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Synthesis of Alicyclic Polyimides from Fluorinated Alicyclic Diamine

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1. Introduction

Recently, polyimides (PIs) with a low dielectric property have been required in their optoelectronic and microelectronic applications. The general methods for reducing dielectric constants of PIs are to introduce low molar polarization atoms such as fluorine or bulky structures such as alicyclic moiety into the PI backbones. Therefore fluorinated PIs [1] and alicyclic PIs [2-4] have been synthesized to obtain low dielectric materials. However the synthesis of alicyclic PIs derived from fluorinated alicyclic monomers have not reported to date. This prompted us to investigate the synthesis of fluorine-containing alicyclic PIs. This paper deals with the synthesis and properties of fluorine-containing alicyclic PIs derived from novel fluorine-containing alicyclic diamine, 4,4'-hexafluoroisopropylidenebis(cyclohexylamine) (6FBCA).

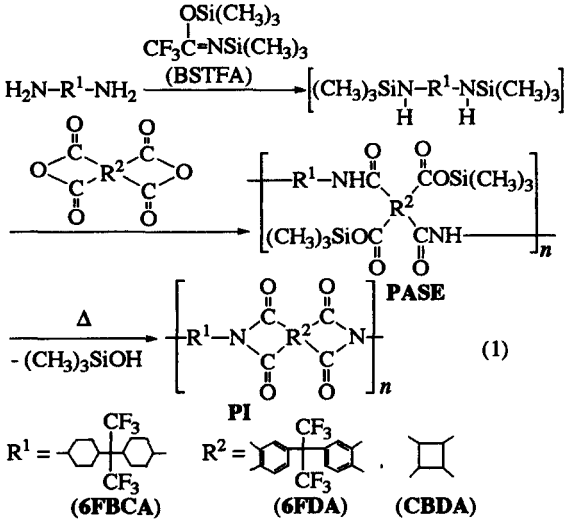
2. Experimental

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). 1,2,3,4-Cyclobutane -tetracarboxylic dianhydride (CBDA) was supplied from Nissan Chemical Industries, Ltd.. CBDA was heated in acetic anhydride at 100°C for 1 h and dried at 100°C under vacuum. 4,4' -(Hexafluoro-isopropylidene)diphthalic anhydride (6FDA) was supplied by Central Glass Co. Ltd.. 6FDA was purified by sublimation. *N,O* -Bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) was used without further purification.

2.2. Synthesis of polyimide

BSTFA (5.0 mmol) was added to a solution of 6FBCA (5.0 mmol) and *N,N*-dimethylacetamide (DMAc) (10 mL) at 0°C with stirring. The solution was stirred at 0-5°C for 30 min. Then, 6FDA or CBDA (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 300°C for 1 h under vacuum.



(1)

3. Results and discussion

3.1. Synthesis of polyimides

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

Polyaddition of dianhydrides and *N*-silylated 6FBCA prepared *in situ* by the reaction with the silylation agent (BSTFA) proceeded in

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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 around 0.5 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	
dianhydride	η_{inh}[c] (dL/g)	**PI** film
6FDA	0.50	self-standing
CBDA	0.52	self-standing

a) Polyaddition was carried out with 5.0 mmol of each monomer and 5.0 mmol of BSTFA in 10 mL of DMAc at 40°C for 3 h. b) **PI** film was prepared by heating **PASE** 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 in DMAc at 30°C.

3.2. Properties of polyimides

PIs dissolved in aprotic polar solvents such as 1,3-dimethyl-2-imidazolidone, *N*-methyl-2-pyrrolidone, and DMAc. The PI derived from 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 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)	
dianhydride	(°C)	in air	in N_2	in air	in N_2
6FDA	271	390	450	420	460
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 PI films. The spectrum of PI derived from CBDA exhibits the cutoff wavelength of 230 nm, which was shorter than that of PI derived from 6FDA. The PIs had colorlessness and good optical transparency.

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 3. The small birefringences (Δn) of PIs were obtained as 0.0007-0.0024. The average refractive indices (n_{AV}) of the PI films derived from 6FDA and CBDA were determined as 1.5001 and 1.4830, respectively. The dielectric constants (ε) 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]

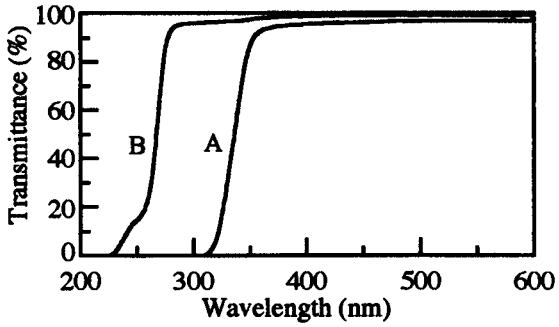

Figure 1. UV-visible spectra of **PI** films:
A, **PI** (6FBCA-6FDA, 13.8 μm);
B, **PI** (6FBCA-CBDA, 8.2 μm)

Table 3. Optical properties of **PI** films

dianhydride	n_{TE}[a]	n_{TM}[b]	n_{AV}[c]	Δn[d]	ε[e]
6FDA	1.5003	1.4996	1.5001	0.0007	2.48
CBDA	1.4838	1.4814	1.4830	0.0024	2.42

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; $\varepsilon = 1.10 n_{AV}^2$ (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 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 dielectric constants of 2.42-2.48, compared with non-fluorinated alicyclic polyimides.

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