

Soluble Polyimides Containing Benzimidazole Rings for Interlevel Dielectrics

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New soluble polyimides with improved adhesion to copper were synthesized from 6,4'-diamino-2-phenylbenzimidazole (BIA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) with 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) via one-pot synthetic method using *N*-methylpyrrolidone (NMP) as a solvent. Precipitation or gelation did not occur during imidization, and the synthesized polyimides having inherent viscosity values of 0.86–1.74 dL/g were dissolved well in polar aprotic solvents and phenolic solvents. Flexible and fingernail-creasable films were formed on casting. T_g values of the polyimides were in the range of 320–351 °C and 5% weight loss in nitrogen occurred above 540 °C in all cases. The polyimides containing an equimolar amount of BIA and TFDB showed good adhesion to copper without any adhesion promoters. Water absorption and dielectric constant of the polyimides were in the ranges of 0.57–1.18% and 2.74–2.94, respectively. The polyimides containing a higher content of benzimidazole rings exhibited higher adhesion to copper.

Introduction

Insulating materials for microelectronics must satisfy various properties such as low dielectric constant, low moisture absorption, high T_g above soldering temperature, high adhesion to the metal used as an interconnecting line, and so on.^{1,2} Polyimides that meet most of the above required properties have been widely used as interlayer dielectrics in high-density multilevel interconnection technology.³ However, polyimides are often insoluble and infusible in fully imidized form due to their rigid chain characteristics, leading to processing difficulties. Therefore, polyimide processing is generally carried out with poly(amic acid) intermediate, and then the poly(amic acid) is converted to polyimide via rigorous thermal treatment. However, this process has some inherent problems, such as emission of volatile byproducts (e.g. H₂O) and storage instability of the poly(amic acid) intermediate.⁴ Also, it is reported that the poly-

(amic acid) has a corrosion problem with copper interconnecting metal.⁵

To overcome these problems, much research effort have been focused on the synthesis of soluble polyimides in fully imidized form without deterioration of their own excellent properties.⁶ Several successful approaches to soluble polyimides including insertion of flexible linkage or bulky substituents on the main chain⁷ and utilization of noncoplanar⁸ or alicyclic⁹ monomers have been de-

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veloped. Copolymerization with two different diamine or dianhydride monomers is also known as an effective way to improve the solubility of insoluble polyimides.¹⁰ Random copolymerization reduces the chain regularity, resulting in improved solubility of the rigid polyimides.¹¹

Among many new diamine monomers for soluble polyimides, 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) has a unique structure, a rigid but non-planar structure with two bulky trifluoromethyl groups.^{7f,8a-c} The polymers made from TFDB show relatively low dielectric constant (ϵ) and low moisture absorption without losing other physical properties. Since the velocity of pulse propagation is inversely proportional to the square root of the ϵ of the medium, reduction of ϵ of the insulating material translates directly into reduction of delay time.¹² While rigid rodlike polyimides with planar structure have many desirable properties for interlevel dielectrics and packaging applications including low thermal expansion and excellent mechanical strength, they are often insoluble and show poor adhesion to copper.¹³ It is known that the incorporation of primary or secondary amine groups, which can interact with metal, into polymer chains enhances the adhesion to metal.¹⁴ Therefore, combination of the two diamine monomers, which have a rigid structure, and secondary amine may produce soluble polyimides that maintain many characteristics of the rigid rodlike polyimides but with improved adhesion and low ϵ . In this study, soluble and rigid rodlike polyimides containing trifluoromethyl groups and benzimidazole rings were prepared from 6,4'-diamino-2-phenylbenzimidazole (BIA) and TFDB with an appropriate aromatic dianhydride, and their properties were investigated.

Experimental Section

Materials. 6,4'-Diamino-2-phenylbenzimidazole (BIA) (mp 217–220 °C) was prepared from 4-nitro-1,2-phenylenediamine and 4-nitrobenzoyl chloride, according to the previously reported procedure, and recrystallized from dimethylformamide (DMF) and water ($v/v = 1/3$).¹⁵ The monomer was sufficiently dried in vacuo at 120 °C prior to polymerization. 2,2'-Bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) (mp 180–182 °C) was prepared from 2-bromo-5-nitrobenzotrifluoride and recrystallized from chloroform and *n*-hexane ($v/v = 1/2$).¹⁶ The monomer was sublimed in vacuo at 135 °C prior to polymer-

ization. 3,3',4,4'-Biphenyl tetracarboxylic dianhydride (BPDA) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) were recrystallized from acetic anhydride and then dried in vacuo at 150 °C for 24 h. *N*-methylpyrrolidone (NMP) was stirred in the presence of P₂O₅ overnight and then distilled under reduced pressure. Xylene and chlorobenzene were stirred in the presence of CaH₂ overnight and then distilled under nitrogen. Other commercially available reagent grade chemicals were used without further purification.

Polymerization. All polymerizations were carried out under argon flow, and equimolar amounts of diamine and dianhydride monomers were used in all cases. Polymerization was carried out with three different diamine ratio (BIA/TFDB), 25/75, 50/50, and 75/25. A representative polymerization procedure is as follows: A 100 mL three-necked flask equipped with an argon inlet and a mechanical stirrer was charged with the appropriate amount of BIA and TFDB. NMP was added to the concentration of 10 wt %, and the mixture was stirred at room temperature. To this mixture, the equimolar amount of BTDA was added in one portion. The solution was stirred for 4 h at room temperature. Within 1 h, the solution became homogeneous. After the solution was diluted with NMP to the concentration of 5 wt %, the temperature was raised to 190 °C slowly and the reaction mixture was stirred for 10 h at 190 °C. Chlorobenzene or xylene was periodically removed from the Dean–Stark trap and replaced with dry chlorobenzene or xylene to ensure cyclodehydration. The polymer was precipitated into a vigorously stirred methanol/water mixture and then filtered. The precipitated polymer was washed with hot water, methanol, and acetone repeatedly and dried in vacuo at 130 °C for 24 h.

PI1. The following quantities of reagents were used: BIA, 0.1821 g (0.5712 mmol); TFDB, 0.5488 g (1.7138 mmol); BTDA, 0.7092 g (2.2010 mmol); and 13 + 13 mL of NMP [1.2755 g (99.5% yield)].

PI2. The following quantities of reagents were used: BIA, 0.1833 g (0.8173 mmol); TFDB, 0.2617 g (0.8172 mmol); BTDA, 0.5267 g (1.6345 mmol); and 10 + 10 mL of NMP [0.9044 g (99.1% yield)].

PI3. The following quantities of reagents were used: BIA, 0.4606 g (2.0538 mmol); TFDB, 0.2192 g (0.6845 mmol); BTDA, 0.8824 g (2.7384 mmol); and 15 + 15 mL of NMP [1.4528 g (99.3% yield)].

Film Preparation. The polymers were dissolved in NMP at a concentration of 5–10 wt % and then filtered through 0.45 μ m filter membranes. The filtered solutions were coated on a glass plate and dried in a vacuum at 100 °C for 24 h. The prepared films were peeled from the plates and dried in a vacuum at 100 °C for 24 h.

General Measurements. FTIR spectra of the compounds were obtained with a Bruker EQUINOX-55 spectrophotometer using KBr pellet or film. NMR spectra of the synthesized compounds were recorded on a Bruker Fourier Transform AC 200 (200 MHz for ¹H and 50.3 MHz for ¹³C) spectrometer. Inherent viscosity data were obtained with a Canon-Ubbelohde type viscometer at 30 °C. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and thermomechanical analysis (TMA) were performed on a TA 2200 thermal analyzer system. T_g 's of the polymers were obtained with DSC or TMA with a heating rate of 10 and 5 °C/min, respectively, in N₂ flow. TGA measurement was made with a heating rate of 10 °C/min in N₂ and air. The coefficients of thermal expansion in the temperature range from 50 to 300 °C were obtained by using TMA with a heating rate of 5 °C/min in N₂. Water absorptions were measured by weight increment of polyimide films after immersed in boiling water for 4 h.

Refractive Index and Dielectric Constant Measurement. Prism coupling measurement was performed in air with ca. 40% relative humidity using a prism coupler.¹⁷ The light source was a He–Ne laser of 632.8 nm wavelength, i.e., 474.08

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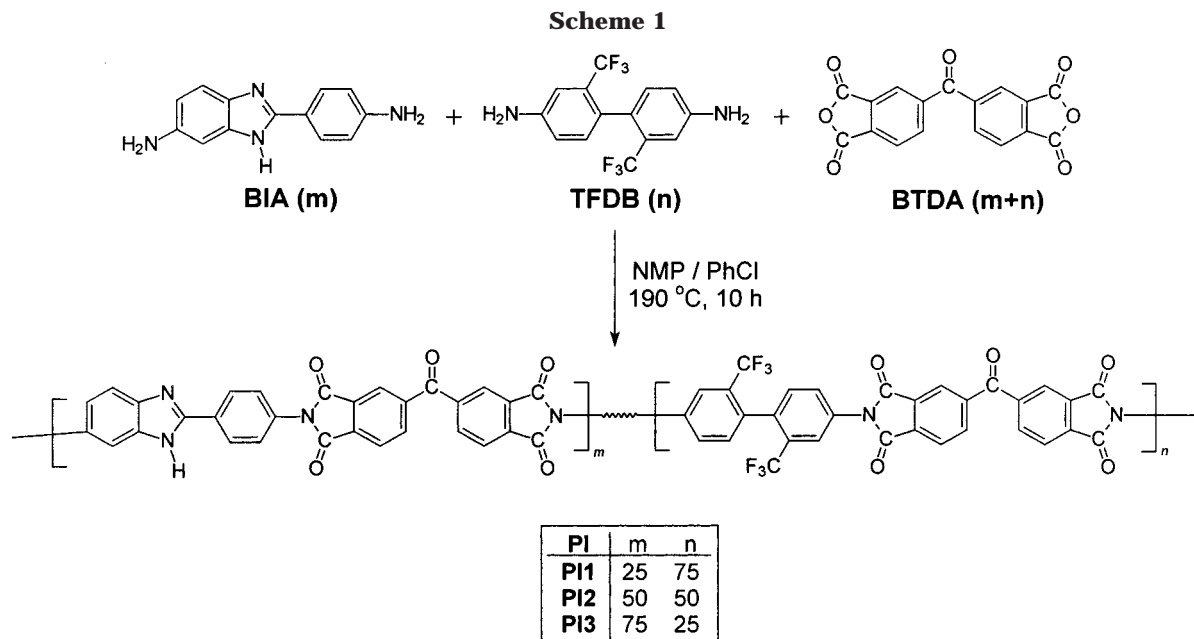
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THz frequency. All measurements were performed using a cubic zirconia prism of $n_{TE} = n_{TM} = 2.1677$ at 632.8 nm. The refractive index (n) of films was measured in transverse electric (TE) and transverse magnetic (TM) modes by choosing the appropriate polarization of the incident laser beam, giving the in-plane refractive index ($n_{TE} = n_x$) and the out-of-plane refractive index ($n_{TM} = n_z$), respectively. The dielectric constant (ϵ) was estimated from the measured refractive indices by the simple Maxwell equation: $\epsilon = n^2$.¹⁸

Adhesion to Copper Test. The polyimide solutions were coated onto the Cu plates and dried at 80 °C for 3 h and 70 °C in a vacuum for 2 h to prepare 8–13 μm thick films. The supporting frame was made by epoxy molding with *o*-cresol novolac epoxy (100), nadic anhydride (80), and benzyl dimethylamine (0.3). The epoxy resin was placed in a silicone molder and cured at 90 °C for 2 h and 150 °C for 4 h. 90° peel test was conducted by peeling the Cu plate. The locus of the fracture was the interface of copper and polyimide.

Results and Discussion

New polyimides were prepared by reacting the appropriate mole ratio (25:75, 50:50, and 75:25) of the two diamines, BIA and TFDB, with BTDA via a one-pot synthetic method, as shown in Scheme 1.

The polymerization was carried out with stoichiometric amounts of a diamine mixture and BTDA in NMP at 10 wt % of solid content. Generally, the one-pot synthetic method produces high molecular weight polyimides even from the diamine with low reactivity, if the final polyimide has sufficient solubility in the reaction solvent.^{4a} The homopolyimide from BIA and BTDA was not soluble in NMP when it was fully imidized. The homopolyimide was precipitated during solution imidization, and fully imidized polyimide could not be made through solution imidization method. However, we expect that the polyimides from the mixed diamine monomers might have sufficient solubility due to the reduced regularity of the repeating unit even though they have planar and rigid rodlike structure.

When the mixture of diamine monomers was placed in NMP, BIA was not completely dissolved in NMP at

room temperature. However, after addition of purified BTDA powder into the heterogeneous solution, the solution became homogeneous and viscous within 1 h. The poly(amic acids) were also prepared at 100 °C, but there were no differences in molecular weight of the final polyimides after solution imidization. The ring-opening polyaddition at room temperature for 4 h yielded poly(amic acid) solutions. After the solid concentration were diluted to 5 wt %, subsequent cyclodehydration by heating at 190 °C for 10 h gave the fully imidized polyimides. It has been reported that benzimidazole ring has a catalytic activity on the imidization reaction.¹⁹ Therefore, imidization was carried out by azeotropic distillation of either chlorobenzene or xylene without any catalysts. Because azeotroping agents are nonsolvents to the conventional polyimides, the maximum volume of the azeotroping agent in imidization media should be kept below 20% (v/v) to prevent premature precipitation. Chlorobenzene, due to its higher polarity, is a better azeotroping reagent than xylene for higher BIA contents. BPDA was also used as a dianhydride when the ratio of BIA and TFDB was 50 to 50, but the polymer **PI2'** was precipitated during the imidization process. The inherent viscosity of the corresponding poly(amic acid) was 1.38 dL/g, and the degree of imidization of **PI2'** determined with FTIR was 91%.²⁰

The structures of the synthesized polyimides **PI1**, **PI2**, and **PI3** were confirmed by FTIR and NMR spectroscopies. Representative ¹H NMR spectra are shown in Figure 1. FTIR spectra of the polyimides show the absorption bands at 1782 (C=O asymmetric stretching), 1728 (C=O symmetric stretching), 1370 (C–N stretching), and 720 (C=O bending) cm^{-1} corresponding

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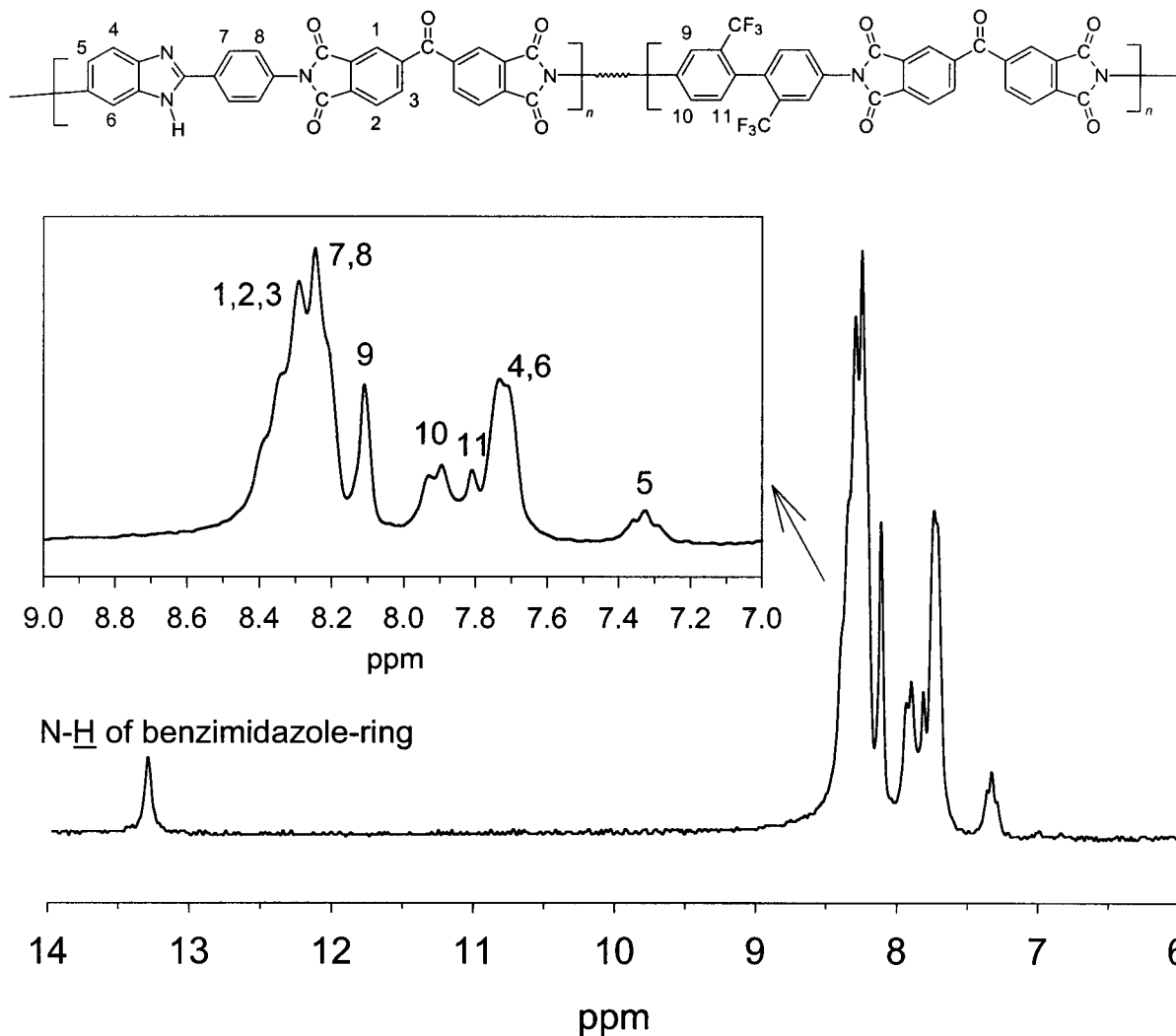


Figure 1. ^1H NMR spectrum of **PI2** (200 MHz, $\text{DMSO}-d_6$).

Table 1. Solubility of the Synthesized Polyimides^a

PIs	NMP	DMAc	DMF	DMSO	<i>m</i> -cresol	THF	CHCl_3	<i>c</i> - H_2SO_4
PI1	++	++	++	++	++	-	-	++
PI2	++	++	++	++	+	-	-	++
PI3	++	+	+	++	+	-	-	+
PI2'	+	-	-	-	+ -	-	-	+

^a ++, soluble at room temperature; +, soluble in hot solvent; + -, partially soluble; -, insoluble.

to the characteristic imide bands. Also, they show the absorption bands around 3300, 1100–1250, and 1670 cm^{-1} corresponding to the N–H stretching in the benzimidazole ring, C–F stretching, and C=O stretching from BTDA, respectively. NMR spectra were also obtained by dissolving the polyimides in methyl sulfoxide- d_6 ($\text{DMSO}-d_6$). ^1H NMR spectra are assigned as shown in Figure 1. ^{13}C NMR spectra show the peaks at 166.11 and 165.96 ($\text{C}=\text{O}$ imide), 193.34 ($\text{C}=\text{O}$ from BTDA), and 120–142 ppm (aromatic carbon).

As expected, the NMR spectra did not show any amide and acid protons as well as the corresponding carbons, indicating that the polyimides were fully imidized. Also, TGA and DSC analyses supported that the polyimides prepared by the one-pot synthetic method were fully imidized.

The solubility of the synthesized polyimides is summarized in Table 1. Though the solubility decreases as TFDB contents decreases, the synthesized polyimides

having inherent viscosities of 0.86–1.74 dL/g are dissolved well in polar aprotic solvents such as NMP, DMSO, DMAc, and NMP and phenolic solvents such as *m*-cresol. But they are insoluble in acetone, tetrahydrofuran (THF), chloroform, and chlorinated benzene. All of the prepared polyimides formed transparent and fingernail-creasable films by solution casting.

The physical properties of the synthesized polyimides are summarized in Table 2. The thermal properties were evaluated by TGA, DSC, and TMA. TGA and DSC curves are shown in Figures 2 and 3, respectively. The 5% weight loss temperatures of the polyimides are above 520 °C in both nitrogen and air regardless of the diamine composition. All of the polyimides show high glass transition temperatures (T_g 's) and low thermal expansion coefficient (CTE) due to their rigid rodlike characteristics. The T_g 's of the polymers are 320, 337, and 351 °C for **PI1**, **PI2**, and **PI3**, respectively, and the CTE in the temperature range from 50 to 300 °C are

Table 2. Physical Properties of the Synthesized Polyimides

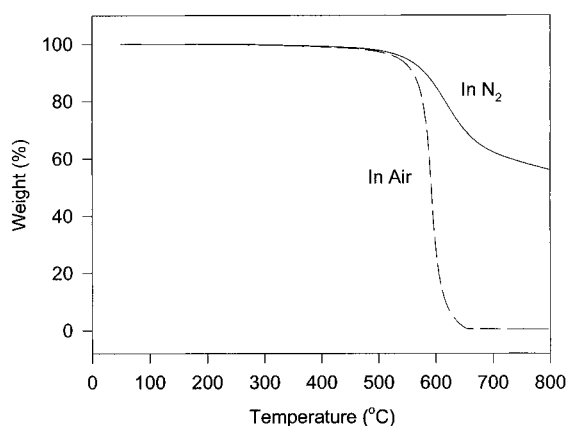
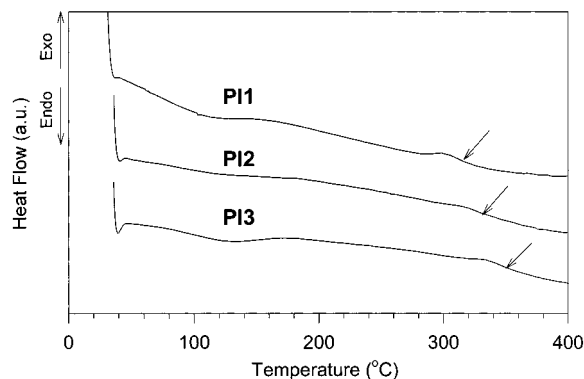
PI	η_{inh}^a (dL/g)	T_{d5}^b (°C)			T_g (°C)		CTE ^e (ppm/°C)	water absorption ^f (%)
		in N ₂	in air	char yield (%)	DSC ^c	TMA ^d		
PI1	0.86	548	535	43	320		55.3	0.57
PI2	1.51	546	533	56	337	340	43.5	0.84
PI3	1.74	540	528	61	351	353	29.6	1.18

^a Inherent viscosity measured at a concentration of 0.5 g/dL in DMAc at 30 °C. ^b The 5% weight loss temperature measured by TGA with a heating rate of 10 °C/min. ^c Measured by DSC with a heating rate of 10 °C/min. ^d Measured by TMA with a heating rate of 5 °C/min. ^e Measured by TMA in temperature range from 50 to 300 °C. ^f Weight increment of polyimide films after soaked in boiling water for 4 h.

Table 3. Optical and Dielectric Properties of the Synthesized Polyimides

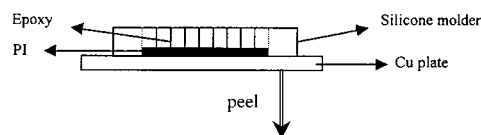
PI	optical properties ^a				dielectric properties ^b				d^c (μm)
	n_{xy}	n_z	n_{av}	Δ	ϵ_{xy}	ϵ_z	ϵ_{av}	Δ	
PI1	1.6823	1.6304	1.6560	0.0789	2.83	2.57	2.74	0.26	7.6
PI2	1.7153	1.6205	1.6837	0.0948	2.94	2.63	2.84	0.31	4.4
PI3	1.7445	1.6563	1.7151	0.0882	3.04	2.74	2.94	0.30	3.9

^a Measured at 632.8 nm (474.58 THz). ^b Estimated from refractive indices using Maxwell's equation. ^c Film thickness.

**Figure 2.** TGA curves of PI2 (heating rate, 10 °C/min).**Figure 3.** DSC curves of the polyimides (heating rate, 10 °C/min, in N₂).

55.3, 44.5, and 29.6 ppm/°C for PI1, PI2, and PI3, respectively. The increment of T_g and the decrement of CTE values with higher incorporation of BIA units may stem from the chain rigidity and the hydrogen bonding characteristics of benzimidazole rings. Water absorption of the polymers decreases as TFDB content increases but is relatively low due to the trifluoromethyl group.

Results of in-plane and out-of plane refractive index (n_{xy} and n_z) measurement at 632.8 nm are summarized in Table 3. All the synthesized polyimides have lower refractive indices (n) than the conventional polyimides such as Kapton. The polyimide with higher content of trifluoromethyl groups has lower refractive index, presumably because of the low polarizability of fluorine.

**Figure 4.** Schematic diagram of the 90° peel test.

And also the synthesized polyimides show slightly higher n_{xy} than n_z . For the most of the polyimides, n_{xy} is higher than n_z because the polarizability along the chain axis is higher than that of normal to the chain axis.²¹ The low Δ of the synthesized polyimides may stem from the twisted structure of the diamine containing two trifluoromethyl groups, which interrupts efficient packing and increases free volume.

Dielectric constants (ϵ) of the synthesized polyimides were estimated from the measured n values using Maxwell's equation ($\epsilon = n^2$). All of the synthesized polyimides have relatively low ϵ and anisotropy (Table 3).

The adhesion to the interconnecting metal is a factor critical to the interlevel dielectric application, as previously described. Benzimidazole ring is known to promote adhesion to copper, but usually the polymers containing fluorine groups have poor adhesion property to most substrates.²² Because the synthesized polymers have both the benzimidazole rings and the trifluoromethyl groups, it is interesting to see which functional group has more effect on the adhesion of the polyimides. The adhesion test to copper was conducted by a 90° peel test, as shown in Figure 4. The locus of failure was not the interface of epoxy and polyimides but that of copper and polyimides.

The results of the adhesion test illustrated in Figure 5 show that the polyimides have the peel strength values ranging from 140 to 390 N/m. The polymers containing more BIA units show better adhesion to copper due to a higher number of benzimidazole rings. Even the incorporation of only 25 mol % of BIA enhances the adhesion to copper significantly, resulting in better

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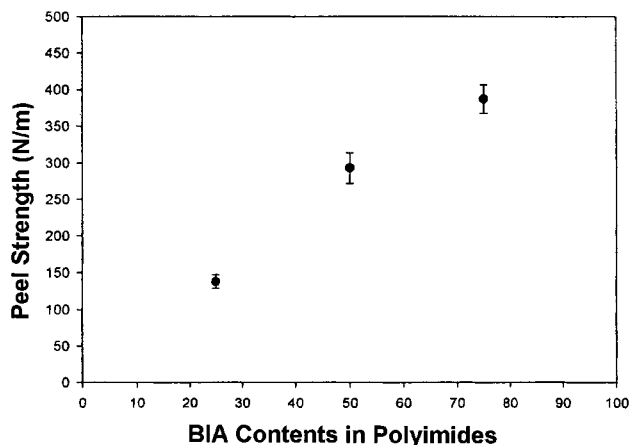


Figure 5. Results of the adhesion to copper by the 90° peel test.

adhesion property of the polyimides than that of Kapton, which has a peel strength less than 100 N/m without adhesion promoter. Previously reported poly(arylene ether benzimidazole) consisting of imidazole rings and aryl ether bonds has excellent adhesion property to copper. When it was utilized as an adhesive layer between polyimide and copper, it showed the adhesion strength over 440 N/m in the 90° peel test,²³ but its glass transition temperature is lower than the polyimides, and the water absorption value is quite high (4%).²⁴ Since the peel strength of 300 N/m or greater is

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acceptable to most microelectronic applications,^{24a} the polyimides containing more than 50 mol % of BIA are good candidates for interlevel dielectric applications without any adhesion promoter.

Conclusions

New rigid rodlike polyimides were synthesized from the two diamines, TFDB and BIA, with BTDA by using a one-pot synthetic method. In the case of the polymerization with BPDA, the polymer was precipitated during imidization. However, the polymerization with BTDA produced the fully imidized soluble polyimides, and the fingernail-creasable, transparent films were obtained. The polyimides show excellent thermal stability and T_g over 300 °C. They have relatively low coefficient of thermal expansion, moisture absorption, and dielectric constant. All the polyimides prepared have a superior adhesion property to copper than Kapton without any adhesion promoter. The polyimides containing higher BIA units showed lower thermal expansion and higher adhesion to copper.

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