

Studies on Synthesis and Properties of Polyimides : IV. 6FDA-Polyimides

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폴리이미드의 제조와 성질에 관한 연구 : IV. 6FDA계 폴리이미드

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Abstract: Using 2,2-Bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, 2,2-bis-[4-(4-aminophenoxy)phenyl]hexafluoropropane and 4,4-diaminodiphenyl ether, the homopolyamic acids, copolyamic acids and blend of homopolyamic acids were prepared and converted to polyimide(PI)s by thermal imidization. In results, it has been found that a exchange reaction of polyamic acids can be occurred during thermal imidization. With measurement of mechanical properties, it was suggested that PI/PI molecular composite can be obtained by copolymerization or physical blending of homopolyamic acids.

요 약 : 2,2-Bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride(6FDA), 2,2-bis-[4-(4-aminophenoxy)phenyl]hexafluoropropane 및 4,4-diaminodiphenyl ether 등을 이용하여 단독폴리아미드산, 공폴리아미드산 및 폴리아미드산의 블렌드를 만들고, 열이미드화로 각각의 폴리이미드를 제조하여 구조와 성질을 조사하였다. 그 결과로 열이미드화 동안에 폴리아미드산 간의 교환반응이 일어난다는 것을 알았다. 그리고 공중합이나 폴리아미드산의 블렌드 방법으로 폴리이미드의 분자복합체를 얻을 수 있었다.

1. Introduction

Polyimide(PI) is one of the thermally and chemically stable polymers and widely used in aerospace and electrical/electronic applications[1, 2]. However, the high softening temperature and insoluble nature in most organic solvents make processing of PI difficult[2, 3].

To improve their solubility and consequent processing characteristics of PI, much effort has been placed on the synthesis of PI with flexibilizing groups such as sulfone, ether, oxyethylene and

bulky group like CF_3 on the polymer backbone[4, 5]. Especially, PI with bulky CF_3 groups has high transparency, low dielectric constant, high gas permeability and water resistance as merits[5, 6]. In addition, it has been announced that a exchange reaction is possible in the mixture of polyamic acid (PAA)s[7, 8].

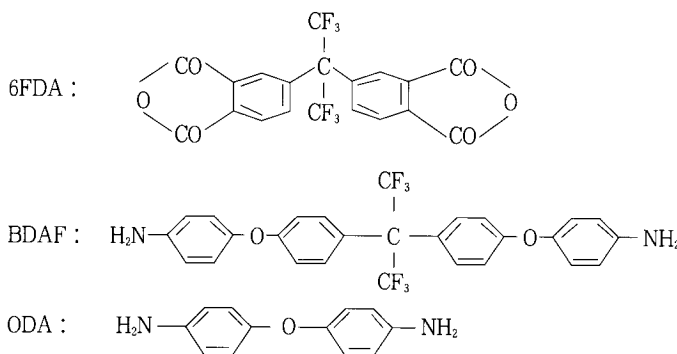
The concept of molecular composite(MC) was first established by T. Helminiak[9], and there has been increasing interest in the preparation of PI/PIMC[10]. Recently it has been reported that the high-strength and high-modulus MC film was pre-

Table 1. Structure and Used Quantity of Monomers

Reagent	Homopolyamic acid (HPAA)		Copolyamic acid (CPAA)		
	HPAA-B	HPAA-O	Random CPAA (RCPAA)	Block CPAA (BCPAA)	
				HPAA-EF	HPAA-EO
6FDA	0.964	0.964	1.93	0.964	0.916
BDAF	0.964		0.964	0.964	
ODA		0.964	0.964		0.964

Unit : Moles $\times 10^{-4}$

* 15wt% in NMP



pared via the physical blending of a rigid PI and a flexible PI[11].

In the present study, the fluorine-containing PAAs were synthesized from 2,2-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 2,2-bis-[4-(4-aminophenoxy)phenyl]hexafluoropropane or 4,4-diaminodiphenyl ether in N-methyl-2-pyrrolidone by polycondensation. To study the effects of structure on properties, the copolyamic acids and homopolyamic acids as well as its blend were prepared. The films of PAAs were converted to PI films by thermal imidization. The structure, solubility, thermal and mechanical properties of the obtained films had been examined with FT-IR, ^{19}F -NMR, DSC, TGA and Universal Testing Machine. In addition, the exchange reaction of polyamic acids and possibilities of copolyimides and blend of homopolyamic acids for PI/PI MC were also considered.

2. Experimental

2.1. Materials

2,2-Bis-(3,4-dicarboxyphenyl)hexafluoropro-

pene dianhydride(6FDA, Hoechst Chem., Germany), 2,2-bis-[4-(4-aminophenoxy)phenyl]hexafluoropropane(BDAF, Central Glass Co., Japan) and 4,4-diaminodiphenyl ether(ODA, Fluka Chemical Co., Switzerland) were purified by sublimation under reduced pressure just before use. N-methyl-2-pyrrolidone(NMP, Aldrich, USA) was purified by vacuum distillation over calcium hydride.

2.2. Preparation of Polyamic Acid(PAA)

For the preparation of PAAs, 6FDA was reacted with BDAF and/or ODA, and solid content was fixed at 15wt%. The structure and used quantity of monomers are shown in Table 1.

2.2.1. Homopolyamic Acid(HPAA)

HPAA of 6FDA-BDAF(HPAA-B) was synthesized by polycondensation; To a solution of 0.500g (0.0964mmol) of BDAF in 5.2ml of NMP, 0.428g (0.0964mmol) of 6FDA was added in one portion. The mixture was stirred at room temperature for 24h under nitrogen atmosphere. The HPAA solution thus obtained was cast onto a glass plate and was dried in air for 8h, and then solvent was re-

moved throughly at 80°C in vacuum. The dried film was stripped from the glass plate by soaking in water. HPAA of 6FDA-ODA(HPAA-O) was also prepared by the procedures described above.

2. 2. 2. Copolyamic Acid(CPAA)

The random CPAA of 6FDA-(BDAF-r-ODA) (RCPAA) and block CPAA of 6FDA-(BDAF-b-ODA)(BCPAA) having 50/50mole% of BDAF and ODA were also synthesized to examine the structure effects on properties. For the preparation of RCPAA, 0.857g (0.193mmol) of 6FDA was added in one portion to a solution of which 0.500g (0.0964mmol) of BDAF and 0.193g(0.0964mmol) of ODA were dissolved in 11.1ml of NMP, and the mixture was reacted for 24h. In addition, BCPAA was synthesized by the following two steps; To a solution of 0.475g(0.0916mmol) of BDAF in 5.2ml of NMP, 0.428g(0.0964mmol) of excess 6FDA was added in one portion at room temperature under nitrogen atmosphere and HPAA with dianhydride end group (HPAA-EF) was obtained by precipitation in methanol after stirring for 12h. To prepare HPAA having diamine end group(HPAA-EO), 0.407g(0.0916mmol) of 6FDA was added in one portion to solution of 0.193g(0.0964mmol) of excess ODA in 5.2ml of NMP. After stirring for 12h, HPAA-EF powder was added to a solution of HPAA-EO and the mixture was stirred for another 24h under nitrogen to obtain BCPAA.

2. 2. 3. Blend of HPAA(BPAA)

BPAA of 50/50mole% ratio was prepared by co-dissolving HPAA-B(0.928g) and HPAA-O (0.622g) in 8.6ml of NMP with stirring for 24h under nitrogen atmosphere.

2. 3. Preparation of Polyimide(PI)

PI films of HPI-B, HPI-O, RCPI, BCPI and BPI were prepared by thermal imidization of HPAA-B, HPAA-O, RCPAA, BCPAA and BPAA films, respectively. The thermal imidization was performed by stepwise heating[3] at 100°C for 1h, 200°C for

1h and 300°C for 1h under air. During heating, the PAA film was fixed with two metal rings to prevent contraction and creasing of the film.

2. 4. Polymer Analysis and Properties Measurement

For structure analyses of the polymers, FT-IR spectrometer(Biorad Digilab, FTS-60) and ¹⁹F-NMR(Bruker 80 spectrometer) were used. The intrinsic viscosity of PAA was measured in NMP at 25°C by using a Ubbelohde viscometer. Solubility was estimated for about 0.3g of PAA or PI in 5ml of solvent at room temperature for 24h. Glass transition temperature was determined by DSC(Dupont 2100) at the second scan. The sample was heated to 350°C at first, cooled and reheated with 20°C/min. The decomposition temperature was measured with TGA (Dupont 2100). Mechanical properties were determined using Instron(Simadzu) with 10mm/min of crosshead speed at 22°C and 45% relative humidity. The measurement was performed with film specimen(20mm gauge length, 10mm width and 0.10~0.13mm thickness) and the result was reported as the average value for three samples.

3. Results and Discussion

3. 1. Structure of Polymers

To examine structure of polymers, FT-IR spectra of HPAA-B and HPI-B were obtained as shown in Fig. 1.

For HPAA-B shown with a dotted line, amide peaks appeared at 1660cm⁻¹ and 1543cm⁻¹. After the thermal imidization(HPI-B), the amide peaks disappeared while imide peaks appeared at 1780cm⁻¹, 1375cm⁻¹ and 720cm⁻¹[12]. From the results, it was confirmed that HPAA-B was converted to HPI-B by thermal imidization. In addition, the fluorine peaks of 6FDA and BDAF appeared near 1200cm⁻¹ [13].

While the absorbances of imide peaks near 1780 and 720cm⁻¹ for film samples can be affected by anisotropy, the band near 1380cm⁻¹ shows little effect from anisotropy when it is normalized to the

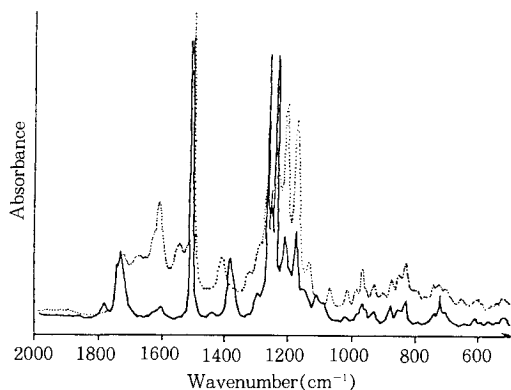


Fig. 1. IR spectra of HPAA-B(.....) and HPI-B (—) films.

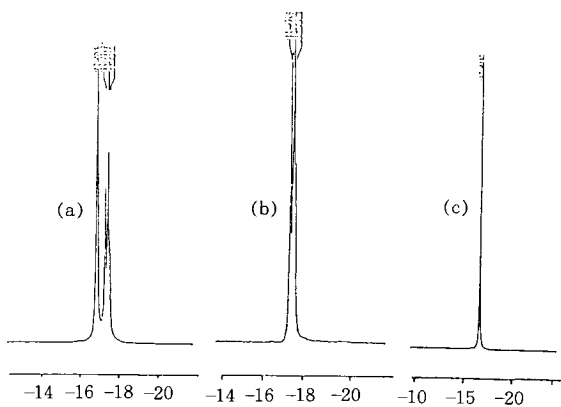


Fig. 2. ^{19}F -NMR spectra of homopolyamic acids in NMP; HPAA-B(a), HPAA-O(b) and BTDA-BDAF(c).

1500cm^{-1} aromatic band[14]. The degree of imidization of the prepared film was found to be 98% referring to a film imidized completely by heating at 350°C for additional 1h.

Because all of the obtained polymers contain fluorines, the ^{19}F -NMR spectra of HPAA-O, HPAA-B and HPAA of 3,3', 4,4'-benzophenonetetracarboxylic dianhydride (BTDA)-BDAF as reference were obtained and given in Fig. 2.

For HPAA-O, the fluorines of 6FDA gave three peaks appearing at -17.4ppm , -17.5ppm , -17.6ppm . On the other hand, HPAA-B showed one more peak at -17.0ppm in addition to three peaks of

6FDA. From ^{19}F -NMR spectrum of HPAA of BTDA-BDAF, it was found that the peak at -17.0ppm is due to the fluorine of BDAF. From the above results, it was concluded that CF_3 groups of 6FDA give three peaks whereas those of BDAF show one peak at ^{19}F -NMR spectrum. The ^{19}F -NMR splitting of CF_3 peaks of 6FDA might be due to different chemical environment. The mol% ratio of 6FDA/BDAF in HPAA-B calculated from the peak intensities of 6FDA and BDAF was good correspondence with feed mole ratio.

To confirm the structure of copolymers, the FT-IR spectra of BCPAA and BCPI are obtained and shown in Fig. 3. Amide peaks of 1660cm^{-1} and 1543cm^{-1} were found for BCPAA. With thermal imidization, amide peaks disappeared and imide peaks appeared at 1780cm^{-1} , 1375cm^{-1} and 720cm^{-1} for BCPI. The ether peak of ODA appearing at 1250cm^{-1} [15] was overlapped with other peaks. From these results, it was also confirmed that BCPAA was converted to BCPI by thermal imidization. The spectra of RCPAA, BPAA RCPI and BPI were found to be very similar patterns as BCPAA and BCPI. In other words, it is almost impossible to distinguish the above three kinds of polymers, BCPI, RCPI and BPI, from each other by FT-IR method.

The formation of BCPAA from HPAA-EF and HPAA-EO was examined by measuring the viscosities of HPAA-EF, HPAA-EO and BCPAA as shown in Table 2.

The intrinsic viscosity of BCPAA was found to be much larger than that of HPAA-EF or HPAA-EO. This increased viscosity was considered due to further polymerization of HPAA-EF with HPAA-EO, and it was concluded that BCPAA is obtained by reaction of dianhydride-terminated HPAA-EF and diamine-terminated HPAA-EO.

3. 2. Solubility of Polymers

Solubility characteristics of PAA and PI in various solvents were observed and listed in Table 3.

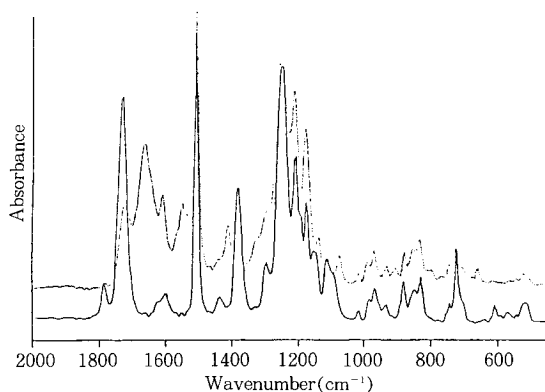
As shown in table 3, all of PAAs, HPAA-B,

Table 2. Intrinsic Viscosities of Homopolyamic Acids and Block Copolyamic Acid

Sample	$[\eta]$
6FDA-BDAF(0.95 : 1) (HPAA-EF)	0.69
6FDA-ODA(1 : 0.95) (HPAA-EO)	0.77
BCPAA (HPAA-EF+HPAA-EO)	1.27

*Unit : (dl/g)

*Condition : in NMP at 25°C

**Fig. 3.** IR spectra of BCPAA(.....) and BCPI (—) films.

HPAA-O, RCPAA, BCPAA and BPAA were dissolved easily in various organic solvents such as NMP, DMAc, DMF, THF, acetone and dichloromethane. HPI-B was soluble in all of solvents which were examined, while HPI-O was insoluble in most of solvents except dichloromethane. As expected[16], HPI-B having more CF₃ groups showed better solubility than HPI-O. In addition, RCPI was soluble in all of organic solvents while BCPI and BPI were swelled except in dichloromethane. From the above results, it was found that dichloromethane is powerful solvent for 6FDA-polyimide systems.

3. 3. Thermal Properties

DSC curves of HPI-B and HPI-O were obtained (Fig. 4) and it was found that glass transition temperature(T_g) of HPI-B(260°C) is about 40°C lower than that of HPI-O(301°C). The lower T_g of HPI-B might be due to C(CF₃)₂ groups in BDAF which increase the bond rotation[16].

Table 3. Solubility of Polyamic Acids and Polyimides at Room Temperature

Sample ^b		Solvent ^a					
		NMP	DMAc	DMF	THF	Acetone	CH ₂ Cl ₂
HPAA	6FDA-BDAF	S	S	S	S	S	S
	6FDA-ODA	S	S	S	S	S	S
HPI	6FDA-BDAF	S	S	S	S	S	S
	6FDA-ODA	I	I	I	I	I	S
CPAA	6FDA-(BDAF-r-ODA)	S	S	S	S	S	S
	6FDA-(BDAF-b-ODA)	S	S	S	S	S	S
CPI	6FDA-(BDAF-r-ODA)	S	S	S	S	S	S
	6FDA-(BDAF-b-ODA)	SW	SW	SW	SW	SW	S
BPAA	6FDA-BDAF/6FDA-ODA	SW	SW	SW	SW	SW	S
	6FDA-BDAF/6FDA-ODA	SW	SW	SW	SW	SW	S

a; NMP : N-Methyl-2-Pyrrolidone

DMA : N, N-dimethylacetamide

DMF : N, N-dimethylformamide

THF : tetrahydrofuran

b; HPAA : homopolyamic acid

HPI : homopolyimide

CPAA : copolyamic acid

CPI : copolyimide

BPAA : blend of HPAAAs

BPI : imidized BPAA

*Solubility Keys; S : soluble,

SW : partially soluble or swelling

I : insoluble

The thermal stability was estimated with TGA and the results were given in Table 4. The initial decomposition temperature(T_{d1}) and maximum decomposition temperature(T_{dmax}) were 526°C and 560°C for HPI-B, whereas those were 536°C and 581°C for HPI-O, respectively. The decomposition temperatures of RCPI, BCPI and BPI were similar and higher than 500°C. The residue remained at 900°C was higher than 50% for all PIs. On the contrary, PI(PMDA-ODA) having no fluorine has higher T_{d1} and T_{dmax} than PIs containing CF₃ groups. From these

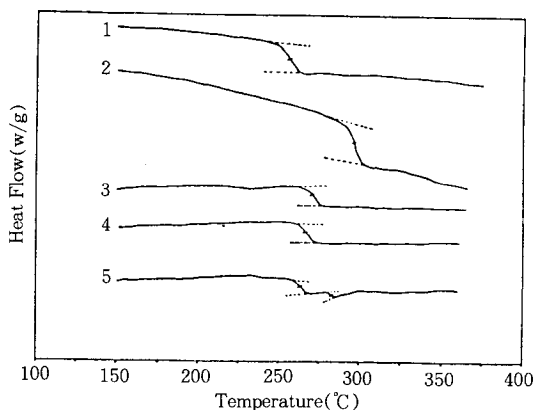


Fig. 4. DSC curves of HPI-B(1), HPI-O(2), RCPI (3), BCPI(4) and BPI(5).

Table 4. Physical Properties of Polyimides and Blend

Samples	$[\eta]^a$ (dl/g)	T_g (°C)	T_{di}^b (°C)	T_{dm}^c (°C)	Residue at 900°C (wt%)
6FDA-BDAF	0.99	260	526	560	50.3
6FDA-ODA	1.12	301	536	581	55.4
6FDA-(BDAF-r-ODA)	1.35	272	529	566	54.8
6FDA-(BDAF-b-ODA)	1.27	269	526	565	54.4
6FDA-BDAF/6FDA-ODA	1.57	270,286	525	564	49.3
PMDA-ODA ^d	1.12	377	584	620	55.0
PMDA-BDAF _d	0.51	319	540	576	57.0
BTDA-BDAF ^d	0.94	249	545	569	58.0

a; Measured in NMP at 25°C for PAA

b; Initial Decomposition Temperature

c; Maximum Decomposition Temperature

d; Reference 17

results, it was confirmed that incorporation of CF₃ group in PI lowers T_g with less reduction of thermal stability.

DSC curves of RCPI, BCPI and BPI are also given in Fig. 4. One T_g of RCPI appeared at 272°C which is an intermediate value of two homopolymer's T_g s, and BCPI has also one T_g at 269°C which is similar to that of RCPI. On the contrary, BPI showed two T_g s at 270 and 286°C, which were shifted from those of HPI-B and HPI-O. From these observations, it could be considered that the block se-

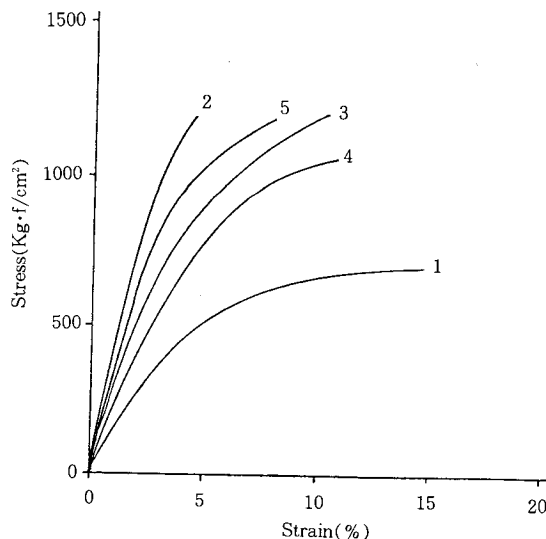


Fig. 5. Stress-strain curves of HPI-B(1), HPI-O (2), RCPI(3), BCPI(4) and BPI(5).

quences of BCPI were disturbed to become randoms RCPI, and BPI turned into a segmented blocky copolymer due to the exchange reaction of PAA amide group during thermal imidization[7, 8].

3.4. Mechanical Properties

To examine mechanical properties, the stress-strain curves of various PIs were obtained and shown in Fig. 5.

As expected from molecular structures, HPI-B exhibited a flexible and soft behavior while HPI-O has a stiff and hard properties. RCPI, BCPI and BPI had the intermediate properties of HPI-B and HPI-O.

The tensile strength and elongation at break of PIs were given in Table 5.

As seen in Table 5, the tensile strength and elongation at break of PI films were greater than those of PAAs. Especially, RCPI and BPI show similar values of tensile strength to that of HPI-O, while their elongation at break were larger than that of HPI-O. Thus, it could be expected that the RCPI and BPI have some possibility of PI/PI molecular composite for high performance materials.

Table 5. Mechanical Properties of Polymers before and after Thermal Imidization

Sample	Tensile Strength(Kgf/cm ²)	Elongation at break(%)
Before imidization;		
6FDA-BDAF	510	11.4
6FDA-ODA	800	2.9
6FDA-(BDAF-r-ODA)	830	8.6
6FDA-(BDAF-b-ODA)	700	7.2
6FDA-BDAF/6FDA-ODA	780	7.5
After imidization;		
6FDA-BDAF (HPI-B)	700	14.8
6FDA-ODA (HPI-O)	1180	4.5
6FDA-(BDAF-r-ODA) (RCPI)	1200	10.3
6FDA-(BDAF-b-ODA) (BCPI)	1060	10.8
6FDA-BDAF/6FDA-ODA (BPI)	1180	8.4

The studies on thermal and mechanical behaviors of BPIs with various compositions are now in progress and the results will be appeared in near future.

3. Conclusions

With 2, 2-Bis-(3, 4-dicarboxyphenyl)hexafluoropropane dianhydride(6FDA), 2, 2-bis-[4-(4-aminophenoxy)phenyl]hexafluoropropane(BDAF) and 4, 4-diamino-diphenyl ether(ODA), the homopolyamic acid(HPAA)s, copolyamic acid(CPAA)s and blend of HPAAs were prepared in N-methyl-2-pyrrolidone and converted to polyimide(PI)s by thermal imidization. By studying the structure, solubility, thermal and mechanical properties of polymers, the followings have been found;

1. For ¹⁹F-NMR spectra of polyamic acid, fluorines of 6FDA give three peaks at -17.4, -17.5, -17.6ppm while BDAF shows only one peak at -17.0ppm.
2. Incorporation of bulky CF₃ group increases solubility of PI and dichloromethane is powerful solvent for 6FDA-PIs.
3. Incorporation of CF₃ group in PI lowers T_g with a little loss of thermal stability.
4. During thermal imidization, exchange reaction of amide groups is possible for CPAA and blend of

HPAAAs to change into blocky copolyimide.

5. Random copolymerization and blending of HPAAAs are possible preparative methods of PI/PI molecular composite for high performance materials.

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