Synthesis of Fluorine-Containing Wholly Alicyclic Polyimides by \textit{In Situ} Silylation Method

Yoshiyuki Oishi\textsuperscript{a}, Shu Onodera, Jan Oravec, Kunio Mori, Shinji Ando\textsuperscript{1}, Yoshiharu Terui\textsuperscript{1}, and Kazuhiko Maeda\textsuperscript{2}

\textsuperscript{a}Department of Chemical Engineering, Iwate University, Morioka 020-8551, Japan
\textsuperscript{1}Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8552, Japan
\textsuperscript{2}Central Glass Co., Ltd., Chiyoda-ku, Tokyo 101-0054, Japan

Keywords: alicyclic polyimide, fluorinated polyimide, fluorinated alicyclic diamine, \textit{in situ} silylation method, optical transparency, low dielectric constant

1. Introduction

Polyimides (PIs) have been widely used as the electronic materials, because of their outstanding characteristics such as high thermal stability, high mechanical strength, and excellent electrical properties. Recently, PIs with high optical transparency and low dielectric property have been required in their optoelectronic and microelectronic applications, as photoresists and interlayer insulators. The dielectric constant ($\varepsilon$) of the material is expressed using the well-known Clausius-Mossotti equation:

$$
\varepsilon = \frac{[1+2 \frac{(Pm)}{Vm}] + [1 - \frac{(Pm)}{Vm}]}{}
$$

where $Pm$ is the molar polarization and $Vm$ is the molar volume. From this relationship of $\varepsilon$, $Pm$, and $Vm$, the general methods for reducing the dielectric constant of the PIs are to introduce low molar polarization atoms such as fluorine or bulky structures such as cardo or alicyclic moiety into the PI backbone. Therefore, fluorinated PIs, cardo PIs, and alicyclic PIs have been synthesized to obtain low dielectric materials. Fluorinated aromatic PIs were obtained from fluorinated aromatic diamines and/or fluorinated aromatic tetracarboxylic dianhydrides.\textsuperscript{[1]} Cardo aromatic PIs were obtained from fluorene-containing aromatic diamines and/or fluorene-containing aromatic tetracarboxylic dianhydrides.\textsuperscript{[2]} Wholly alicyclic PIs derived from alicyclic diamines and alicyclic tetracarboxylic dianhydrides exhibited the better transparency and the lower dielectric constant with little sacrifice in their thermal properties.\textsuperscript{[3-8]}

Generally, the synthesis of wholly alicyclic PIs with high molecular weights by the conventional two step method starting from alicyclic diamines and tetracarboxylic dianhydrides is sometimes difficult due to the salt formation of pendant carboxyl group of the poly(amic acid)s with high basic amino group of the alicyclic diamines.

We demonstrated that wholly alicyclic PIs could be synthesized satisfactorily from $N,N'$-bis(trimethylsilyl)-substituted alicyclic diamines and tetracarboxylic dianhydride by the silylation method.\textsuperscript{[8]} The polyaddition of $N$-silylated diamines to tetracarboxylic dianhydride produced poly(amic acid silyl ester)s having high molecular weights without the formation of any salts during polymerization. In spite of the advantage of the silylation method, the main drawback of the use of $N$-silylated alicyclic diamine as PI-forming monomer is a relatively complicated handling because of their tendency to be hydrolyzed. Recently, we have developed the \textit{in situ} silylation method for the synthesis of wholly alicyclic polyimides by the use of amide-type silylation agent.\textsuperscript{[7]}

Since we have taken much interest in the incorporation of fluorine atom into the wholly alicyclic PI\textsuperscript{[9]}, this paper deals with the synthesis and properties of fluorine-containing wholly alicyclic PIs from novel fluorinated alicyclic diamines and alicyclic dianhydride.

2. Experimental

2.1. Materials

4,4'-Hexafluoroisopropylidenebis(cyclohexylamine) (6FBCA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobicyclohexyl (6FDAC) were supplied from Central Glass Co. Ltd. They were prepared by the catalytic hydrogenation of corresponding fluorinated aromatic diamines,
4,4′-(hexafluoroisopropylidene)dianiline and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl. 1,2,3,4-Cyclobutanetetracarboxylic dianhydride (CBDA) was supplied from Nissan Chemical Industries, Ltd. and used without further purification. N,N′-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) was used as received. N-Methyl-2-pyrrolidone (NMP) was dried over calcium hydride and purified by distillation.

2.2. Synthesis of polyimide

6FBCA (5.0 mmol) was dissolved in NMP (10 mL) in a flame-dried flask (100 mL) under nitrogen. The solution was cooled to 0°C with an ice bath. BSTFA (5.0 mmol) was added to this solution with stirring. The solution was stirred at 0°C for 15 min and at room temperature for 30 min. Then, CBDA (5.0 mmol) was added to the solution at 0°C in one portion. The mixture was stirred at 0°C for 1 h and at room temperature for 6 h under nitrogen. The clear and viscous poly(amic acid silyl ester) (PASE) solution was obtained. The inherent viscosity of the polymer was 0.64 dL/g, measured at a concentration of 0.5 g/dL in NMP at 30°C.

The PASE solution was cast on a poly(ethylene terephthalate) film. The PI film was obtained by drying PASE solution at room temperature for 1 h at a pressure of 10 Torr and for 12 h under vacuum, and then by heating at 60°C for 6 h, 100°C for 6 h, 200°C for 1 h, and 250°C for 1 h, and 300°C for 1 h under vacuum. The IR spectrum of the film showed absorptions at 1773, 1702 cm⁻¹ (C=O), and 1366 cm⁻¹ (C-N), due to imide group.

2.3. Measurements

Infrared (IR) spectra were recorded on a Jasco FT-IR 7300 spectrophotometer. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed with a Seiko TG/DTA 320 and DSC 220, respectively. Dynamic mechanical analysis (DMA) were performed with a Seiko DMS 210. UV-visible spectra were recorded on a Jasco V-570 spectrophotometer. Reflective index was measured by a Metricon model PC-2000 prism coupler at a wavelength of 1320 nm.

3. Results and discussion

3.1. Synthesis of polyimides

Fluorine-containing wholly alicyclic PIs were prepared in two step: the ring-opening polyaddition of in situ N-silylated fluorinated alicyclic diamines to alicyclic tetracarboxylic dianhydride, producing PASEs, which in turn undergo subsequent thermal imidization [Eq. (1)].

\[
\begin{align*}
\text{OSi(CH}_3)_3 \\
\text{CF}_3 \text{C}=\text{NSi(CH}_3)_3
\end{align*}
\]

The polyaddition of CBDA and N-silylated fluorine-containing alicyclic diamines, which were prepared in situ by the reaction with the silylation agent (BSTFA). The polymerization at room temperature for 6 h smoothly proceeded in homogeneous solutions without any salt formation, giving the clear and viscous PASE solutions. Table 1 summarized the results of the synthesis of PASEs. The inherent viscosities of the PASEs were in the range from 0.61 to 1.00 dL/g, indicating enough molecular weights to form cast films.

| Table 1. Synthesis of PASEs and PIs |

<table>
<thead>
<tr>
<th>diamine</th>
<th>( \eta_{inh} ) (dL/g)</th>
<th>PI film</th>
</tr>
</thead>
<tbody>
<tr>
<td>6FBCA</td>
<td>0.64</td>
<td>self-standing</td>
</tr>
<tr>
<td>6FDAC</td>
<td>1.00</td>
<td>self-standing</td>
</tr>
<tr>
<td>6FBCA/6FDAC (50/50)</td>
<td>0.61</td>
<td>self-standing</td>
</tr>
</tbody>
</table>

The PASEs were subjected to thermal imidization at 300°C for 1 h to be converted to fluorinated wholly alicyclic PI films in the elimination of trimethyl silanol (Figure 1). The PI films were colorless, transparent, and self-
standing. From the IR spectrum of PI (6FBCA-CBDA) film, characteristic imide absorptions of 1773, 1702, and 1366 cm⁻¹ were observed, and the absorptions at 3309 and 1648 cm⁻¹ due to the amide group completely disappeared.

Figure 1. IR spectra of PASE (6FBCA-CBDA) heated at 100°C, 200°C, and 300°C.

3.2. Properties of polyimides

PI films derived from 6FBCA or 6FDAC were not soluble in organic solvents, but the copolyimide film from 6FBCA/6FDAC (50/50) were slightly soluble in N,N-dimethylacetamide (DMAc), NMP, and 1,3-dimethyl-2-imidazolidione (DMI).

The thermal properties of PI films were shown in Table 2. The glass transition temperatures (T_g) of PI films were in the range of 306-335°C. The PI derived from 6FDAC had higher T_g than that of PI from 6FBCA due to more rigidity of bicyclohexyl structure.

The thermal decompositon temperatures (T10) of PI films in air and nitrogen were in the range of 395-400°C and 430-440°C, respectively.

Table 2. Thermal properties of PI films

<table>
<thead>
<tr>
<th>diamine</th>
<th>T_g a)</th>
<th>T10 b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°C)</td>
<td>in air</td>
</tr>
<tr>
<td>6FBCA</td>
<td>326</td>
<td>400</td>
</tr>
<tr>
<td>6FDAC</td>
<td>335 c)</td>
<td>395</td>
</tr>
<tr>
<td>6FBCA/6FDAC (50/50)</td>
<td>306 c)</td>
<td>400</td>
</tr>
</tbody>
</table>

a) Determined by DSC on the second heating at a heating rate of 20°C/min in nitrogen. b) Temperature at which 10% weight loss recorded by TG at a heating rate of 10°C/min. c) Determined by DMA at a heating rate of 2°C/min in nitrogen.

Figure 2 shows UV-visible spectrum of PI film derived from 6FBCA. PI films exhibited the cutoff wavelength (λ_cutoff) of 230-240 nm. These values are close to those of non-fluorinated wholly alicyclic PIs.[3-8] The transmittance of wholly fluorinated PI films were more than 80% above 270 nm. This indicates the fluorinated groups enhance the transparency of PI films (Table 3).

Table 3. Optical transparency of PI films

<table>
<thead>
<tr>
<th>diamine</th>
<th>thickness λ_cutoff a) (nm)</th>
<th>λ_80 b) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6FBCA</td>
<td>8.7</td>
<td>230</td>
</tr>
<tr>
<td>6FDAC</td>
<td>5.7</td>
<td>270</td>
</tr>
<tr>
<td>6FBCA/6FDAC (50/50)</td>
<td>17.3</td>
<td>240</td>
</tr>
</tbody>
</table>

a) Cutoff wavelength b) Transmittance of 80%

The refractive indices of PI films at 1320 nm were determined by a prism coupler. Table 4 shows the in-plane (n_π), out-of-plane (n_DM), and average (n_AV) refractive indices, and birefringences (Δn) of PI films. The birefringences of PI films were obtained as 0.0016-0.0128. These relatively small values reveal that the polymers have low polarizability anisotropy and the polymer chains are randomly oriented in the film. The average refractive indices of the PI films were determined as 1.471-1.478, which are lower than those of non-fluorinated wholly alicyclic PIs (1.498-1.522).[6-8]

The dielectric constant (ε) of the material at optical frequencies can be estimated roughly from the refractive index (n) according to Maxwell's equation: ε ≈ n². The dielectric constant around 1 MHz have been evaluated to be ε = 1.10n², including an additional
contribution of approximately 10% from the infrared absorption. The $n_{AV}$ of 1.471-1.478 of fluorinated alicyclic PI films can be translated into dielectric constants of 2.38-2.40. These values are lower than those of non-fluorinated wholly alicyclic PIs (2.47-2.55).

Table 4. Optical properties of PI films

<table>
<thead>
<tr>
<th>Diamine</th>
<th>$n_{TE}^{a)}$</th>
<th>$n_{TM}^{b)}$</th>
<th>$n_{AV}^{c)}$</th>
<th>$\Delta n^{d)}$</th>
<th>$\varepsilon^{e)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6FBCA</td>
<td>1.4784</td>
<td>1.4768</td>
<td>1.4779</td>
<td>0.0016</td>
<td>2.40</td>
</tr>
<tr>
<td>6FDAC</td>
<td>1.4800</td>
<td>1.4672</td>
<td>1.4757</td>
<td>0.0128</td>
<td>2.40</td>
</tr>
<tr>
<td>6FBCA</td>
<td>1.4724</td>
<td>1.4692</td>
<td>1.4713</td>
<td>0.0032</td>
<td>2.38</td>
</tr>
<tr>
<td>/6FDAC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) In-plane refractive indices. b) Out-of-plane refractive indices. c) Average refractive index; $n_{AV} = (2n_{TE} + n_{TM})/3$. d) Birefringence; $\Delta n = n_{TE} - n_{TM}$. e) Optically estimated dielectric constant; $\varepsilon = 1.10n_{AV}^2$ (at 1 MHz).

4. Conclusion

The polyaddition of CBDA and N-silylated fluorinated alicyclic diamines prepared by the in situ silylation with $N,O$-bis(trimethylsilyl)trifluoroacetamide afforded poly(amic acid silyl ester)s with high molecular weights. The poly(amic acid silyl ester)s were converted to the films of fluorinated wholly alicyclic polyimides with the elimination of trimethylsilanol by the thermal imidization. The fluorinated polyimides were colorless and transparent, and had high glass transition temperatures above 300°C and good thermal stability with the 10% weight loss temperatures around 400°C in air. The polyimide films exhibited lower refractive indices of 1.47-1.48 and the estimated dielectric constants of 2.38-2.40. Thus, the fluorinated wholly alicyclic polyimides are considered to be one of the promising polymeric materials with excellent transparency and low dielectric constants in the opto- and microelectric application.

References