Synthesis and Properties of Semiaromatic 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 externally covered 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. It has a nanometer-sized cage structure and can be functionalized with various organic groups. The incorporation of POSS into some polymers has offered the opportunity to develop high-performance materials that contain many desirable properties of conventional organic and inorganic components such as good thermal and mechanical properties, solubility, nonflammability, and excellent dielectric properties. Because the surface of the polymer is converted into an SiO2 layer further decomposition of the bulk polymer material is prevented when these polymers are exposed to active (atomic) oxygen. 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. The introduction of POSS into polyimides can improve these properties further. Recently, some POSS-containing polyimides have been reported by Leu et al. 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. In most reported cases, the POSS-based materials were prepared with POSS as a side chains or as an end group in hybrid polymers. There are few examples for the synthesis of main chain POSS in the literature. We previously reported the synthesis of a POSS, double-decker-shaped silsesquioxane (DDSQ). In this paper we reported the synthesis of double-decker-shaped silsesquioxane dianhydride (DDSQDA) via hydroisilylation 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 semi-aromatic polyimides containing POSS in main chain (POSS-PIs) from the DDSQ-diamine with various aromatic tetracarboxylic dianhydrides were synthesized and characterized.

Experimental Section
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): ν = 1860, 1782 (anhydride C=O), 1265 (Si – CH3), 1220 (Si – Ph), 1132, 1090 (Si – O – Si) cm−1. 1H NMR (300 MHz, CDCl3): 7.48 – 7.19 (40H, m), 3.25 – 3.20 (2H, 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. 13C NMR (75 MHz, CDCl3): 172.1, 171.6, 133.9, 131.1, 127.8, 52.3, 49.6, 41.7, 40.2, 26.3, 24.6, –1.9 ppm. 29Si NMR (60 MHz, CDCl3): –22.1, –77.9, –78.9 ppm. Anal. Calcld for C92H84O2N10Si2O16 (%): C, 59.84; H, 4.59; N, 2.81. Found: C, 59.86; H, 4.48; N, 2.81.

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): ν = 3406 (–NH2), 1770, 1707 (amide C=O), 1384 (C – N), 1265 (Si – CH3), 1236 (Si – Ph), 1133, 1051 (Si – O – Si) cm−1. 1H NMR (300 MHz, acetone-d6): 7.72 – 7.65 (8H, d, 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), 3.24 (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. 13C 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, 41.0, 40.3, 26.9, 25.4, –1.8 ppm. 29Si NMR (60 MHz): –21.8, –78.3, –78.9 ppm. Anal. Calcld for C92H84N10O2N10Si2O16 (%): C, 59.84; H, 4.59; N, 3.03. Found: C, 59.86; H, 4.48; N, 2.81.

Synthesis of POSS-PAAs. 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): v = 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.

Scheme 1.

**Results and Discussion**

**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 180 °C by one-step high temperature solution polymerization procedure 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 deactivation of the anhydride ring by the norbornene moiety.

**Table 1. Synthesis of Polyamic Acid (5)**

<table>
<thead>
<tr>
<th>Ref (^a)</th>
<th>Temp (°C)</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Inherent Viscosity (^b) (dL/g)</th>
<th>Weight % of (\Phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>DMAc</td>
<td>24</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>NMP</td>
<td>24</td>
<td>0.16</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>DMAc</td>
<td>24</td>
<td>0.16</td>
<td>Dicarboxylic</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>a-cored temperature</td>
<td>24</td>
<td>0.16</td>
<td>Dicarboxylic</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>a-cored temperature</td>
<td>30</td>
<td>0.20</td>
<td>Dicarboxylic</td>
</tr>
</tbody>
</table>

\(^a\)Polymerization was carried out with 0.5mmol of each monomer in the solvent under nitrogen. \(^b\)Measured at a concentration 0.5 g/ mL in each solvent at 30 °C.

**One-step high temperature solution polymerization procedure .**

**Figure 1.** \(^1\)H, \(^13\)C NMR spectra of POSS-PAA 7d in DMSO-\(d_6\) and 4 in acetone-\(d_6\).
Polymer Characterization. POSS – PAAs 7 containing POSS in the main chain have high molecular weights were synthesized by functional group conversion method. Figure 1 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 due to the proton of the methyl group signal, seven peaks (1 to 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 (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.

$^{29}$Si NMR spectra of monomer 3, monomer 4 and POSS-PAA 7d.

Thermal Properties of POSS – PIs 8. The thermal properties of the POSS – PIs were evaluated by DSC and TGA (Table 2). The $T_g$ values of POSS – PIs in nitrogen ranged from 255 °C to 267 °C. The $T_g$ is very typical compared to those of polyimides. $^{11}$ 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 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 ($T_{5\%}$) and 10% weight loss temperatures ($T_{10\%}$) in air are improved up to 514 °C and 551 °C (8e), respectively. The results indicate that the POSS moiety improves the thermal stability over current semiaromatic polyimides used in the microelectronics applications.

Table 2. Summary of the Properties of the POSS – PIs and PMDA/ODA

<table>
<thead>
<tr>
<th>PI</th>
<th>$T_g$ (°C)</th>
<th>$T_d$ (°C)</th>
<th>$T_{5%}$ (°C)</th>
<th>density (g/cm$^3$)</th>
<th>contact Angle (°)</th>
<th>solubility index/td (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a</td>
<td>264</td>
<td>504</td>
<td>541</td>
<td>1.41</td>
<td>84</td>
<td>0.25</td>
</tr>
<tr>
<td>8b</td>
<td>261</td>
<td>501</td>
<td>536</td>
<td>1.42</td>
<td>86</td>
<td>0.27</td>
</tr>
<tr>
<td>8c</td>
<td>255</td>
<td>495</td>
<td>521</td>
<td>1.43</td>
<td>79</td>
<td>0.53</td>
</tr>
<tr>
<td>8d</td>
<td>262</td>
<td>503</td>
<td>537</td>
<td>1.42</td>
<td>83</td>
<td>0.45</td>
</tr>
<tr>
<td>8e</td>
<td>257</td>
<td>514</td>
<td>551</td>
<td>1.44</td>
<td>84</td>
<td>0.38</td>
</tr>
<tr>
<td>8f</td>
<td>248</td>
<td>498</td>
<td>537</td>
<td>1.40</td>
<td>85</td>
<td>0.30</td>
</tr>
</tbody>
</table>

POMDA/ODA: 82, 470, 530, 1.44, 54, 2.04

*From DSC on the second heating at a heating rate of 30 °C/min in nitrogen.
*Temperature at which 5% weight loss was recorded by thermogravimetry at a heating rate of 10 °C/min in air. Temperatures at which 10% weight loss was recorded by thermogravimetry at a heating rate of 10 °C/min in air. Polyamic Acid (7) measured at a concentration 0.5 g/dL in each solvent at 30°C.

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 properties 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, and it was observed that 92 – 97% of the film mass was retained after 3 days. The film after acid treatment was too brittle 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.

Thermal Properties of POSS – PIs 8. The thermal properties of the POSS – PIs were evaluated by DSC and TGA (Table 2). The $T_g$ values of POSS – PIs in nitrogen ranged from 255 °C to 267 °C. The $T_g$ is very typical compared to those of polyimides. $^{11}$ 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 due to the $T_g$ of the polyimides. The POSS unit has no noticeable effect on $T_g$. However, while the $T_g$ is
what it cannot interact with. Second, the unique molecular “silicone-oxygen” frame (silsesquioxane combination) of POSS (SiO2) with the middle character of silicone (SiO) and silica (SiO2), 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. The combination of a hydrophobic polymer to minimize swelling and chemical stability of the POSS moiety imparts high resistance to acid and alkaline solutions.

### Table 4. Mechanical properties and Dielectric Constant of POSS—Pls 8a-e

<table>
<thead>
<tr>
<th>POSS -PI</th>
<th>tensile strength (MPa)</th>
<th>elongation (%)</th>
<th>initial modulus (GPa)</th>
<th>Dielectric Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a</td>
<td>42.1</td>
<td>2.9</td>
<td>2.32</td>
<td>2.38</td>
</tr>
<tr>
<td>8b</td>
<td>74.1</td>
<td>6.0</td>
<td>2.15</td>
<td>2.63</td>
</tr>
<tr>
<td>8ba</td>
<td>65.9</td>
<td>3.8</td>
<td>1.96</td>
<td>-</td>
</tr>
<tr>
<td>8c</td>
<td>58.9</td>
<td>5.9</td>
<td>1.82</td>
<td>2.36</td>
</tr>
<tr>
<td>8d</td>
<td>52.3</td>
<td>5.0</td>
<td>1.51</td>
<td>2.55</td>
</tr>
<tr>
<td>8e</td>
<td>65.8</td>
<td>5.4</td>
<td>2.18</td>
<td>2.74</td>
</tr>
</tbody>
</table>

*Immersed in the solution of 5% NaOH in water at 40 °C for 72 h.* Dielectric Constant measured at 1 MHz.

### Dielectric Constant of POSS—Pls 8. The POSS—Pls 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 reduces the dielectric constant. The fluorinated semiaromatic polyimide and 8a had similar dielectric constants. This indicates that the POSS unit is 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. They are slightly lower than the optically estimated dielectric constant of typical alicyclic polyimide (2.47) and a fluorinated semiaromatic polyimide (2.6) and significantly lower than that of a typical semiaromatic polyimide (2.83).

### Conclusions

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—Pls 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—Pl 8a and 8e possessed low dielectric constants of 2.38 and 2.36, respectively.

### References and Notes


