

# Synthesis and Properties of 6FDA-BisAAF-PPD Copolyimides for Microelectronic Applications

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**ABSTRACT:** In this work, fluorine-containing copolyimides were synthesized from 6FDA dianhydride and different ratios of BisAAF and PPD diamines. Properties, such as composition, viscosity, dielectric constant, glass-transition temperature, thermal decomposition temperature, tensile characteristics, and transmittance, were investigated by using elemental analysis, viscometry, Fourier transform infrared spectrometry, differential scanning calorimetry, a thermogravimetric analyzer, a tensile tester, and UV-visible spectrophotometry. After curing at 300°C for 1 h, imidization was observed, as indicated the appearance of an absorption peak of the carbonyl of the imide at 1780  $\text{cm}^{-1}$  (C=O asymmetry stretching). The inherent viscosity increased with an increasing PPD mole fraction, from 0.40 dL/g of

pure 6FDA-BisAAF to 0.84 dL/g of pure 6FDA-PPD. The dielectric constant decreased with increasing fluorine content. The glass-transition temperature increased with an increasing PPD mole fraction; the values increased from 317°C with pure 6FDA-BisAAF polyimide to 364°C with pure 6FDA-PPD polyimide. The 5% weight loss temperature ( $T_d$ ) of the copolyimides was around 530°C in air and 540°C in a nitrogen atmosphere. The tensile modulus and tensile strength gradually increased with an increasing PPD molar fraction. The transmittance of 6FDA-BisAAF-PPD copolyimides was greater than 90% at wavelengths above 500 nm. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2064–2069, 2005

**Key words:** fluoropolymers; dielectric property; polyimide

## INTRODUCTION

Polymers have been used in many applications in microelectronic devices, such as passivation layers, substrate materials, and interlayer dielectrics. Polyimides, with their low dielectric constant, good thermal property, superior resistance to chemicals, and excellent mechanical properties, have been considered some of the best polymers for these applications.<sup>1,2</sup>

Polyimides containing fluorine have drawn much attention in recent research, because of their low dielectric constants, and have been considered new candidate materials for intermetal dielectrics (IMD).<sup>3</sup> The introduction of fluorine into polyimide will significantly decrease the dielectric constant, reduce moisture absorption, and improve the optical property.<sup>3–8</sup> However, C–F bonding also will reduce the glass-transition temperature ( $T_g$ ) of polyimide.<sup>7</sup> In addition to dielectric constant, the water absorption, chemical properties,  $T_g$ , thermal stability, and mechanical properties of the polymers also are critical for the application of IMD because the dielectrics

must survive the postannealing and chemical mechanical polishing (CMP) process.

It has been reported that 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA)-based polyimides have dielectric constants below 3.0.<sup>9–11</sup> The glass-transition temperature ( $T_g$ ) of 6FDA-based polyimides is around 300°C,<sup>9,12</sup> and the thermal decomposition temperature ( $T_d$ ) is around 500°C.<sup>12</sup> In addition, 6FDA-based polyimides show good transparency in the UV-visible region.<sup>12</sup> Hence, they may serve as transparent thin-film materials.

In this study, 6FDA was used as the only source of dianhydride, reacting with various mole fractions of 2,2'-bis-(4-aminophenyl)-hexafluoropropane (BisAAF) and *p*-phenylene diamine (PPD) to form fluorine-containing copolyimides. The purpose of this work was to synthesize a series of fluorine-containing copolyimides by controlling composition and structure in order to obtain a high  $T_g$ , low dielectric constant polyimide. This polyimide may be of use in integrated circuits for advanced applications.

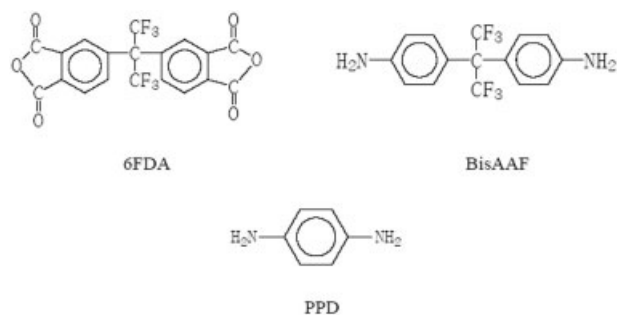
## EXPERIMENTAL

### Materials

2,2'-Bis-(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (6FDA), 2,2'-bis-(4-aminophenyl)-hexafluoropropane (BisAAF), *p*-phenylene diamine (PPD),

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Scheme 1

dimethylacetamide (DMAc), tetrahydrofuran (THF), and anhydrous *N*-methylpyrrolidine (NMP) were obtained from commercial sources without further purification. The structures of the monomers are shown in Scheme 1.

### Synthesis of 6FDA-BisAAF-PPD copolyimides

The 6FDA-BisAAF-PPD copolymers were prepared as follows: Different ratios of BisAAF and PPD mixed with an appropriate amount of anhydrous NMP were added to a dry 250-mL three-necked flask equipped with a nitrogen inlet and a mechanical stirrer. After the BisAAF and PPD dissolved, a stoichiometric amount of 6FDA was added. The solid content of the solution was 16 wt %. The compositions of the samples, referred to as PI-1–PI-5, are shown in Table I. After the monomers were added, the reaction mixture was stirred at room temperature in an  $N_2$  atmosphere for 6 h to form a viscous poly(amic acid) solution. The solution was cast on glass and dried in a vacuum oven at 80°C for 8 h. After the baking process, the film on the glass was converted to polyimide by heating in air at 300°C for 1 h. The film was cooled to room temperature and stripped from the glass. Scheme 2 shows the synthesis of 6FDA-BisAAF-PPD polyimide.

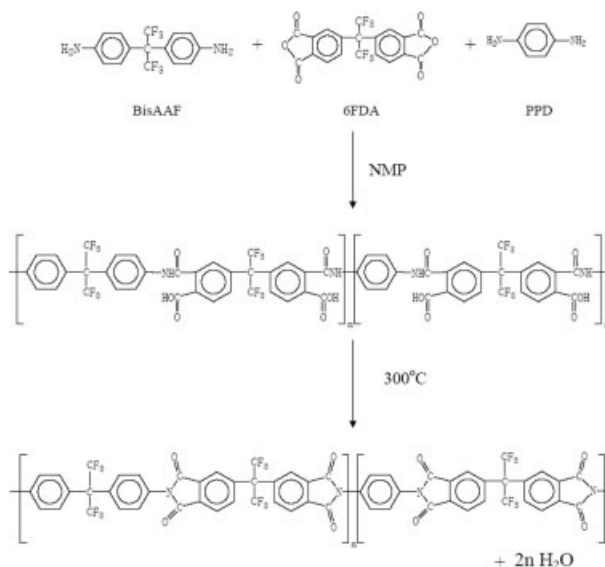
### Characterization

The elemental analysis of these copolyimides was determined by a Elementar vario EL III instrument. The

TABLE I  
Composition of Copolyimides PI-1–PI-5

Sample	Composition			Molar ratio
	6FDA (mol) <sup>a</sup>	BisAAF (mol) <sup>a</sup>	PPD (mol) <sup>a</sup>	
PI-1	0.015	0.015	0	1:1:0
PI-2	0.015	0.0105	0.0045	1:0.7:0.3
PI-3	0.015	0.0075	0.0075	1:0.5:0.5
PI-4	0.015	0.0045	0.0105	1:0.3:0.7
PI-5	0.015	0	0.015	1:0:1

<sup>a</sup> The molecular weights of 6FDA, BisAAF, and PPD are 444.2, 334, and 108.1 g/mol, respectively.



Scheme 2

IR spectra were recorded on a Jasco 460 FTIR spectrometer. The inherent viscosities of the 6FDA-BisAAF-PPD precursors was measured with a Cannon-Ubbelohde No. 100 viscometer at a concentration of 0.5 g/dL in NMP at 30°C. The dielectric constants were examined with an HP 4291B at frequencies of 1 MHz and 1 GHz. The solubility tests were performed by soaking the cured polymers in the solvents for 24 h with stirring at 25°C. The glass-transition temperature ( $T_g$ ) of the 6FDA-BisAAF-PPD films was determined with a TA Instrument (model 2920) differential scanning calorimeter (DSC) at a heating rate of 10°C/min in a nitrogen atmosphere. Thermal stability was determined with a TA Instrument thermogravimetric analyzer (TGA), Q500, at a heating rate of 20°C/min in an air and nitrogen atmosphere. The tensile properties of the 6FDA-BisAAF-PPD copolyimides were measured with a SHIMADZU AG-1S with a loading of 50N and an elongation rate of 5 mm/min. The samples for measuring the tensile properties were 6 cm in length and 0.75 cm in width and had a thickness ranging from 50 to 100  $\mu\text{m}$ . The UV–vis transmittance spectra were examined with a Hitachi U-2001 UV–vis spectrophotometer with a wavelength ranging from 200 to 1100 nm.

## RESULTS AND DISCUSSION

### Synthesis of 6FDA-BisAAF-PPD copolyimides

The compositions of these polyimides were examined after samples were cured at 300°C for 1 h in air. Both the calculated and measured data on composition are given in Table II. Because the content of fluorine could not be measured by elemental analysis, the fluorine content listed in Table II was determined by calcula-

**TABLE II**  
Results of Elemental Analysis of Copolyimides PI-1–PI-5

Sample	Elemental analysis (%)				
		C	H	N	F
PI-1	Calc.	54.4	1.86	3.73	30.4
	Found	54.71	1.95	3.59	
PI-2	Calc.	55.25	1.88	4.12	28.5
	Found	55.29	2.02	3.88	
PI-3	Calc.	55.92	1.89	4.42	27.0
	Found	55.91	2.04	4.18	
PI-4	Calc.	56.70	1.91	4.78	25.3
	Found	56.30	2.08	4.49	
PI-5	Calc.	58.14	1.94	5.42	22.1
	Found	57.46	2.11	5.12	

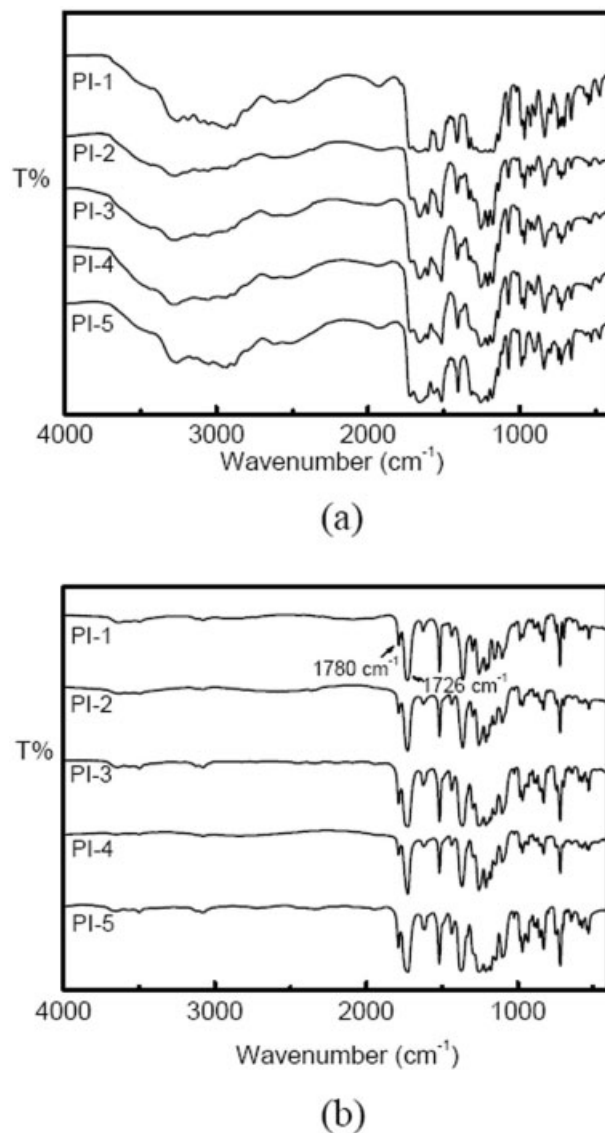
tion. The fluorine content decreased from PI-1 to PI-5 (30.4–22.1 wt %). The results of elemental analysis showed that the actual compositions agreed with the calculated data.

To ensure that the poly(amic acid) was imidized after curing at 300°C for 1 h, the structures of the polymers, before and after curing, were identified by IR measurement. Figure 1(a,b) shows the IR spectra of PI-1–PI-5 before and after curing. It was observed that the polymers exhibited a broad absorption band around 3100–3400  $\text{cm}^{-1}$  because of the amino (N–H), carboxyl (COOH), and hydroxyl (OH) groups. The dehydrative cyclization of the poly(amic acid) precursors was confirmed by the disappearance of the broad absorption peak around 3100–3400  $\text{cm}^{-1}$  and the appearance of absorption peaks at 1780  $\text{cm}^{-1}$  (C=O asymmetry stretching) and 1726  $\text{cm}^{-1}$  (C=O symmetry stretching), characteristic of the carbonyl of imide. These results suggest that imidization was achieved after curing at 300°C for 1 h.

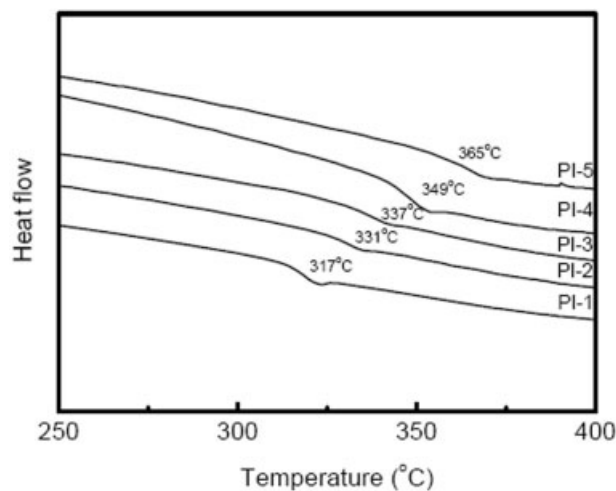
### Properties of 6FDA-BisAAF-PPD copolyimides

The inherent viscosity of the polyimide precursors was measured at a concentration of 0.5 g/dL in NMP at 30°C. The dielectric constant was examined by a parallel-plate capacitor at frequencies of 1 MHz and 1 GHz. The results for dielectric constant and inherent viscosity are summarized in Table III. It was observed that the viscosity of pure 6FDA-BisAAF poly(amic acid) (PI-1) was about 0.40 dL/g. However, the viscosity increased significantly with the addition of the PPD. The PI-2–PI-4 precursors showed a viscosity of around 0.6 dL/g, and the pure 6FDA-PPD poly(amic acid) (PI-5) had a viscosity of 0.84 dL/g. The increased viscosity may be attributed to the introduction of the rigid PPD molecule.

Table III shows that the dielectric constant gradually increased from PI-1 to PI-5 at the measured frequencies of 1 MHz (from 2.63 to 2.87) and 1 GHz (from 2.55 to 2.64). The increased dielectric constant may be at-



**Figure 1** IR spectra of copolyimides PI-1–PI-5: (a) before curing at 300°C for 1 h, (b) after curing at 300°C for 1 h.



**Figure 2** DSC curves of copolyimides PI-1–PI-5.

**TABLE III**  
Inherent Viscosities of precursors and Dielectric Constants of Copolyimides PI-1–PI-5

	Inherent viscosity <sup>a</sup> (dL/g)	Dielectric constant <sup>b</sup>	
		1 MHz	1 GHz
PI-1	0.40	2.63	2.55
PI-2	0.63	2.67	2.58
PI-3	0.61	2.70	2.59
PI-4	0.67	2.77	2.65
PI-5	0.84	2.87	2.64

<sup>a</sup> Inherent viscosity was measured at a concentration of 0.5 g/dL in NMP at 30°C.

<sup>b</sup> Dielectric constant was measured at the frequency of 1 MHz and 1 GHz.

tributed to the content of the bulky CF<sub>3</sub> groups from decreasing PI-1 to PI-5. It has been reported in the literature<sup>13,14</sup> that the presence of CF<sub>3</sub> groups may result in less efficient chain packing, increasing the free volume. In addition, the strong electronegativity of fluorine will result in very low polarizability of C—F bonds, which also decreases the dielectric constant. The experimental results corresponded with those of the elemental analysis and those reported in the literature. The lower dielectric constant at high frequency (1 GHz) may have been a result of the reduction in electronic polarization.

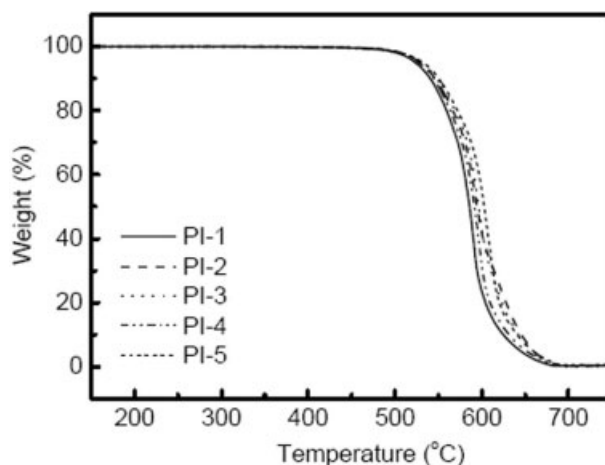
The solubility of the PI-1–PI-5 copolyimides after being cured at 300°C for 1 h is shown in Table IV. It was observed that all samples were soluble in acetone, NH<sub>4</sub>OH, and H<sub>2</sub>SO<sub>4</sub> (96%). However, it also was found that the dissolution behavior of PI-1–PI-5 was different in THF and DMAc. It was totally insoluble in alcohol and H<sub>2</sub>O<sub>2</sub>. It was observed that the solubility behavior changed gradually from soluble to insoluble going from PI-1 to PI-5 in THF and DMAc solvents. These results may have occurred because of the increased molecular rigidity and the decreased free volume going from PI-1 to PI-5, which decreased the paths and possibility of the solvent molecules being able to pass through and dissolve the polymers.

**TABLE IV**  
Solubility of Copolyimides PI-1–PI-5 in Different Solvents

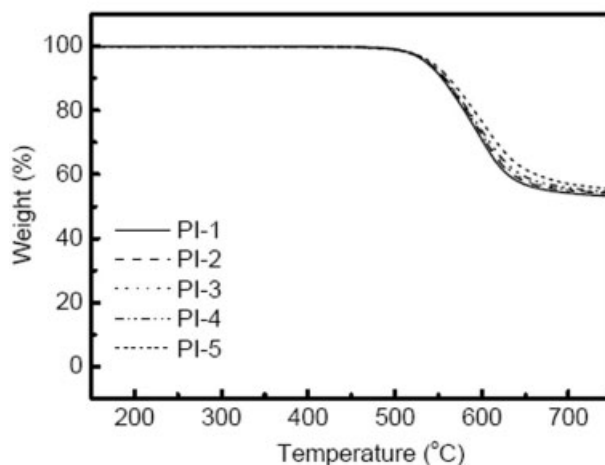
	PI-1	PI-2	PI-3	PI-4	PI-5
Acetone	+	+	+	+	±
THF	+	+	+	±	–
DMAc	+	+	–	–	–
NH <sub>4</sub> OH	+	+	+	+	+
Alcohol	–	–	–	–	–
H <sub>2</sub> SO <sub>4</sub> (96%)	±	+	+	+	+
H <sub>2</sub> O <sub>2</sub>	–	–	–	–	–

+, Soluble; ±, partially soluble, –, insoluble.

All samples were soaked in the solvent with stirring for 24 h.



(a)



(b)

**Figure 3** TGA thermograms of copolyimides PI-1–PI-5: (a) in air, (b) in N<sub>2</sub>.

The glass-transition temperature ( $T_g$ ) and thermal decomposition temperature ( $T_d$ ) of PI-1–PI-5 were measured by DSC (in nitrogen) and TGA (in air and nitrogen). The spectra from the DSC measurement are shown in Figure 2. Thermal decomposition temperature was measured in both air and nitrogen. In our study, all the  $T_d$  values were defined at the temperature of 5% weight loss. The TGA thermograms of PI-1–PI-5 in air and in an N<sub>2</sub> atmosphere are shown in Figure 3(a,b). All the  $T_g$  and  $T_d$  values (in air and nitrogen) of PI-1–PI-5 are listed in Table V. It was observed that the  $T_g$  of pure 6FDA-BisAAF polyimide (PI-1) was 317°C. However, the  $T_g$  increased with an increasing PPD mole fraction, and the  $T_g$  of pure 6FDA-PPD polyimide (PI-5) reached a temperature of 365°C. This increased glass-transition temperature may be attributed to the addition of a rigid PPD molecule, which enhances the stiffness of backbones and reduces the flexibility of the fluorine-containing polyimide structure.

**TABLE V**  
Glass-Transition Temperatures and Thermal Decomposition Temperatures of PI-1–PI-5

Sample	$T_g^a$ (°C)	$T_{d-air}^b$ (°C)	$T_{d-N_2}^c$ (°C)
PI-1	317	523	536
PI-2	331	529	538
PI-3	337	530	536
PI-4	349	527	539
PI-5	365	532	542

<sup>a</sup> Determined by DSC at a heating rate of 10°C/min in a nitrogen atmosphere.

<sup>b</sup> 5% Weight loss temperature in air.

<sup>c</sup> 5% Weight loss temperature in nitrogen.

The  $T_d$  values of PI-1–PI-5 are given in Table V, which shows that the  $T_d$  was higher in nitrogen than in air for the same sample. The thermal decomposition temperature slightly increased with the addition of PPD, but to a lesser extent than did the  $T_g$ . The  $T_d$  of these five samples ranged from 524°C to 532°C in air and from 536°C to 542°C in nitrogen.

The thermal properties of several 6FDA-based polyimides synthesized from 6FDA and various aromatic diamines were reported by Li et al.<sup>12</sup> Their research showed that 6FDA-based polyimides had glass-transition temperatures ranging from 263°C to 336°C, as measured by a thermal mechanical analyzer (TMA), and the thermal decomposition temperatures ranging from 341°C to 507°C in air and from 413°C to 525°C in nitrogen. However, in the current study, the  $T_g$  values were found to range from 317°C to 365°C and the  $T_d$  in air and nitrogen to be around 530°C and 540°C, respectively. Therefore, the 6FDA-based copolyimides synthesized in our experiments exhibited similar or even better thermal properties.

The thermal stability of polyimides is determined by the bonding strength in the molecular structure and is also related to the molecular weight of the polymers. 6FDA monomer contains a hexafluoropropane linkage that interrupts aromaticity. It has been reported in the literature<sup>15,16</sup> that the incorporation of 6FDA will lead to a decrease in thermal stability. In this study, both the 6FDA and the BisAAF monomers had a structure of hexafluoropropane linkage. The difference in the compositions of PI-1–PI-5 was the molar ratio of the BisAAF to the PPD diamines. The quantity of 6FDA was the same in all samples, and the  $T_d$  values of all samples were rather close to each other. The slight increase in decomposition temperature may have been a result of the increase in the rigid PPD monomer content in the copolyimides.

It is believed that in polymers there is a highly correlated relationship between flexibility and the glass-transition temperature. Aromatic rings on the backbone of polymers will significantly increase the rigidity of the molecular chain.<sup>17</sup> In addition, the res-

**TABLE VI**  
Tensile Properties of Copolyimides PI-1–PI-5

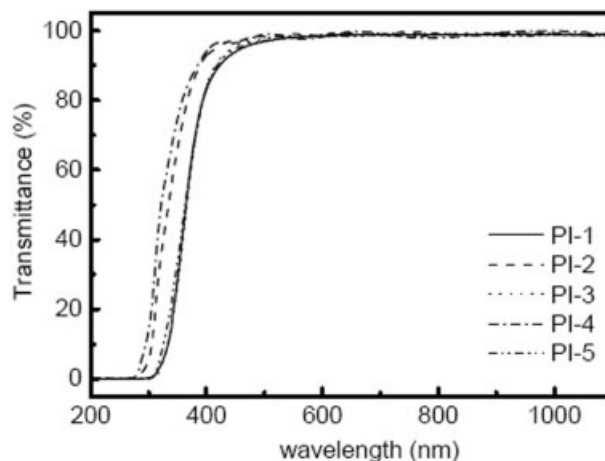
	Tensile modulus (GPa)	Tensile strength <sup>a</sup> (MPa)	Elongation <sup>b</sup> (%)
PI-1	0.97	50.3	7.3
PI-2	1.06	65.5	14.0
PI-3	1.10	66.6	7.5
PI-4	1.23	67.8	6.4
PI-5	1.46	70.4	4.9

<sup>a</sup> Tensile strength was measured at the break point of the test.

<sup>b</sup> Elongation was recorded at the break point.

onance planarity of phenyl will impose a flat planar structure and reduce the free rotation and flexibility of the molecule.<sup>17</sup> In contrast, the C—C single bond on the backbone will increase the probability of free rotation and will decrease the glass-transition temperature.<sup>17</sup> With the substitution of BisAAF by PPD, the number of C—C single bonds was reduced and replaced by rigid phenyl groups in the backbone of the structure. Therefore, the an increased  $T_g$  was measured.

Table VI shows the tensile properties of PI-1–PI-5. The modulus of PI-1 was 0.97 GPa, which increased with an increasing PPD molar fraction. PI-5 had a modulus of 1.46 GPa. It is believed that the increase in the modulus was a result of the incorporation of the rigid PPD structure. The tensile strength of the PI-1–PI-5 copolyimides was measured at the break point of the test, and the tensile strength also showed the same pattern. Elongation at break also was recorded and is shown in Table VI. No significant trend toward elongation was observed in samples PI-1–PI-5. The elongation varied from 4.85% (PI-5) to 14.04% (PI-2). The mechanical properties of a low-k dielectric constant material for use in ULSI required that the tensile modulus be greater than 1 GPa and that the elongation at



**Figure 4** Uv-vis spectra of copolyimides PI-1–PI-5.

break be greater than 5%.<sup>18</sup> In addition to PI-1 and PI-5, samples PI-2–PI-4 also were able to satisfy the requirement of this application. Even the properties of the PI-1 and PI-5 samples had values close to the requirement.

Figure 4 shows the UV–vis transmittance spectra of PI-1–PI-5 in wavelengths ranging from 200 to 1100 nm. The thickness of the measured films ranged from 10 to 25  $\mu\text{m}$ . The transmittance of the PI-1–PI-5 copolyimides at a wavelength of 500 nm was above 90%. The wavelengths of the onset transmittance and the 80% transmission for these copolyimides were about 276–304 and 359–395 nm, respectively. Thus, the copolyimides produced in this research were found to have excellent transparency in the UV–vis wavelength regions. In principle, the wavelengths of the onset transmittance and the 80% transmission correspond to the electron conjugation length of the backbone. The superior transparency of these copolyimides may be attributed to the limited electronic conjugation along the backbone of these 6FDA-based polyimides<sup>19</sup> and may have applications in optical devices.

### CONCLUSIONS

A new series of 6FDA-BisAAF-PPD copolyimides were synthesized and characterized in this study. The polyimides had a higher glass-transition temperature and greater thermal stability with an increasing PPD/BisAAF ratio. The dielectric constants of these copolyimides ranged from 2.63 to 2.87 (@1 MHz). The introduction of more  $\text{CF}_3$  groups by BisAAF monomer resulted in a lower dielectric constant. The introduction of a rigid and thermally stable aromatic structure of PPD enhanced both the thermal and mechanical properties of the 6FDA-based copolyimides. The results of tensile tests of these copolymers showed acceptable mechanical properties for use in the ULSI application. The UV–vis measurement revealed excellent transparency of the copolyimides. As a result,

these copolyimide films may find applications for optical devices. The superior properties of these polyimides indicate their potential use in microelectronic processes; however, the integration between these copolyimides and metal interconnects must be characterized in the future.

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