYPE
Technical Paper

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE

Synthesis of Polyimides Produced from Novel High Temperature Polyhedral Oligomeric Silsesquioxane Dianilines

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
23030521

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NUMBER

AFRL-RZ-ED-TP-2009-118

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
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10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)
AFRL-RZ-ED-TP-2009-118

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited (PA #09182).

13. SUPPLEMENTARY NOTES
For presentation at the American Chemical Society National Meeting, Washington D.C., 16-20 August 2009.

14. ABSTRACT

Polyimides (PIs) are used extensively in a variety of applications such as circuit-printing films and semiconductor coatings in the microelectronics industry, spacecraft materials including solar arrays, thermal insulation blankets, and space inflatable structures, and in components in modern aircraft. PIs are well known for their thermal stability but are prone to long-term oxidative degadation and are notorious for having hygrothermal issues, especially when used in fiber-reinforced composites. A potential approach to mitigating these shortcomings is nanoscale reinforcement. In previous work, we have demonstrated protection of PIs in the low earth orbit environment through chemical bonding of a host of polyhedral oligomeric silsesquioxanes (POSS) into polyimide backbones by copolymerization through amine groups located in the POSS organic periphery. We have recently synthesized a novel high temperature POSS diamine that exhibits a strictly aromatic periphery that when copolymerized into the backbone of a growing polyimide enables the POSS molecule to assume a pendant-type conformation. We report an initial assessment of the resultant properties offering a glimpse of the potential benefits realized from the use of the monomer in applications demanding performance in challenging environments.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:

a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Dr. Joseph Mabry
Unclassified	**Unclassified**	**Unclassified**	SAR	3	**19b. TELEPHONE NUMBER** *(include area code)* N/A

Preprint

SYNTHESIS OF POLYIMIDES PRODUCED FROM NOVEL HIGH TEMPERATURE POLYHEDRAL OLIGOMERIC SILSESQUIOXANE DIANILINES

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Introduction

Polyimides (PIs) are used extensively in a variety of applications such as circuit-printing films and semiconductor coatings in the microelectronics industry[1], spacecraft materials[2] including solar arrays, thermal insulation blankets, and space inflatable structures, and in components in modern aircraft[3]. PIs are well known for their thermal stability but are prone to long-term oxidative degradation and are notorious for having hygrothermal issues[4], especially when used in fiber-reinforced composites. A potential approach to mitigating these shortcomings is nanoscale reinforcement. In previous work[5], we have demonstrated protection of PIs in the low earth orbit environment through chemical bonding of a host of polyhedral oligomeric silsesquioxanes (POSS) into polyimide backbones by copolymerization through amine groups located in the POSS organic periphery. Such protection is derived from the formation of passivating silica-rich layers during polymer erosion in severely oxidative environments. To date, much of the relevant research performed in the area of POSS-polyimides has been focused on cages exhibiting aliphatic peripheries which introduce an inherent thermal stability and solubility mismatch with the polyimide matrix. We have recently[6] synthesized a novel high temperature POSS diamine that exhibits a strictly aromatic periphery that when copolymerized into the backbone of a growing polyimide enables the POSS molecule to assume a pendant-type conformation. We report an initial assessment of the resultant properties offering a glimpse of the potential benefits realized from the use of the monomer in applications demanding performance in challenging environments.

Experimental

Instrumentation. ^{1}H and ^{29}Si NMR Spectra were obtained on a Bruker 300-MHz spectrometer using 5 mm o.d.tubes. $CDCl_3$ and Me_4Si was used as the internal and external reference standards, respectively. Dynamic mechanical analysis (DMA) was performed on a TA Instruments Q800 on thin imidized films prepared from solution casting on glass. Dynamic thermogravimetric analysis (TGA) experiments were conducted on a TA Instruments Q1000 IR instrument.

Materials. 1M 3-[Bis(trimethylsilyl)amino]phenylmagnesium chloride, 4-Bromo-N,N-bis(trimethylsilyl)aniline and magnesium turnings were obtained from Aldrich and used as received. Trisilanolphenyl-POSS, $Ph_7Si_7O_9(OH)_3$, was obtained from Hybrid Plastics. Silicon tetrachloride and trichloromethylsilane were obtained from Hulls Chemicals and distilled before use. Triethylamine was obtained from Aldrich and was also distilled before use. Anhydrous THF (Aldrich) and hexane (Aldrich) were further dried through an alumina column and were degassed prior to use. Pyromellitic dianhydride (PMDA) was obtained from Aldrich and recrystallized in dioxane (Aldrich) before use. 4, 4'-Diaminodiphenyl ether (ODA) was obtained from Lancaster Synthesis and recrystallized in DMF (Aldrich) and Toluene (Aldrich) mixture. Dimethylacetamide (DMAC) was obtained from Aldrich and was purified by distillation under reduced pressure over BaO and stored over 4A^0 molecular sieves. All reactions were carried out under an inert atmosphere of dry N_2 unless otherwise stated in the procedure.

Synthesis of Monomer A Precursor, *p*-$ClMeSi[PhN(TMS)_2]_2$: A solution of 4-Bromo-N,N-bis(trimethylsilyl)aniline (9.48 g, 30 mmol) in 25 mL of anhydrous THF was taken in an addition funnel and slowly added to a stirring mixture of Mg (0.912 g, 38 mmol) and anhydrous THF initiated with a crystal of I_2 and a drop of 4-Bromo-N,N-bis(trimethylsilyl)aniline[7]. The reaction was allowed to stir overnight at ambient temperature, cannulated to a 250 mL round bottomed flask and very slowly added to a stirring mixture of THF (10 mL) and trichloromethylsilane (2.252 g, 15 mmol). This was allowed to stir overnight. The solvent was removed *in vacuo* from the reaction mixture and dry hexane added to extract the product by filtration through celite. After removing all volatiles under a dynamic vacuum, the residual yellow colored filtrate was transferred to a 25 mL flask and distilled using a Kugelrohr apparatus to give di(N,N-bis(trimethylsilyl)aminophenylchloromethylsilane, as a colorless, very viscous liquid in 90% yield. ^{1}H NMR ($CDCl_3$) 0.09 ppm (s, 36H, $NSiCH_3$), 0.92ppm (s, 3H, $SiCH_3$), 6.96 ppm (m, 4H), 7.49 ppm (m, 4H). ^{29}Si NMR ($CDCl_3$) 4.83 ppm, 10.70 ppm (ratio = 4:1)

Synthesis of Monomer B Precursor, *m*-$ClMeSi[PhN(TMS)_2]_2$: A solution of 1M 3-[Bis(trimethylsilyl)amino]phenylmagnesium chloride (30 mL 30 mmol) in 25 mL of anhydrous THF was taken in an addition funnel and slowly added to a stirring mixture of trichloromethylsilane in 15 mL anhydrous THF (2.252 g, 15 mmol) and stirred overnight. After using a work up procedure described above, meta product was obtained as a colorless, viscous liquid in 90% yield. ^{1}H NMR ($CDCl_3$) 0.08 ppm (s, 36H, $NSiCH_3$), 0.93 ppm (s, 3H, $SiCH_3$), 7.32 ppm (m, 2H), 7.28 ppm (t, 2H, J=7.5 Hz), 7.16 ppm (m, 2H), 7.00 ppm (dt, 2H, J=7.5 Hz, 1.8 Hz). ^{29}Si NMR ($CDCl_3$) 4.83 ppm, 9.89 ppm (ratio = 4:1)

Synthesis of Phenyl POSS-silanol, $Ph_7(Si_8O_{12})OH$: A solution of distilled silicon tetrachloride (1.915 g, 11.3 mmol) in anhydrous THF was added slowly to a stirring solution of 10 g (10.7 mmol) of Phenyl triol in 50 mL anhydrous THF . This was followed by addition of NEt_3 (3.585 g, 35.4 mmol) in 5 mL anhydrous THF over a period of ½ h. The reaction mixture was stirred overnight followed by filtration. The filter cake was washed with distilled H_2O, THF and finally with chloroform. The organic layer was separated and stirred with 20 mL distilled water and 2 mL 0.1M dilute hydrochloric acid for 1 h. The organic layer was washed with H_2O, dilute HCl and brine solution followed by rotary evaporating to slurry and fully precipitated in 150 mL tech. methanol. After two hours of stirring, the mixture was filtered and the filter cake dried to give 9.19 g (92%) of pure Phenyl POSS-silanol. ^{29}Si NMR ($CDCl_3$) -77.93, -78.21, -78.27, -100.386 (ratio = 3:3:1:1)

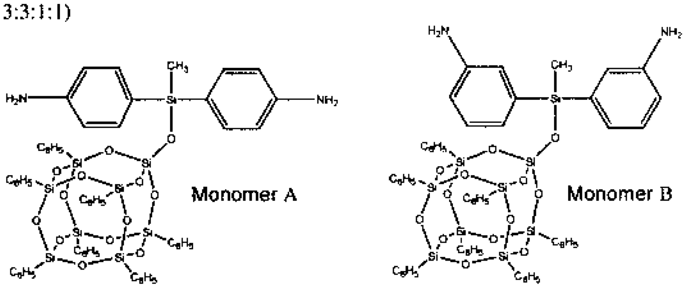

Figure 1 Two New Poss Diamine Monomers.

Synthesis of POSS diamine Monomer A and B: Monomer A and B are made via the same method. To make monomer A, a solution of di(N,N-bis(trimethylsilyl)aminophenylchloromethylsilane, monomer A/B precursors (0.67 g, 1.216 mmol), in 2 mL dry ether was added very slowly to a stirring solution of POSS-silanol (1.08 g , 1.1 mmol) in 5mL dry ether and 2 mL anhydrous THF. To this was very slowly added a solution of distilled triethylamine in dry ether (0.116 g, 1.15 mmol). This was left stirring over night. The solution was filtered to remove $NEt_3.HCl$ precipitates and rotary evaporated to slurry. The slurry was precipitated fully in 150 mL reagent grade methanol acidified with glacial acetic acid to give POSS dianiline monomer in 98% yield. ^{29}Si NMR ($CDCl_3$) -8.185, -77.95, -77.77, -109.25 (ratio = 1:3:4:1).

Copolymerization. Various proportions of POSS-diamine monomer and 4, 4'-oxydianiline (ODA) were reacted with pyromellitic dianhydride (PMDA) to form PMDA-(ODA/POSS-diamine) copoly(amic) acid. The copoly(amic acid) of 5 wt.% POSS/PMDA-ODA (1.9% Si_9O_{13}) was prepared by first putting 0.083 mmol (0.1 g) of POSS-diamine in 4 mL DMAC into a stirring solution of 4.50 mmol (0.901 g) of ODA in 4 mL DMAC in inert atmosphere. Then, after POSS-diamine and ODA had dissolved completely, 4.585 mmol (1 g) of PMDA in 4 mL DMAC was slowly added to the stirring mixture of POSS-diamine and ODA. The solution was stirred continuously overnight and a viscous poly(amic) acid (PAA) solution was obtained. 10 wt. % (3.8% Si_9O_{13}), 15 wt. % (5.7% Si_9O_{13}) and 20 wt. % (7.7% Si_9O_{13}) copoly (amic) acid were obtained similarly by changing the various loadings.

	5% POSS	10% POSS	15% POSS	20%POSS
POSS	0.1 g	0.209 g	0.328 g	0.460 g
ODA	0.901 g	0.883 g	0.863 g	0.841 g
PMDA	1 g	1 g	1 g	1 g

PMDA-ODA/POSS-diamine mixtures were cast on glass slides and subsequently put in vacuum oven at 80° C for 4 hours under a nitrogen purge. Imidization of POSS-PMDA-ODA was carried out by putting the samples in a nitrogen circulated vacuum oven at 120, 160, 200, 250 for 1 h each and then at 280 °C for 2h to ensure complete imidization.

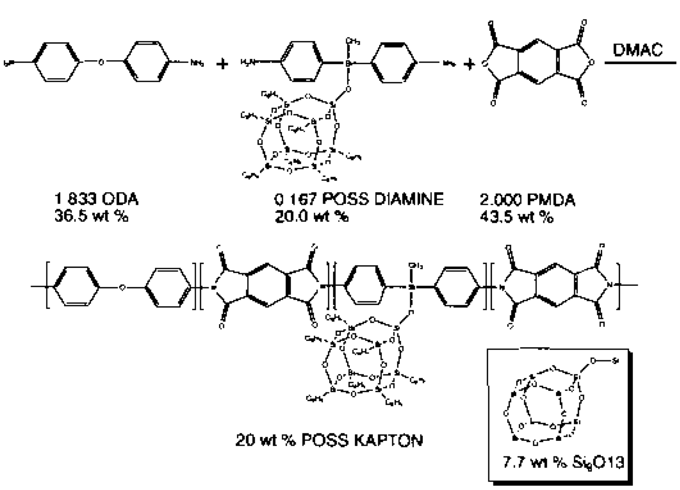

Figure 2 Polymerization to form POSS Kapton.

Results and Discussion

Effects of Copolymerized Phenyl POSS on the Dynamic Mechanical Properties, Dampening, and Glass Transition Temperature of Kapton

Copolymerization with side-chain type POSS adversely affects the "Young's" modulus in film tension experiments due to a decrease in chain interactions caused by the presence of pendant POSS molecules. However, the mechanical properties can be tuned by varying Phenyl POSS content due to a competition between introducing free volume and the interactions of assembled POSS peripheries in the equilibrated structure. 15 weight % Phenyl POSS demonstrates superior elastic properties to the other copolymers (Fig. 3a). The damping factor, δ, is a measure of a material's propensity for energy absorption through molecular rearrangement, the peak of which is often regarded as the glass transition temperature of a polymer. Phenyl POSS-Kapton copolymers containing more than 10 weight % POSS feature higher glass transition temperatures (~20°C) and less deformation under stress in comparison with the control, highlighting the benefits of the aromatic interactions between assembled POSS molecules in the equilibrium structure of the resultant copolymers (Fig. 3b).

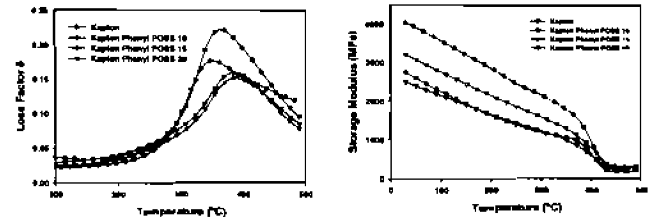

Fig 3. (a) Tan delta and (b) storage modulus curves vs. temperature for Kapton and Phenyl POSS Kapton copolymers.

Effects of Copolymerized POSS on Thermal and Thermo-Oxidative Stability

Copolymerization of Phenyl POSS with Kapton slightly improves the thermal stability of the resultant copolymers in an inert atmosphere as evidenced by thermal gravimetric analysis in a nitrogen environment, also improving their char yields (scan rate 10°C/minute), despite the likely increase in free volume introduced by copolymerization with POSS molecules. The thermo-oxidative stability of Kapton is substantially improved by the incorporation of 15 weight percent Phenyl POSS as evidenced by TGA experiments conducted in an air atmosphere (scan rate 10°C/minute).

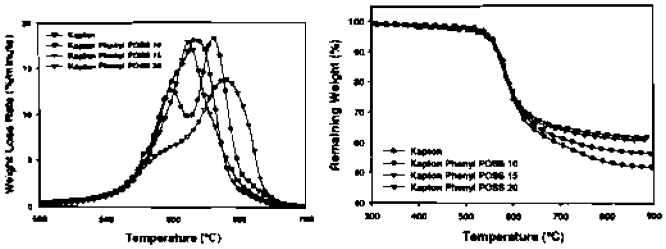

Figure 4. (a) Weight loss profiles and (b) weight loss rates vs. temperature for Kapton and Phenyl POSS Kapton copolymers.

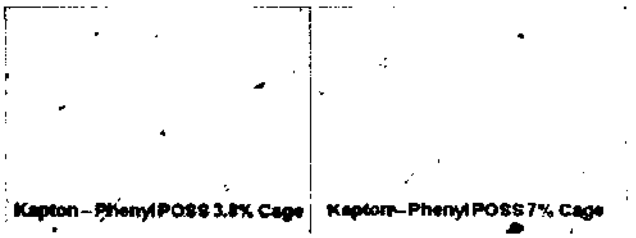

Figure 5. Optical micrographs of Phenyl POSS Kapton copolymers demonstrating POSS assembly and low refractive index mismatch.

Conclusions

The synthesis of a novel POSS diamine containing an aromatic periphery targeting applications with challenging temperature and oxidation requirements has been reported. Copolymerization of the diamine monomer with Kapton imparts improvements in mechanical relaxation response under stress and thermo-oxidative stability. POSS aggregation in copolymers is likely a main contributor to the observed performance improvements although the phase separation comes at little cost to film clarity and light transmission.

Acknowledgements.

The authors of this paper would like to thank Air Force Office of Scientific Research and the Air Force Research Laboratory, Propulsion Directorate for financial support of this research.

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