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

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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 degradation 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.
SYNTHESIS OF POLYMIDES 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, spacecraft materials including solar arrays, thermal insulation blankets, and space inflatable structures, and in components of modern aircraft. 1 PIs are well known for their thermal stability but are prone to long-term oxidative degradation 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 polyoligomeric silsesquioxanes (POSSs) 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 synthesized a novel high temperature POSS diamine that exhibits a strictly aromatic periphery that when covalently incorporated into the backbone of a growing polyimide provides 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 monomers in applications demanding performance in challenging environments.

Experimental

Instrumentation. 1H and 13C NMR Spectra were obtained on a Bruker 300-MHz spectrometer using 5 mm o.d. tubes. CDCl3 and Me2Si 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. 1H NMR and 13C NMR Spectra were obtained on a Bruker 300-MHz spectrometer using 5 mm o.d. tubes. CDCl3 and Me2Si 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.

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Synthesis of POSS-diamine Monomer A and B were made via the same procedure. To make monomer A, a solution of di(N,N-bis(trimethylsilyl)aminophenylchloromethylsilane, monomer A/B precursors (0.67 g, 1.21 mmol), in 2 mL dry ether was added very slowly to a stirring solution of POSS-silanol (1.08 g, 1.11 mmol) in 5 mL dry anhydrous THF. To this was very slowly added a solution of distilled triethylamine in dry ether (0.115 g, 1.15 mmol). This was left stirring overnight. The solution was filtered and the filter cake dried to give 1.98 g (92%) of pure POSS-silanol. 13C NMR (CDCl3) 37.95, 57.57, 7.32 ppm. After two hours of stirring, the reaction mixture was filtered and the filter cake dried to give 1.24 g (97%) of pure POSS-silanol.

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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 circulatied vacuum oven at 120, 160, 200, 250 for 1 h each and then at 280°C for 2 h to ensure complete imidization.

Results and Discussion

Effects of Copolymerized Phenyl POSS on the Dynamic Mechanical Properties, Damping, 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 equilibrium 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).

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 2. Polymerization to form POSS Kapton.

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References

(6) Manuscript in progress.