Synthesis and Characterization of Novel Fully Aliphatic Polyimidosiloxanes Based on Alicyclic or Adamantyl Diamines

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ABSTRACT: A series of fully aliphatic polyimidosiloxanes (APISiO) were prepared by poly(addition/condensation) reaction of bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride or cyclobutane-1,2,3,4-tetracarboxylic dianhydride and varying compositions of 1,3-bis(3-amino propyl)-tetra methyl disiloxane and rigid adamantyl diamines (1,3-diaminoadamantane or 3,3'-diamino-1,1'-diadamantane) or flexible alicyclic diamines (4,4'-methylene bis(cyclohexylamine) or 4,4'-methylene bis(2-methylcyclohexylamine)). High temperature one-step synthesis in m-cresol was employed to obtain APISiOs with intrinsic viscosity in the range of 0.28–0.59 dL/g. The final materials were characterized by $^1$H and $^{13}$C NMR, $^{29}$Si-MAS-NMR and IR spectroscopic analysis, thermogravimetric and differential scanning calorimetric analysis, and wide angle X-ray diffractometry. UV–visible spectra revealed the optical behavior of the polyimides. It was found that the APISiOs containing appropriate ratio of adamantyl moieties together with flexible aliphatic siloxane groups exhibit good thermal and mechanical stabilities, solubility, fair transparency, and low dielectric constant (2.4–2.7). © 2006 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 44: 5254–5270, 2006

Keywords: aliphatic polyimides; adamantane; low dielectric constant; mechanical properties; siloxanes

INTRODUCTION

Polyimides (PI) possess excellent thermal, mechanical, and electrical properties and thus have found immense applications in many technologies ranging from microelectronics to high temperature matrices and adhesives to gas separation membranes since 1970s.1–4 Fully aliphatic and alicyclic polyimides (API) are currently being considered for their applications in optoelectronics and interlayer dielectric materials, thanks to their higher transparencies and lower dielectric constants, when compared with aromatic polyimides, which result from their low molecular density and polarity and low probability of undergoing inter- or intramolecular charge transfer.5–7 Nevertheless, polyimides derived from aliphatic monomers are most suited for applications that have less-stringent thermal requirements.8 Previous studies revealed that adamantane (tricycle[3.3.3.1.1.3,7]decanec), a rigid alicyclic compound composed of three cyclohexane rings in chair conformations,9 is the most salutary alicyclic candidate for incorporation into aliphatic polyimides to enhance thermal stability without sacrificing their high transparency, solubility, and low dielectric constants.10,11 Adamantane can also reduce the coefficient of thermal expansion of poly-
imides because of its rigid-rod structure. Thus, adamantane-based aliphatic polyimides have gained much attention recently.

On the other hand, increasing importance of polyimides for gas-separation, microelectronics, and optoelectronics applications have paved the way for the introduction of silicon moieties into the backbone of PIs, promoting significant increase in permeability, perm-selectivity, and adhesive ability.13–16 Thus, more recently, silicon containing aromatic polymers have attracted much scientific and technological interest because of their superior permeability and adhesive ability between substrates and polyimides together with low dielectric constant.17–19 Polyimide-siloxanes (PISiO), the segmented copolymers containing siloxane segment along the intractable backbone chain of aromatic polyimides, maintain some of the excellent properties of PIs, e.g., high thermal stability and mechanical strength and some of the desirable properties of siloxanes, such as ductility and adhesion as well as low moisture permeability. Superior solubility even in organic solvents with low boiling point meliorate the processibility of fully imidized PISiOs by replacing a prolonged polymer curing step at elevated temperature with a baking procedure at a lower one, while maintaining the thermal and mechanical stability.20,21

In this work, we wish to discuss how adamantyl group and siloxane moieties influence the basic properties of aliphatic polyimides (APIs), by synthesizing various fully aliphatic polyimide-siloxanes (APISiO). Here, we adopt a one-step imidization approach to directly synthesize a series of APISiOs by the copolymerization of adamantyl or alicyclic diamine monomer, along with 1,3-bis (3-amino propyl)-tetra methyl disiloxane (APTMS) and dianhydride monomers. For that purpose, we synthesized the monomers 1,3-diaminoadamantane (DAA) and 3,3’-diamino-1,1’-diadamantane (DADA). The molar ratio of APTMS and aliphatic diamines is varied and this in turn produces APISiOs with tunable dielectric constant. Apart from the main stream of synthesis of physically cross-linked polyimide/silica hybrid materials, our investigation tells a different story of chemically embedding siloxanes into polyimide backbone. Moreover, to the best of our knowledge, we are the first to deal with fully aliphatic polyimidosiloxanes (API-SiO), especially, adamantane-based APISiOs. We have focused mainly on studying the solubility, crystallinity, thermal, dielectric, optical, and mechanical properties of all the synthesized APISiOs and the effects that the incorporation of adamantane units had on the basic characteristics of the flexible APISiO.

EXPERIMENTAL

Materials

The structures of the monomers used in this study are shown in Figure 1.
ene-2,3,5,6-tetracarboxylic dianhydride (BOCA) and cyclobutane-1,2,3,4-tetracarboxylic dianhydrides (CBDA) were recrystallized from acetic anhydride and dried at 150 °C under vacuum before use. The alicyclic diamine, 4,4’-methylene bis(cyclohexylamine) (MCA), was distilled under reduced pressure and stored in the dark prior to use. 4,4’-Methylene bis(2-methylcyclohexylamine) (MMCA) was recrystallized from hexane and dried at 50 °C. 1,3-Bis(3-amino propyl)-tetra methyl disiloxane (APTMS) obtained from Gel est–AZmax (Chiba, Japan) was used without purification. The solvent m-cresol was dried over CaCl₂, then over 4 Å Linde type molecular sieves, distilled under reduced pressure, and stored under nitrogen in the dark. All reagents and chemicals except APTMS were purchased from Aldrich Chemical Company.

Monomer Synthesis

1,3-Diaminoadamantane (DAA) and 3,3’-diamino-1,1’-diadamantane (DADA) were synthesized according to literature procedures starting from 1-bromoadamantane and purified through vacuum sublimation. Details of the synthesis of DAA and DADA are provided as the supplemental materials. Though DADA was stable to air, DAA was rapidly transformed to a colorless liquid and then reformed into a white solid, when exposed to air. Because of its instability and moisture sensitivity, the IR spectra of this compound did not agree with its proposed structure.

1,3-Diaminoadamantane: ¹H NMR (300 MHz, benzene-d₆): δ (ppm) = 1.23 (2H, s, H-2), 1.32 (10H, m, H-4, H-6, H-8, H-9, H-10), 1.44 (4H, NH₂), 1.95 (2H, m, H-5, H-7); ¹³C NMR (75.45 MHz, benzene-d₆): δ (ppm) = 31 (C-5, C-7), 35.4 (C-6), 45.3 (C-4, C-8, C-9, C-10), 49.22 (C-1, C-3), 54.7 (C-2).

3,3’-Diamino-1,1’-diadamantane: IR (KBr): v (cm⁻¹) = 3425 (NH₂), 3005, 2900, 1680, 1382–1270, 1206, 1110, 820, 760 cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆): δ (ppm) = 1.29 (4H, m, H-5, H-7), 1.33–1.45 (24H, m, H-2, H-4, H-6, H-8, H-9, H-10), 2.01 (4H, s, NH₂); ¹³C NMR (75.45 MHz, DMSO-d₆): δ (ppm) = 32 (C-5, C-7), 33.5 (C-8, C-9), 35.3 (C-6), 39.2 (C-1), 44.7 (C-2), 45.3 (C-4, C-10), 47.2 (C-3).

Preparation of APIs and APISiOs Through One-Step Polymerizations

The sample preparation is outlined in Scheme 1. First, the APTMS was added, with stirring, to a solution containing diamine in m-cresol under nitrogen atmosphere. Equimolar amount of the dianhydride was added slowly to this mixture preheated to 60 °C, initiating the reaction. The solution is then heated to 100 °C for 12 h followed by 150 °C for 4 h and 200 °C for 48 h for completion of the reaction. The resulting viscous yellow solution is cooled, diluted by adding m-cresol, and added drop wise to rapidly stirred methanol to precipitate the APISiOs. The precipitation procedure was carried out several times. The white powder thus obtained is then filtered, washed with methanol, and dried in vacuum oven at 60 °C. The molar ratio between APTMS and aliphatic diamine is varied to obtain APIs with different silicon content. For polymerizations involving DAA, the steps prior to the initial heating were performed in a nitrogen glove box because of the air sensitivity of the monomer.

Film Casting

A 5–7 wt % solution of polymer in chloroform was prepared and filtered to remove the nondissolved materials and dust particles and was poured into a Petri dish. The casting process took about 8 h at room temperature. The casting films were dried in an oven at 40 °C for 6 h without vacuum and for another 6 h with vacuum, and the resulting films samples were dried at 80 °C for 6 h and then at 100 °C for 10 h. To perform the dielectric constant and transparency measurements, the solutions of APIs after dissolving in CHCl₃ were spin-coated onto clean ITO glass and quartz plates, respectively, and then subjected to the...
heating cycle described earlier. The quartz plates were cleaned with diluted water and then with hot piranha solution (7:3 M ratio of conc. H$_2$SO$_4$ and 30% H$_2$O$_2$)\(^{24}\) and the ITO plates were washed using a detergent bath in an ultrasonicator for at least 30 min, then thoroughly rinsed with distilled water, dried, and stored in a nitrogen-filled glove box. Before coating the polyimide solution onto ITO, the coated sides of the electrode were subjected to plasma and immediately spin coated with the polymer.\(^{25}\) The series of polymers synthesized are listed in Table 1.

**Measurements**

Infrared spectra (KBr disks) were recorded on a Shimadzu IR Prestige-21 spm using a Ge-KBr beam splitter.\(^{1}\)H and \(^{13}\)C NMR spectra were recorded on a Varian Unity Plus-300 (300 MHz) NMR spectrometer, and chemical shifts are reported in ppm units with tetramethylsilane as internal standard. Molecular structure of the solid materials was confirmed from Bruker DSX400 spectrometer at room temperature with a 4 mm zirconia rotor spinning at 6 kHz (Resonance frequency of 79.5 MHz; 90° pulse width of 5 µs, contact time 2 ms, recycle delay 50 s). Inherent viscosities were measured with a Cannon Fenske viscometer in NMP or H$_2$SO$_4$ solution (0.5 g/dL, 25 °C). Average molecular weight ($M_n$) and PDI of the soluble APIs were estimated by Gel permeation chromatograph (GPC) using a Waters 515 Differential Refractometer with two Styrogel HR 5E columns in DMF (0.1 mg/L) solvent at 42 °C, calibrated with polystyrene standards. The solubility test was performed using equal amounts of polymer in matched quantities of commonly used solvents. Thermogravimetric analysis (TGA) was performed under nitrogen on TGA Q50 Q Series thermal analyzer. The sample was heated using a 10 °C/min heating rate from 50 to 600 °C. Differential scanning calorimetry (DSC) was conducted under nitrogen with TA instruments Q 100 differential scanning calorimeter. The sample was heated at 20 °C/min from 50 to 500 °C. Tensile properties were determined from stress–strain curves obtained with a universal testing machine (KSU 05, Kyungsang Instrument) with a load cell of 10 kgf at room temperature. A gauge of 2 cm and a strain rate of 0.5 cm/min were used for this study. The transparencies of the polyimide films were measured from ultraviolet–visible spectra recorded from one accumulation on a SHIMADZU UV-1650 PC spectrometer optimized with a spectral width of 200–800 nm, a resolution of 0.5 nm, and a scanning rate of 200 nm/min; the thickness of each film was ~1 µm. Wide-angle X-ray diffraction (WAXD) measurements of the pulverized samples were conducted at room temperature in the reflection mode using a Rigaku diffractometer (Model Rigaku Miniflex). The Cu K$_\alpha$ radiation ($\lambda = 1.54$ Å) source was operated at 50 kV and 40 mA. The 2θ scan data were collected at 0.01° intervals over the range 1.5–70° and at a scan speed of 0.5° (2θ)/min. The dielectric constant was obtained at 1 MHz using an impedance-gain phase analyzer (HP4194A) and the formula $K = C d / A \varepsilon_\infty$, where $C$ is the observed capacitance, $d$ is the film thickness, $A$ is the area, and $\varepsilon_\infty$ is the free permittivity. The thickness of each film was 1.0 ± 0.05 µm. Plasma treatment of the ITO plates were done using Plasma cleaner; Harrick Plasma PDC-32A. Water absorption experiments were performed for dried film samples

<table>
<thead>
<tr>
<th>Table 1. Preparation of APIs and API-SiOs</th>
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<tr>
<td>Polymer$^a$</td>
</tr>
<tr>
<td>APTMS:MCA:BOCA</td>
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<tr>
<td>APTMS:MMCA:BOCA</td>
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<tr>
<td>APTMS:DDA:BOCA</td>
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<td>APTMS:DADA:BOCA</td>
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<td>APTMS:MCA:CBCA</td>
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<td>APTMS:MMCA:CBCA</td>
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<tr>
<td>APTMS:DAA:CBCA</td>
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<tr>
<td>APTMS:DADA:CBCA</td>
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</table>

$^a$ Values indicate monomer ratio.
with masses ranging from 150 to 200 mg. The dried samples were immersed in water at 25 °C and water absorption equilibrium was attained after 13 days. The weight gains were measured as the percentage of water absorption.

RESULTS

Synthesis of APISiOs

One-pot polyimide syntheses performed at a high temperature without isolating any polyamic acid is employed for the synthesis of fully APISiO. Generally, the reactions of dianhydrides with highly basic diamines, such as aliphatic and alicyclic diamines, result in the formation of carboxylic acid salts together with polyamic acids. This salt formation prevents the formation of high molecular-weight polyamic acids. So, One-pot polyimide seemed to be a useful method for preparing high-molecular-weight polyimides because the amines used for the salt formation can be regenerated during thermal cyclization.26 Therefore, we prepared our APISiOs of interest by the following steps: 100 °C for 12 h, 150 °C for 4 h, and 200 °C for 48 h, in m-cresol under nitrogen atmosphere without isolating any polyamic acids. These polymerizations proceeded in the homogeneous state to produce APISiOs quantitatively. Copolyimides of aliphatic diamines and APTMS with various ratios 1:0, 9:1, 7:3, 1:1, 3:7, 0:1 respectively, were synthesized with the purpose of having the most appropriate ratio of Si content and alicyclic moieties. Adamantane groups were incorporated to enhance the thermal stability of the resulting APISiOs. Table 2 summarizes the results of these polymerizations.

![Table 2. Properties of Fully Aliphatic Polyimidosiloxanes](image-url)

- NA, no transition was observed in the range 40–500 °C.
- a Polymers cannot be dissolved in DMF.

The polymer viscosities ranged from 0.28 to 0.59 dL/g, implying that they have an appreciable molecular weight. According to GPC data, $M_n$ and PDI of the polymers ranged from 5200 to 47,000, and 1.12 to 2.9 respectively. Unfortunately, the values of very rigid backboned API cannot be obtained because of their low solubility. The lower $M_w/M_n$ values comparative to those of...
conventional PIs may be due to the some-what low reactivity of monomers containing the rigid and bulky groups.\textsuperscript{27}

**Structural Analysis**

Previous study on PISiO\textsuperscript{28} reports that APTMS does not react with dianhydride, i.e., pyromellitic dianhydride, and is eliminated during the precipitation step. So, we have given special emphasis on the structural analysis of the synthesized API-SiOs, confirming the addition of APTMS into our fully aliphatic polyimide backbone. For the structural confirmation at molecular level, we have used IR, \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, and \textsuperscript{29}Si-MAS NMR spectroscopy. All the analysis techniques were found to be in good agreement with our expectations as described as follows.

Structural characteristics of the polymers obtained by IR analysis contains the earmark absorption bands of imide group around 1780, 1720, 1380, and 730 cm\textsuperscript{-1} for all samples. Among them, the peaks at 1720 cm\textsuperscript{-1} of C=O asymmetric stretching, representing an imide group and at 1780 cm\textsuperscript{-1} of C=O symmetric stretching, indicating a cyclic five-member ring, confirmed imide formation. The bands at 1380 and 730 cm\textsuperscript{-1} are attributed to the C–N–C bond and the imide ring deformation, respectively. C–H stretching (2800–2900 cm\textsuperscript{-1}), CH\textsubscript{2} bending (1465 cm\textsuperscript{-1}), and CH\textsubscript{3} bending (1375 cm\textsuperscript{-1}) arising from the alicyclic moieties of the polymer were clearly seen in all API-SiOs. The major difference between the pure APIs and silicon containing API-SiOs is the bands of Si domain stretching between 1000 and 1180 cm\textsuperscript{-1} together with around 850 cm\textsuperscript{-1} (Si–O–Si asymmetric stretching), around 1400 cm\textsuperscript{-1} (Si–CH\textsubscript{3}), and at 787 cm\textsuperscript{-1} (Si–C). The intensities of these bands gradually increases as the amount of APTMS residue increased in the polyimide backbone, while the intensity of the absorption bands corresponding to that of aliphatic moieties decreased as shown in Figure 2.

In addition, as Figures 3 and 4 indicates, NMR spectra confirmed the polyimidosiloxanes. In the \textsuperscript{1}H NMR study of the model compounds, PISiO1, API2, API-Si\textsubscript{2}\textsubscript{5}, API1, API-Si\textsubscript{1}\textsubscript{5} (Fig. 3), protons of APTMS residue appear at 0.41 ppm (Si–CH\textsubscript{3}), 1.65–1.5 ppm (CH\textsubscript{2}), and at 3.48 ppm (N–CH\textsubscript{2}) and that of BOCD at 6.06 ppm (C=C) and 2.56–2.63 ppm (Bicyclic dianhydride ring) together with all the desired peaks of the diamine group. The appearance of C=C peak (around 6 and 176 ppm in \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra respectively) rules out the possibility of the double bond of the dianhydride to rapture and react at elevated temperatures of polymerization. The bicyclic proton signals were broadened through the interaction with the nearby C=C groups. The copolymers showed the characteristic peaks of both the diamine residue and APTMS, confirming that the siloxane diamine is successfully added to the polyimide backbone. The stoichiometry of the reactants was controlled by \textsuperscript{1}H NMR by comparing a specific proton signal for APTMS group and alicyclic diamine residue. For MCA, the peak at 1.6 ppm, MMCA that at 1.06 ppm, DAA the proton at 1.32 ppm, and for DADA the peak at 1.4 ppm were chosen as the standards for comparison with the siloxane peak at 0.41 ppm to give relative composition of APTMS and alicyclic units. The varying composition of the API-SiO backbone was clarified by the \textsuperscript{1}H NMR integration method and the results are tabulated in Table 3.

\textsuperscript{13}C NMR spectra also endorse the successful formation of expected polymers. Figure 4 showing the carbon peaks of PISiO\textsubscript{2}, API-Si\textsubscript{7}\textsubscript{5}, API-Si\textsubscript{8}\textsubscript{3} proves the peaks of adamantane or bia-damantane moieties assembled with that of CBDA and APTMS. The splitting of carbon peak of C=O around 176 ppm occurs in copolymides, proving the presence of different moieties in the two sides of the imide ring.
\[ ^{29}\text{Si-MAS NMR spectra of polyimidosiloxanes, PISiO1, APISi2, APISi2_{(5)}, APISi2_{(7)}, are presented on Figure 5.}\]

The \[ ^{29}\text{Si-MAS NMR spectroscopy showed the signals of the internal silicon atoms of the polymer backbone around +7.6 ppm corresponding to Si (CH}_3_{2} – O – Si (CH}_3_{2}.\] The signal located around +7.6 ppm is attributed to the silicon atom close to the methylene group.\[ ^{29}\text{Si-MAS NMR spectrum of PISiO1 exhibits a narrow single peak at +7.6 ppm. The narrow peak results from a single ordered environment around Si. The spectrum of copolymers (e.g.: APISi2_{(5)} as shown in Fig. 5) exhibits two broad peaks around +17.5 and +7.6 ppm. Multiple peaks are the result of disordered atmosphere around Si atom.}\]

\text{Figure 3.} \[ ^{1}\text{H NMR (CDCl}_3\text{) spectra of PISiO1, API2, APISi2_{(5)}, AP11, APISi1_{(5)}.}\]
increasing alicyclic diamine components, which suggests increasing disorder accompanying addition of cyclohexane or adamantane moieties. The peak near 17.5 ppm is due to the enhanced segmental motions. This result indicates that the chain mobility of PISiO1 and PISiO2 are restricted and the incorporation of the alicyclic moieties enhances the mobility of the siloxane group of the polymer.

**Thermal Stability and Phase Transitions**

We used DSC and TGA to evaluate the thermal behavior of the polyimides. The polymers under-
went their 5% weight losses within the temperature range from 325 to 455 °C. The temperatures for 10% gravimetric loss ($T_{10}$), which is an important criterion for evaluating thermal stability, were in the range 353–476 °C. Figure 6 displays representative TGA curves; Table 2 summarizes the results.

Taking the rigidity factor into account it was assumed that the APIs based on adamantyl units will show the highest thermal stability. Despite the rigid backbones, the thermal stability of homopolyimides derived from the diamines DAA and DADA were lower than that with MCA and MMCA diamines. This unexpected behavior may be due to the low degree of intermolecular interactions because of the steric hindrance provided by the bulky adamantyl groups. Thermal stability was further improved when silica was introduced. The APISiO containing 50% silica (APISiO(5)) had the maximum $T_{d}$ in the range 460–470 °C. The increase in the thermal stability may be resulted from high thermal stability of silica and the pseudocrosslinking nature of silicon particles.32 On the other hand, too much amount of APTMS affected contrarily, since it increases the amount of thermally fragile aliphatic chains.

**Table 3.** Experimental and Theoretical Silicon Content Obtained on the Various APISiOs

<table>
<thead>
<tr>
<th>Polymer</th>
<th>APISi1(7)</th>
<th>APISi1(5)</th>
<th>APISi1(3)</th>
<th>APISi4(7)</th>
<th>APISi4(5)</th>
<th>APISi4(3)</th>
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<tr>
<td>W.R. (E)</td>
<td>21.1</td>
<td>6.1</td>
<td>10.8</td>
<td>15</td>
<td>6.1</td>
<td>10.6</td>
</tr>
<tr>
<td>W.R. (T)</td>
<td>21.7</td>
<td>6.6</td>
<td>11</td>
<td>15.5</td>
<td>6.6</td>
<td>11</td>
</tr>
<tr>
<td>Percentage of Si</td>
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<td></td>
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<td></td>
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<tr>
<td>NMR$^a$</td>
<td>100</td>
<td>27</td>
<td>45</td>
<td>65</td>
<td>26.5</td>
<td>47</td>
</tr>
<tr>
<td>TGA$^b$</td>
<td>97</td>
<td>27.7</td>
<td>49</td>
<td>68</td>
<td>27.7</td>
<td>48</td>
</tr>
</tbody>
</table>

$^a$ W.R. (E) is weight percentage of final residue obtained from thermogravimetric curves. $^b$ W.R. (T) is theoretical silica content (wt %).

$^a$ Obtained from NMR integration method.

$^b$ Obtained from char yield calculations of TGA curves.

**Figure 5.** $^{29}$Si-MAS NMR spectra of APISiOs.

**Figure 6.** TGA curves of representative fully API-SiO.

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Adamantane-based polyimidosiloxanes (APISi3(5), APISi4(5), APISi7(5), APISi8(5)) showed enhanced thermal stability, which can be attributed to the precise balance of rigidity and interchain interactions. Among them, the biadamantyl-based API-SiOs (APISi4, APISi8) have higher thermal resistance than those with mono adamantane units (APISi3, APISi7), mainly because of the dilution effect of aliphatic imide moieties. In addition, APISiOs containing consecutive adamantyl units have linear structure when compared with those containing an adamantyl unit. These results suggest that the synthesized fully APISiO have such high thermal stability, though not as high as those derived from aromatic monomers, as being suitable for electronic materials. Moreover, the TGA curves indicate that water or solvent has been successfully removed from the final polymers because there is no severe weight loss below 100 °C. This may be due to the presence of hydrophobic methyl group (Si—CH₃), which facilitates the escape of water during the heat treatment in the polyimide synthesis and should have imparted hydrophobic properties to the material.

The thermogravimetric curves were also used for estimating the proportion of siloxane units in the polymer chain. The char yield at 600 °C was estimated from the curves. The increase in final weight residue suggests the successful incorporation of higher amount of silica into polymer backbone. The varying ratios of APTMS and alicyclic diamine residues in the synthesized APISiOs were confirmed by comparing the experimental and theoretical char yield. Theoretical values are calculated on the assumption that every Si atom can be converted into silicon oxide. Table 4 presents the experimental and theoretical values of silicon oxide obtained in the various polyimidosiloxanes materials. The NMR integration results and final residue calculations confirm that the proportion of APTMS in APISiOs was found to coincide with each other within the experimental errors.

\[ T_g \] was recorded according to the DSC thermograms of the second heating, since the influence

<table>
<thead>
<tr>
<th>Solvents</th>
<th>NMP</th>
<th>DMAc</th>
<th>DMF</th>
<th>THF</th>
<th>DMSO</th>
<th>m-Cresol</th>
<th>CHCl₃</th>
<th>H₂SO₄</th>
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<td>API1</td>
<td>+</td>
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<td>+</td>
<td>+</td>
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* Solubility: (++) soluble at room temperature; (+) soluble upon heating; (±) partially soluble or swells; (−) insoluble.

Table 4. Solubility of Synthesized PI-PIsOs

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of residual water or solvent and the history of thermal annealing were occasionally observed in the initial DSC heating run. The glass transition temperatures of the polyimides were in the range 197–270 °C (Table 2), with the exception that we could not detect \( T_g \) values for the most rigid homo-APIs, i.e., those derived from DAA and DADA. The \( T_g \) values of the APISiOs based on adamantyl diamines shifted to higher temperatures. The \( T_g \) of polyimides can be explained mainly in terms of chain rigidity without considering specific intermolecular interactions. Thus, in the present study the bulky adamantane groups inhibited chain mobility and generated extra chain rigidity. The enhanced values of \( T_g \) of the polymers possessing MMCA backbones, relative to those possessing MCA units, suggest that the glass transition temperatures of these types of polymers increase gradually upon increasing the chain rigidity induced by the methyl substitution. Figure 7 presents typical DSC thermograms. In general, the increased chain rigidity due to the pendant cardo groups restricted the free rotation about the polymer backbone to yield polyimidosiloxanes with high glass transition temperatures. As the amount of silicon increased in the polyimide backbone, glass transition temperature showed an increasing trend followed by a decrement when the APTMS amount further increased. According to the previous report, even when a small amount of silicon is introduced into polyimide matrix scales down the \( T_g \) notably due to the plasticizing effect of low molecular weight silica. In the present study, the incorporation of APTMS should have limited the chain motion, leading to the enhancement of \( T_g \). But, as the amount of siloxane rose again, the plasticizing effect should have imparted better influence as evidenced by the diminish in \( T_g \).

**Mechanical Properties**

Figure 8 shows the effect of silica content on the tensile strength and the elongation at break of the APISiOs obtained from the stress–strain curves. The tensile strength ranged from 99 to 121 MPa and elongation at break varied between 10 and 22%. Though the homo polyimide films (API3, API4, API7, and API8) were too brittle to be analyzed, DAA- and DADA-based APISiOs showed higher tensile strength, which can be attributed to the rigidity of the adamantane species. At the same time, they showed the minimum elongation at break. The higher elongations of MCA- and MMCA-based polymers likely to be resulted from the more flexible nature of the backbone because of the presence of flexible cyclohexane units. Comparison between BOCA- and CBDA-based APISiOs also supported the assumption that the chain rigidity enhanced tensile strength, while the flexibility endorsed elongation at break. A special trend was not noted on tensile strength on increasing the amount of Si, except that the tensile strength shows a maximum for the 1:1 ratio of APTMS and alicyclic diamines. For polyimide/silica hybrid networks, the strength and toughness of the hybrid is dependent on the density of the physical crosslinking between polyimide molecules and silica networks. In an appropriate range of the crosslink density, the crosslinks could exhibit the strengthening and toughening effects. In general, decrease in mechanical stiffness is seen with an increase in particle concentration for a particle-filled system because of the loss of homogeneity of the hybrids and a decrease of both stress and energy at break is observed. Unlike hybrids, in our present study, APTMS is directly bonded to the polyimide backbone chemically and so in this context, the balance of chain rigidity, flexibility, and interchain interactions should have played important roles effectively to maximize the ten-

![Figure 7. DSC thermograms of fully APISiO demonstrating the increment in \( T_g \) as a result of adamantane group incorporation.](image-url)
sile strength because chemical bonds between the organic and inorganic phases allows the polyimide and siloxane phases to interact at the molecular level.\(^{37}\) As the amount of APTMS units increased, the tensile strength was decreased, maybe due to the less tough linear aliphatic unit enhancement in the chain. On the other hand, the elongation at break went on increasing as the number of the flexible units increased. Unfortunately, the case of 100% APTMS cannot be evaluated presently because we were not able to make good films of PISiO1 and PISiO2.

**Solubility and WAXD Studies**

We performed WAXD experiments in an attempt to evaluate the crystallinities of our synthesized polyimidosiloxanes; Figure 9 displays representative WAXD results. The APIs based on MCA and MMCA showed peaks at \(2\theta > 9^\circ\) and at \(9^\circ < 2\theta < 40^\circ\). The peaks in the low-angle region results from the polymer chain ordered along the chain axis, whereas the broad peak is due to the diffraction of a poor intermolecular packing combined with amorphous halo.\(^{38}\) The peak around 16.4° (\(d\)-spacing 5.4 Å) for API1, API2, API5, and API6 is sharp and strong, suggesting a more ordered internal structure. As the siloxane unit was incorporated, the peaks at \(2\theta > 9^\circ\) disappeared and the amorphous halo was evident at \(9^\circ < 2\theta < 40^\circ\). The intermolecular distance, which was estimated from the maxima of the broad peak at \(9^\circ < 2\theta < 20^\circ\), increased slightly and while the peaks broadened as a result of lattice strain as the amount of APTMS raised. But, as the amount of Si units increased, slight sharpening of the amorphous halo and appearance of peak at 5.2° (\(d\)-spacing 16.4 Å) was observed, pointing the regain of ordered internal arrangement in APISiO chains, as shown in Figure 9.
For APISiOs with DAA and DADA units, only a broad amorphous halo over the range 10–20° (2θ) was seen, indicative of the existence of a very poorly developed crystal structure. Incorporation of adamantyl moieties resulted in a lowering of the peak intensity and broadening of the peaks at 2θ < 20°. The decreased scattering intensity suggests a disruption of the internal order; the broadening of peaks arises from the lattice strain that result from the presence of the bulky and rigid pendent adamantane groups. We observed a lower crystallinity for the copolyimides containing DAA and DADA residues, presumably because of the low degree of dipolar interchain interactions between the bulky moieties; this result is consistent with their higher solubility. PISiO1 and PISiO2 showed six distinct diffraction peaks at 2θ = 7.8, 11.7, 14.52, 16.65, 18.61 and 27° corresponding to d-spacing of 11.3, 7.5, 6.07, 5.3, 4.8, and 3.3 Å respectively. The splitting of the broad peak at 2θ < 20° points high intermolecular regularity and chain packing arising from the highly flexible nature of APTMS.

We determined the solubility of the PISiO in various kinds of organic solvents using powdery samples; Table 4 lists the results. The homopolyimides obtained from DAA and DADA were soluble only in m-cresol and sulfuric acid because of the rigidity of their backbones. Copolymerization of both rigid and flexible diamines produced API-SiOs that had improved solubility relative to those of the corresponding single-diamine APIs and PISiOs. Enhanced solubility in polyimides is generally governed by the presence of flexible backbones, bulky noncoplanar groups, and kink linkages; all of these factors reduce the degree of polymer chain interaction and their rigidity. In our case, the improved solubility of the API-SiOs with adamantane backbone, when compared with MCA- and MMCA-based polymers, clearly arose from the presence of a flexible aliphatic backbone together with the bulky noncoplanar adamantyl moieties, which create steric hindrance and curtail both interchain interactions and chain packing. The solubility was increased by the addition of APTMS till 50% while further increases caused a decline because of the increased interchain interactions.

**Trends in Dielectric Constant of the Synthesized API-SiOs**

We observed appreciably low dielectric constants (ε) for all the API-SiOs. The influence of Si content as well as that of adamantane units upon ε of API-SiOs based on BOCA is demonstrated in Figure 10. Dielectric constant values measured at several different positions of each API-SiO film were averaged to rule out their thickness dependence. Such low dielectric constants are due to the fact that polymers are fully aliphatic, subsequently having low hydrophobicity and polarity. Inefficient chain packing, which induces free volume, is the reason for the lower values of ε of the API. As the amount of APTMS increased in polymer chain, the dielectric constant decreased first. This can be explained in terms of an overall enhancement of small scale molecular mobility by the incorporation of silica domains in the polyimidosiloxanes backbone, arising from loosened molecular packing of API-SiO chains when compared with API chains. But as the amount of siloxane units increased, no further decrease in ε value was seen owing to the improved degree of close chain packing. API-SiOs based on DAA and DADA showed lower ε values than that based on MCA and MMCA, which can be ascribed to the loosening of chain packing originating from steric hindrance to dense molecular packing of polymer input by the bulky diamond-like adamantyl pendent as is well known from earlier reported studies that lowering chain packing density is...
the most common way to reduce $\varepsilon$. Unexpect-
edly, we found that the values of $\varepsilon$ of the APISiOs containing biadamantyl groups were higher than those containing adamantyl groups, regardless of the increased dilution of the polar imide groups that is caused by the bulkier biadamantyl moieties. Similar trend was, however, observed also in earlier research based on adamantyl and diadamantyl moieties. Thus, we can explain this finding on the basis of the linear structures of the biadamantane-containing APIs relative to those of the noncoplanar adamantane-containing APIs; i.e., the former species have smaller molar volumes. The two adamantane units linked in the 1,1’ position arranges them to be in a least hindered manner. On the other hand, the mono adamantane aligns in a nonlinear fashion to become more stable. In general, an increased free volume correlates with a decreased dielectric constant for these polymers of our interest. Typical water uptake data of the samples showed that water absorption decreases (2.4–1.1%) as the amount of APTMS increases, which agrees with our observation that as the amount of siloxane group increases, the $\varepsilon$ value decreases (see supplemental materials). Adamantane and biadamantane moieties showed only a negligibly narrow difference in water uptake, which points that the differences in $\varepsilon$ value especially the higher $\varepsilon$ values of diadamantyl groups can be attributed mainly to its linear arrangement rather than its water uptake nature.

**Transparency Measurements**

Fully aliphatic polyimides exhibit high transparency because of their low molecular density, polarity, and probabilities of mediating inter- and intramolecular charge transfer. We expected that these combined factors would result in all of our
synthesized APIs having transparencies above 80%, especially those based on DAA and DADA \sim 95\%. This enhanced transparency as a result of the incorporation of the adamantyl groups is designated to the loosening of the intermolecular packing that results from the low polarizability and bulkiness of these pendent groups. Unfortunately, Si content adversely affected the transparency of the polymers because of the interchain crosslinking nature of siloxane in the APISiO backbones. It is noteworthy, however, that the transparency of APISiO3(5), APISiO4(5), APISiO7(5), APISiO8(5), is still above 90\% because of the presence of bulky adamantyl moieties. This trend is demonstrated in Figure 11, which presents the UV–vis spectra of \sim 1\,\mu m-thick polyimide films based on API5, API7, APISi5(5), and APISiO7(5).

**DISCUSSION**

Among the wide studies on polyimide/silica hybrid materials, a different method of chemically implanting siloxanes into polyimide backbones can be considered. Unlike the widely used sol–gel process of physically interlocking polyimide and siloxanes with the chances of preferential hydrolysis, microheterogeneity, cracking, and delamination, we have applied one-step poly (condensation/addition) reaction for synthesizing fully APISiO. Recently, the syntheses of wholly APIs from N-silylated alicyclic diamines and by in situ silylation method have been reported. But, due to the complexity of the methods reported previously, we chose the simple one-step synthesis and were able to obtain APISiOs with reasonable molecular weights and effective chemical bonding in expected ratios of APTMS and alicyclic diamine. Structural confirmation done using NMR and IR spectral analysis perfectly evidences our assessment. To the best of our knowledge, this is the first successful approach of its kind, since fully APISiO is a totally untouched research area. Moreover, the incorporation of adamantyl moieties has ameliorated the uniqueness of our study. This study of fully APISiO also reveals a number of interesting facts. The synthesized APISiOs with \langle M_\text{n} \rangle \sim 5200 to 47,000 possess \langle T_g \rangle as high as 270 °C, 10\% weight decomposition ranging from 353 to 476 °C, ε values 2.47–2.68, and tensile strength 99–121 MPa along with excellent solubility in common solvents. Si and adamantane moieties attributed shoulder to shoulder for the lower dielectric constants of adamantyl-based APISiOs among which APISiO3(5) credits the lowest value 2.47 emerging as a strong competent among technologically significant materials. Notably high \langle T_g \rangle values of APISiO3(7), APISiO3(5), and APISiO7(5), together with their transparency above 90\% anticipate them to be promising candidates for transparent, thermally stable substrates in microelectronics and photoelectronics having ease of processibility owing to their better solubility. If one compares with the previously reported fluorinated APIs, our PISiO do have a comparable thermal stability, dielectric constant, and transparency up to specific amount of siloxane together with mechanical stability, often where fluorinated polyimides fail. Previous studies prove that though fluoropolymers exhibit some outstanding characteristics, such as low water absorption, low dielectric constants, water and oil repellency, chemical and thermal stability, and fire retardancy, the decrease in adhesiveness is frequently troublesome, and the deterioration of mechanical strength (elastic modulus) occurs in some cases, whereas silicon polymers are well known for their good adhesiveness and in the present case the good solubility and mechanical stiffness adds credit to our fully APISiO. Moreover, fluorinated hybridsiloxane incorporation in polyimides was found to decrease the thermo-oxidative stabil-
ity. Thus, our study resolves that fully APISiO obtained from the reaction of BOCA with 1,3-diaminoadamantane and APTMS (APISiO$_3$(7) and APISiO$_3$(5)) excelled other APISiOs in their traits presumably due to a balance among stiffness, polarity, free volume, flexibility, and silicon content of their backbone units. Nevertheless, our present study suggests that fully APISiO, especially based on adamantane/biadamantane units and APTMS residues in the ratio 1:1, possess high transparency (~90%), high values of $T_g$, enhanced solubility, and low dielectric constants, together with marginal thermal stability and mechanical stiffness; these properties suggest that they may find an immense range of applications in flexible polymer light emitting diode substrates, soft-printed circuit boards, interlevel dielectric insulators, high-speed passivation or dielectric films, and alignment films.

CONCLUSIONS

We synthesized a series of fully APISiO based on BOCA/CBDA and varying ratios of aliphatic/adamantyl diamines and APTMS through polyaddition/polycondensation reactions. These APISiOs possessed inherent viscosities of 0.28–0.59 dL/g. Spectroscopic studies proves the effective addition of APTMS into the polyimide backbones in the desired ratios. The organic-soluble APISiOs that we prepared exhibited low dielectric constants and appropriate thermal and mechanical stability. Our study reveals that copolymides containing a suitable ratio of adamantyl moieties together with flexible aliphatic siloxanes groups display improved thermal and mechanical stabilities, solubility, fair transparency, and lower dielectric constant. Thus, the APISiOs have potential for applications within micro- and optoelectronic devices.

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REFERENCES AND NOTES