Synthesis and Characterization of Polyimides Containing Pyridine Moiety

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ABSTRACT: A series of new polyimides was prepared by reacting 2,6-diaminopyridine with various aromatic dianhydrides in DMF in 1 : 1 mole ratio. All the resulting polyimides were readily soluble in organic solvents such as dimethylformamide, *N,N*-dimethylacetamide, pyridine, *m*-cresol, THF, etc. They also show good film-forming ability. The polyimides exhibit good thermal stability and mechanical properties. The polymers have high T_g in the range of 252–296°C. The inherent viscosities of the polymers vary from 0.81 to 1.28 dL/g. A new class of bismaleimide and polyaspartimide as also synthesized. All the resulting polymer structures were characterized by FTIR and elemental analysis. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1846–1853, 2004

Key words: high performance polymers; pyridine containing; thermal properties; film properties; solubility

INTRODUCTION

The syntheses of new polyimides have been an important goal in polymer science for many years, as these polymers exhibit unique mechanical, chemical, and thermal properties. Polyimides have found usage as films, coatings, adhesives, and matrix resins because of their excellent electrical and mechanical properties, high thermal and chemical stability, good solvent resistance, and dimensional stability.[1–8] In particular, aromatic polyimides have found wide application in both microelectronics and aerospace industries as flexible circuitry carriers, stress buffers, and inter-dielectric layer, passivation layers, varnishing resin, fibers, and matrix materials.[9–12] Aromatic polyimides without sidegroups have higher molecular packing coefficient, which provides higher mechanical modulus as well as low thermal expansion coefficient and low interfacial stress. Apart from microelectronics applications, polyimides are widely used in structural applications, because of their high thermal stability. The most popular class of thermosetting polyimides is bismaleimides. The bismaleimides have more advantages in comparison to high molecular weight condensation type polyimides as they usually suffer from processing problems because of their insolubility, infusibility, and the volatiles evolved during the ring formation. Epoxy resins are widely used as matrix resin for structural composites, but they have some limitations, which restrict their utility. They have poor hot/wet performance.[16] Bismaleimides can be used as potential substitutes for epoxy resin. They play a vital role in thermosetting engineering plastic in multilayer printed circuit board in large scale for computers and as advanced composites for aerospace industries.[17–20] The double bonds in bismaleimides are highly electron deficient because of the two flanking imide carbonyl groups; the double bond can undergo Michael addition reaction with primary or secondary amine to effect chain extension prior to thermal curing to reduce the polymer crosslinking density and brittleness.[21–23] The polyaspartimides obtained have more facile properties in processing than condensation polyimides.[24,25]

In the present study, a series of polyimides containing pyridine group were synthesized by reacting 2,6-diaminopyridine with different aromatic dianhydrides. A new class of bismaleimide and polyaspartimide was also synthesized by using pyridine diamine. It is expected that the incorporation of the pyridine group in the main chain would increase the chemical, mechanical, and thermal stability, which is a vital property in the aerospace application of polyimides. So, an attempt was made to synthesize and study the polyimides, bismaleimide, and polyaspartimide-containing pyridine moiety.

EXPERIMENTAL

Materials

All dianhydrides and other chemicals of high purity were obtained from various commercial sources. 2,6-Diaminopyridine (E-Merck, Darmstadt, Germany), py-

Polyimide

a

PMDA

b

BPTDA

c

BPDA

d

ODPA

e
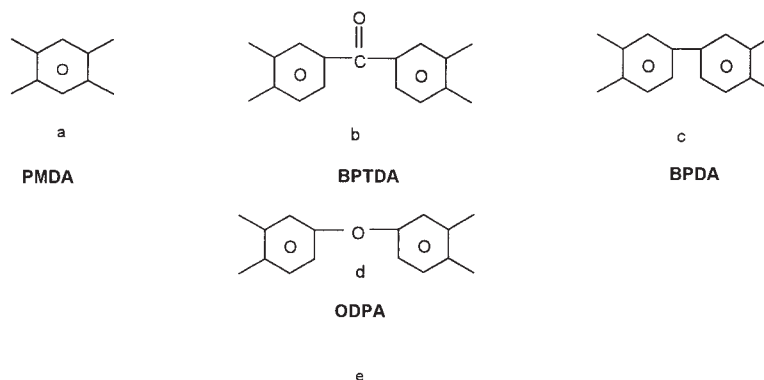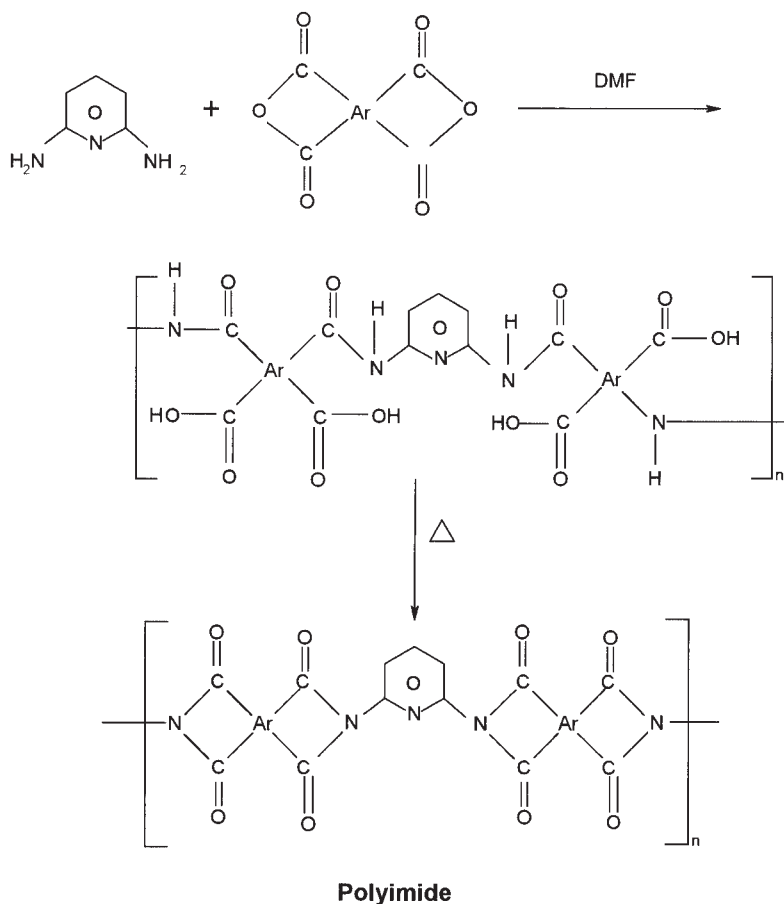
Scheme 1

romellitic dianhydride (PMDA, Sigma), 3,3′,4,4′-biphenyltetracarboxylicdianhydride (BPTA, E-Merck), 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride (BPTDA, E-Merck), maleic anhydride (Spectrochem, Mumbai, India), oxydiphthalic anhydride (ODPA, Fluka, Mumbai, India), acetic anhydride (Fluka), sodium acetate (E-Merck), N,N-dimethyl formamide (DMF, E-Merck), Tetrahydrofuran (THF, Fluka) and m-cresol (Spectrochem) were used in the present study.

Polymer synthesis

The polymer was synthesized by adopting a two-stage method involving polyamic acid intermediate, as shown in Scheme I. A three-necked flask equipped with an addition funnel and N_2 inlet was charged with a solution of 2,6-diaminopyridine 10.8 g (0.1 mol) in DMF. Then, 21.8 g (0.1 mol) of solid dianhydride (PMDA) was added at once to avoid a side reaction. The mole ratio of the diamine/dianhydride mixture was 1 : 1 and the reaction mixture was stirred at room temperature for 5 h in N_2 atmosphere to get a viscous polyamic acid solution. To this viscous solution, $\sim$ 38 ml of toluene was added and allowed to reflux at a temperature of about 150°C for 7 h. The water formed during the reaction was removed by Dean–Stark apparatus. The resulting viscous solution was cooled to

TABLE I
Elemental Analysis of Polyimides

Sample No.	Polymer	Molecular formula and weight	Carbon (%)	Hydrogen (%)	Nitrogen (%)
1	IV_a	$(C_{15}H_5N_3O_4)_n$ $(291.22)_n$	C = 61.86 F = 60.80	C = 1.73 F = 1.49	C = 14.43 F = 14.62
2	IV_b	$(C_{22}H_9N_3O_5)_n$ $(395.33)_n$	C = 66.84 F = 66.23	C = 2.29 F = 2.51	C = 10.63 F = 10.71
3	IV_c	$(C_{21}H_9N_3O_4)_n$ $(367.32)_n$	C = 68.66 F = 67.90	C = 2.47 F = 2.34	C = 11.44 F = 11.47
4	IV_d	$(C_{21}H_9N_3O_5)_n$ $(383.32)_n$	C = 65.80 F = 65.24	C = 2.37 F = 2.24	C = 10.96 F = 11.07
5	BMI	$(C_{13}H_7N_3O_4)_n$ $(269.20)_n$	C = 58.01 F = 56.90	C = 2.62 F = 2.57	C = 15.61 F = 15.58
6	Polyaspartimide	$(C_{19}H_{13}N_5O_4)_n$ $(377.34)_n$	C = 60.48 F = 60.52	C = 4.00 F = 3.84	C = 18.66 F = 18.59

C, calculated value; F, found value.

room temperature and poured into methanol to yield a pale yellow solid. It was filtered, washed, and dried in a vacuum oven at 65°C for 14 h. All other polyimides were synthesized $IV_{(b-d)}$ by adopting the same procedure mentioned above. Yield: 83%, IR (KBr, cm^{-1}). The bands at 1777, 1720 are related to an asymmetric and symmetric stretch of imide carbonyl group and those at 1100 and 720 cm^{-1} are related to vibrations of imide group; the band at 1383 cm^{-1} is due to C–N–C stretching vibrations. The IR spectra of all other polyimides are almost identical, indicating the formation of polyimides. Elemental analysis data of all polyimides are tabulated in Table I, which is in good agreement with the polymer structure.

Bismaleimide synthesis

Bismaleimide (BMI) was synthesized by a two-stage method involving bismaleamic acid intermediate. The reactions involved in the synthesis are given in Scheme II. A three- necked flask equipped with an addition funnel and N_2 inlet was charged with a solution of 19.6 g (0.2 mol) of maleic anhydride in THF. Added dropwise was 10.8 g (0.1 mole) of 2,6-diamino pyridine dissolved in THF to the above solution. Because the reaction was exothermic, the addition was carried out in an ice bath; the reaction mixture was stirred at room temperature for 5 h and then at 60°C for an additional 2 h. The reaction mixture was poured into methanol to get bismaleamic acid. The precipitate was washed with fresh THF to remove unreacted reactant. It was then dried in a vacuum at 60°C for 12 h.

To a 150-ml round-bottomed flask, 0.04 mol (12.2 g) of bismaleamic acid in 25 mL DMF was added. The solution was heated to 70°C with stirring. Acetic anhydride (35 mL) and 2.86 g sodium acetate were added to the reaction solution. The temperature of the reaction mixture was raised to 85°C and then stirred at that temperature for 6 h. The reaction mixture was poured into methanol to yield bismaleimide. The solid was washed with hot methanol and dried in a vacuum oven at 60°C for 12 h.

Yield: 92%, IR (KBr (cm^{-1}) 1775, 1714 (imide carbonyl stretch), 1383 cm^{-1} (C—N—C stretch), 691 cm^{-1} (C=C in maleimide ring). Elemental analysis of $(C_{13}H_7N_3O_4)_n$ calculated: C, 58%; H, 2.62%; N, 15.61%. Found: C, 57.98%; H, 2.59%; N, 15.58%.

Synthesis of polyaspartimide

The general procedure for preparation of linear polyaspartimide is by nucleophilic addition of diamines to aromatic bismaleimide (Michael addition reaction), as shown in Scheme II.

A 100-ml three-necked flask equipped with a magnetic stirrer, reflux condenser, thermometer, and nitrogen inlet was charged with 2.69 g (0.1 mol) of BMI in 25 ml of m-cresol. When all the BMI was dissolved, 1.08 g (0.1 mol) of p-phenylene diamine was added. Then, 0.1 ml glacial acetic acid (catalyst) was added to the mixture when all the diamine was completely dissolved. The reaction mixture was then allowed to reflux at 100–110°C for about 96 h. The resulting dark-colored, viscous solution was poured into excess methanol with vigorous stirring. The precipitated polymer was collected by filtration and washed with hot ethanol to remove the contaminated m-cresol and unreacted reactant.

Yield: 94%, IR KBr (cm^{-1}) 3380, 1620 (due to N—H stretching vibrations), 1777, 1720 (imide carbonyl stretch), 1380 cm^{-1} (C—N—C stretching vibrations). Elemental analysis of $(C_{19}H_{13}N_5O_4)_n$ calculated: C, 60.48%; H, 4.00%; N, 18.66%. Found: C, 60.52%; H, 3.84%; N, 18.59%.

BMI

+

p-phenylene diamine

Poly aspartimide
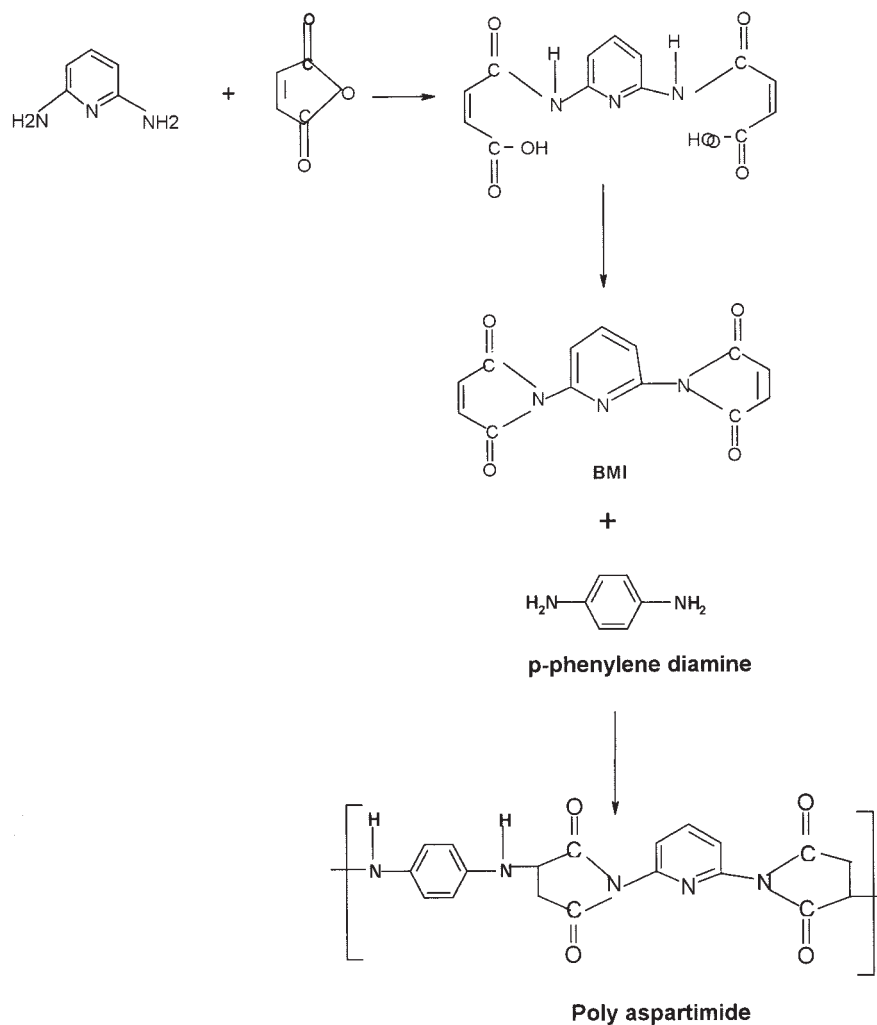
Scheme II

Measurements

The structures of all the polymers were confirmed by elemental analysis and FTIR spectra. The FTIR spectra were recorded on a Jasco IR-700 spectrometer. Elemental analysis was performed on a Carlo Erba EA 1108 microanalyzer. The inherent viscosity of all the polymers was measured by using a Ubbelohde viscometer with 0.5 g/dL in N-methyl-2-pyrrolidone (NMP) at 30°C. Differential scanning calorimetric (DSC) analysis was performed on a Perkin–Elmer differential scanning calorimeter DSC 7 at a scan rate of 20°C per minute in flowing nitrogen. Theremogravimetric analysis (TGA) was conducted with the thermal analyzer instrument TGA 2050. Experiments were carried out with ~ 10 mg of samples in flowing nitrogen at a heating rate of 20°C per minute. Mechanical properties of the films were measured with an Instron model 1130 tensile tester with a 5 kg load cell at a crosshead speed of 5 cm/min on strips approximately 30–40 μm and 0.5 cm wide with a 2-cm gauge length. Dielectric properties were studied on polymer films by the parallel plate capacitor method by using

HP-4194A Impedance/Gain phase analyzer at a frequency of 1 kHz. Gold electrodes were vacuum deposited on both the surfaces of dried films. Moisture absorption was measured by immersing the specimens in water at room temperature for 3 days and the weight difference was determined.

RESULTS AND DISCUSSION

Polymer synthesis

A new class of polyimides containing pyridine group in the main chain was synthesized by conventional two-step method starting from 2,6-diaminopyridine and different aromatic tetracarboxylic acid dianhydrides through thermal cyclodehydration, as shown in Scheme I. In this study, effects of pyridine ring in the polyimide chain were correlated. The polyimides obtained were characterized by FTIR and elemental analysis. Elemental analysis data for all the polyimides (Table I) agree with the calculated values. Figure 1
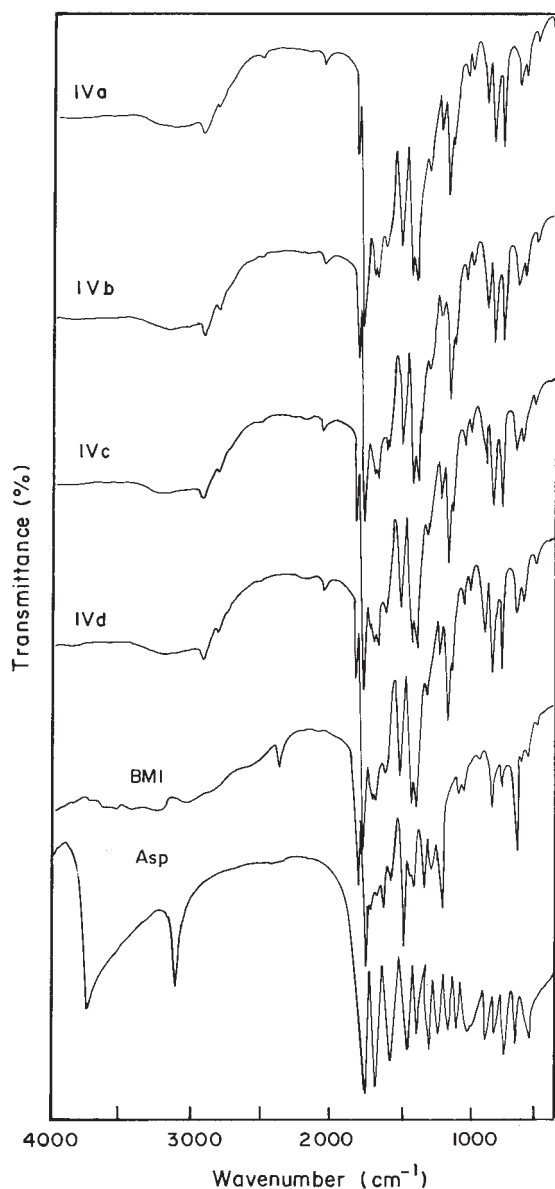
Figure 1 FTIR spectra of polyimides.

depicts the FTIR spectra of polyimides in which the absorption at 1777 and 1720 cm^{-1} is related to asymmetric and symmetric stretching vibrations of the imide carbonyl group. The band at 1383 cm^{-1} is due to

C—N—C stretching vibration and the band at 1106 cm^{-1} is due to vibration of imide ring. The FTIR spectrum of all other polyimides (IV$_{a-d}$) is almost identical, indicating the formation of polyimides.

The bismaleimide monomer was synthesized in two steps, as shown in Scheme II. The diamine was reacted with the respective amount of maleic anhydride in THF at ambient temperature to give the bismaleamic acid. The bismaleamic acid was cyclodehydrated to give bismaleimide. The absence of a band around 3400 cm^{-1} in the IR spectrum confirms the completion of reaction of diamine with maleic anhydride; the bismaleimide shows a strong absorption at 1720 and 1780 cm^{-1} because of symmetric and asymmetric carbonyl stretching vibrations of the imide ring. The structure of bismaleimide compound was confirmed by elemental analysis (Table I). The results were in good agreement with the proposed structure.

The structure of polyaspartimide was confirmed by means of elemental analysis and FTIR spectroscopy. The elemental analysis of this polymer (Table I) was found to be in good agreement with the calculated values for the proposed structure. Some of the characteristic absorption bands of IR spectrum are as follows. There is a medium intensity band at 1638 cm^{-1}, due to N—H bending, ensuring the formation of a succinimide group. The absence of a band at 690 cm^{-1} confirms the complete addition of diamine to the double bond and the band at 3370 cm^{-1} is due to N—H stretching vibrations.

Polymer solubility

The solubilities of polyimides in various test solvents were determined and is tabulated in Table II. The solubilities were determined by dissolving 0.05 g of sample in 8 mL of the test solvent at room temperature and the solution was stirred in inert atmosphere. The solubility was determined visually.

All the polyimides were completely soluble in polar aprotic solvents such as DMF, DMAc, and NMP. Depending upon the dianhydride used, the solubility varies. Polyimide (IV$_d$) was soluble in most of the test solvents, as this imide has flexible linkage in the dian-

TABLE II
Solubility of Polyimides

Sample No.	Polymer	Pyridine	NMP	DMF	CHCl$_3$	THF	*m*-Cresol	DMAc
1	IV$_a$	−	++	++	−	−	±	++
2	IV$_b$	±	++	++	−	±	++	++
3	IV$_c$	++	++	++	−	−	++	++
4	IV$_d$	++	++	++	±	−	++	++
5	BMI	++	++	++	++	++	±	++
6	Polyaspartimide	++	++	++	++	±	±	++

++, Completely soluble; ±, sparingly soluble; −, insoluble.

TABLE III
Inherent Viscosity of the Polyimides

Sample No.	Polymer	Inherent viscosity $(\eta_{dl/g})$	Film quality
1	IV$_a$	1.06	Brittle
2	IV$_b$	1.28	Flexible
3	IV$_c$	1.14	Flexible
4	IV$_d$	0.81	Flexible
5	Polyaspartimide	0.71	—

hydride. Similarly, polyimide (IV$_b$) was also soluble in test solvents because in BPTDA the bridging carbonyl group enhances the electron polarizability; hence, the solubility, while (IV$_a$) exhibits poor solubility because of the rigidity of the polymer. The bismaleimide and aspartimide exhibit good solubility in test solvents.

Inherent viscosity

The inherent viscosity of all the polyimides (IV$_{a-d}$) was measured by using 0.5 g/dL solutions in NMP at 30°C. The values of inherent viscosity of the polyimides are summarized in Table III. The inherent viscosity values were in the range of 0.81–1.28 dL/g. The inherent viscosity values indicate that high molecular weight polymers were obtained. Polyimide (IV$_a$) has high viscosity due to high molecular rigidity. The inherent viscosity of polyaspartimide was 0.71 dL/g. All polyimides exhibit good film-forming property and are creasable except IV$_a$, which may be due to high molecular rigidity of the polymer. Hence, it is brittle in nature.

Thermal properties of polyimides

DSC and TGA were used to evaluate the thermal properties of the polyimides. The thermal behavior data of polyimides are presented in Table IV. Figure 2

Figure 2 DSC curves of polyimides.

shows the DSC curves of the polyimides. The T_g values of all polyimides IV$_{(a-d)}$ recorded are in the range of 252–296°C, depending on the structure of the dianhydride used and with increasing stiffness of the polymer backbone. As expected, polyimide IV$_d$ has the lowest T_g because of the presence of flexible ether bridge. Polyimide IV$_a$ showed highest T_g as a result of the rigid pyromellitic imide unit.

DSC curves of BMI and BMI/p-phenylene diamine (1:1) blend curing characteristics were studied and the results are shown in Figure 3. In the case of BMI, an endothermic curve was observed at 280°C because of melting and an exothermic curve at 320°C was observed because of polymerization reaction of double bonds. In the case of BMI/p-phenylene diamine adduct, DSC was first scanned up to 150°C; then, the sample was quenched and rescanned. A broad endothermic peak was observed at a lower temperature of about 243°C in comparison to the neat bismaleimide.

TABLE IV
Thermal Properties of Polyimides

Sample No.	Polymer	$(T_g$ in °C$)^a$	$(T_{10}$ °C$)^b$	Char yield $(\%)^c$
1	IV$_a$	296	502	52
2	IV$_b$	283	492	48
3	IV$_c$	278	497	60
4	IV$_d$	252	473	54
5	Polyaspartimide	—	403	—

^{a} Midpoint temperature base line shift on the second DSC heating trace (scan rate = 20°C/min) of the sample after quenching from 400°C.
^{b} Temperature at which 10% weight loss was recorded by TGA at a heating rate of 20°C/min.
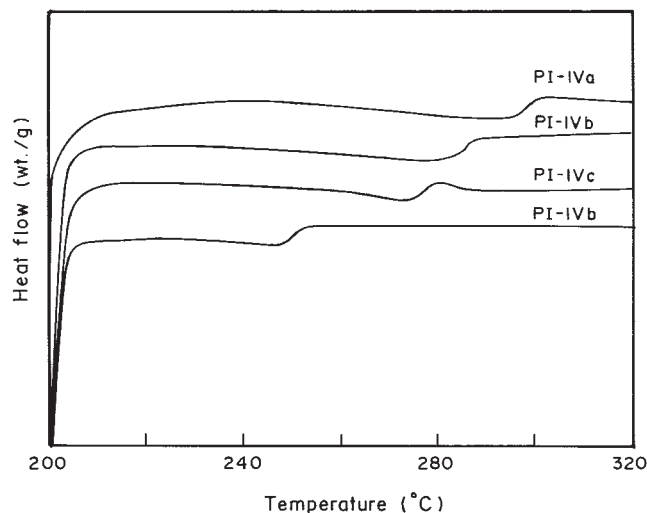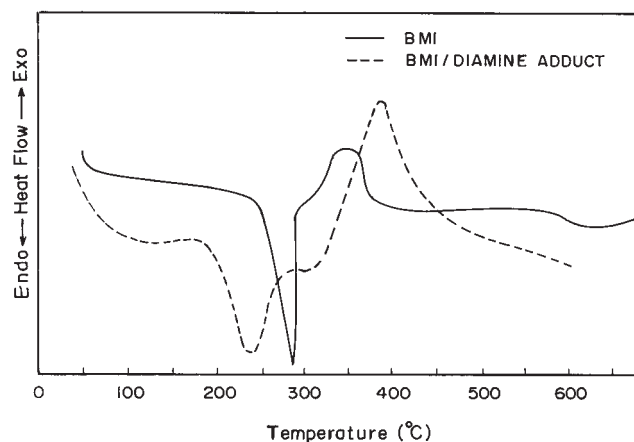^{c} Residual weight % at 800°C in nitrogen.

Figure 3 DSC curves of BMI and BMI/diamine adduct.

TABLE V
Mechanical Properties of Polyimide Films

Sample No.	Polymer	Tensile strength (mPa)	Tensile elongation (%)	Tensile modulus (GPa)
1	IV_a	—	—	—
2	IV_b	114	10	2.2
3	IV_c	96	9	1.8
4	IV_d	92	10	1.7

A similar type of phenomenon was observed by Wang and Hwang.[16] Because the maleimide double bonds of bismaleimide are electron deficient by the electron withdrawing nature of the adjacent carbonyl groups, nucleophilic addition of amines to the maleimide occurs readily at low temperature and at higher temperature the homopolymerization reaction of the maleimide double bond will occur.[26]

Thermogravimetric analysis (TGA) data of polymers are tabulated in Table V. Figure 4 shows T_{10} values of polymers, where temperature at which 10% weight loss occurs was determined from the original thermogram. The T_{10} values of the polyimides are in the range of 473–502°C in nitrogen atmosphere. The char yield at 800°C in nitrogen atmosphere was in the range of 60–48%, confirming that incorporation of the pyridine group in the main chain enhanced the thermal stability of the polymers. Figure 5 shows the thermogram of polyaspartimide in which maximum weight loss occurs (T_{max}) at 465°C, showing that the polymer has good thermal stability.

Mechanical properties of polyimides

All the polyimides afford good quality and creasable films, except polyimide IV_a, which is noncreasable; this may be due to high molecular rigidity. The tensile
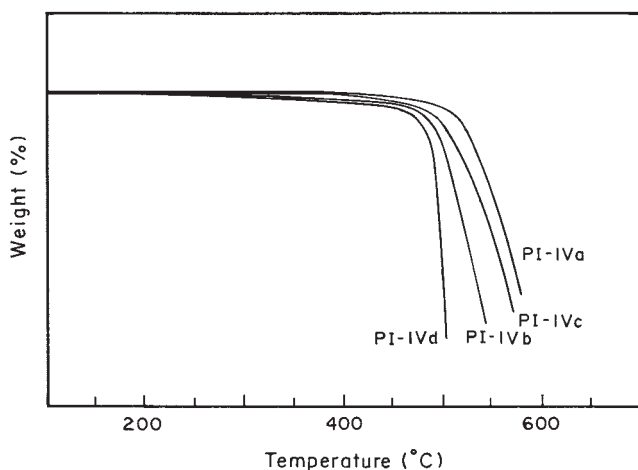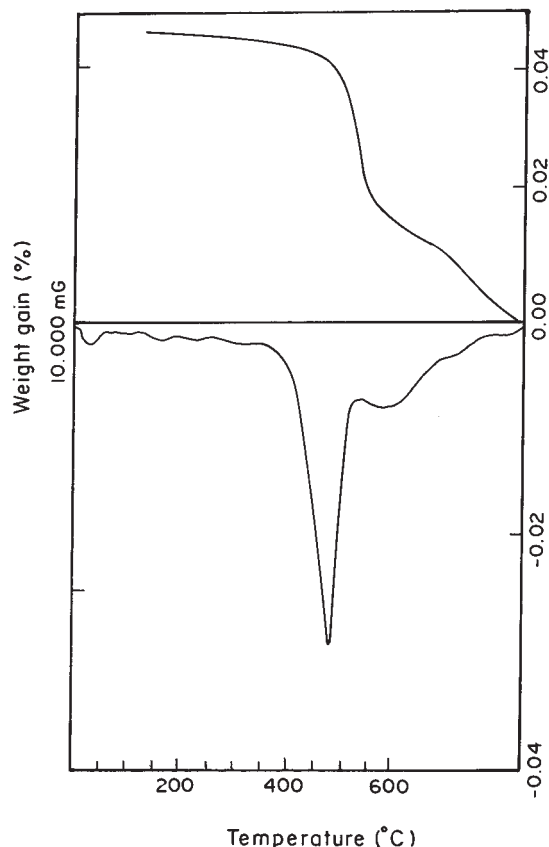

Figure 5 Thermogram of polyaspartimide.

properties of flexible films are summarized in Table V. They showed an ultimate tensile strength of 92–114 mPa, an elongation at break 9–10%, and initial modulus at 1.7–2.2 mPa. The values show that the films obtained are very tough, because elongation at break is very high (9–10%). The residual stress will be very low, which is very vital for semiconductor applications.[13]

Dielectric properties and moisture absorption

The moisture absorption and dielectric properties of the polyimide films were studied and tabulated in Table VI. The dielectric constant values of the polyimide films were in the range of 3.26–3.58, which were comparable with the standard polyimide films (PMDA/ODA = 3.5). Moisture absorption values of the polyimides films were in the range of 0.76–1.1%, which were very low in comparison to reference polyimide films (2%).

CONCLUSIONS

A new series of polyimides was prepared from 2,6-diaminopyridine and with different dianhydrides. These polyimides show good solubility, good film

Figure 4 TGA curves of polyimides.

TABLE VI
Dielectric Constant and Moisture Absorption
of Polyimides

Sample No.	Polymer	Dielectric constant	Moisture absorption (%)
1	IV$_a$	—	—
2	IV$_b$	3.51	1.1
3	IV$_c$	3.26	0.82
4	IV$_d$	3.58	0.76
5	Ref	3.5	2.0

property, and thermal stability with excellent mechanical properties; also, a new class of bismaleimide and polyaspartimide was synthesized and characterized. Polyimide films have good toughness, low moisture absorption, and comparable dielectric constant value with the reference polyimide.

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