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Synthesis and properties of novel polyaspartimides from 2,7-bis(4-maleimidophenoxy)naphthalene and aromatic diamines

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A new aromatic bismaleimide containing bis(phenoxy)naphthalene unit, 2,7-bis(4-maleimidophenoxy)-naphthalene, was synthesized from 2,7-bis(4-aminophenoxy)naphthalene and maleic anhydride by the usual two-step procedure that included ring-opening addition to give bismaleamic acid, followed by cyclodehydration to bismaleimide. The monomer was characterized by IR, ^{1}H-NMR, EA and mass spectrometry. In addition, a series of polyaspartimides containing a naphthalene unit in the polymer backbone were prepared by the polyaddition of this bismaleimide and various diamines via a Michael-type addition in *m*-cresol with glacial acetic acid as a catalyst. The polymers were characterized by EA, IR and inherent viscosity. They were amorphous and soluble in various organic solvents such as *N*-methylpyrrolidone, DMAc, DMF, DMSO. Dark-brown and brittle films were obtained by casting from NMP or DMAc solutions. The glass transition temperatures of the polyaspartimides were in the range of 192–231°C, and the 5% weight loss temperatures were above 300°C in nitrogen.

(Keywords: 2,7-bis(4-maleimidophenoxy)naphthalene; bismaleimide; polyaspartimide with naphthalene)

INTRODUCTION

Bismaleimides (BMI) are a class of thermosetting resins well known for their high thermal stability, hot-wet strength and fatigue resistance[1]. The double bonds in bismaleimide are highly electron deficient due to the two flanking imide carbonyl groups. As a result, BMI resins can be thermally selfpolymerized through their reactive maleic double bonds to give a highly crosslinked network without the formation of volatile by-products, which offers considerable advantage in processing over the conventional condensation-type polyamide. The network exhibits chemical stability, and thermal and mechanical properties superior to most epoxy resins[2,3]. They have become one of the important high-performance thermosetting engineering plastics for various applications, such as multilayer printed circuit boards for large-scale computers[4–6], advanced composites for aerospace industries[7,8], structural adhesives, potting resin, etc.

Any nucleophilic difunctional reagents can also be added to the maleic double bonds to yield linear, high-molecular-weight polyimides. The addition of hydrogen sulfide and bisthiols to bismaleimides has been reported to yield linear polyimidothioether[9–11]. The addition reaction between amine nucleophiles and maleimide unsaturation has also been investigated[12,13]. Although many studies have been devoted to bismaleimides and their polymers, none concerns bismaleimides containing a naphthalene structure. This paper reports the synthesis and characterization of a new bismaleimide containing a 2,7-substituted bis(phenoxy)naphthalene unit in the backbone. Michael addition of this bismaleimide with several diamines was carried out in *m*-cresol, to produce polyaspartimides. Incorporation of the naphthalene structure is expected to increase the thermal stability of the resultant polymer.

EXPERIMENTAL

Materials

2,7-Dihydroxynaphthalene (from Aldrich), *p*-chloronitrobenzene (from TCI), ferric chloride hexahydrate (from Ishizu), hydrazine monohydrate (from Katayama), and maleic anhydride (from Merck) were used as received. Reagent-grade aromatic diamines, such as *p*-phenyldiamine (IIIa) was sublimed at about 100°C under vacuum (2–3 mm Hg), 4,4-diaminodiphenylmethane (IIId) and 4,4-diaminodiphenylsulfone (IIIf) were recrystallized from benzene and ethanol, respectively. 9,9-Bis[4-(*p*-aminophenoxy)phenyl]fluorene (IIIh) was prepared by the condensation of *p*-chloronitrobenzene with 9,9-bis(4-hydroxyphenyl)fluorene, followed by catalytic reduction of the dinitro compound in methoxyethanol via a modified method of Kuenzel; m.p. 178–179°C (ref. 14: 177–179°C). N,N′-dimethylformamide (DMF), N,N′-dimethylacetamide (DMAc) and N-methyl-2-pyrrolidone (NMP) were purified by distillation under

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reduced pressure over calcium hydride and stored over 4A molecular sieves. *m*-Cresol was distilled and stored in a dark bottle. All other solvents were obtained from various commercial sources and used without further purification.

Monomer synthesis

2,7-Bis(4-nitrophenoxy)naphthalene. Into a reactor equipped with a stirrer, a reflux condenser, a thermometer, a Dean-Stark water separator and a nitrogen inlet were charged 250 ml of DMF, 80.05 g (0.5 mole) of 2,7-dihydroxynaphthalene, 173.35 g (1.1 mole) of *p*-chloronitrobenzene, 82.8 g (0.6 mole) of potassium carbonate, and 75 ml of toluene. The reaction mixture was refluxed at 140–145°C for 8 h under a nitrogen atmosphere. Water produced by the reaction was successively removed from the system by azeotrope with toluene. After completion of the reaction, the resulting inorganic salts were removed by hot filtration. These salts were washed with 90 ml of DMF, then the combined filtrate was heated again to 100–110°C. To the mixture, 60 ml of water were added and slowly cooled to room temperature. The crude product precipitated gradually, and was collected by filtration. The solid was washed with 500 ml of methanol, filtered and dried under vacuum. The product was recrystallized again from 2-methoxyethanol to produce green crystals. The yield was 176.9 g (88%); m.p. 167–168°C (ref. 15: 168–169°C); IR (KBr) cm^{-1}: 3100 (aromatic C–H), 1510, 1335 (N=O), 1240 (C–O–C); ^1H-NMR (DMSO-d_6) δ (ppm): 7.1–8.2 (m, 14H, aromatic); mass spectrum EI *m/e* intensity (%): 402 (100 M^+). Analysis calculated for $C_{22}H_{14}N_2O_6$: C, 65.67%; H, 3.48%; N, 6.97% found C, 65.66%; H, 3.47% N; 6.92%.

2,7-Bis(4-aminophenoxy)naphthalene (BAPN). To 34.2 g (0.1 mole) of the dinitro compound in 200 g of 2-methoxyethanol was added 2 g of charcoal and 0.18 g of ferric chloridehexahydrate. Over a period of 1 h, 50 ml of 85% hydrazine monohydrate were added to the above mixture at 100°C and then maintained at that temperature for 4 h. After the removal of active carbon, 40 ml water were added to the hot solution. Upon cooling, pale, orange coloured needles precipitated which were collected by filtration, washed well with water, and then dried *in vacuo*. The yield was 29.8 g (87.2%); m.p. 166–167°C (ref. 15: 166–167°C); IR (KBr) cm^{-1}: 3395, 1630 (N–H), 1210 (C–O–C); ^1H-NMR (DMSO-d_6) δ (ppm): 6.5–7.8 (m, 14H, aromatic), 5.0 (s, 4H, NH_2); mass spectrum EI *m/e* intensity: 342 (100, M^+). Analysis calculated for $C_{22}H_{18}N_2O_6$: C, 77.19%; H, 5.26%; N, 8.19% found C, 76.97%; H, 5.26%; N, 8.18%.

2,7-Bis(4-maleamidophenoxy)naphthalene (I). A three-necked flask equipped with an additional funnel and a nitrogen inlet was charged with a solution of 2,7-bis(4-aminophenoxy)naphthalene (34.2 g, 0.1 mole) in THF (100 ml). Under a nitrogen atmosphere, maleic anhydride (21.56 g, 0.22 mole) dissolved in THF (50 ml) was added dropwise to the above mixture. An exothermic reaction and product precipitation were observed immediately. The mixture was stirred for 4 h at room temperature and at 60°C for an additional 1 h. The yellow precipitate was collected, washed with fresh THF to remove excess maleic anhydride, and then dried in vacuum. The yield of bismaleamic acid was 52.7 g (98%); m.p. 240–241°C; IR (KBr) cm^{-1}: 3300 (N–H), 3050 (aromatic C–H), 1720 (C=O, stretching), 1540 (N–H), 1240 (C–O–C). ^1H-NMR (DMSO-d_6) δ (ppm): 10.44 (s, 2H, COOH), 7.02–7.94 (m, 14H, aromatic), 6.26–6.50 (m, 4H, olefinic); FAB mass spectrum intensity (%); 538 (18, M^+). Analysis calculated for $C_{30}H_{22}N_2O_8$: C, 66.91%; H, 4.09%; N, 5.20% found C, 66.88%; H, 4.13%; N, 5.21%.

2,7-Bis(4-maleimidophenoxy)naphthalane (BMPN, II). To a 500 ml round-bottomed flask was added 26.9 g (0.05 mole) of bismaleamic acid and 100 ml of DMF. The solution was heated to 60–65°C with stirring. Acetic anhydride (30 ml) and 2.7 g of sodium acetate (300 ml and 27 g, respectively, per mol of water condensed)[16] were added to the preheated solution. The temperature of the reaction mixture was raised to 80–90°C and then allowed to stir at that temperature for 6 h. The solution was cooled to room temperature stirring constantly and then poured into ice-water, stirring for 1 h. The precipitate was filtered, dissolved in methylene chloride and washed with a dilute solution of sodium carbonate. The organic layer was dried with anhydrous calcium chloride and then evaporated in a rotary evaporator. A pale yellow solid was obtained, 22.8 g (91%), m.p. 162–164°C. IR (KBr) cm^{-1}: 1780, 1720 (imide ring C=O), 1390 (C–N–C), 690 (C=C, maleimide ring), ^1H-NMR (DMSO-d_6) δ (ppm): 7.15 (s, 4H, olefinic), 7.18–8.00 (m, 14H, aromatic), FAB mass spectrum intensity (%): 502 (20, M^+). Analysis calculated for $C_{30}H_{18}N_2O_6$: C, 71.71%; H, 3.59%; N, 5.58% found C, 71.67%; H, 3.75%; N, 5.42%.

Polymer synthesis

The general procedure for polyaddition was as follows. To a 100 ml three-necked flask fitted with a paddle stirrer, thermometer and nitrogen inlet was charged: 5.02 g (0.01 mole) of BMPN(II), 1.08 g of *p*-phenyldiamine (IIIa), 0.2 ml of glacial acetic acid and 40 ml of *m*-cresol as a solvent. The reaction mixture was maintained at 100–105°C for 3 days with constant stirring. During this time, an increase in the solution viscosity and darkening in colour were noticed. The reaction mixture was trickled into excess methanol with vigorous stirring. The precipitated polymer was collected by filtration, washed thoroughly with methanol and dried. The polymer was ground to powder, extracted with hot ethanol using a soxhlet extractor and subsequently dried in a vacuum oven at 60°C. The polymer had an inherent viscosity of 0.2 dL/g, measured at a concentration of 0.5 g/dL in NMP at 30°C. The IR spectrum exhibited absorption at 3380, 1640 cm^{-1} (N–H), 1720 cm^{-1} (C=O). Other polymers of IV series were synthesized by an analogous procedure.

Measurements

Melting points were obtained on a polarizing microscope (Laboratory Devices MEL-TEMP. II.). The melting-point apparatus was uncorrected. Infrared (IR) spectra were recorded on a Jusco IR-810 spectrometer with KBr pellets. Nuclear magnetic resonance (NMR) spectra were obtained using a Burker WP-100 spectrometer at 200 MHz with DMSO-d_6 as a solvent and tetramethysilane as an internal standard. Elemental analyses were carried out with Heraeus CHN-Rapid elemental analyzer. Mass spectrometric analyses were performed on a VG 70-250 S GC/MS spectrometer with a solid inlet. Wide-angle X-ray diffraction patterns were obtained at room temperature (ca 25°C) on a Geiger Flex D-Max/IIIA apparatus with nickel-filtered CuK radition (40 kV, 15 mA) at a scanning rate of 2°/min. The inherent viscosities of polymers were determined with solutions of 0.5 g/dL in NMP at 30°C using an Ubbelohde suspended level viscometer. A 1% solution (w/w) was taken as measure of solubility. TMA measurements were made with a Du Pont Model 943 thermomechanical analyzer using film samples. Thermogravimetric analyses (TGA) were performed on a Du Pont 951 thermal analyzer, using a heating rate of 20°C/min in N_2 at a flow rate of 40 cm^3/min.

RESULTS AND DISCUSSION

Monomer synthesis

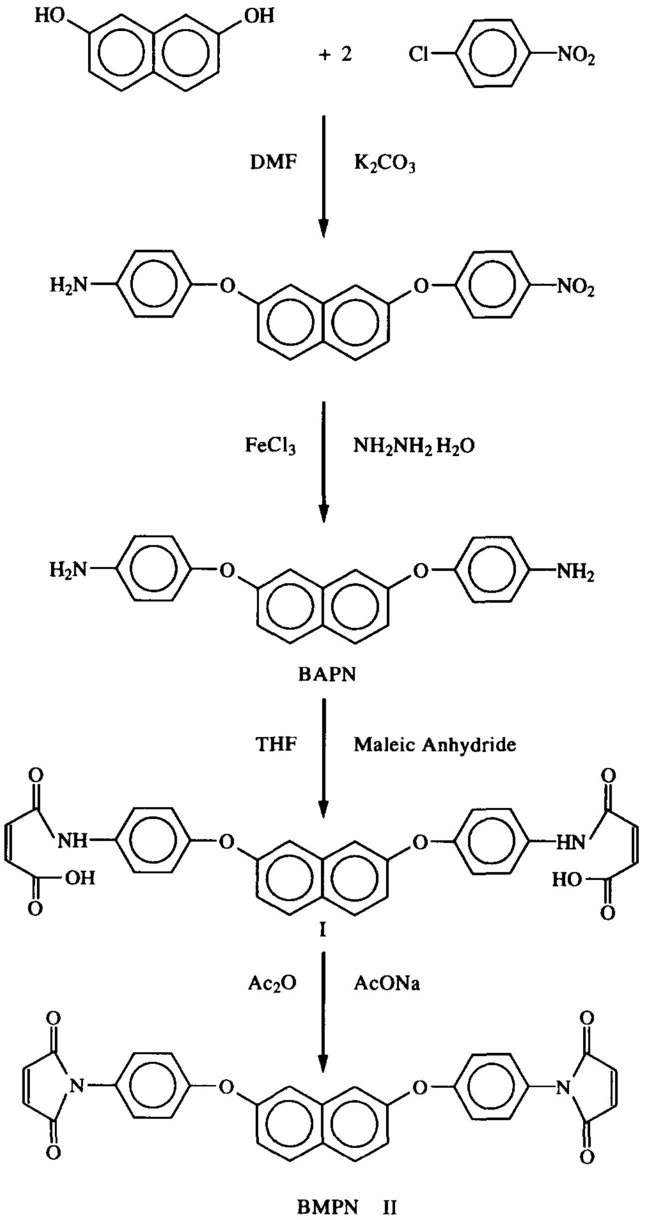
The diamine containing a naphthalene and aryl ether linkage, 2,7-bis(4-aminophenoxy)naphthalene (BAPN), was obtained from 2,7-dihydroxynaphthalene according to *Scheme 1*, according to the modified procedure of Hiroko *et al.*[17]. The diamine (BAPN) was then reacted with the respective amount of maleic anhydride in THF at ambient temperature to give the bismaleamic acid (I). The bismaleamic acid was cyclodehydrated by moderate heating, using acetic anhydride and sodium acetate in DMF. The infrared spectra of the bismaleimide (BMPN) and the corresponding bismaleamic acid (I) exhibited several distinctive differences. Bismaleimide showed a strong absorption at 1720 cm^{-1} and a weak absorption at 1780 cm^{-1}, assigned to asymmetric and symmetric C=O stretching vibration of imide ring respectively; it also lacked the absorptions at 3400–3000 cm^{-1} associated with the carboxylic OH stretching vibration and 1540 cm^{-1} for the -NH stretching of the amide group. Consequently imidization could be mointored by means of these absorptions.

Synthesis and properties of polymers

The nucleophilic addition of diamines to aromatic bismaleimide, the Michael-type addition, is a well known route to linear polyaspartimides. In the present work, 2,7-bis(4-maleimidophenoxy)naphthalene and an equivalent amount of aromatic diamines were stirred together in *m*-cresol containing a catalytic amount of glacial acetic acid to promote the polymerization (*Scheme 2*). The polymer was preciptated in methanol, then extracted with warm ethanol so as to remove the contaminated *m*-cresol and unreacted starting materials.

Inherent viscosities (η_{inh}) of the polymers are summarized in *Table 1*. Polyaspartimides IVb and IVf with lower inherent viscosities of 0.14 and 0.08, respectively, were obtained by the same polymerization procedure. The lower inherent viscosity for IVb can be attributed to the lower reactivity of the diamine monomer containing a meta-oriented amine group, and that for IVf is due to the electron-withdrawing character of the sulfone group reducing the basicity of the diamine.

The structure of polymers were confirmed by means of elemental analysis and IR spectroscopy. The results of



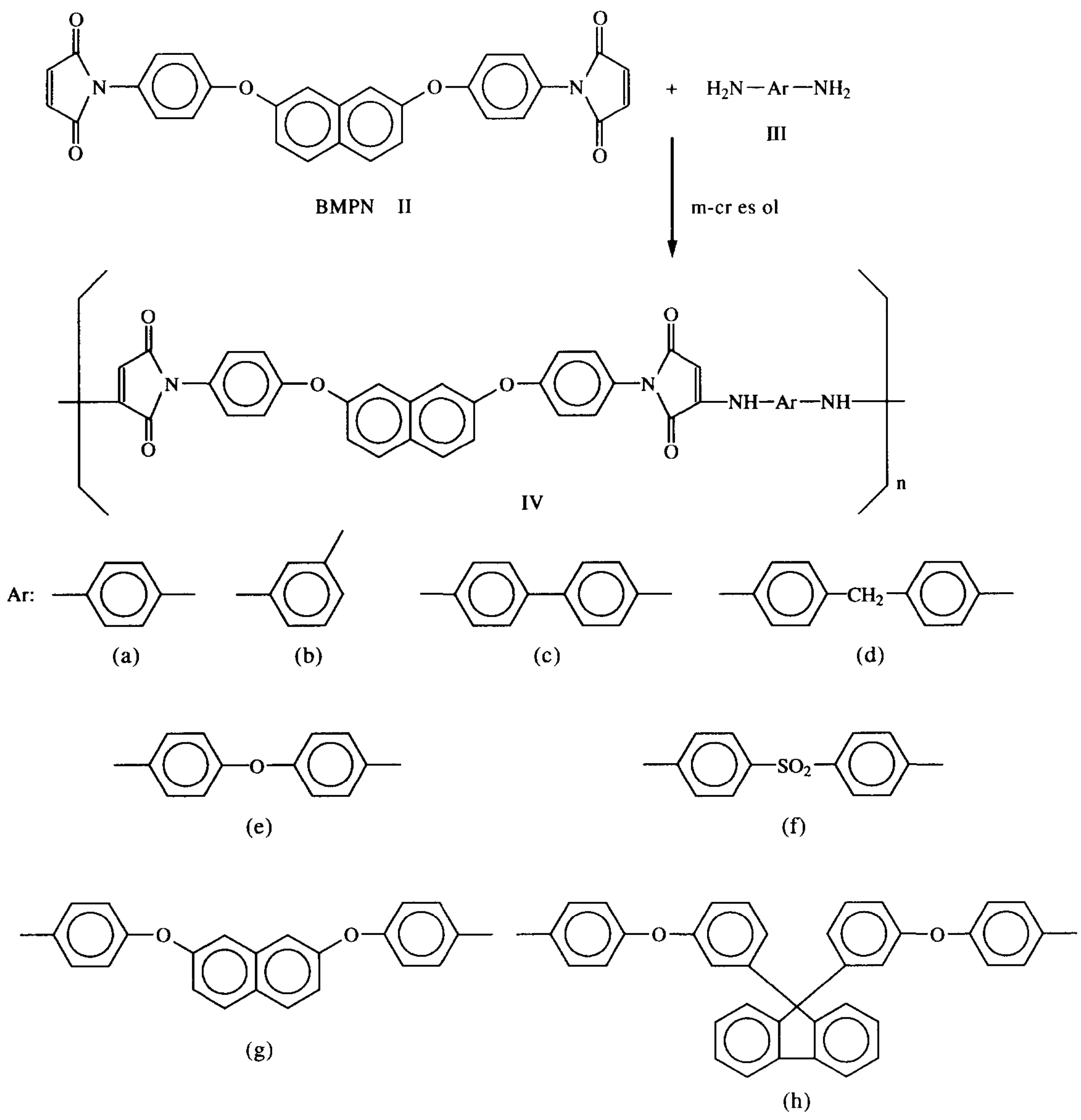
Scheme 1

Table 1 Synthesis of polyaspartimides[a]

Polymer code	η_{inh}[b] dl/g	Formula		Elemental analysis C(%)	H(%)	N(%)
IVa	0.32	$(C_{36}H_{26}O_6N_4)_n$	Calc.	70.82	4.26	9.18
			Found	69.56	4.68	9.48
IVb	0.14	$(C_{36}H_{26}O_6N_4)_n$	Calc.	70.82	4.26	9.18
			Found	70.57	4.73	9.49
IVc	0.21	$(C_{42}H_{30}O_6N_4)_n$	Calc.	73.46	4.40	8.16
			Found	73.09	5.18	7.92
IVd	0.28	$(C_{43}H_{32}O_6N_4)_n$	Calc.	73.70	4.60	8.00
			Found	71.12	5.18	7.28
IVe	0.23	$(C_{42}H_{30}O_7N_4)_n$	Calc.	71.80	4.30	7.97
			Found	70.40	4.89	6.98
IVf	0.08	$(C_{42}H_{30}O_8N_4S_1)_n$	Calc.	67.20	4.00	7.47
			Found	67.46	3.55	7.02
IVg	0.19	$(C_{52}H_{36}O_8N_4)_n$	Calc.	73.92	4.29	6.63
			Found	73.90	4.39	6.53
IVh	0.20	$(C_{67}H_{46}O_8N_4)_n$	Calc.	77.76	4.45	5.42
			Found	76.62	3.89	4.95

[a] Polymerization was carried out with 0.01 mol each of monomer and 0.2 ml glacial acetic acid in 40 ml *m*-cresol at 100–105°C, for 72 h under nitrogen

[b] Measured at a concentration of 0.5 g/dl in NMP at 30°C



Scheme 2

elemental analyses of these polymers were in good agreement with the calculated values for the proposed structures (*Table 1*). Some of the characteristic differences observed in the IR spectra of the Michael addition product compared to the spectrum of BMPN are as follows: there is a medium intensity band at 1640 cm^{-1} which might be due to -NH bending, suggesting the formation of a succinimide group; characteristic maleimide double bond at –690 cm^{-1} had disappeared[16] and a new band at –3380 cm^{-1} for -NH stretching confirmed the addition reaction of the imide ring.

Table 2 Solubility of polyaspartimide[a]

Solvent[b]	Polymer IVa	IVb	IVc	IVd	IVe	IVf	IVg	IVh
NMP	+h	++	+h	++	++	++	++	++
DMAc	+h	++	−h	++	++	++	++	++
DMF	+h	++	−h	++	++	++	+h	++
DMSO	−h	++	−h	++	++	++	+h	++
m-Cresol	−h	++	−h	+h	+h	++	+h	+h
Py	−h	++	−h	+h	+h	++	+h	+h
o-Chlorophenol	−h	++	−h	+h	−h	++	−h	+h
$CHCl_3$	−	−	−	−	−	−	−	−

[a] (++) soluble at room temperature; (+h) soluble on heating; (−h) partically soluble on heating; (−) insoluble

[b] NMP: *N*-methyl-pyrrolidone
DMAc: *N*,*N*-dimethylacetamide
DMF: *N*,*N*-dimethylformamide
DMSO: dimethyl sulfoxide
Py: pyridine

The X-ray diffraction studies revealed that the prepared polymers are amorphous, as generally found for the addition polyimides obtained via the Michael reaction. The solubilities of polyaspartimide IVa–g in various solvents were investigated and the results are summarized in *Table 2*. Most polymers were readily soluble in polar aprotic solvents such as NMP, DMAc, DMF and DMSO. Polymers containing *m*-phenylene (IVb) and aryl sulfone (IVf) were soluble even in *m*-cresol, *o*-chlorophenol and pyridine, but all of them were entirely insoluble in chloroform. Polymers IVa and IVc containing *p*-phenylene and biphenylene exhibited somewhat limited solubility, due to their symmetric and rigid structures. The high solubility of polymer IVh is attributed to the bulky fluorene unit in the main chain.

Thin films were prepared from the polyaspartimides

Table 3 Thermal properties of polyaspartimides

Polymer code	T_g[a] (°C)	T_5[b] in N_2	Char yield[c]
IVa	231	364	66.7
IVb	192	314	45.5
IVc	–	371	46.4
IVd	200	350	48.2
IVe	203	346	53.7
IVf	–	303	53.4
IVg	206	377	45.8
IVh	194	354	51.3

[a] Determined by TMA at heating rate of 20°C/min

[b] Temperature at which 5% weight loss was recorded by means of thermogravimetry at a heating rate of 20°C/min

[c] Residual weight % at 600°C in nitrogen

by casting the polymer solutions onto an alumina mould followed by an appropriate drying procedure. All polymers could be cast from NMP and DMAc. These polymers produced dark brown and brittle films. The brittleness may be due either to an innate structural effect or to the low molecular weight of the polymers. The thermal behaviour of the polymers was evaluated by means of TG and TMA. The thermal data of polymers are given in *Table 3*. Representative thermograms are shown in *Figure 1*. The glass transition temperature (T_g) of polymers IV ranged between 192–231°C, depending on the structure of the diamine component. It increased with increasing rigidity and symmetry of the diamines. The 5% decomposition temperature of the polymers ranged between 303–377°C in nitrogen. Polymer IVg, which had naphthalene rings in both bismaleimide and diamine had the highest decomposition temperature, and polymer IVa, with a *p*-phenylene structure, had the highest anaerobic char yield.

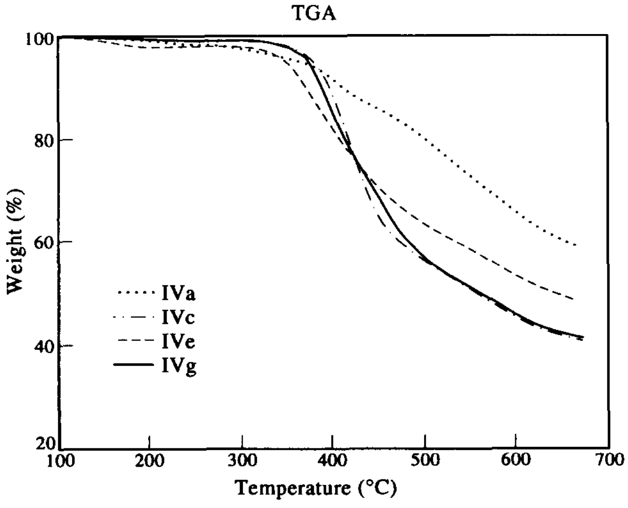


Figure 1 TG curves of some polyaspartimides

CONCLUSIONS

Novel bismaleimide containing naphthalene was synthesized and polymerized with various diamines to yield a new class of polyaspartimides. The basicity of diamine controls the reactivity of polymerization. Solubility and thermal properties of the polymers were influenced by the rigidity and symmetry of the polymer main chain. Polyaspartimides IV are stable up to 300°C in N_2 and give dark-brown brittle films.

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