# Synthesis and Properties of Fluorine-Containing Polyimides Derived from Fluorinated Alicyclic Diamine

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## 1. Introduction

Recently, polyimides with a low dielectric property have been required in their optoelectronic and microelectronic applications. The general methods for reducing dielectric constants of polyimides are to introduce low molar polarization atoms such as fluorine or bulky structures such as alicyclic moiety into the polyimide backbones. Therefore, fluorinated polyimides [1] and alicyclic polyimides [2-4] have been synthesized to obtain low dielectric materials. We have taken much interest in the synthesis of fluorine-containing alicyclic polyimides. However, the polyimides derived from fluorinated alicyclic monomers have not yet reported to date.

This paper deals with the synthesis and properties of fluorine-containing alicyclic polyimides derived from novel fluorinated alicyclic diamine, 4,4'-hexafluoroisopropylidenebis(cyclo-hexylamine) (6FBCA).

## 2. Experimental

### 2.1. Materials

6FBCA was supplied from Central Glass Co., Ltd.. 6FBCA was prepared by the catalytic hydrogenation of 4,4'-(hexafluoroisopropylidene)-dianiline and purified by distillation: mp 40-42°C, bp 115°C (0.2 Torr). 4,4'-Methylenebis(cyclo-hexylamine) (MBCA) and 4,4'-methylenebis(2-methylcyclohexylamine) (MBMCA) were purified by distillation before use. 1,2,3,4-Cyclobutane-tetracarboxylic dianhydride (CBDA), supplied from Nissan Chemical Industries, Ltd., was heated in acetic anhydride at 100°C for 1 h and dried at 100°C under vacuum. 4,4'-(Hexafluoroisopropylidene)-diphthalic anhydride (6FDA), supplied by Central Glass Co. Ltd., was purified by sublimation. *N,O*-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) was used without further purification. *N,N*-Dimethyl-acetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), and 1,3-dimethyl-2-imidazolidone (DMI) were dried over calcium hydride and purified by distillation.

### 2.2. Synthesis of polyimide

BSTFA (5.0 mmol) was added to a solution of the diamine (5.0 mmol) and the solvent (10 mL) at 0°C with stirring. The solution was stirred at 0-5°C for 30 min. Then, the tetracarboxylic dianhydride (5.0 mmol) was added to the solution at 0°C in one portion. The mixture was stirred at 0-5°C for 1 h and 40°C for 3 h under nitrogen. The clear and viscous poly(amic acid silyl ester) (PASE) solution was obtained. The solution was cast on a glass plate or poly(ethylene terephthalate) film. The polyimide film was obtained by heating PASE at 100°C for 2 h, 200°C for 1 h, 250°C for 1 h, and then 300°C for 1 h under vacuum.

## 3. Results and discussion

### 3.1. Synthesis of polyimides

We have reported that alicyclic polyimides could be prepared satisfactorily by the *N*-silylated diamine method.[3,4] We applied this method to the synthesis of fluorinated alicyclic polyimides (PIs) [Eq. (1)].

Polyaddition of dianhydrides and *N*-silylated 6FBCA prepared *in situ* by the reaction with the silylation agent (BSTFA) proceeded in homogeneous system and afforded clear and viscous PASE solutions. Table 1 summarizes the results of the synthesis of PASEs. The inherent viscosities of

PASEs were in the range of 0.35-1.42 dL/g. PASEs were subjected to thermal imidization at 300°C for 1 h to be converted to PIs in the elimination of trimethylsilanol.

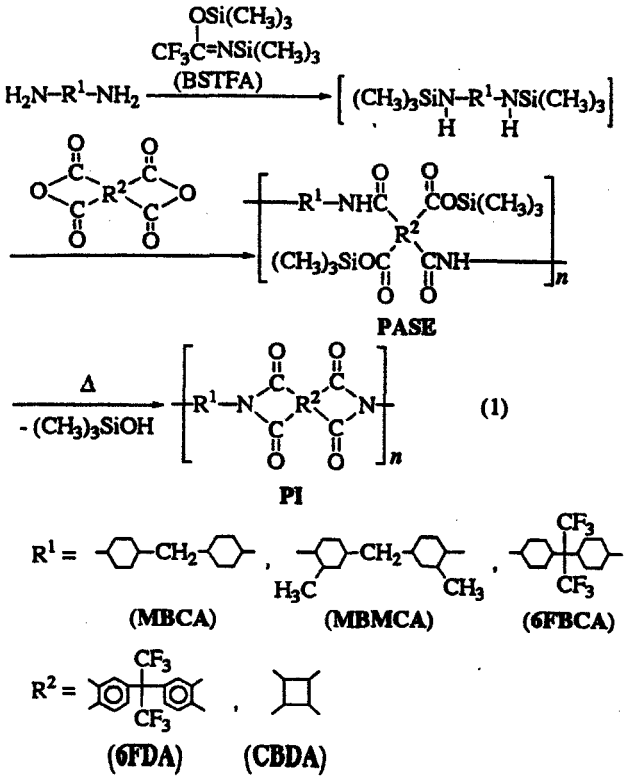


Table 1. Synthesis of PASEs[a] and PIs[b]

| | PASE | |
|---|---|---|
| diamine-dianhydride | $\eta_{inh}$[c] (dL/g) | PI film |
| MBCA-6FDA | 0.82(NMP) | self-standing |
| MBCA-CBDA | 0.35(NMP) | self-standing |
| MBMCA-6FDA | 1.42(DMI) | self-standing |
| MBMCA-CBDA | 0.84(DMI) | self-standing |
| 6FBCA-6FDA | 0.54(DMAc) | self-standing |
| 6FBCA-CBDA | 0.52(DMAc) | self-standing |

a) Polyaddition was carried out with 5.0 mmol of each monomer and 5.0 mmol of BSTFA in 10 mL of the solvent at 40°C for 3 h.
b) PI films were prepared by heating PASEs at 200°C for 1 h, 250°C for 1 h, and 300°C for 1 h under vacuum.
c) Measured at a concentration of 0.5 g/dL at 30°C.

3.2. Properties of polyimides

PIs dissolved in aprotic polar solvents such as DMI, NMP, and DMAc. The PI derived from 6FBCA and 6FDA had better solubility and were also soluble in tetrahydrofuran and chloroform.

The thermal properties of PIs were shown in Table 2. The glass transition temperatures ($T_g$) of 6FBCA-based PIs derived from 6FDA and CBDA were 271 and 283°C, respectively. The thermal decomposition temperatures ($T_5$) of PIs in air and nitrogen were in the range of 390-395°C and 435-450°C, respectively.

Table 2. Thermal properties of PI films

| | $T_g$[a] | $T_5$[b] (°C) | | $T_{10}$[c] (°C) | |
|---|---|---|---|---|---|
| polyimide | (°C) | in air | in $N_2$ | in air | in $N_2$ |
| MBCA-6FDA | 278 | 380 | 460 | 410 | 465 |
| MBCA-CBDA | 293 | 360 | 400 | 395 | 425 |
| MBMCA-6FDA | 265 | 370 | 445 | 395 | 460 |
| MBMCA-CBDA | 280 | 365 | 405 | 400 | 420 |
| 6FBCA-6FDA | 271 | 390 | 450 | 420 | 460 |
| 6FBCA-CBDA | 283 | 395 | 435 | 415 | 440 |

a) Determined by DSC on the second heating at a heating rate of 20°C/min in nitrogen.
b) Temperature at which 5% weight loss recorded by TG at a heating rate of 10°C/min.
c) Temperature at which 10% weight loss recorded by TG at a heating rate of 10°C/min.

Figure 1 shows UV-visible spectra of 6FBCA-based PI films. The spectrum of PI derived from 6FBCA and CBDA exhibits the cutoff wavelength of 230 nm, which was shorter than that of PI derived from 6FDA. The wholly PIs had complete colorlessness and good optical transparency (Table 3).

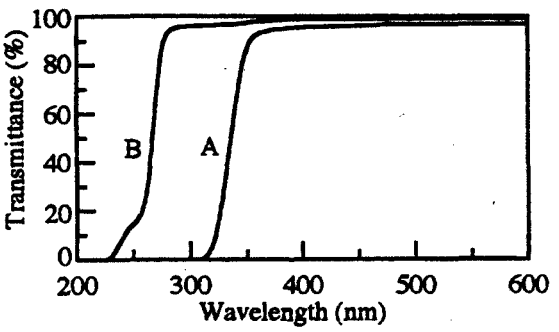


**Figure 1.** UV-visible spectra of PI films:
A, PI (6FBCA-6FDA, 13.8 μm);
B, PI (6FBCA-CBDA, 8.2 μm)

Table 3. Cutoff wavelengths of PI films

| polyimide | $d$ (μm) | $\lambda_{cutoff}$ (nm) |
|---|---|---|
| PI(MBCA-6FDA) | 14.2 | 310 |
| PI(MBCA-CBDA) | 12.6 | 230 |
| PI(MBMCA-6FDA) | 4.0 | 292 |
| PI(MBMCA-CBDA) | 13.4 | 240 |
| PI(6FBCA-6FDA) | 13.8 | 306 |
| PI(6FBCA-CBDA) | 8.2 | 230 |

The in-plane and out-of-plane refractive indices of PI films at 632.8 nm were measured by a prism coupler and listed in Table 4. The small birefringences ($\Delta n$) of 6FBCA-based PIs were

obtained as 0.0007-0.0024. The average refractive indices ($n_{AV}$) of the 6FBCA-based PI films derived from 6FDA and CBDA were determined as 1.5001 and 1.4830, respectively. The dielectric constants ($\varepsilon$) around 1 MHz for PIs have been evaluated from refractive indices.[2] The $n_{AV}$ of 1.5001 and 1.4830 can be translated into the dielectric constants of 2.48 and 2.42, respectively. These values are lower than those of non-fluorinated alicyclic polyimides.[2-4]

**Table 4.** Optical properties of PI films

| polyimide | $n_{TE}$[a] | $n_{TM}$[b] | $n_{AV}$[c] | $\Delta n$[d] | $\varepsilon$[e] |
|---|---|---|---|---|---|
| **MBCA-6FDA** | 1.5278 | 1.5245 | 1.5267 | 0.0033 | 2.56 |
| **MBCA-CBDA** | 1.5407 | 1.5345 | 1.5386 | 0.0062 | 2.60 |
| **MBMCA-6FDA** | 1.5182 | 1.5167 | 1.5177 | 0.0015 | 2.53 |
| **MBMCA-CBDA** | 1.5207 | 1.5181 | 1.5198 | 0.0026 | 2.54 |
| **6FBCA-6FDA** | 1.5003 | 1.4996 | 1.5001 | 0.0007 | 2.48 |
| **6FBCA-CBDA** | 1.4838 | 1.4814 | 1.4830 | 0.0024 | 2.42 |

a) In-plane refractive indices at 632.8 nm.
b) Out-of-plane refractive indices at 632.8 nm.
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

Fluorine-containing alicyclic polyimides were successfully prepared from fluorine-containing alicyclic diamine and tetracarboxylic dianhydrides by *in situ* silylation method. The 6FBCA-based polyimides are colorless and transparent and have high glass transition temperatures of 271-283°C. These films have lower refractive indices of 1.48-1.50 and estimated dielectric constants of 2.42-2.48, compared with non-fluorinated alicyclic polyimides.

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