

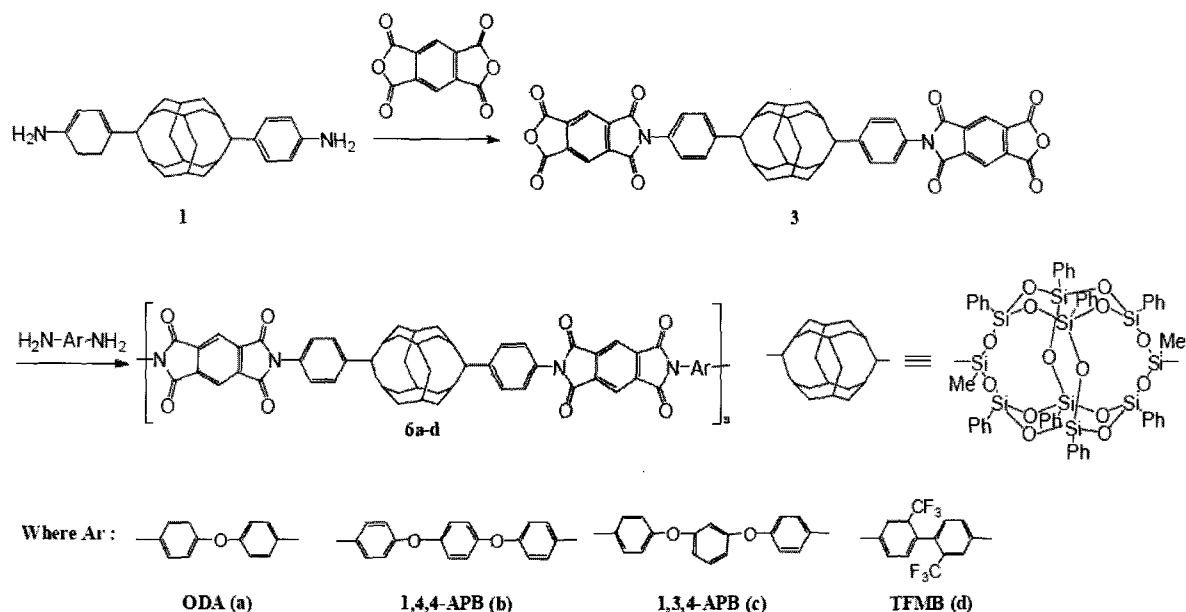
Preparation and Properties of Soluble-Controlled Aromatic Polyimides Containing POSS in Main Chain Derived from DDSQ

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Introduction

Polyhedral oligomeric silsesquioxane (POSS), an inner cage with an inorganic silicon and oxygen framework which is covered externally by organic substituents, are cube-octameric molecules of nanoscale dimensions that may be functionalized with reactive groups suitable for the synthesis of new organic-inorganic hybrids, thus providing the opportunity to design and build materials with extremely well-defined dimensions possessing nanophase behavior.¹⁻⁶ The incorporation of POSS into some polymers has offered the opportunity to develop high-performance materials that combine many desirable properties of conventional organic and inorganic components such as good thermal and mechanical properties, solubility, nonflammability, oxidative resistances, and excellent dielectric properties.¹⁻⁶ In particular, a 31 wt % POSS (15 wt % Si₈O₁₂) content material was tested for active (atomic) oxygen (AO) resistance and found to show exceptionally good characteristics with no detectable erosion relative to Kapton.^{1,3,4} And the polymers based on POSS were reported to show 10 times higher durability than the aromatic polyimide Kapton, which has the highest resistance among the conventional polymers against active oxygen.⁴ Because the surface of the polymer is converted into a SiO₂ layer further decomposition of the bulk polymer material is prevented when these polymers are exposed to AO.^{1,3,4}



Scheme 1. Synthesis of DDSQDA (3) and POSS-PIs 6.

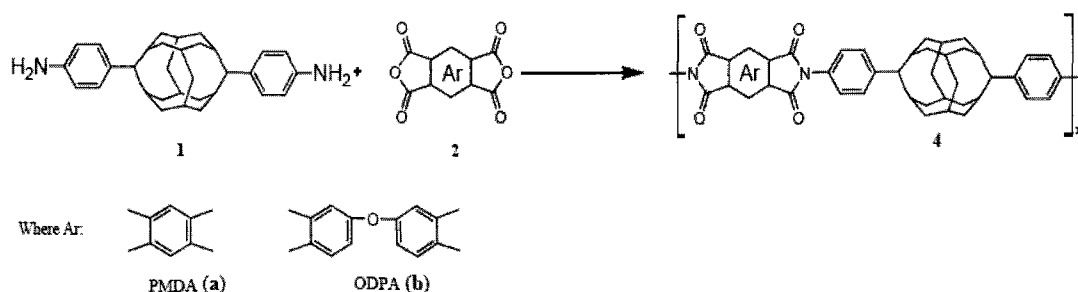
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We previously reported the synthesis and characterization of a series of linear semiaromatic polyimides containing double-decker-shaped silsesquioxane (DDSQ) in the main chain (POSS – PIs) for low dielectric films.^{6, 8} After the low dielectric constant for requirement of interlayer polymers, the second most important requirement for novel intermetal dielectrics is thermal stability. This paper presents the synthesis of double-decker-shaped silsesquioxane aromatic tetracarboxylic dianhydride (DDSQDA). This dianhydride is derived from DDSQ-diamine **1** by the functional group conversion method, i.e., conversion of functional group from low reactivity to high reactivity for preparing high molecular weight polymers.⁶ This aromatic tetracarboxylic dianhydride is designed to increase the thermal stability and mechanical properties while maintaining a low dielectric constant. The POSS – PIs from DDSQDA and various aromatic diamines are synthesized by a one-step high temperature solution polymerization and two-step low-temperature polymerization procedure.

Results and Discussion

Synthesis of POSS – PI 4. The polymerization of DDSQ-diamine **1** with PMDA or ODPA was carried out by two different methods: a one-step high temperature solution polymerization and two-step low-temperature polycondensations. But only low-molecular-weight polymers (POSS – PI **4** < 0.10 dL/g) could be isolated from solution. The inherent viscosity remained unchanged even when the reaction temperature was elevated to 180 °C and prepared from solvent-catalyst combinations of 1,2-dichlorobenzene and 2-hydroxypyridine (Method 1) or *m*-cresol and isoquinoline (Method 2) as shown in Table 1. The low molecular weights are likely due to a less reactive molecular structure.^{6, 8}

Table 1. Synthesis of Polymer (**4**)



Run ^a	Polymer	Solvent	Dianhydride	Catalyst	Inherent Viscosity ^c (dL/g)
1	4a	1,2-dichlorobenzene	PMDA	2-hydroxypyridine	0.07
2	4a	<i>m</i> -cresol	PMDA	isoquinoline	0.06
3	4a^b	DMAc	PMDA	-	0.04
4	4b	1,2-dichlorobenzene	ODPA	2-hydroxypyridine	0.09
5	4b	<i>m</i> -cresol	ODPA	isoquinoline	0.09
6	4b^b	DMAC	ODPA	-	0.08

^aPolymerization was carried out with 0.5 mmol of each monomer in the solvent under nitrogen.

^bPolyamic acid from two-step low-temperature polycondensation. ^cDetermined at a concentration 0.5 g/dL in DMAc at 30 °C.

Synthesis of DDSQDA (3). In order to obtain polyimides containing the main chain POSS units with high molecular weights, the monomer was redesigned.⁶ As shown in Scheme 1, DDSQDA **3** was

synthesized through functional group conversion method from **1** and excess PMDA in toluene at 105 °C in high yield. In contrast to the aromatic dianhydride, such as PMDA and ODA, DDSQDA has better solubility in solvents in which it was readily soluble in conventional such as acetic anhydride, acetone, and Chloroform at room temperature. Thus, it is difficult to recrystallize DDSQDA from acetic anhydride. However, we observed that after a precisely controlled drop gave a high yield. The solid was heated under vacuum at 230 °C to ensure all of unreacted PMDA was removed, and a slightly yellow solid with high purity was obtained. The structure of monomer **3** was confirmed by FT IR, ¹H, ¹³C, and ²⁹Si NMR spectroscopies, MALDI – TOF MS and elemental analysis. The IR spectrum of DDSQDA shows characteristic absorptions at 1861 and 1794 cm⁻¹ due to C=O stretching of a dianhydride ring group, and 1796 and 1732 due to C=O stretching of a imide ring group (Figure 1). In addition, the absorptions of the Si–O–Si are observed at 1132 and 1083 cm⁻¹. The ¹H, ¹³C NMR of DDSQDA are presented in Figures 2. They were also consistent with the formation of **3** (*vide infra*). In addition, the observed elemental compositions of C, H, and N elements and MALDI–TOF MS agree well with the calculated values. Based on the above data, it is clear that the novel dianhydride **3** was obtained with sufficient purity for the polymerization.

Synthesis of POSS–PI 6. A series of POSS–PIs **6** were prepared from dianhydride **3** and aromatic diamines **5** including ODA (**a**), 1,4,4-APB (**b**), 1,3,4-APB (**c**), and TFMB (**d**) by a one-step high temperature solution polymerization employing solvent-catalyst combinations of 1,2-dichlorobenzene and 2-hydroxypyridine (Scheme 1). The prepared polymers have inherent viscosities in the range of 0.48 – 0.61 dL/g (Table 2). Flexible and tough POSS–PI films were obtained by heating the corresponding POSS–PIs solution cast onto a quartz plate in nitrogen, followed by immersion in warm water. The resulting POSS–PIs films were dried in vacuo at 100 °C for 8 h prior to performing measurements.

Table 2. Summary of the Properties of the POSS–PIs

POSS-PI ^a	diamine	T _g (°C) ^b	T _{5%} (°C) ^c		T _{10%} (°C) ^d		contact angle (deg)	inherent Viscosity ^e (dL/g)
			in N ₂	in air	in N ₂	in air		
6a	ODA	ND ^f	515	505	565	555	92	0.61
6b	1,4,4-APB	ND	510	505	560	550	88	0.51
6c	1,3,4-APB	325	505	500	545	540	87	0.56
6d	TFMB	ND	520	495	570	553	102	0.48

^aPolymerization was carried out with 0.2 mmol of each run in solvent at room temperature under nitrogen. ^bFrom DSC on the second heating at a heating rate of 30 °C/min in nitrogen. ^cTemperature at which 5 % weight loss was recorded by thermogravimetry at a heating rate of 10 °C/min in N₂ or air. ^dTemperature at which 10 % weight loss was recorded by thermogravimetry at a heating rate of 10 °C/min in N₂ or air. ^eDetermined at a concentration 0.5 g/dL in each solvent at 30 °C. ^fND: not detect.