Synthesis and Characterization of Organosoluble Aromatic Polyimides Containing POSS in Main Chain Derived from Double-Decker-Shaped Silsesquioxane

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ABSTRACT: Preparation of low dielectric constant polyimides containing double-decker-shaped silsesquioxane (DDSQ) in the main chain with high molecular weights ($\eta_{\text{inh}} = 0.61$ dL/g) is reported. Double-decker-shaped silsesquioxane aromatic tetracarboxylic dianhydride (DDSQDA) was prepared by reaction of DDSQ aromatic diamine and pyromellitic dianhydride through functional group conversion method. The polyimides were synthesized from DDSQDA and several aromatic diamines by a one-step high temperature solution method. Introduction of DDSQ unit in polyimides endowed properties such as solubility in organic solvents, 10% weight loss temperatures (T_{d10}) up to 570 °C in nitrogen, the glass transition temperatures (T_g) higher than 300 °C, good mechanical properties (tensile strengths of 72.3–82.1 MPa, initial modulus of 1.8–2.6 GPa, and elongation at breakage of 8.0–15.9%), transmittances over 80% at 400 nm, and a dielectric constant of 2.43 at 1 MHz. The polyimides were soluble in organic solvents such as DMAc, chloroform, THF, and acetone.

Introduction

Polyhedral oligomeric silsesquioxanes (POSS), having 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 unique molecular “silicone−oxygen” frame (silsesquioxane combination) of POSS (Si_2O_3) with the character of silicone (SiO) and silica (SiO_2), has the features of both an inorganic substance (silicone base) and an organic matter (carbon base). It has been reported that POSS has a dramatic effect on properties of the materials composed of it such as chemical resistance.[5–11] POSS-based hybrid polymers have generated much interest recently from both academic and industrial points of view. By incorporating these Si−O cages into organic polymers, properties superior to the organic material alone are realized, offering to possibilities for the development of novel materials.[10–16] In addition, 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(atomic) oxygen.[1,7,8] Because the surface of the polymer is converted into an SiO_2 layer further decomposition of the bulk polymer material is prevented when these polymers are exposed to active (atomic) oxygen.[1,8]

Recently, POSS nanocomposites, have been reported by Kannan et al., who summarize the combination of the unique POSS molecules and polymers holds great promise for the future of biomedical devices, especially at cardiovascular interfaces.[5] 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.[16–22]

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.[6,23] After the low dielectric constant for requirement of interlayer polymers, the second most important requirement for novel intermetallic phase dielectrics is thermal stability.[20–27] Unlike aluminum metallization, copper metallization can be achieved by electroplating or electroless plating (chemical reduction) in addition to PVD (physical vapor deposition) and CVD (chemical vapor deposition) techniques. These processes can be conducted at temperatures below 250 °C. Unfortunately, an annealing step is necessary to ensure void free copper deposits. Since this step is performed at temperatures in the range 400–450 °C for up to 1 h, any low-*k* material must be able to withstand this temperature for several hours. In addition to the dielectric constant and thermal stability, there are a large number of additional issues, which must be addressed before a novel material can be used as intermetallic phase dielectric. Important issues are, for example, moisture uptake, purity, solubility, adhesion to Si, SiO_2, Al, Cu, and other inorganic materials, planarization behavior, plasma etching behavior, and others. Recently low dielectric constant PIs with good processability have been desired in microelectronics in order to meet the requirements of high-density interconnection.[25–27] However, their application is somewhat limited due to difficulties such as insolubility in conventional solvents. Therefore, considerable efforts have been made to address these issues and to design polyimides with the desired properties.[27–30]

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

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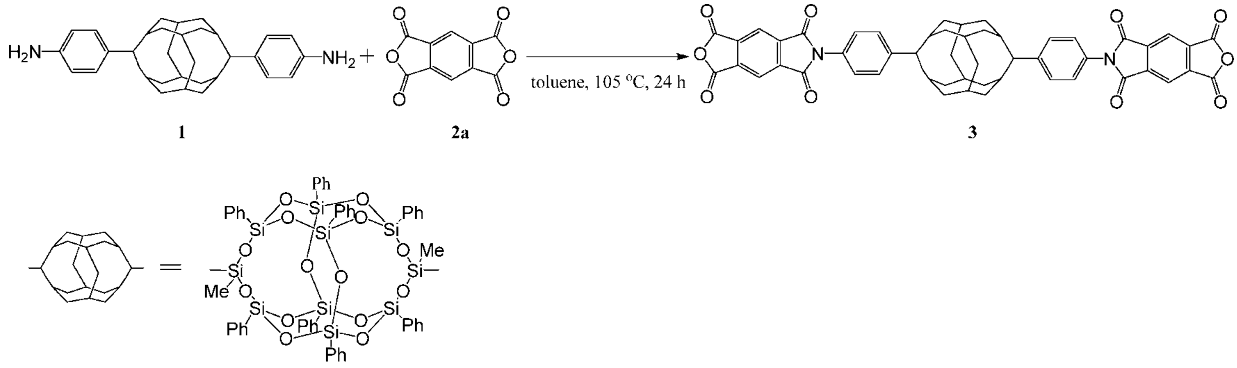
Scheme 1



diamines are synthesized by a one-step high temperature solution polymerization procedure.

Experimental Section

Materials. *N*,*N*-Dimethylacetamide (DMAc) (TCI) was purified by vacuum distillation over CaH_2 prior to use. Tetrahydrofuran (THF) and toluene (TCI) were distilled over sodium. 1,2-Dichlorobenzene was purified by standard procedures and stored under an argon atmosphere. *m*-Cresol (Aldrich Chemical Corp.) was distilled under nitrogen before use. 2-Hydroxypyridine (Aldrich) was sublimed in vacuo and then recrystallized from chloroform/diethyl ether. Pyromellitic dianhydride (PMDA) and 4,4′-oxydiphthalic dianhydride (ODPA)(TCI) were purified by recrystallization from acetic anhydride/acetic acid and dried in a vacuum oven at 120 °C for 8 h. 4,4′-Oxydianiline (ODA), 1,3-bis(4-aminophenoxy)benzene (1,3,4-APB), and 1,4-bis(4-aminophenoxy)benzene (1,4,4-APB) were purified by sublimation before use. 2,2′-Bis(trifluoromethyl)benzidine (TFMB) (Aldrich Chemical Corp.) was recrystallized from methanol and then dried at 50 °C for 2 h prior to use. DDSQ−diamine **1** was synthesized according to a reported procedure.[23] Other reagents and solvents were used as received.

Monomer Synthesis. *Synthesis of DDSQDA (3).* In a 20 mL two-necked round-bottomed flask equipped with an drop funnel and a stirrer, a solution of DDSQ−diamine **1** (534.4 mg, 0.40 mmol) in THF (1 mL)/toluene (2 mL) was added slowly to a solution of PMDA (436.2 mg, 2.0 mmol) in THF (2 mL) under an argon stream at 80 °C for 2 h. After the addition was finished, the mixture was stirred at 105 °C for 24 h. After solvent removal, the solid was heated under vacuum at 230 °C to ensure all of the PMDA was removed. The solid were purified by recrystallization from acetic anhydride and dried in a vacuum oven at 200 °C for 8 h to afford **3** (680.5 mg, 98% yield): mp >350 °C; MALDI−TOF MS = 1760.6 (M + Na^+, calcd value of 1736.2). IR (KBr): ν = 1861, 1794 (C═O, dianhydride), 1796, 1732 (imide, C═O), 1376 (C−N), 1132, 1083 (Si−O−Si) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 8.55 (4H, s), 7.80 (4H, d, *J* = 7.2 Hz), 7.52–7.14 (44H, m), 0.56 (6H, s) ppm. ^{13}C NMR (75 MHz): 164.4, 161.0, 138.7, 134.9, 134.6, 134.5, 132.6, 131.0, 128.3, 125.7, 121.6, 0.0 ppm. ^{29}Si NMR (60 MHz): −24.7, −71.3, −72.5 ppm. Anal. Calcd for $C_{82}H_{58}N_2O_{24}Si_{10}$: C, 56.73; H, 3.37; N, 1.61. Found: C, 57.86; H, 3.48; N, 1.81.

Polymer Synthesis. *Synthesis of POSS−PI 4.* The procedure for POSS−PI **4a** is given as an example. The POSS−PI **4a** was prepared from solvent–catalyst combinations of 1,2-dichlorobenzene and 2-hydroxypyridine (method 1) or *m*-cresol and isoquinoline (method 2). Method 1: DDSQ−diamine **1** (1335.9 mg, 1.0 mmol) and PMDA (218.1 mg, 1.0 mmol) were dissolved in 5.0 mL of 1,2-dichlorobenzene in a 25-mL three-necked flask. Then, 2-hydroxypyridine (46.6 mg, 3 wt%) was added, and the system was equipped with an overhead mechanical stirrer, a Dean–Stark trap with condenser, and a nitrogen inlet. The mixture was warmed to 100 °C for 0.5 h to dissolve the monomers and catalyst then was maintained at 180 °C for 8 h. The solution was poured into methanol. The precipitate was filtered off, washed with water, and dried under vacuum at 180 °C for 24 h.

Method 2: DDSQ−diamine **1** (1335.9 mg, 1.0 mmol) and PMDA (218.1 mg, 1.0 mmol) were dissolved in 5.0 mL of *m*-cresol in a 25 mL three-necked round-bottom flask. After the solution was stirred at room temperature for 30 min, isoquinoline (ca. 5 drops) was added and further stirring was conducted. The mixture was then heated at 180 °C for 6 h. The water formed during the imidization was continuously removed using a stream of nitrogen. At the end of the reaction, the mixture was cooled and precipitated into 500 mL of methanol. The polymer was separated by filtration, washed repeatedly with methanol, and dried in a vacuum oven at 80 °C for 24 h.

In addition, the general two-step low-temperature polycondensation procedure of DDSQ−diamine **1** with PMDA was carried out in DMAc (17 or 28 wt % solids) to give POSS−poly(amic acid) (POSS−PAA), which was then thermally imidized to produce POSS−PI **4a**. The inherent viscosity of the POSS−PI **4a** or POSS−PAA is 0.06–0.07 dL/g, determined at a concentration of 0.5 g/dL in DMAc at 30 °C. IR (KBr): ν = 1862, 1793 (C═O, dianhydride), 1795, 1731 (imide C═O), 1377 (C−N), 1133, 1084 (Si−O−Si) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 8.55 (2H, br), 7.83–7.79 (4H, m), 7.53–7.15 (44H, m), 0.56 (6H, br) ppm. ^{13}C NMR (75 MHz): 164.1, 161.3, 138.8, 134.7, 134.6, 134.4, 132.1, 131.2, 128.8, 125.3, 121.4, −0.1 ppm. ^{29}Si NMR (60 MHz): −24.5, −71.8, −72.6 ppm.

Synthesis of POSS−PIs 6. As a typical experiment, **3** (694.5 mg, 0.4 mmol) and 1,4,4-APB (116.9 mg, 1.0 mmol) were dissolved in 4.0 mL of 1,2-dichlorobenzene in a 25-mL three-necked flask. Then 2-hydroxypyridine (24.3 mg, 3 wt %) was added, and the system was equipped with an overhead mechanical stirrer, a Dean–Stark trap with condenser, and a nitrogen inlet. The mixture was warmed to 100 °C for 0.5 h to dissolve the monomers and the catalyst then was maintained at 180 °C for 8 h. The solution was noticeably more viscous after 8 h and was then poured into methanol. The resulting precipitate was filtered off, washed with water, and dried under vacuum at 180 °C for 24 h. The inherent viscosity of the POSS−PI **6b** obtained is 0.51 dL/g, determined at a concentration of 0.5 g/dL in DMAc at 30 °C. IR of **6b** (film): ν = 1779, 1731 (imide C═O), 1366 (C−N), 1264 (Si-CH_3), 1230 (Si-Ph), 1133–1084 (Si−O−Si) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 8.48 (4H, br), 7.79–7.69 (4H, m), 7.53–6.96 (52H, m), 6.82 (4H, br),0.55 (6H, br) ppm. ^{13}C NMR (75 MHz): 165.2, 165.1, 151.2, 150.9, 137.5, 136.2, 134.8, 134.4, 131.9, 131.0, 128.1, 128.0, 125.9, 123.5, 121.6, 119.0 −0.03 ppm. ^{29}Si NMR (60 MHz): −24.8, −71.4, −72.7 ppm.

Other POSS−PIs, **6a**, **6c**, and **6d**, were prepared in a similar procedure by the polymerization of 1 equiv of **3** to 1 equiv of diamines ODA (**5a**), 1,3,4-APB (**5c**), and TFMB (**5d**) as shown in Scheme 2.

Polyimide films were prepared by casting the polyimide solution from DMAC onto a silicon wafer then cured by a stepped thermal sequence (80 °C/1 h, 120 °C/1 h, 220 °C/2 h) under nitrogen atmosphere to gain films of POSS−PI s **6a**−**d.**

IR of **6a** (film): ν = 1779, 1730 (imide *C*═O), 1371 (C−N), 1264 (Si-CH_3), 1242 (Si-Ph), 1132, 1078 (Si−O−Si) cm^{-1}. ^1H

Scheme 2

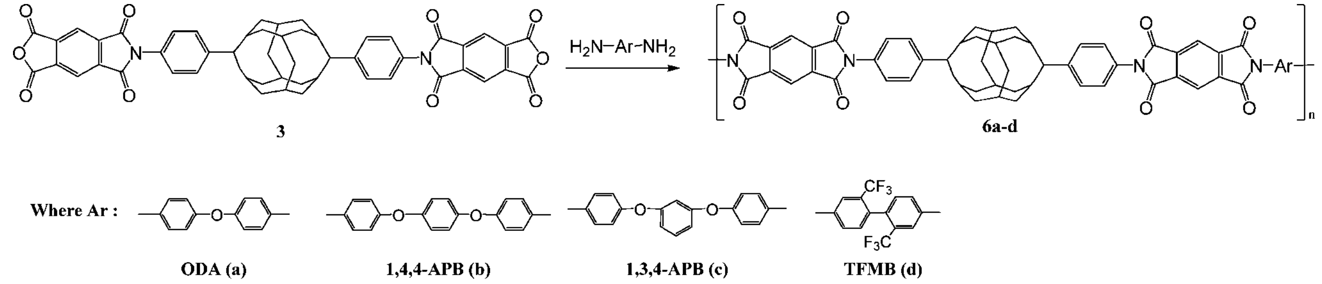
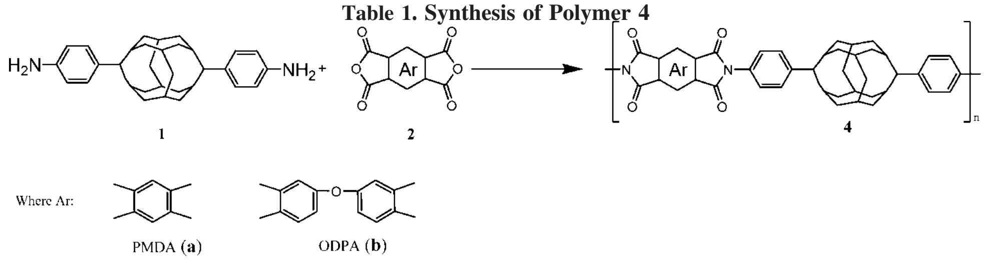


Table 1. Synthesis of Polymer 4



run[a]	polymer	solvent	dianhydride	catalyst	inherent viscosity[c] (dL/g)
1	**4a**	1,2-dichlorobenzene	PMDA	2-hydroxypyridine	0.07
2	**4a**	*m*-cresol	PMDA	isoquinoline	0.06
3	**4a**[b]	DMAc	PMDA		0.04
4	**4b**	1,2-dichlorobenzene	ODPA	2-hydroxypyridine	0.09
5	**4b**	*m*-cresol	ODPA	isoquinoline	0.09
6	**4b**[b]	DMAC	ODPA		0.08

[a] Polymerization was carried out with 0.5 mmol of each monomer in the solvent under nitrogen. [b] Polyamic acid from two-step low-temperature polycondensation. [c] Determined at a concentration 0.5 g/dL in DMAc at 30 °C.

NMR (300 MHz, $CDCl_3$): 8.48 (4H, br), 7.79 (4H, br), 7.51–6.90 (52H, m), 0.55 (6H, br) ppm. ^{13}C NMR (75 MHz): 165.5, 165.2, 157.1, 137.4, 137.2, 134.8, 134.4, 134.3, 131.2, 130.9, 128.0, 126.7, 125.9, 121.1, 119.7, −0.04 ppm. ^{29}Si NMR (60 MHz): −24.6, −71.5, −72.9 ppm.

IR of **6c** (film): $\nu = 1778$, 1731 (imide $C{=}O$), 1372 (C−N), 1262 ($Si-CH_3$), 1243 (Si−Ph), 1131–1091 (Si−O−Si) cm^{-1}.

IR of **6d** (film): $\nu = 1781$, 1733 (imide $C{=}O$), 1365 (C−N), 1264 ($Si-CH_3$), 1228 (Si−Ph), 1114, 1071 (Si−O−Si) cm^{-1}.

Measurements. ^1H NMR, ^{13}C NMR, and ^{29}Si NMR measurements were carried out by a JEOL JNM-AL 300 MHz spectrometer in $CDCl_3$, acetone-d_6, or DMSO-d_6 without TMS. Infrared spectra were obtained using a JASCO Corp. FT-IR 460 Plus Fourier-transform infrared spectrophotometer. The ultraviolet–visible (UV–vis) spectra were recorded on a JASCO Corp. UV-2800 spectrophotometer at room temperature. The thickness of the specimen for Fourier transform infrared (FT-IR) and UV–vis measurements was controlled to be ~13 μm. The inherent viscosities were determined using 0.5 g/dL concentration in a Kinematic TV-5S viscometer at 30 °C. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using a Seiko TGA 6200 and a Seiko DSC 6200 with a heating rate of 10 °C min^{-1} under air and nitrogen, respectively. MALDI−TOF MS spectra were taken on a SHIMADZU AXIMA-CFR mass spectrometer, which was equipped with a nitrogen laser ($\lambda = 337$ nm) and pulsed ion extraction. The operation was performed with an accelerating potential of 20 kV by a linear-positive ion mode. The sample monomer solution (1 g/L) was prepared in tetrahydrofuran (THF). The matrix components, 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol, Aldrich) and sodium trifluoroacetate (Aldrich), were dissolved in THF (25 and 2 g/L, respectively). The monomer solution (50 μL) was then mixed with 250 μL of the matrix solution. A 1 μL portion of the final solution was deposited onto a sample target plate and allowed to dry in air at room temperature. Dielectric constants were measured by Agilent Technologies 4294A Precision Impedance Analyzer at 1–1000 kHz. Mechanical properties were measured on a TOYO BALDWIN CO. Ltd. TENSILON/UTM-11-20 with a load cell of 5 kg and 4 mm/min drawing speed. Tensile properties were calculated from the stress–strain curves. Measurements were performed at ambient conditions with film specimens (0.5 cm wide, 6 cm long, thickness 20–30 μm), and calculations are an average of at least five samples. Contact angles were taken on a Face CA-A contact angle meter.

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. However, only low-molecular-weight polymers (POSS−PI 4 < 0.10 dL/g) could be isolated from the 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.[6,22]

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 ODPA, DDSQDA has better solublility 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 and ^1H, ^{13}C, and ^{29}Si NMR spectroscopies, MALDI−TOF MS, and elemental analysis. The IR spectrum of DDSQDA shows

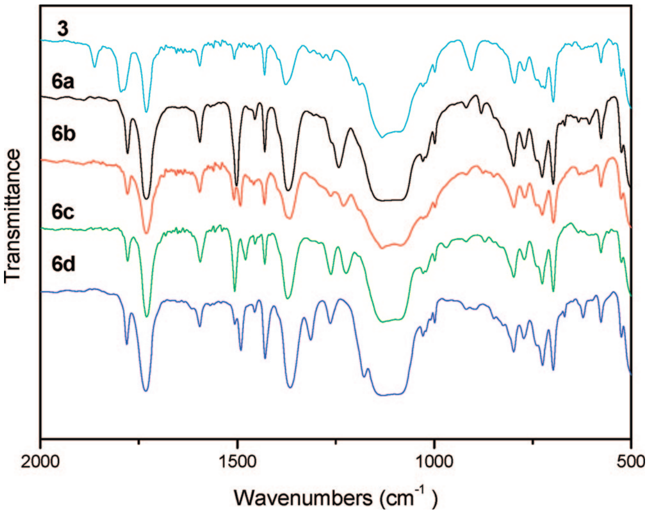


Figure 1. FT-IR spectra of monomer **3** and POSS−PIs **6**.

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 ^{1}H, ^{13}C, and ^{29}Si NMR of DDSQDA are presented in Figures 2–4. 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. On the basis of 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 2). 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. The FT IR spectra of the POSS−PIs **6** show characteristic absorptions due to imide ring at 1780($\nu_{as,C=O}$), 1730($\nu_{s,C=O}$), and 1372–1365 ($\nu_{as,C-N}$) cm^{-1} (Figure 1), and disappearance of the characteristic absorptions at 1861 and 1794 cm^{-1}due to C=O stretching of a dianhydride ring group of monomer **3**. This indicates that monomer **3** has completely reacted the resulting PAA has also completely converted to PI. The presence of the Si−O−Si asymmetric stretching absorptions between 1071 and 1133 cm^{-1} confirms that the structure of the POSS unit remains intact.

Furthermore, POSS−PIs **6** were identified by NMR spectroscopy. Figures 2 and 3 show the ^{1}H and ^{13}C NMR spectra of POSS−PI **6b** and monomer **3**, respectively. The ^{1}H NMR peaks for POSS−PI **6b** are less resolved than those of monomer **3**, which is typically observed for polymeric materials. These are on small shifts between peaks 1 of monomer **3** and **6**, assigned to the $SiMeO_2$ proton. The comparison of the ^{1}H NMR spectra of **3** and **6** shows that there are three new peaks (5, 7, 6) in polymer **6**, which are attributed to the protons of 1,4,4-APB moiety. In Figure 3, the singlet peak 1, due to the proton of the methyl group signal, is relatively unshifted. The comparison of the ^{13}C NMR spectra of **3** and polymer **6b** shows that there are six new peaks (11–16) in polymer **6**, which are attributed to the 1,4,4-APB moiety. In particular, there is significantly shifts of peak 10 due to the C=O dianhydride ring carbon of monomer **3** and the C=O imide ring carbon of POSS−PI **6b**. The ^{29}Si NMR spectra of polymer **6b**, monomer **3**, and **1** are shown in Figure 4, in which the signal of **6b** was barely shifted compared with those of monomers **1** and **3**. It provides direct evidence that the silsesquioxane cages remain intact during the reaction.[6] On the basis of the above data, it is clear that the polyimide is obtained successfully.

Solubility of POSS−PIs 6. The effects of POSS groups on the properties of PIs were evaluated through the study of their solubility, thermal properties, optical properties, water adsorption, and dielectric properties. The PIs **6** have larger contact angles than conventional polyimides[6,27] against water as shown in Table 2. The larger contact angle due to the present of the hydrophobic nature of the silsesquioxane segments in the polymer backbone. As shown in Table 3, POSS−PIs **6** were

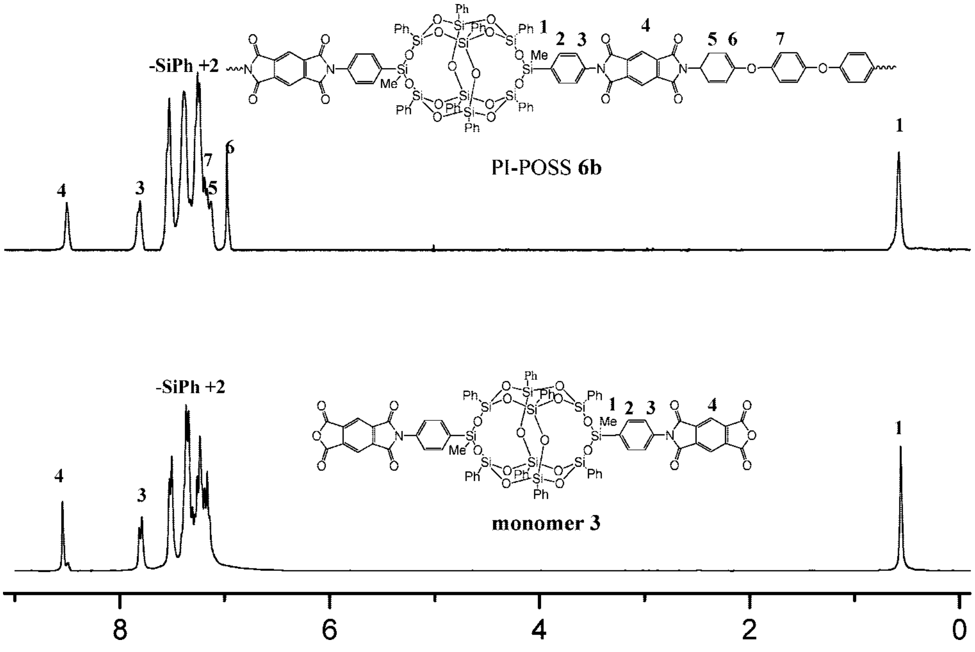


Figure 2. ^{1}H NMR spectra of POSS−PI **6b** and monomer **3** in $CDCl_3$.

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

POSS−PI[a]	diamine	T_g (°C)[b]	T_{d5} (°C)[c] in N_2	T_{d5} (°C)[c] in air	T_{d10} (°C)[d] in N_2	T_{d10} (°C)[d] in air	contact angle (deg)	inherent viscosity[e] (dL/g)
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

[a] Polymerization carried out with 0.2 mmol of each run in solvent at room temperature under nitrogen. [b] From DSC on the second heating at a heating rate of 30 °C/min in nitrogen. [c] Temperature at which 5% weight loss was recorded by thermogravimetry at a heating rate of 10 °C/min in N_2or air. [d] Temperature at which 10% weight loss was recorded by thermogravimetry at a heating rate of 10 °C/min in N_2 or air. [e] Determined at a concentration 0.5 g/dL in each solvent at 30 °C. [f] ND: not detected.

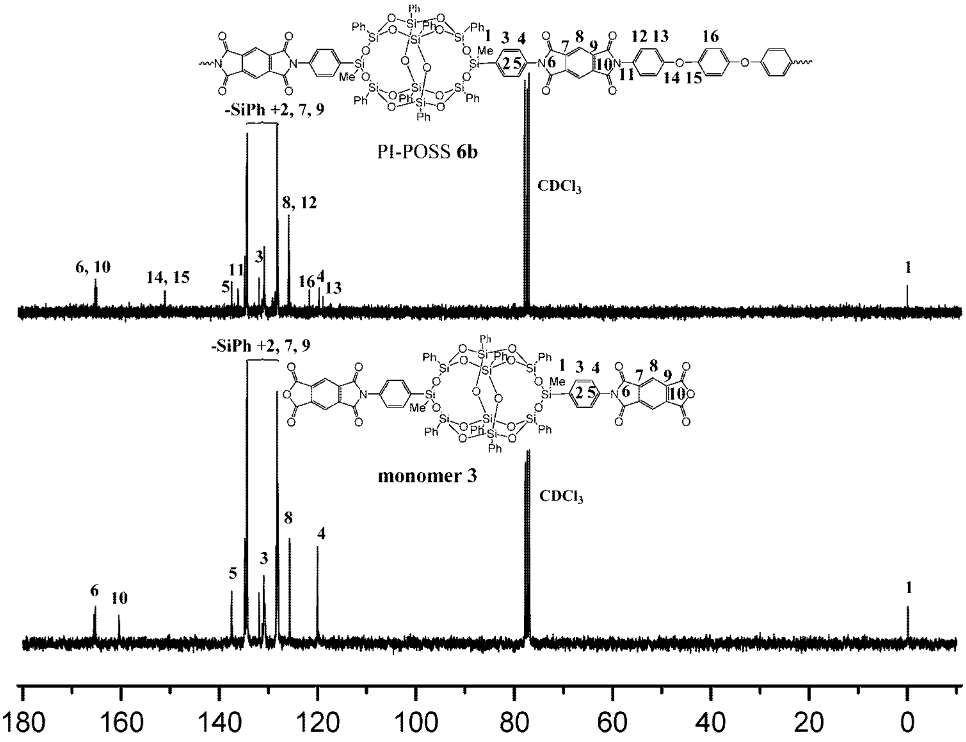


Figure 3. ^{13}C NMR spectra of POSS−PI **6b** and monomer **3** in $CDCl_3$.

soluble in organic solvents such as DMAc, chloroform, THF, acetone and could be dissolved at 5% w/v at room temperature, excluded POSS−PIs **6a** derived from the two-step low-temperature polycondensation, which was insoluble even when in polar amide type solvents such as NMP and DMAc at elevated temperatures.

Thermal Properties of POSS−PIs 6. The thermal properties of the POSS−PIs were evaluated by TGA and DSC measurements. The results are summarized in Table 2. As shown in Figure 5 (TGA), the POSS−PIs exhibit good thermal stability up to 500 °C. Residual weights ranging from 64% to 76% are observed at 700 °C in air. The PI films had T_{d10} values of 540–555 °C in the following decreasing order, PI **6a** > PI **6d** > PI **6b** > PI **6c** in air, and values of 545–570 °C in the following decreasing order, PI **6d** > PI**6a** > PI**6b** > PI **6c** in nitrogen. This tendency is consistent with the structural characteristics of the PIs. For example, in contrast to the rigid molecular structures of POSS−PIs **6a** and **6d**, that of **6c** is more flexible due to the flexible ether linkages present in its molecular chains; therefore, the T_{d10} value of POSS−PI**6c** is much lower. A similar tendency is also observed with regard to the DSC measurements. The T_g of POSS−PIs **6** were not detected except **6c**, which has T_g of 325 °C. It should be probably explained that POSS−PIs **6a**, **6b**, and **6d** have T_g values that are too high to be detected due to the rigid molecular structures, but **6c,** which is derived from 1,3,4-APB has a rather lower T_g, which may be observed due to the flexible ether linkages present in its molecular chains. The thermal properties of the POSS−PIs are significantly higher than those of POSS−PIs having a semi-aromatic polymer backbone as we have previously reported.[6]

Mechanical Properties of POSS−PIs 6. The mechanical properties of POSS−PIs **6** films are summarized in Table 4. The polyimide films have tensile strengths of 72.3–82.1 MPa, initial modulus of 1.8–2.6 GPa, and elongation at breakage of 8.0–15.9%. It indicates that they could be cast as transparent, flexible, and tough films. This material shows higher mechanical properties compared with the POSS−PIs having composed of semiaromatic groups in the polymer backbone.[6]

Electrical Properties of POSS−PIs 6. The POSS−PIs films showed good dielectric properties, and possessed low dielectric constants of 2.43–2.65 at 1 MHz (Table 4). This can be attributed to the relatively increased free volume by the POSS cubic silica core. Second, the POSS molecules have a lower polarity, which also helps to reduce the dielectric constant.[6,12] The POSS−PIs **6d** exhibited the lowest dielectric constant (2.43 at 1 MHz), which could be explained by high POSS content and the low electronic polarizability of the fluorine substituents.

Optical Properties of POSS−PIs 6. The transmission UV–vis spectra of films **6a** and **6d** are shown in Figure 6. The POSS containing polyimide films exhibit cutoffs at 318 nm (**6a**) and 320 nm (**6d**) and transmittances over 80% at 400 nm. A cutoff wavelength is defined here as the point where the transmittance becomes less than 1% in the spectrum. These

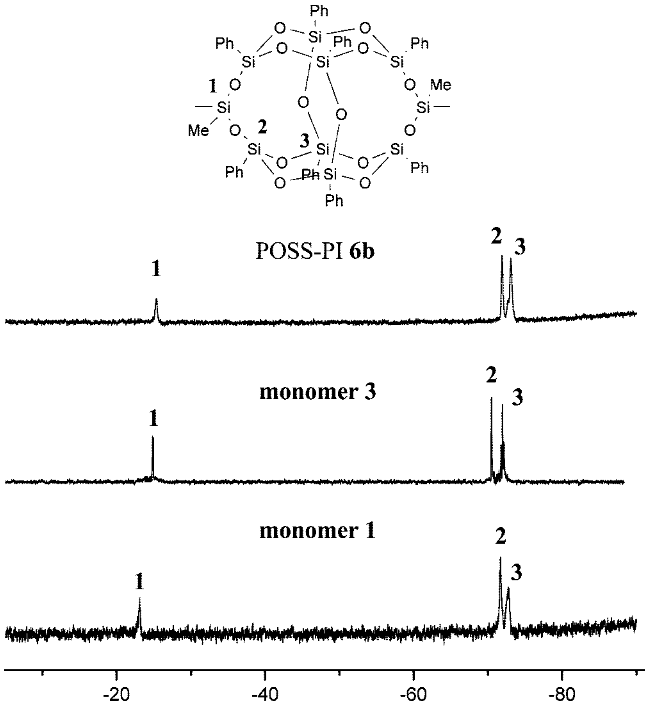


Figure 4. ^{29}Si NMR spectra of POSS−PI **6b** and monomer **3** in $CDCl_3$.

Table 3. Solubility of OSS−PIs[a]

PI	NMP	DMAc	DMF	THF	acetone	methanol	chloroform
6a	+	+	+	+ −	+ −	−	+
6a[b]	−	−	−	−	−	−	−
6b	+	+	+	+	+	−	+
6c	+	+	+	+ −	+ −	−	+
6d	+	+	+	+	+	−	+

[a] Solubility: (+) soluble at room temperature; (−) insoluble even on heating. (+ −) partially soluble or swelling on heating. [b] Two-step low-temperature polycondensation.

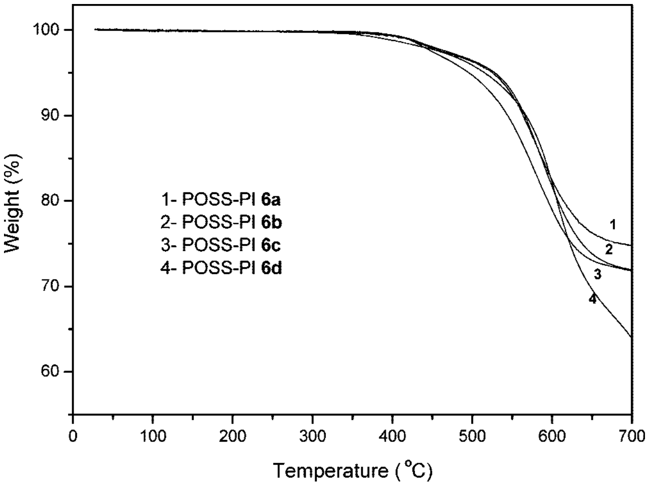


Figure 5. TGA curves of POSS−PI **6** in air with a heating rate of 10 °C/min.

values are a few nanometers higher than those of other siloxane containing polyimides (289 nm)[21] and are similar to those of other semiaromatic polyimides, which can be attributed to POSS units. In addition, POSS−PI **6a** provides an example of very high POSS loading (up to 61 wt % POSS, up to 27 wt % SiO) while maintaining excellent film qualities and appearing essentially transparent and showing only a slight brown coloration (Figure 7).

Table 4. Mechanical and Electrical Properties of POSS−PIs

POSS−PI	tensile strength (MPa)	elongation (%)	initial modulus (GPa)	dielectric constant[a]
6a	82.1	10.9	2.6	2.56
6b	78.1	13.6	2.4	2.59
6c	76.0	15.9	1.9	2.65
6d	72.3	8.0	1.8	2.43

[a] Dielectric constant measured at 1 MHz.

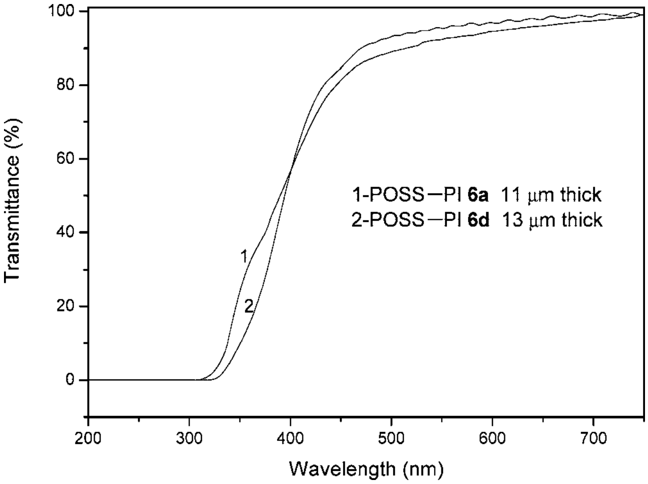


Figure 6. UV–vis spectra of POSS−PI films: **6a** and **6d**.

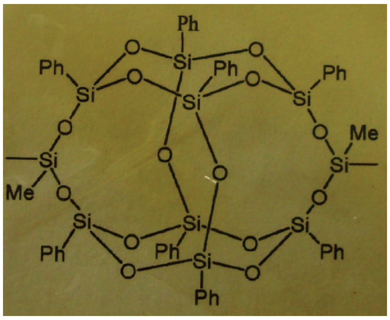


Figure 7. Photograph of the POSS symbol (actual size 4 cm × 4 cm) taken through a thick film (25 μm) of POSS−PI**6a** supported on a glass slide.

Conclusions

To increase the thermal stability and mechanical properties with maintaining a low dielectric constant, DDSQDA, a double-decker-shaped silsesquioxane aromatic tetracarboxylic dianhydride, was synthesized through the functional group conversion method. One-step high temperature solution polymerization procedure of DDSQDA with several aromatic diamines gave the polyimides containing POSS in the main chain (POSS−PI) having high molecular weights (up to $\eta_{inh} = 0.61$ dL/g). POSS−PI thus obtained have outstanding thermal properties, good mechanical properties, and low dielectric constant. In particular, POSS−PI **6d** demonstrates good combined characteristics, including low dielectric constant of 2.43, T_{d10} of 570 °C, good mechanical properties (tensile strengths of 72.3 MPa, initial modulus of 1.8 GPa, and elongation at breakage of 8.0%), excellent optical properties, and is organosoluble; hence, it is a good candidate for polymeric material against advanced microelectronic applications.

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References and Notes

(1) (a) Wright, M. E.; Petteys, B. J.; Guenthner, A. J.; Faillis, S.; Yandek, G. R.; Tomczak, S. J.; Minton, T. K.; Brunsvold, A. *Macromolecules* **2006**, *39*, 4710. (b) Svejda, S. A.; Phillips, S. H.; Gonzalez, R. I.; Feher, F. J.; Lichtenhan, J. D.; Reinerth, W. A. U.S. Patent 6,767,930, 2004. (c) Lichtenhan, J. D.; Vu, N. Q.; Gilman, J. W.; Feher, F. J. United States Patent 5,412,053, 1995.

(2) Provatas, A.; Matisons, J. G. *Trends Polym. Sci.* **1997**, *5*, 327.

(3) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409.

(4) Pescarmona, P. P.; Maschmeyer, T. *Aust. J. Chem.* **2001**, *54*, 583.

(5) Kannan, R. Y.; Salacinski, H. J.; Butler, P. E.; Seifalian, A. M. *Acc. Chem. Res.* **2005**, *38*, 879.

(6) (a) Wu, S. M.; Hayakawa, T.; Kikuchi, R.; Grunzinger, S. J.; Kakimoto, M.; Oikawa, H. *Macromolecules* **2007**, *40*, 5698. (b) Seino, M.; Hayakawa, T.; Ishida, Y.; Kakimoto, M.; Watanabe, K.; Oikawa, H. *Macromolecules* **2006**, *39*, 3473.

(7) (a) Kawakami, Y. *React. Funct. Polym.* **2007**, *67*, 1137. (b) Ikeda, M.; Saito, H. *React. Funct. Polym.* **2007**, *67*, 1148.

(8) Brunsvold, A. L.; Minton, T. K.; Gouzman, I.; Grossman, E.; Gonzalez, R. *High Perform. Polym.* **2004**, *16*, 303.

(9) Su, R. Q.; Müller, T. E.; Prochazka, J.; Lercher, J. A. *Adv. Mater.* **2002**, *14*, 1369.

(10) Kim, H. C.; Wilds, J. B.; Kreller, C. R.; Volksen, W.; Brock, P. J.; Lee, V. Y.; Magbitang, T.; Hedrick, J. L.; Hawker, C. J.; Miller, R. D. *Adv. Mater.* **2002**, *14*, 1637

(11) Koh, K.; Sugiyama, S.; Morinaga, T.; Ohno, K.; Tsujii, Y.; Fukuda, T.; Yamahiro, M.; Iijima, T.; Oikawa, H.; Watanabe, K.; Miyashita, T. *Macromolecules* **2005**, *38*, 1264.

(12) (a) Leu, C.; Reddy, G. M.; Wei, K.; Shu, C. *Chem. Mater.* **2003**, *15*, 2261. (b) Leu, C.; Chang, Y.; Wei, K. *Chem. Mater.* **2003**, *15*, 3721.

(13) Zhang, C.; Babonneau, F.; Bonhomme, C.; Laine, R. M.; Soles, C. L.; Hristov, H. A.; Yee, A. F. *J. Am. Chem. Soc.* **1998**, *120*, 8380.

(14) Xu, H.; Kuo, S.; Lee, J.; Chang, F. *Macromolecules* **2002**, *35*, 8788.

(15) Fu, B. X.; Zhang, W. H.; Hsiao, B. S.; Rafailovich, M.; Sokolov, J.; Sauer, B. B.; Phillips, S.; Blanski, R. *High Perform. Polym.* **2000**, *12*, 565.

(16) Haddad, T. S.; Lichtenhan, J. D. *Macromolecules* **1996**, *29*, 7302.

(17) Lichtenhan, J. D.; Otonari, Y. A.; Carr, M. J. *Macromolecules* **1995**, *28*, 8435.

(18) Devaux, E.; Rochery, M.; Bourbigot, S. *Fire Mater.* **2002**, *26*, 149.

(19) Gonzalez, R. I.; Phillips, S. H.; Hoflund, G. B. *J. Spacecraft Rockets* **2000**, *37*, 463.

(20) Yi, M. H.; Huang, W.; Jin, M. Y.; Choi, K. Y. *Macromolecules* **1997**, *30*, 5606.

(21) Wu, S. M.; Hayakawa, T.; Kakimoto, M. *High Perform. Polym.,* 000

(22) Wright, M. E.; Schorzman, D. A.; Feher, F. J. Jin, R. Z. *Chem. Mater.* **2003**, *15*, 264.

(23) Kato, T.; Kikukawa, T.; Ito, K.; Yoshida, K.; Yamamoto, Y. Jpn. Kokai Tokkyo Koho 2006265243A 2006.

(24) Cardoen, G.; Coughlin, E. B. *Macromolecules* **2004**, *37*, 5123.

(25) Kim, K.; Keum, D.; Chujo, Y. *Macromolecules* **2003**, *36*, 867.

(26) Kim, B.; Mather, P. T. *Macromolecules* **2002**, *35*, 8378.

(27) Maier, G. *Prog. Polym. Sci.* **2001**, *26*, 3.

(28) Matsuura, T.; Yamada, N.; Nishi, S.; Hasuda, Y. *Macromolecules* **1993**, *26*, 419.

(29) Mi, Q.; Gao, L. X.; Ding, M. X. *Polymer* **1997**, *38*, 3663.

(30) Kato, J.; Seo, A. S.; Shiraishi, S. *Macromolecules* **1999**, *32*, 6400.

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