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

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Received March 6, 2007; Revised Manuscript Received June 6, 2007

ABSTRACT: A series of semiaromatic polyimides containing polyhedral oligomeric silsesquioxane (POSS) in main chain (POSS−PIs) from a double-decker-shaped silsesquioxane diamine (DDSQ−diamine) (**4**) with various aromatic tetracarboxylic dianhydrides were prepared and the structures were characterized by IR and NMR spectra. A double-decker-shaped silsesquioxane dianhydride (DDSQDA) (**3**) was synthesized by hydrosilylation reaction from double-decker-shaped silsesquioxane (DDSQ) (**1**) and *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (**2**), which then reacted with 4,4′-oxydianiline (ODA) to produce the DDSQ-diamine. The POSS−PIs possessed good thermal stability and mechanical properties, low water absorption, and alkali resistance as well as low dielectric constant. The 5% weight loss temperatures (T_{d5}) in air were observed at 495−514 °C. The polymer films had good mechanical properties with elongation at breakage of 2.9−6.0%, in which POSS−PI **8c** derived from 4,4′-oxydiphthalic anhydride (ODPA) exhibits the highest elongation of 6.0%. The water absorption of POSS−PI **8b** (<1%) was much lower than that of PI from pyromellitic dianhydride (PMDA)/ODA (6.0%). POSS−PIs **8** possessed excellent alkaline and acid resistance. POSS−PI **8b** kept its flexible mechanical properties when immersed in 5% NaOH solution at 40 °C for 72 h. The dielectric constant of POSS−PI **8c** measured by precision impedance method was 2.36.

Introduction

Polyhedral oligomeric silsesquioxane (POSS) is a cube-octameric molecule with an inner inorganic silicon and oxygen framework which is externally covered by organic substituents.[1−5] It has a nanometer-sized cage structure and can be functionalized with various organic groups.[6,7] One set of members of the POSS family are octamers with the general formula $(RSiO_{1.5})_8$ consisted of a rigid and cubic silica core with a nanopore diameter of ca. 0.3−0.4 nm.[8,9] 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,[10−13] solubility, nonflammability,[14] oxidative resistances,[15] and excellent dielectric properties.[8,16−19]

Polyimides (PIs) have outstanding thermal resistance, good mechanical properties and excellent dielectric properties necessary for use in microelectronics as the interlayer dielectrics in integrated circuit fabrication.[21,22] The introduction of POSS into polyimides can improve these properties forther. Recently, some POSS-containing polyimides have been reported by Leu et al.[8,16,17] who prepared polyimide-side-chain tethered POSS nanocomposites for low dielectric films. While side-chain incorporation of POSS did reduce the dielectric constant, no significant effect on the mechanical properties was observed.[8,16,17] In most reported cases, the POSS-based materials were prepared with POSS as a side chains[8−20] or as an end group[23−26] in hybrid polymers. There are few examples for the synthesis of main chain POSS in the literature.[27] For a step-polymerization system, it is important for the monomer to possess exactly two functional groups in order to obtain linear polyimides with a high molecular weight. Because of multiple site on POSS with equivalent reactivity it is rather difficult to introduce only two functional groups, so polymerization from the POSS monomers typically generates insoluble cross-linked polymers from small amounts of POSS containing more than two functional groups.[28−31]

We previously reported the synthesis of a POSS, double-decker-shaped silsesquioxane (DDSQ).[7,32] Since the DDSQ possesses precisely two reactive hydrosilane groups, linear organic−inorganic hybrid polymers should be obtainable without cross-linking.

In this paper, we reported the synthesis of double-decker-shaped silsesquioxane dianhydride (DDSQDA) (**3**) via hydrosilylation of *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (**2**) with double-decker-shaped silsesquioxane (DDSQ), and its subsequent reaction with 4,4′-oxydianiline (ODA) to produce a double-decker-shaped silsesquioxane diamine (DDSQ-diamine) (**4**). A series of linear semiaromatic polyimides containing POSS in main chain (POSS−PIs) from the DDSQ-diamine with various aromatic tetracarboxylic dianhydrides were synthesized and characterized. The thermal and mechanical properties, alkali resistance, and dielectric properties were also investigated.

Experimental Section

Materials. 1-Methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylacetamide (DMAc), and toluene were purified by vacuum distillation

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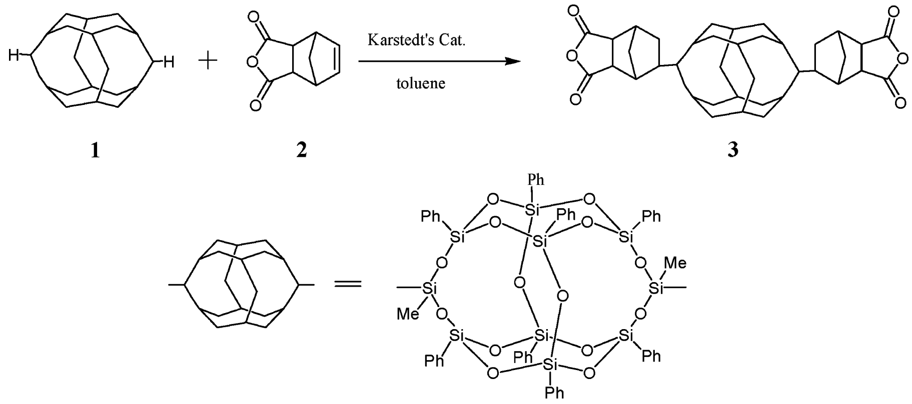
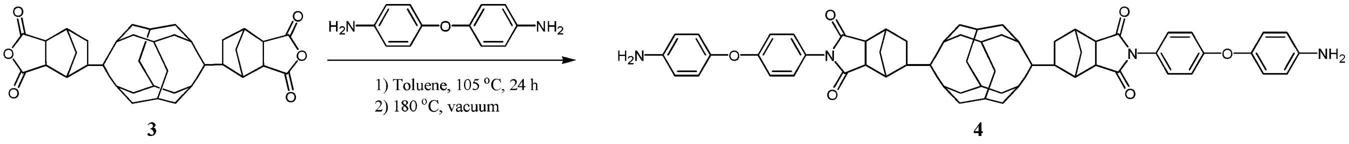
10.1021/ma070547z CCC: $37.00

Scheme 1



Scheme 2



over CaH$_2$ prior to use. *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (**2**) was purified by recrystallization from acetic anhydride and sublimation before use. 4,4′-Oxydianiline (ODA) and pyromellitic dianhydride (PMDA) were purified by sublimation before use. 4,4′-Oxydiphthalic anhydride (ODPA), 3,3′,4,4′-biphenyltetracarboxylic anhydride (BPDA), and 3,3′,4,4′-benzophenonetetracarboxylic anhydride (BTDA) were heated to 90 °C in acetic anhydride and toluene, stirred for 1 h, filtered, and then dried at 150 °C for 2 h prior to use. 4,4′-(Hexafluoro-isopropylidene) diphthalic anhydride (6FDA) was dried at 150 °C for 2 h before use. 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 a magnetic stirrer were placed the DDSQ (0.50 g, 0.43 mmol), **2** (0.56 g, 3.4 mmol), and toluene (4 mL) under an argon stream. The reaction was carried out catalyzed by 0.2 mol % of Karstedt's catalyst (Pt(dvs)) in toluene at 75 °C for 24 h to afford **3** (0.61 g, 96% yield): mp >350 °C. IR (KBr): $\nu = 1860$, 1782 (anhydride C═O), 1265 (Si−CH$_3$), 1220 (Si−Ph), 1132, 1090 (Si−O−Si) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): 7.48−7.19 (40H, m), 3.25−3.20 (4H, m), 2.89 (2H, s), 2.67 (2H, s), 1.80−1.57 (6H, m), 1.28 (2H, m), 0.83 (2H, t, $J = 7.8$ Hz), 0.28 (6H, s) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): 172.1, 171.6, 133.9, 131.1, 127.8, 52.3, 49.6, 41.7, 40.9, 40.2, 26.3, 24.6, −1.9 ppm. ^{29}Si NMR (60 MHz, CDCl$_3$): −22.1, −77.9, −78.9 ppm. Anal. Calcd for $C_{68}H_{64}O_{20}Si_{10}$ (%): C, 55.11; H, 4.35. Found: C, 54.96; H, 4.38.

Synthesis of DDSQ—Diamine (4). A mixture of **3** (0.50 g, 0.34 mmol), and ODA (0.41 g, 2.04 mmol) were added into a 100 mL two-necked round-bottomed flask, which was then stirred in toluene at 105 °C for 24 h, and dried under vacuum at 180 °C to give a yellow solid (**4**) in a 98%: mp >350 °C. IR (KBr): $\nu = 3406$ (−NH$_2$), 1770, 1707 (amide C═O), 1384 (C−N), 1265 (Si−CH$_3$), 1236 (Si−Ph), 1133, 1051 (Si−O−Si) cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6): 7.72−7.65 (8H, dd, $J = 7.2$, 6.9 Hz), 7.60−7.53 (8H, dd, $J = 7.8$, 7.2 Hz), 7.47−7.24 (24H, m), 7.10 (4H, d, $J = 8.7$ Hz), 6.93−6.88 (8H, m), 6.78 (4H, d, $J = 8.7$ Hz), 4.67 (4H, s), 3.28 (4H, s), 3.02 (2H, s), 2.72 (2H, s), 1.92 (4H, d, $J = 8.4$ Hz), 1.74−1.57 (4H, m), 1.05 (2H, t, $J = 8.4$ Hz), 0.42 (6H, s) ppm. ^{13}C NMR (75 MHz): 177.8, 177.7, 160.0, 147.1, 146.5, 134.6, 131.6, 129.0, 127.1, 122.2, 119.9, 117.2, 116.1, 51.7, 49.3, 41.8, 41.1, 40.3, 26.9, 25.4, −1.8 ppm. ^{29}Si NMR (60 MHz): −21.8, −78.3, −78.9 ppm. Anal. Calcd for $C_{92}H_{84}N_4O_{20}Si_{10}$ (%): C, 59.84; H, 4.59; N, 3.03. Found: C, 59.86; H, 4.48; N, 2.81.

Polymer Synthesis. Synthesis of POSS—PAA 5. The general polymerization procedure of **3** with ODA was carried out in DMAc (17 or 28 wt % solids) to give POSS−PAA **5**, which was then thermally imidized to produce POSS−PI **6**. The inherent viscosity of the POSS−PAA **5** is 0.14−0.20 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C. IR (KBr): $\nu = 3434$ (N−H), 1648 (C═O, carboxylic acid), 1262 (Si−Me), 1221 (Si−Ph), 1131, 1087 (Si−O−Si) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): 11.65−11.49 (2H, m), 10.05−9.89 (2H, m), 7.82−7.21 (40H, m), 7.03−6.63 (16H, m), 3.26 (4H, br), 3.04 (2H, br), 2.77 (2H, br), 1.84 (4H, m), 1.65−1.47 (4H, m), 1.00 (2H, br), 0.39 (6H, br) ppm. ^{13}C NMR (75 MHz): 178.1, 177.3, 159.8, 146.7, 146.4, 135.1, 132.2, 128.8, 127.3, 122.4, 120.1, 116.7, 115.8, 51.6, 48.9, 42.1, 40.8, 40.4, 27.1, 25.5, −1.9 ppm. ^{29}Si NMR (60 MHz): −21.5, −78.8, −78.6 ppm.

IR of **6** (KBr): $\nu = 1806$, 1714 (amide C═O), 1379 (C−N), 1262 (Si−CH$_3$), 1240 (Si−Ph), 1135, 1048 (Si−O−Si) cm^{-1}.

Synthesis of POSS—PAAs 7. In a typical experiment, **4** (0.50 g, 0.27 mol) was dissolved in 10 mL DMAc in a 25 mL three-necked, to which, BPDA (**d**, 0.08 g, 0.27 mol) was added while stirring. The suspension was stirred for 24 h at room temperature to yield a viscous solution, which was then poured into methanol. The precipitate was filtered off, washed with water, and dried under vacuum at 40 °C. The inherent viscosity of the resulting POSS−PAA **7d** is 0.38 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C. IR (KBr): $\nu = 3445$ (N−H), 1767, 1709 (amide C═O), 1634 (C═O, carboxylic acid), 1264 (Si−Me), 1234 (Si−Ph), 1132, 1083 (Si−O−Si) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): 10.55 (2H, br), 8.12−7.95 (8H, m), 7.79 (2H, br), 7.46 (2H, br), 3.40(4H, br), 3.25(2H, br), 2.86(2H, br), 1.74 (4H, br), 1.51 (4H, br), 0.83 (2H, br), 0.32 (6H, br) ppm. ^{13}C NMR (75 MHz, DMSO-d_6) : 177.6, 177.5, 167.7, 167.2, 157.8, 156.4, 151.6, 136.4, 133.7, 131.5, 130.9, 130.1, 128.6, 127.1, 121.7, 120.5, 119.5, 118.1, 50.9, 48.6, 40.7, 40.1, 39.3, 26.3, 24.6, −1.7 ppm. ^{29}Si NMR (60 MHz, DMSO-d_6) : −21.6, −77.7, 78.3, −79.2 ppm.

Other POSS−PAAs, **7a**, **7b**, **7c**, and **7e**, were prepared in a similar procedure by the polymerization of 1 equiv of **4** to 1 equiv of dianhydride PMDA (**a**), ODPA (**b**), 6FDA (**c**), and BTDA (**e**) as shown in Scheme 3.

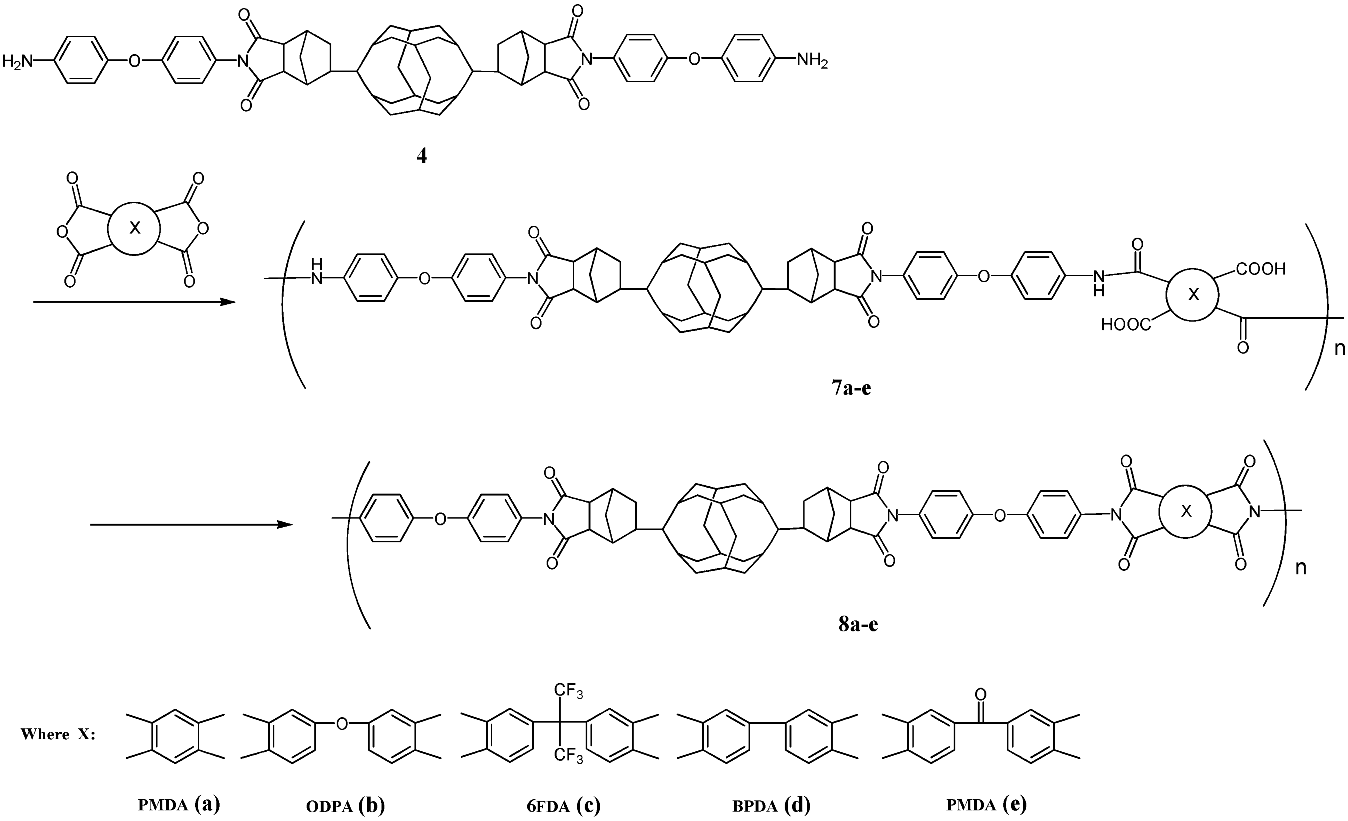
Polyimide films were prepared by casting the polyamic acid solution from DMAC onto a silicon wafer then cured by a stepped thermal sequence (80 °C/2 h, 120 °C/1 h, 250 °C/2 h, 300 °C/1 h) under nitrogen atmosphere to produce the imidized POSS−PIs **8a**−**e**.

IR of **8a** (KBr): $\nu = 1781$, 1714 (amide C═O), 1376 (C−N), 1261 (Si−CH$_3$), 1242 (Si−Ph), 1136, 1078 (Si−O−Si) cm^{-1}.

IR of **8b** (KBr): $\nu = 1776$, 1718 (amide C═O), 1380 (C−N), 1268 (Si−CH$_3$), 1241 (Si−Ph), 1143−1087 (Si−O−Si) cm^{-1}.

IR of **8c** (KBr): $\nu = 1783$, 1716 (amide C═O), 1375 (C−N), 1264 (Si−CH$_3$), 1243 (Si−Ph), 1142−1090 (Si−O−Si) cm^{-1}.

Scheme 3



IR of **8d** (KBr): $\nu = 1780$, 1716 (amide C═O), 1378 (C−N), 1266 (Si−CH_3), 1234 (Si−Ph), 1114, 1071 (Si−O−Si) cm^{-1} (Figure 4).

IR of **8e** (KBr): $\nu = 1781$, 1717 (amide C═O), 1378 (C−N), 1265 (Si−CH_3), 1242 (Si−Ph), 1115, 1088 (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 FT-IR 460 Plus Fourier-transform infrared spectrophotometer. The inherent viscosities were determined using 0.5 g/dL concentration in a Kinematic TV-5S viscometer at 30 °C. Thermo gravimetric 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, 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, 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

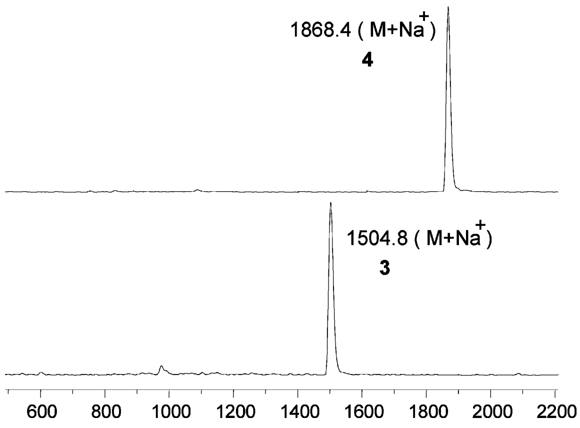


Figure 1. MALDI−TOF MS spectra of **3** and **4**.

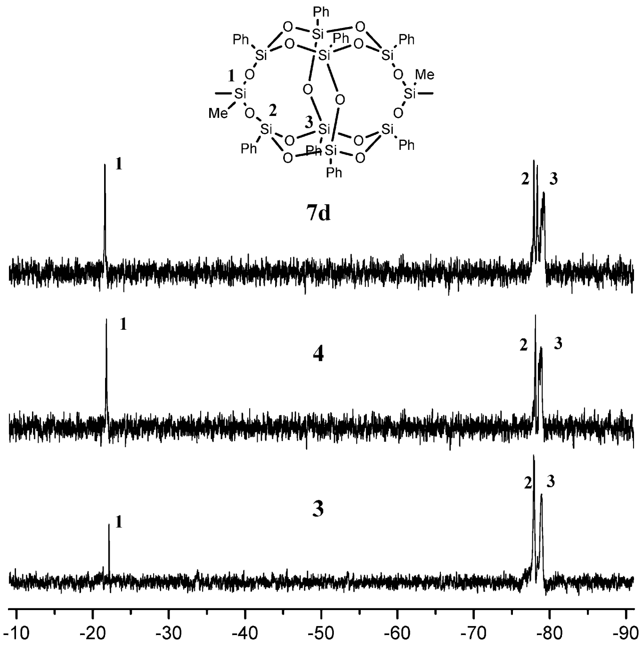


Figure 2. ^{29}Si NMR spectra of monomer **3**, monomer **4** and POSS−PAA **7d**.

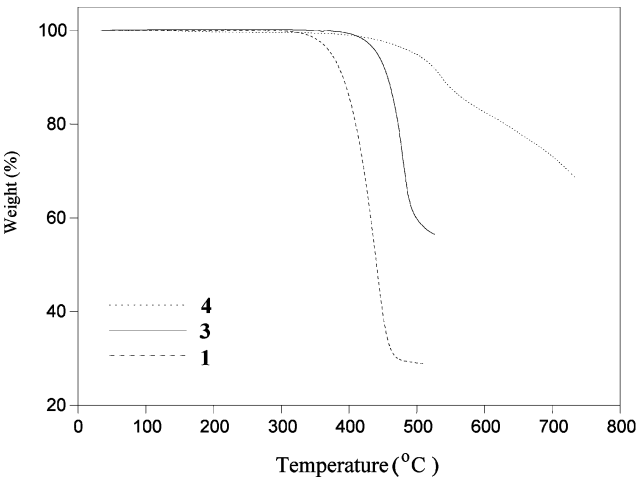


Figure 3. TGA curves of **1**, **3**, and **4** in air with a heating rate of 10 °C/min.

performed at ambient conditions with film specimens (0.5 cm wide, 6 cm long, thickness 33−42 μm) and calculations are an average of at least five samples. Polyimide density was measured on films by a flotation method in a solution of calcium nitrate in water at 25 ± 0.1 °C.[33] Contact angle were taken on a Face CA-A contact angle meter. The treatment with acid: the film immersed in the solution of 95% sulfuric acid at 40 °C for 72 h. The treatment with base: the film immersed in the solution of 5% NaOH in water at 40 °C for 72 h. Testing methods for water absorption of PIs were performed by according to the measuring method described in Japanese Standards Association (JIS) K7209.[34,35]

Results and Discussion

Synthesis of DDSQDA(3). **3** was prepared by hydrosilylation reaction of DDSQ with *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (**2**) (Scheme 1). The reaction was quenched after the 8 h and indicated by a preliminary test reaction that monitored the disappearance of the Si−H peak in ^{1}H NMR spectrum. After solvent removal, the solid was heated under vacuum at 150 °C to ensure all of anhydride **2** was removed. Success in the isolation of **3** depends upon the rigorous exclusion of anhydride **2**. The Pt catalyst was extracted from the solid by refluxing in acetone with active carbon for several hours; the precipitate was filtered though celitile 545, and washed with acetone. Remaining trace impurities were extracted by ether via Soxhlet extraction. Finally, the solid was refluxed in acetic anhydride and toluene for 2 h, followed by solvent removal, and then dried at 180 °C. The molecular weight of **3** was confirmed by MALDI−TOF MS spectrum (Figure 1). A signal observed at 1504.8 (M + Na$^+$) was observed which is consistent with the calculated analysis value of 1480.2.

Synthesis of POSS—PAA 5. The polymerization of **3** with ODA was carried out in DMAc at room temperature to give POSS−PAA **5**. The inherent viscosity is low (0.14−0.20 dL/g) implying that POSS−PAA **5** has a relatively low molecular weight. The inherent viscosity remained unchanged even when the reaction temperature was increased to 65 °C and reaction time prolonged to 30 h as shown in Table 1. The POSS−PI **6** prepared from POSS−PAA **5** by thermal imidization was also fragile. The low molecular weights are likely due to a deactivation of the anhydride ring by the norbornae moiety.[21]

On the other hand, the copolymerization of **3**, ODPA and ODA was performed in DMAc at room temperature for 24 h. The mole ratio of monomers was 1:1:2, respectively. The obtained PAA showed low inherent viscosities of 0.22 dL/g. The copolymerization was carried out at other mole ratio of **3** (1 equiv) and ODPA (2 equiv) with ODA (3 equiv) again, but also no discernible effect on the inherent viscosity was observed.

Synthesis of DDSQ—Diamine (4). To obtain polyamic acids containing main chain POSS units with high molecular weights, bis-amine monomer **4** was prepared from **3** and excess ODA in toluene at 105 °C (Scheme 2). Comparison of the ^{29}Si NMR spectra of **4** with that of **3** (Figure 2), indicates that the silsesquioxane cages remains intact throughout the reaction. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were also consistent with the formation of **4** (*vide infra*). A singlet peak observed at 1868.4 (M+Na$^+$) for MALDI−TOF MS agrees well with the calculated value of 1844.4 (Figure 1). Additionally, the thermal properties of monomers were evaluated by TGA as shown in Figure 3. The 5% weight loss temperatures (T_{d5}) in air were observed at 373−497 °C, and 10% weight loss temperatures (T_{d10}) in air were observed at 390−528 °C, respectively, which shows that the POSS-containing monomers possess good thermal stability similar to semiaromatic polyimides.[22,36]

Synthesis of POSS—PAA 7. A series of POSS−PAAs were prepared from **4** and a series of aromatic dianhydrides (Scheme 3).

To investigate the solvent effect, polymerizations of PMDA and ODPA with diamine **4**, were studied in different solvents of NMP and DMAc, respectively (Table 2). It was found that reaction in DMAc generated a product with relative higher inherent viscosity than reaction in NMP.

Polymer Characterization. POSS−PAAs **7** were identified by NMR spectroscopy. Figure 5 and 6 show the ^{1}H and ^{13}C NMR spectra of POSS−PAA **7d** and monomer **4**, respectively. The ^{1}H NMR peaks for POSS−PAA **7d** are less resolved than those of monomer **4**, typical of polymeric materials. The peak due to the amine proton (4.67 ppm) of monomer **4** is absent in **7d**, and a new peak typical of an amide proton is observed at 10.55 ppm. The comparison of the ^{1}H NMR spectra of **4** and **7d** indicates that peak 2 which split into two broad groups 2 and 2* in the monomer **4** became a single broad signal in the polymer **7d**. This might be attributed to the rotation hindrance of polymer chain. The data are consistent with the formation of a polyamic acid. In the ^{13}C NMR spectra, the singlet peak 8 due to the proton of the methyl group signal, seven peaks (1−7) due to the carbons of methylene groups in the norbornane moiety. These are relatively unshifted from monomer **4** to POSS−PAA **7d**. It indicates that the methyl group and norbornane moiety remain intact following the reaction. The ^{29}Si NMR spectra of polymer **7d** (DMSO-d_6) and **4** (acetone-d_6) are shown in Figure 2, in which the signal $SiMeO_2$ (peak 1) of **7d** was barely shifted compared with **4**. It provides direct evidence that the silsesquioxane cages remain intact following the reaction. The broad peak 2 centered at −78.3 ppm in **4** split into a doublet at −77.7 and −78.3 ppm in **7d**. A chiral center can cause the splitting of ^{29}Si NMR signal, which means that different stereo-configurations cause this splitting.[37]

POSS−PIs **8** were identified by FT-IR spectroscopy. The FT-IR spectrum of POSS−PI **8d** is given as an example (Figure 4). The appearance of characteristic imide absorptions at 1780 and 1716 cm^{-1} and disappearance of the absorption of 1707 cm^{-1} which attributed to the carboxylic acid indicates conversion from PAA to PI. The presence of the Si−O−Si asymmetric stretching absorptions between 1071 and 1114 cm^{-1}, Si−Me absorptions at 1266 cm^{-1} and of Si−Ph absorptions at 1234 cm^{-1}, confirms that the POSS unit's structure remains intact.

Thermal Properties of POSS—PIs 8. The thermal properties of the POSS−PIs were evaluated by DSC and TGA (Table 3). The T_g values of POSS−PIs in nitrogen ranged from 255 to

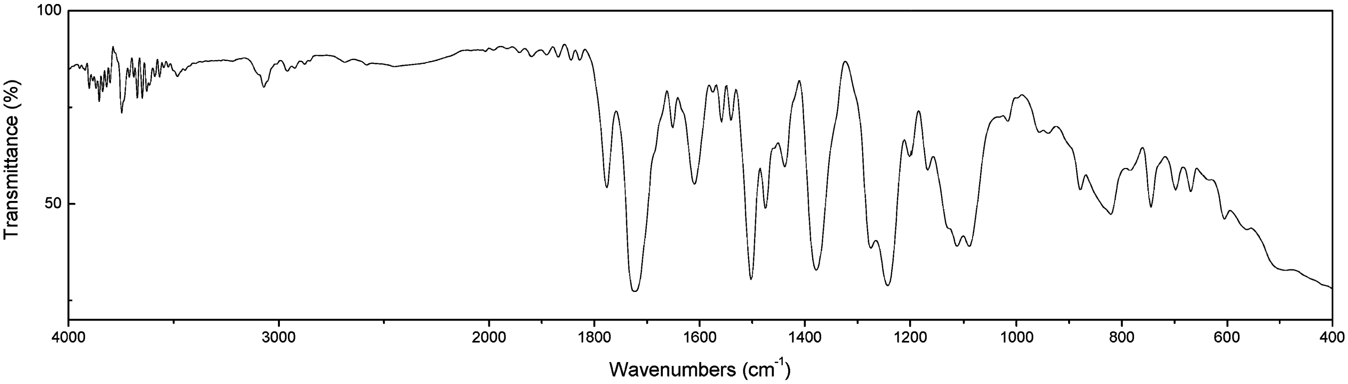
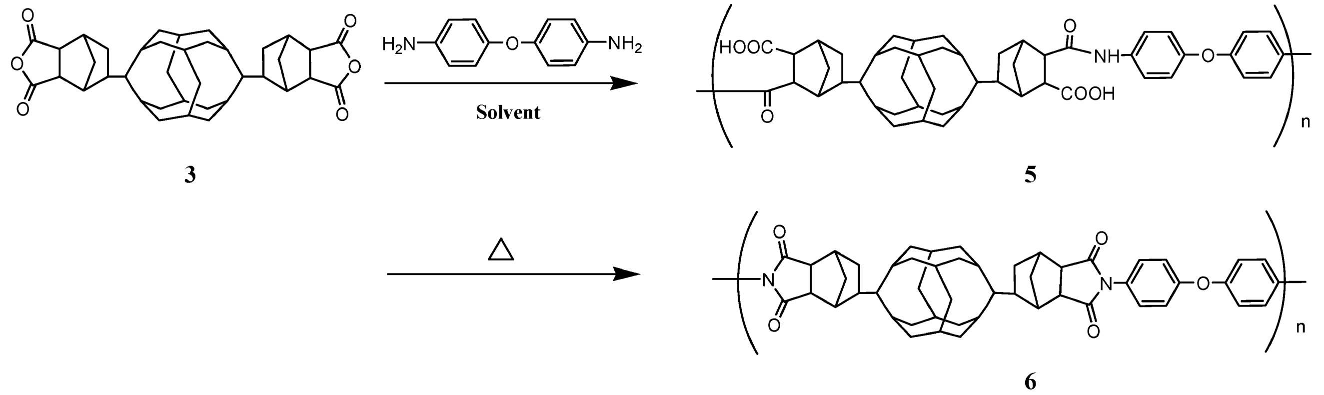


Figure 4. FT-IR spectrum of POSS−PI **8d**.

Table 1. Synthesis of Polyamic Acid (5)



run[a]	temp (°C)	solvent	amt (mL)	time (h)	inherent viscosity[b] (dL/g)	film quality of **6**
1	25	DMAc	5	24	0.15	
2	25	NMP	5	24	0.14	
3	25	DMAc	3	24	0.18	brittle
4	25−65[c]	DMAc	5	30	0.19	brittle
5	25−65[c]	DMAc	3	30	0.20	brittle
6	65	DMAc	3	30	0.16	

[a] Polymerization was carried out with 0.5 mmol of each monomer in the solvent under nitrogen. [b] Measured at a concentration 0.5 g/dL in each solvent at 30 °C. [c] Reaction at 25 °C for 7 h and at 65 °C for 23 h.

Table 2. Summary of the Effects of Solvent on the Inherent Viscosity of POSS−PAAs

POSS−PAA[a]	solvent	dianhydride	yield (%)	inherent viscosity[b] (dL/g)
7a	NMP	PMDA	98	0.25
7a	DMAc	PMDA	99	0.27
7b	DMAc	ODPA	>99	0.53
7b	NMP	ODPA		0.45
7c	DMAc	6FDA	>99	0.48
7d	DMAc	BPDA	>99	0.38
7e	DMAc	BTDA	>99	0.39

[a] Polymerization was carried out with 0.2 mmol of each run in solvent at room temperature under nitrogen. [b] Measured at a concentration 0.5 g/dL in each solvent at 30 °C.

267 °C. The T_g is very typical compared to those of other polyimides.[22,36] The T_g of POSS−PI **8e** (267 °C) is highest and not that for **8a** (264 °C), which is basically the same as for the other polyimides. It can be explained that the flexible ODA unit of monomer **4** is due to the T_g of the polyimides. The POSS unit has no noticeable effect on T_g. However, while the T_g is unchanged, the 5% weight loss temperatures (T_{d5}) and 10% weight loss temperatures (T_{d10}) in air are improved up to 514 and 551 °C (**8e**), respectively. The results indicate that the POSS moiety improves the thermal stability over current semiaromatic polyimides used in the microelectronic applications.[21,22,36]

Mechanical Properties of POSS—PIs 8. Table 4 summarizes the mechanical properties of POSS−PIs **8** series. The polyimide films (**8**) have tensile strengths of 42.1−74.1 MPa, initial modulus of 1.51−2.32 GPa, and elongation at breakage of 2.9−6.0%. The elongation of **8a** is unusually low (2.9%). This is likely due to the lower molecular weight of **8a** as compared with the other polyimides. However, **8b** derived from ODPA showed the highest elongation of 6.0%, which might be attributed to the higher molecular weight and the flexible ether linkage in the polymer backbone.

Alkali and Acid Resistance. In order to investigate the alkali and acid resistance of the present PIs, the mechanical properties of POSS−PI **8b** and the polyimide (PMDA/ODA) were measured before and after immersion in the 5 wt % NaOH solution and in 95 wt % sulfuric acid, respectively. As shown in Table 4, after immersion in 5% NaOH at 40 °C for 72 h the POSS−PI **8b** still remained flexible and its mechanical properities were only slightly degraded: tensile strength of 65.9 MPa, elongation of 3.8%, and initial modulus of 1.96 GPa. However, the reference PMDA/ODA film lost its flexibility and its mechanical properties could not be remeasured. Immersion of the PMDA/ODA film in 95% sulfuric acid dissolved within minutes. However, the sulfuric acid only swelled POSS−PIs **8**, and it was observed that 92−97% of the film mass was retained after 3 days. The film after acid treatment was too brittle

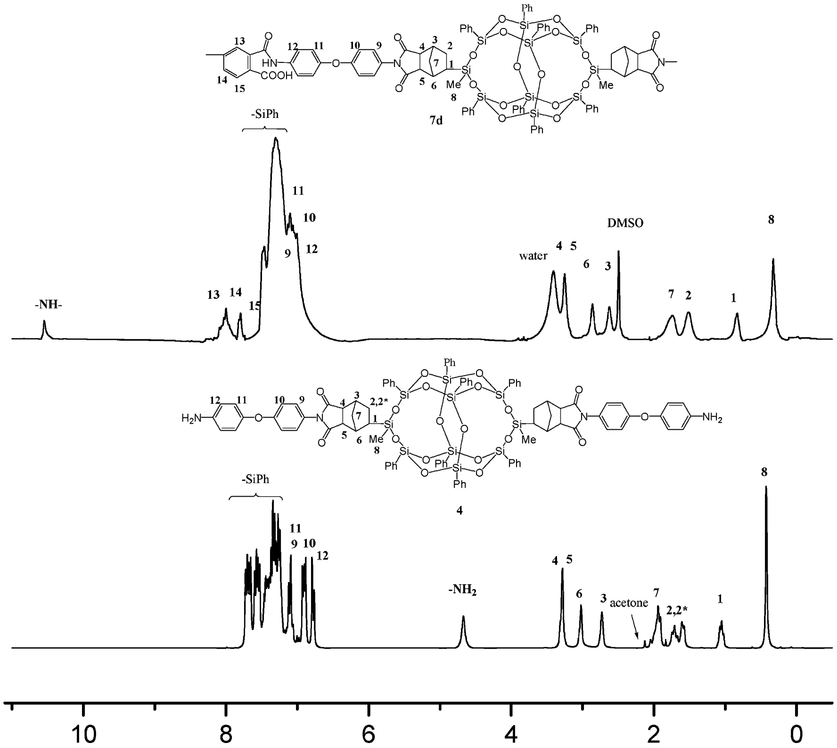


Figure 5. ^{1}H NMR spectra of POSS−PAA **7d** in DMSO-d_6 and **4** in acetone-d_6.

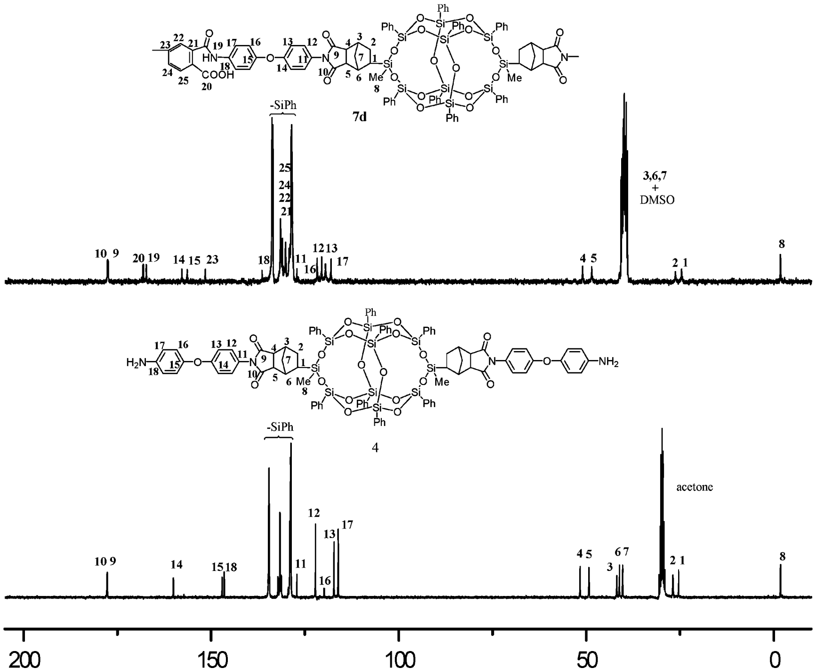


Figure 6. ^{13}C NMR spectra of POSS−PAA **7d** in DMSO-d_6 and **4** in acetone-d_6.

to mechanically test, possibly indicating that the mass loss is due to extraction of low molecular weight species that were acting as a plasticizer. Overall, the POSS moiety added exceptional acid and base resistance to the PI.

The high resistance to acid and base is likely due to two main factors. First, the POSS−PI contact angle of water is significantly higher than that of the PMDA/ODA PI (Table 3). This correlates well with the low water absorption (Figure 7) of the POSS−PI **8b** (<1%) to the PMDA/ODA film (4.8−6%). It is reasonable to conclude that the base solution cannot degrade what it cannot interact with. Second, the unique molecular “silicone−oxygen” frame (silsesquioxane combination) of POSS (Si_2O_3) with the middle character of silicone (SiO) and silica (SiO_2), has the features of both an inorganic substance (silicone base) and organic matter (carbon base). It indicates POSS has a dramatic effect in chemical resistance etc.[3,10−15] The combination of a hydrophobic polymer to minimize swelling and chemical stability of the POSS moiety imparts high resistance to acid and alkaline solutions.

Dielectric Constant of POSS—PIs 8. The POSS−PIs **8** possessed low dielectric constants of 2.36−2.74 at 1 MHz (Table 5). This can be attributed to the POSS of cubic silica core with the homogeneity nanopore increasing in the free volume. Second, the POSS molecules have a lower polarity, which also

Table 3. Summary of the Properties of the POSS−PIs and PMDA/ODA

PI	T_g[a] (°C)	T_{d5}[b] (°C)	T_{d10}[c] (°C)	density (g/cm^3)	contact angle (deg)
8a	264	504	541	1.41	84
8b	261	501	538	1.42	86
8c	255	495	521	1.43	79
8d	262	503	537	1.42	83
8e	267	514	551	1.44	84
6	248	498	537	1.40	85
PMDA/ODA	362	470	530	1.44	54

[a] From DSC on the second heating at a heating rate of 30 °C/min in nitrogen. [b] Temperature at which 5% weight loss was recorded by thermogravimetry at a heating rate of 10 °C/min in air. [c] Temperature at which 10% weight loss was recorded by thermogravimetry at a heating rate of 10 °C/min in air.

Table 4. Mechanical Properties of POSS−PIs 8a−e

POSS−PI	tensile strength (MPa)	elongation (%)	initial modulus (GPa)
8a	42.1	2.9	2.32
8b	74.1	6.0	2.15
8b[a]	65.9	3.8	1.96
8c	58.0	5.9	1.82
8d	52.3	5.0	1.51
8e	65.8	5.4	2.18

[a] Immersed in the solution of 5% NaOH in water at 40 °C for 72 h.

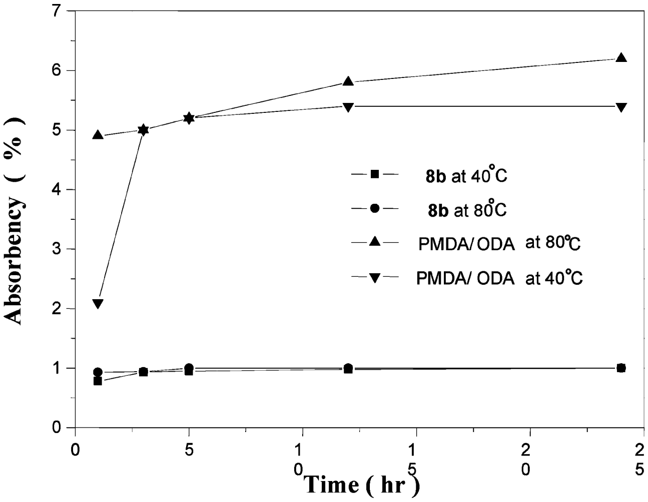


Figure 7. Water absorption of POSS−PI **8b** and PMDA/ODA at 40 and 80 °C, respectively.

reduces the dielectric constant.[17] The fluorinated semiaromatic polyimides **8c** and **8a** had similar dielectric constants. This indicates that the POSS unit is a effective, if not more effective, at decreasing the dielectric constant as fluorinated units. The values for POSS−PI **8a** and **8c** are similar to those for POSS-containing polyimides nanocomposites (2.32 ± 0.05) without significantly affecting the mechanical properties.[16] They are slightly lower than the optically estimated dielectric constants of typical alicyclic polyimide (2.47)[21] and a fluorinated semiaromatic polyimide (2.6)[38] and significantly lower than that of a typical semiaromatic polyimide (2.83).[36]

Conclusions

Table 5. Dielectric Constant of Polyimides

PI	10 kHz	100 kHz	1 MHz
8a	2.43	2.39	2.38
8b	2.69	2.65	2.63
8c	2.39	2.37	2.36
8d	2.59	2.57	2.55
8e	2.79	2.76	2.74
PMDA/ODA	3.46	3.44	3.39

The polymerization of double-decker-shaped silsesquioxane diamine **4** with aromatic tetracarboxylic dianhydrides in DMAc at room temperature afforded polyamic acids containing POSS in main chain with high molecular weights ($\eta_{inh} = 0.53$ dL/g). POSS−PI **8** had good thermal stability with the 5% weight loss temperature in air over 490 °C. The polyimide films have good mechanical properties with elongation at breakage of 2.9−6.0%, in which POSS−PI **8b** showed the highest elongation (6.0%). The water absorption of POSS−PI **8b** (<1%) was lower than that of the PMDA/ODA film. POSS−PIs **8** possessed excellent alkaline and acid resistance. POSS−PI **8b** kept its flexible mechanical properties after immersion in 5% NaOH solution at 40 °C for 72 h. POSS−PI **8a** and **8c** possessed low dielectric constants of 2.38 and 2.36, respectively.

Acknowledgment. The authors acknowledge Dr. Makoto Seino for helpful discussions, and Dr. Ziyi Ge, Dr. Qinghua Duan, and Dr. Jiro Hamaya of Tokyo Institute of Technology are thanked for many discussions on the synthesis. We are also grateful to Professor Yasuyuki Tezuka for use of the MALDI−TOF MS instrumentation.

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MA070547Z