

Synthesis and Characterization of Soluble Polyimides Containing Phthalazinone and Bicarbazole Moieties in the Main Chain

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ABSTRACT:

Soluble aromatic polyimides with good comprehensive properties are favorable for their applications. A novel aromatic diamine, bis(N-4-amine-phenyl)-3,3'-bicarbazole was synthesized and characterized. The structure of the diamine was determined via IR and ¹H-NMR spectroscopy and elemental analysis. A series of soluble polyimides were prepared from the diamines and dianhydrides by one-pot solution polymerization in sulfolane. Experimental results indicated that all the polyimides had excellent thermal stability. The glass transition temperature was between 295 °C and 304 °C, the temperature at 5% weight loss were all higher than 505 °C in nitrogen. The polyimides exhibited excellent solubility in a variety of organic solvents, such as *N*-methyl-2-pyrrolidinone (NMP), *m*-cresol, and *N,N*-dimethyl acetamide (DMAc). The polyimide solutions in NMP were processed into flexible films which exhibited good adhesive property (2.32 ~ 3.42 N mm⁻¹) and showed predominantly amorphous nature measured by wide-angle X-ray diffraction. These free-standing films held dielectric constants of 3.08-3.26 (100 kHz) and low water absorption in the range of 0.92-1.06%. These outstanding properties make the obtained polyimides good candidates for the fields of microelectronics or processable high-temperature engineering plastic.

Key words: Polyimides; Thermal properties; Diamine; Phthalazinone; Bicarbazole

INTRODUCTION

Aromatic polyimides are useful high performance polymers, which exhibit excellent mechanical properties, high thermal stability, low dielectric constants and electrical properties.¹⁻³ They have been widely applied in the aerospace, microelectronics, adhesives, gas separation membranes, composites and so on.⁴⁻⁸ However, most of the polyimides are difficult to process because they are infusible at the common processible temperature and insoluble in the common organic solvents.⁹ Conventional processing techniques generally involve preparing the poly(amic acid) precursors and then converting into polyimides by thermal or chemical imidization. Unfortunately, a series of problems can be caused by thermally and hydrolytically unstable of the poly(amic acid)s. Besides, voids in bulk materials can be formed when the water evolves during imidization. Therefore, it is important to synthesize soluble polyimides in fully imidized form without destruction of their own excellent properties.¹⁰⁻¹⁴ Furthermore, the use of soluble polyimides is capable of forming cover films on foils with simple casting processes at lower temperatures simply for solvent evaporation.

Considerable research approaches of synthesis soluble polyimides include introduction of flexible or kinked linkages,¹⁵⁻¹⁷ bulky lateral substituents,¹⁸⁻²⁰ crank, non-coplanar structures²¹⁻²³ into the polymer backbone. Furthermore, copolycondensation is one of the possible ways which could disrupt the

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symmetry or reduce regularity.²⁴⁻²⁶ Among these methods, introducing crank, non-coplanar groups into polyimide backbones has been considered to be efficient, which can impart solubility and not reduce thermal stability. Recently a lot of research efforts have been focused on synthesizing of new diamine or dianhydride monomers with crank, non-coplanar structure. These structural modifications have led to new polyimides with good solubility, excellent thermal properties and other desirable properties.

In the present paper, a new aromatic diamines, bis(*N*-4-amine-phenyl)-3,3'- bicarbazole was synthesized and characterized. A series of new soluble and thermally stable polyimides based on diamine monomers containing non-coplanar structure with phthalazinone and bicarbazole moieties, was prepared as expected to modify their solubility, due to increasing the disorder of the chains, accompanied by having still high glass transition temperature (T_g). Our results has shown that herein the reported polyimides exhibited good solubility, excellent thermal properties and high adhesive properties.

EXPRIMENTAL

Materials

The dianhydride monomers, 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA,99%) and 2-bis[4-(3,4-dicarboxyphenoxy) phenyl] propane dianhydride (BPADA, 99%) were recrystallized from acetic anhydride and then dried in vacuo at 120 °C for 24 h before used. *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethyl acetamide (DMAc), toluene and sulfolane were purified by distillation under reduced pressure over calcium hydride and stored over 4Å molecular sieves. Bicarbazole and 1,2-Dihydro-2-(4-aminophenyl) -4-[4-(4-(aminophenoxy) phenyl)](2*H*)phthalazin-1-one (DHPZDA) were synthesized according to the literature, respectively.^{27,28} The other reagents were used without further purification.

Instruments

Infrared measurements were recorded on KBr pellets with a Thermo Nicolet Nexus 470 Fourier transform infrared (FT-IR) spectrometer over the range of 400-4000 cm^{-1} . ^1H - NMR spectra were obtained with a Varian Unity Inova 400 spectrometer at an operating temperature of 25 °C using DMSO- d_6 as a solvent and were listed in parts per million downfield from tetramethylsilane (TMS). Elemental analysis was carried out by an ario EL III elemental analyzer. Thermo gravimetric analysis (TGA) was investigated on a Mettler TGA/DTA851 thermo gravimetric analysis instrument in a nitrogen atmosphere at a heating rate of 20 °C min^{-1} from 100 to 800 °C. The glass transition temperature (T_g) was recorded on a Mettler DSC822 differential scanning calorimeter in nitrogen at a heating rate of 10 °C min^{-1} from 50 to 350 °C. GPC analyses were carried out on a HP 1090 HPLC equipped with 5 mm Phenogel columns (linear, 4×500 Å) arranged in series with chloroform as solvent and a UV detector at 254 nm. And the values were calibrated versus polystyrene standard. Inherent viscosities (η_{inh}) of the polymers were measured by Ubbelohde capillary viscometer in NMP at a concentration of 0.5 g dL^{-1} at 25 °C. Wide-angle X ray diffraction (WAXD) was measured at room temperature on a Shimadzu XRD-6000 automatic X-ray diffractometer with NI-filtered Cu Ka radiation. The rotated velocity of the goniometry was 4° min^{-1} . The copper/polyimide laminate samples were cut into strips with dimensions of 10 mm ×100 mm. All peel tests were performed three times for each sample and the reported values were the average. Surface and volume resistances were measured with film specimens 80 mm in diameter and 50 μm thick on an EST121 micrometer of current instrument at room temperature. The

dielectric constants of the polyimide films were detected by the parallel plate capacitor method using a HP4194A Impedance/Gain phase analyzer at a frequency of 100 kHz, and calculated on the base of the measured capacitance data using the following equation:

$$\varepsilon = CL/\varepsilon_0 A \quad (1)$$

Where C is the capacitance, ε_0 is the permittivity of free space ($= 8.85 \times 10^{-12}$ MKS unit), L is the film thickness and A is the electrode area, respectively.

Water absorption (W_A) was performed by immersing the polyimide film into water at 25 °C for 24 h. Then the film was taken out, wiped with a cotton paper very quickly, and weighed on a microbalance. Water uptake was calculated from equation:

$$W_A = (W_0 - W) \times 100 \% \quad (2)$$

Where W and W_0 are the weights of dry and corresponding water swollen films, respectively.

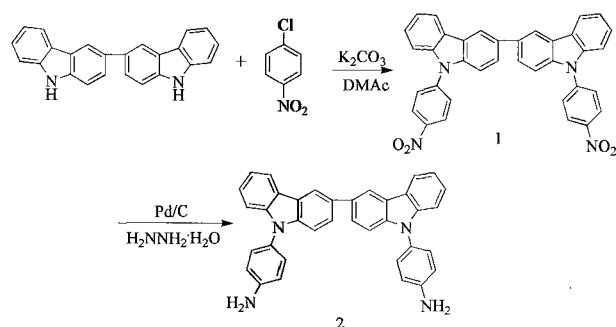
Synthesis of diamine containing bicarbazole moieties

Synthesis of bis(*N*-4-nitro-phenyl)-3,3'-bicarbazole(BCZDN)

The Synthesis of bis(*N*-4-nitro-phenyl)-3,3'-bicarbazole (BCZDN) was carried out in a 250-mL three-necked round bottom flask equipped with a mechanical stirrer, a nitrogen inlet, a Dean-Stark trap with a condenser and a nitrogen outlet. A mixture of 3,3'-bicarbazole (6.648 g, 2 mmol), 4-chloro-nitrobenzene (7.878 g, 5 mmol), potassium carbonate (4.140 g, 5 mmol) of DMAc (100 mL) and toluene(50 mL) was heated to 150 °C for 8 h to ensure complete dehydration. After removing toluene, the mixture was heated to 160 °C for 2 h under a nitrogen atmosphere, and then poured into 1 L of ethanol. The crude product was recrystallized from DMAc to give yellow power (10.660 g, 92.86%), mp: 346~348 °C. FT-IR (KBr, pellet): 1500, 1320 cm^{-1} (-NO₂ stretching), 1220 cm^{-1} (C-N-C stretching), 852 cm^{-1} (C-NO₂ stretching). ¹H-NMR (400 MHz, DMSO-*d*₆, δ): 8.76 (s, 2H), 8.56, 8.54 (d, 4H). Elemental analysis: Calcd for C₃₆H₂₂N₄O₄ (574.60): C, 75.25%; H, 3.86%; N, 9.75%. Found: C, 74.84%; H, 3.76%; N, 9.35%.

Synthesis of bis(*N*-4-amine-phenyl)-3,3'-bicarbazole (BCZDA)

The intermediate dinitro compound 1 (5.746 g, 1 mmol) and 5% Pd/C (0.1 g) were suspended in a 250-mL three-necked, round-bottom flask containing 200 mL of methyl glycol. The mixture was heated to reflux, and added dropwise with 80% hydrazine monohydrate (15 mL) over 1 h. The darkened solution was filtered hot to remove Pd/C after a further 4 h of refluxing. The filtrate was distilled to remove some solvent. After being poured into 1 L of deionized water, the grey precipitate was collected by filtration and dried under vacuum at 60 °C for 12 h. The crude product was purified by recrystallizing from isopropanol/DMF (5:1) to provide white powder diamine 2 was obtained (3.660 g, 71.19%), mp: 172~174 °C. FT-IR (KBr pellet): 3452, 3373 cm^{-1} (NH₂, stretching), 1325, 1230 cm^{-1} (C-N stretching). ¹H-NMR (400 MHz, DMSO-*d*₆, δ): 8.63 (s, 2H), 7.41 (s, 2H), 6.82, 6.84 (d, 4H), 5.54(s, 4H). Elemental analysis: Anal. Calcd for C₃₆H₂₂N₄H₄: C, 84.02%; H, 5.09%; N, 10.89%. Found: C, 83.86%, H, 5.18%; N, 10.82%.

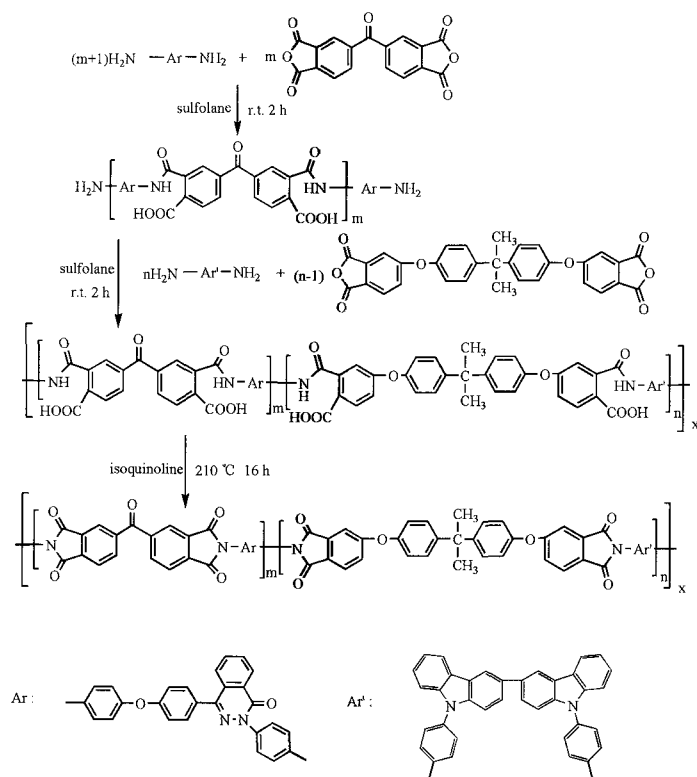


Scheme 1. Synthesis of aromatic diamine BCZDA

Synthesis of the polyimides

The polyimides were prepared by one-pot polycondensation procedure, as illustrated in Scheme 2. The number in the sample name was listed as table 1. All of the polyimides were synthesized with similar methods.

The general procedure for the preparation of the polyimides was shown as follows. Diamine DHPZDA (1.02 mmol) and dianhydride monomer BTDA (1.0 mmol) were firstly dissolved in 8.0 mL of sulfolane in a 100 mL three-necked round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube. After the mixture was stirred at room temperature for 2 h, BCZDA (1.0 mmol) and BPADA (1.02 mmol) with 7.0 mL of sulfolane were added together into the above reaction solution, and the resulting mixture was further stirred for 2 h at room temperature. Then isoquinoline (catalyst, several drops) was added and the mixture was heated to 210 °C for another 16 h. Water formed during the imidization was continuously removed with a stream of nitrogen. At the end of the reaction, the mixture was cooled and precipitated into 300 mL ethanol. The polymer was separated by filtration and washed with ethanol for several times and dried in a vacuum oven at 120 °C for 10 h.



Scheme 2. Synthesis of the polyimides

Preparation the polyimide films and their flexible copper clad laminates

The polyimides were dissolved in NMP at a concentration of 10 wt% and then filtered through buchner funnel. One portion of the filtered solutions was cast on a glass plate and dried at 100 °C for 10 h. The prepared films were peeled from the plates and dried in a vacuum at 100 °C for 24 h. Another portion was cast on copper foil laminate and dried at 100 °C for 10 h and then at 150 °C for another 24 h.

RESULTS AND DISCUSSION

Monomer synthesis and characterization

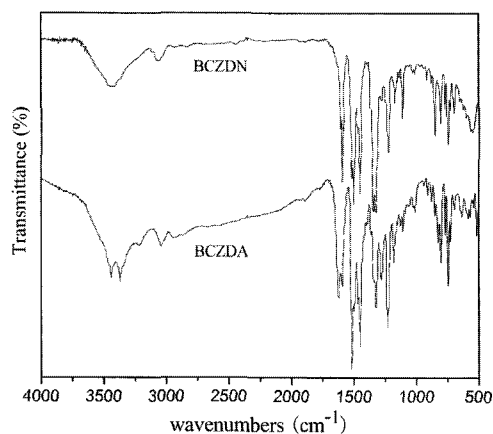


Figure 1. FT-IR spectra of the intermediate

BCZDN and diamine BCZDA. Dinitro compound showed two characteristic absorptions at 1500 and 1320 cm^{-1} (NO_2 asymmetric and symmetric stretching). The characteristic absorptions of the nitro groups disappeared after reduction. Furthermore, the amino groups gave the pair of N-H characteristic absorptions at the region of 3300-3500 cm^{-1} . Figure 2 shows the $^1\text{H-NMR}$ spectra of BCZDA, and the assignments of each proton are given in Figure 2. The amine proton appeared at 5.44 ppm was observed. Moreover, the elemental analysis result was good confirmation of the calculated values for the all proposed chemical compositions. As shown in Figure 3, the molecular model of diamine was simulated by chemoffice, which demonstrated obvious non-coplanar structure. Therefore, the structure of diamine was designed to endow some desired properties to the objective polyimides, such as good solubility and thermal stability.

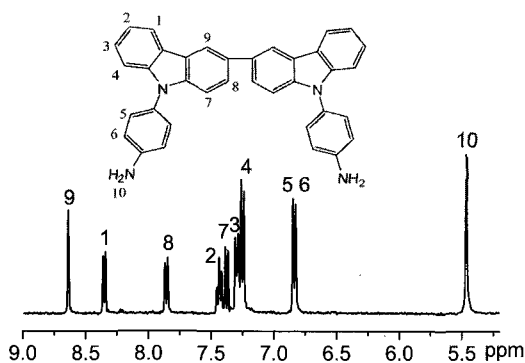


Figure 2. $^1\text{H-NMR}$ spectrum of the diamine BCZDA (in DMSO-d_6)

As shown in Scheme 1, BCZDA was synthesized via a two-step reaction using 3,3'-bicarbazole and 4-chloro-nitrobenzene as starting materials. Firstly, the carbazole-based dinitro compound BCZDN was synthesized by nucleophilic substitution reaction in the presence of potassium carbonate in DMAc. Then the diamine BCZDA was obtained by hydrazine Pd/C-catalyzed reduction in methyl glycol at 100 °C. A polymer-grade diamine was obtained by recrystallizing from DMF/isopropanol with a yield of 71.19%. Figure 1 compares the FT-IR spectra of the intermediates BCZDN and diamine BCZDA.

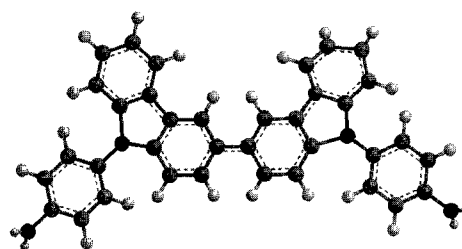


Figure 3. The molecular model of

Polymer synthesis and characterization

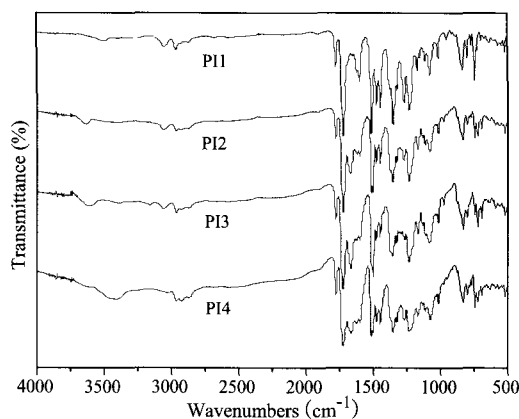


Figure 4 FT IR spectra of the polyimides

As shown in Table 1, the soluble polyimides had high inherent viscosities of 0.94~1.25 dL/g. According to GPC data, the number-averaged molecular weights (M_n) of these polyimides were $1.05 \sim 2.76 \times 10^4$. Their molecular weight distribution index (MDI) of them was ranged from 2.3 to 5.2.

Table 1. Inherent viscosities and GPC molecular weights of the polyimides

Polyimides	BCZDA:BPADA:DHPZDA:BTDA (molar ratio)	η_{inh}^a (dL/g)	M_n^b ($\times 10^4$)	M_w^b ($\times 10^4$)	MDI ^c
PI1	1:1:0:0	0.94	1.05	2.40	2.3
PI2	2:2:1:1	1.25	2.76	14.16	5.1
PI3	1:1:1:1	1.08	1.88	6.75	3.6
PI4	1:1:2:2	1.13	2.11	10.94	5.2

^a Measured in NMP at a concentration of 0.5 g dL⁻¹ at 25 °C.

^b Measured by GPC using CHCl₃ as an eluent and polystyrene as standard.

^c PDI= M_w/M_n .

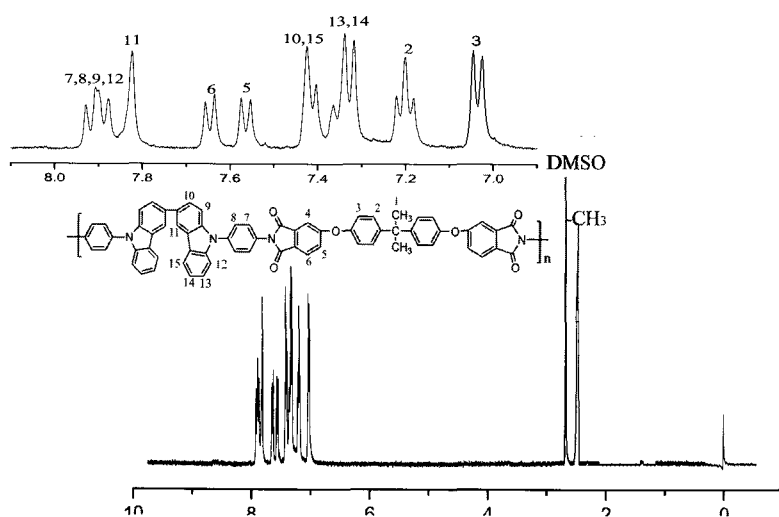


Figure 5. ¹H-NMR spectrum of the PI1(in DMSO-*d*₆)

The polyimides were prepared via the one-pot method in sulfolane at 210 °C (Scheme 2). The formation of polyimides was confirmed by IR and ¹H-NMR spectroscopy. The FT-IR spectra of polyimides PI1-PI4 is illustrated in Figure 4. All polyimides showed the characteristic imide absorptions around 1780 and 1720 cm⁻¹ (imide carbonyl asymmetrical and symmetrical stretchings), and 1380 cm⁻¹ (C-N stretching). No characteristic band of polyamic acid (1680 cm⁻¹) was found. Figure 5 describes ¹H-NMR spectrum of polyimide PI1, and the assignments of each proton are given in Figure 5. The spectrum generally agrees with the proposed polymer structure.

Polymer solubility

The solubility of these polyimides was tested in various organic solvents by dissolving 10 mg of polymers in 1 mL of solvent at room temperature or upon heating, as shown in Table 2. All the obtained polyimides could be soluble in polar organic solvents at room temperature, such as NMP, DMAc and *m*-cresol. Comparison of the solubility of these polyimides, we

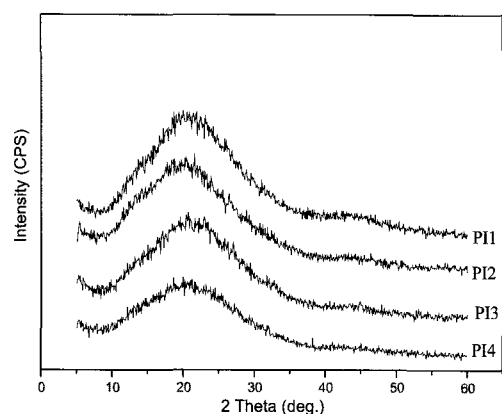
could know that polyimides with phthalazinone structure show an enhanced solubility in organic solvents by the virtue of the twisted non-coplanar phthalazinone structure, which increased the chain-packing distances, reduced the intermolecular interactions of macromolecular chains.²³ The solubility of the polyimides decreased with the increasing bicarbazole contents. The result can be explained by the more rigid molecular structure of the diamine BCZDA than that of DHPZDA.

Table 2. Solubility of the polyimides in different solvents^a

Polyimides	Solvent ^b								
	NMP	m-cresol	DMAc	DMF	DMSO	Chloroform	Sulfolane	Acetone	THF
PI1	++	++	++	+	+	+	+	-	-
PI2	++	++	++	+	+	+	+	-	-
PI3	++	++	++	+	+	++	+	-	-
PI4	++	++	++	++	+	++	+	-	-

^a Solubility: ++, soluble at room temperature; +, soluble on heating; -, insoluble.

^b NMP: *N*-methyl pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.



X-Ray diffraction of the polyimides

The crystallinity of the polyimides was characterized by a Shimadzu XRD-6000 automatic wide angle X-ray diffractometer (WAXD) with Ni-filtered Cu K α radiation, the 2 θ degrees ranging from 5° to 60° using the polyimide films as samples. The WAXD result is shown in Figure 6. All of the polyimides had only one large broad peak at 10~30° without obvious peak features, indicating that the polyimides obtained were amorphous. This might be attributed to no regularly ordered structure

of the polymer backbones.

Thermal properties

The thermal analysis data of the polyimides are presented in Table 3. The T_g values of the polyimides evaluated by DSC were recorded in the range of 295~305 °C. The T_g of polyimide PI1 was higher than T_g of the polyimides prepared with similar dianhydrides those reported by other researchers.^{29,30} The high T_g values were mainly attributed to the introduction of bicarbazole moiety into the imide ring, which hindered the rotation of nitrogen atoms around the two phenyl ring, and further increased rigidity of polymer chains. As shown in Figure 7, these polyimides had no notable weight loss below 500 °C in nitrogen atmosphere. The 5% weight loss temperatures ($T_{5\%}$) were in the range of 505~526 °C and $T_{10\%}$ in the range of 542~561 °C. The amount of residue of these polymers was more than 65 % at 800 °C in nitrogen atmosphere. Among the obtained polyimides, the PI1 has higher thermal stability than other polymers which can be related to increase the content of carbazole moiety in polyimide backbones. As mentioned above, all PIs possessed excellent thermal stability.

Table 3. Thermal properties of the polyimides

Polyimides	T_g^a (°C)	$T_{5\%}^b$ (°C)	$T_{10\%}^b$ (°C)	C_d^c (%)
PI1	305	526	561	66
PI2	303	517	543	65
PI3	296	516	548	67
PI4	295	505	542	69

^a: glass transition temperature measured by DSC with a heating rate of 10 °C min⁻¹ in N₂.

^b: measured by TGA with a heating rate of 20 °C min⁻¹ in N₂.

^c: Residual weight percentage at 800 °C in nitrogen.

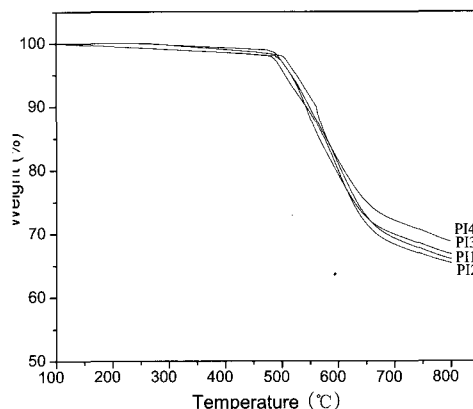


Figure 7. TGA curves of the polyimides

Adhesion properties

The adhesive properties of the polyimides were evaluated with an Instron H10KS at a peel rate of 50 mm min⁻¹. The obtained soluble polyimides could form cover films on foils with simple casting procedure at room temperature followed by distilling the solvent below 200 °C. Table 4 lists the dependence of the adhesion between the copper foil and polyimides on the composition of the polymers. The adhesion strength increased in the order of PI1 (2.32 N mm⁻¹) < PI3 < PI4 < PI2 (3.42 N mm⁻¹). Moreover, the adhesion strength between copper and polyimide thin film decreased when intermolecular distance of the polymer increased. The polyimide films exhibited good adhesion to copper without complicated surface treatment as described in literature.³¹⁻³³

Table 4. Peel strength of the polyimides

Polyimides	Peel force ^a (N)	Peel strength ^a (N mm ⁻¹)
PI1	17.5	2.32
PI2	23.8	3.42
PI3	21.4	3.08
PI4	18.3	2.57

^a Measured with an Instron H10KS at a peel rate of 50 mm min⁻¹.

Electrical properties and water absorption

Electrical properties and water absorption of the polyimide films are presented in Table 5. The polyimides presented good electrical properties with surface and volume resistances on the order of magnitude of 10¹⁵ Ω and 10¹⁷ Ω·cm, respectively. The dielectric constants of the polyimide films evaluated by capacitance method were in the range of 3.08-3.26, much lower than the standard polyimide films (PMDA/ODA 3.5).³⁴ The dielectric behavior of polymers is strongly related to their chemical structures. The change in the polarizability and free volume of the polymer molecular chains is the main reason for the alteration of the dielectric constants. A polymer with a lower polarizability or higher free volume has a lower dielectric constant.^{2,35} The low dielectric constant of the synthesized polyimides could be attributed to the introduction of the non con-planar phthalazinone and bicarbazole moieties, which loosens the chain packing and increases the molecular free volumes. Water absorption values of the polyimides films were in the range of 0.92~1.06%. The low water absorptions also ensure the polyimides with stable dielectric property. Water absorption in even small amounts can increase the dielectric constant of the polyimides because water has a quiet high dielectric constant. Furthermore, a structurally flexible polymer with bulky chemical groups showed lower water absorption than a rigid

polymer. The low dielectric constants and low water absorption of these polyimides indicate their potential applications in the microelectronics industry.

Table 5. Electrical properties and water absorption of the polyimides

Polyimides	$\rho_s^a \times 10^{-15} (\Omega)$	$\rho_v^a \times 10^{-17} (\Omega \cdot \text{cm})$	Dielectric constant ^b	Water absorption ^c (%)
PI1	1.2	0.9	3.26	1.06
PI2	1.6	1.1	3.18	0.98
PI3	1.8	1.3	3.13	0.94
PI4	1.9	1.2	3.08	0.92

^a ρ_s , Surface resistance, ρ_v , Volume resistance.

^b Measured by HP4194A Impedance/Gain phase analyzer at a frequency of 100 kHz.

^c Measured by immersing the polyimides in distilled water at 25 °C for 24 h.

CONCLUSIONS

A novel diamine with bicarbazole moiety (BCZDA), was successfully synthesized in this article, and the obtained BCZDA was employed to react with various aromatic dianhydrides by one-pot high-temperature polycondensation procedure. The introduction of bicarbazole and phthalazinone groups into polymer's main chain resulted that the novel polyimides obtained had a good balance in the solubility, thermal stability and adhesive properties. These features make our polyimides potential candidate in the field of such as cover layer material.

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