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Synthesis and characterization of new polymaleamides from N,N'-bisisomaleimide and N,N'-methylenedianilinobisisomaleimide with some aromatic diamines by ring-opening polyaddition

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Polymaleamides from bisisomaleimides and diamines have been prepared by ring-opening polyaddition. These polymaleamides were found to have inherent viscosity in the range 0.30–0.42 g dl^{-1}. The identities of the polymaleamides were confirmed by elemental analysis, and i.r., u.v.–visible and ^{1}H n.m.r. spectoscopies. The thermal degradation behaviour of the polymaleamides was studied by mass spectrometry and thermogravimetric analysis; fragmentation schemes for the polymaleamides are proposed. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

Polymers possessing potential cross-linking groups can be cured to products having high thermal and chemical stabilities. The introduction of group >C=C< into a polymer backbone increases its chain rigidity[1]. The structure–property studies of polyoxadiazoles with phenylene and vinylene functions in the backbone reveal that (1) replacing the phenylene by vinylene group increases the solubility of the polymer (before curing) and (2) the wholly vinylene oxadiazole is quite similar in stability to vinylene–phenylene oxadiazole copolymer[2-4]. The main advantage of incorporating unsaturation units in the backbone of the polymer is that no volatile products are given off during the curing process; otherwise, the volatile products, if present, will naturally produce voids in the polymer, thus causing deterioration in the mechanical properties of the polymeric material[5]. When melt methods are adopted for the production of aliphatic–aromatic polyamides, the polymers frequently become discoloured and they have a branched/network structure. In the solution and interfacial procedures using a diacid chloride and a diamine, there is a competing side reaction between the solvent and the diacid chloride, forming monoalkylamide and dialkylamide[1], thus retarding the growth of the polymer. These difficulties are circumvented by employing a ring-opening technique.

Diamines undergo ring-opening polyaddition (ROPA) to various reactive heterocyclic compounds[6-11]. Bisiso-imides constitute an interesting class of potentially reactive compounds[2,13]. This paper describes the synthesis of polymaleamides by ROPA, respectively of N,N'-methylenedianilinobisisomaleimide with diamines in N-methyl-2-pyrrolidinone (NMP) containing 4% (w/v) LiCl under ambient conditions.

EXPERIMENTAL

Bisisoimides

4,4'-Diaminobibenzyl (DABB; Fluka AG) was purified by vacuum sublimation, m.p. 135°C. Aniline was purified by distillation. NMP was purified by a standard procedure[14].

3,3'-Dibromo-4,4'-diaminodiphenylmethane. Methylenedianiline (0.05 mol) was refluxed with a mixture of acetic anhydride (11 ml) and glacial acetic acid (25 ml) for 2 h and diluted with H$_2$O to precipitate the diacetyl derivative; this derivative (0.035 mol) was dissolved in glacial acetic acid (25 ml) and brominated in the presence of anhydrous sodium acetate (0.098 mol) by bromine (4 ml)

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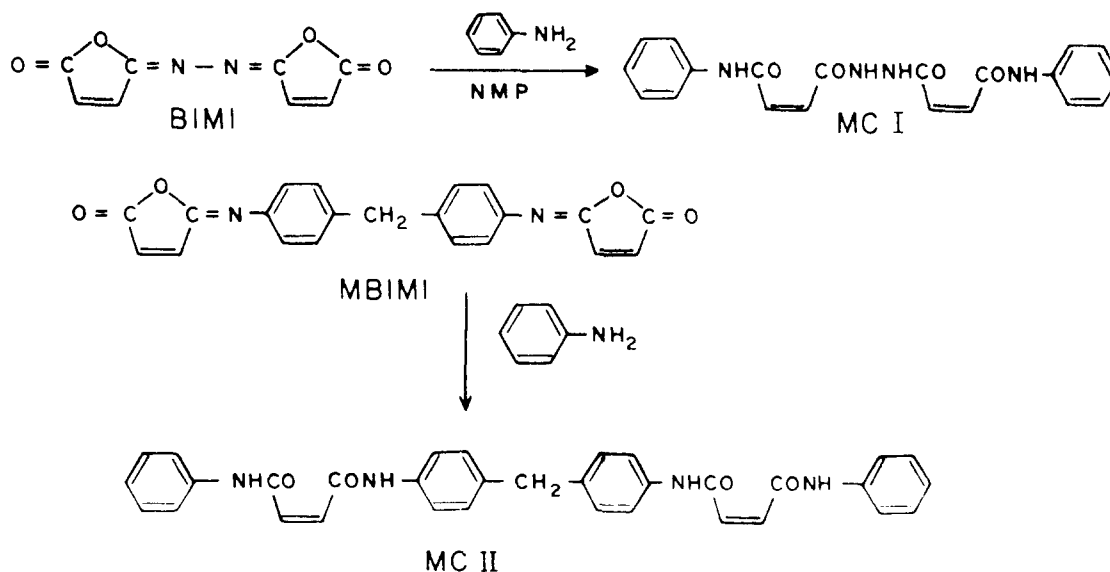
Scheme 1 Synthesis of model compounds (MC I and MC II)

in glacial acetic acid (20 ml). The excess of bromine was boiled off and the mixture was poured into ice. The dibromo derivative, dibromoacetamidodiphenylmethane, recrystallized from ethanol, was hydrolysed by refluxing with concentrated HCl in ethanol for 5 h; its hydrochloride, which separated on cooling, was recrystallized from hot H_2O by NaOH, washed and dried (yield 98%), m.p. 118°C.

N,N'-Bisisomaleimide (BIMI). A solution of hydrazine hydrate (0.1 mol) in glacial acetic acid (25 ml) was added in drops with stirring to maleic anhydride (0.2 mol) in glacial acetic acid (100 ml); during the addition and afterwards for 3 h, the temperature was maintained below 25°C. The product, 1,2-bis(3-carboxyacryloyl) hydrazine, was washed with H_2O, ethanol and dried, m.p. 185°C; this purified product (0.088 mol), dissolved in pure, dry dichloromethane (200 ml), was treated with trifluoroacetic anhydride (33.6 ml) and the mixture was refluxed for 5 h. The product, BIMI, was filtered, washed successively with water, a very dilute solution of $NaHCO_3$ and H_2O, then dried and recrystallized from *N,N*-dimethylformamide, (yield 60%), m.p. 260°C.

N,N'-Methylenedianilinobisisomaleimide (MBIMI). To an ice-cold solution of maleic anhydride (0.2 mol) in dry ether (200 ml) was added methylenedianiline (0.1 mol) in dry ether (200 ml) with stirring; the mixture was allowed to stand overnight[15]. The resulting methylenedianilinobismaleamic acid was purified[16] by dissolution in dilute $NaHCO_3$ and reprecipitation with HCl, washed with water and dried, m.p. 195°C. This amic acid (0.05 mol) was treated with 1,3-dicyclohexylcarbodiimide (0.1 mol) in a mixture of dichloromethane (50 ml) and dry ether (20 ml)[17] and allowed to stand overnight. The precipitated 1,3-dicyclohexylurea was filtered off and the product MBIMI was recovered from the filtrate by removing the solvent under reduced pressure. It was recrystallized from a 1/1 benzene/ether mixture (yield 85%), m.p. 155°C.

Model compounds

Model compounds were synthesized from each of the bisisoimides, BIMI and MBIMI (0.005 mol) and aniline (0.011 mol) employing NMP as solvent under nitrogen, allowing the reaction to proceed for 24 h. The respective reaction product was separated by adding ice–water, filtered, washed and vacuum dried. The model compounds obtained from BIMI and MBIMI are designated, respectively, as MC I and MC II (*Scheme 1*). Elemental analysis–percentage composition–experimental (calculated): for MC I ($C_{20}H_{18}N_4O_4$): C, 63.39 (63.49); H, 4.78 (4.76); N, 14.90 (18.81); for MC II ($C_{33}H_{28}N_4O_4$); C, 72.95 (72.79); H, 5.14 (5.15); N, 10.35 (10.29).

Solution polymerization

An appropriate diamine (0.005 mol) was dissolved in NMP containing 4% (w/v) LiCl in a polymerization kettle provided with a nitrogen inlet, guard tube and a mechanical stirrer. The isoimide monomer (0.005 mol) was then added rapidly to the kettle cooled in an ice–water bath without disturbing the inert atmosphere; the stirring (3500 rev min^{-1}) was continued at room temperature for 72 h to complete the slow polymerization. The polymer was precipitated with H_2O, filtered, washed successively with dilute HCl, dilute $NaHCO_3$ and H_2O and vacuum dried at 65°C (*Scheme 2*).

Analytical methods

The inherent viscosity of a 0.5 g dl^{-1} solution of the polymer in concentrated sulfuric acid (AnalaR) was determined using a modified Ubbelohde viscometer at 25°C. Elemental analyses were performed on a Perkin-Elmer 240 B analyser. The i.r. spectra of the polymers were recorded in KBr pellets on a Perkin-Elmer model 598 spectrophotometer. The electronic spectra in concentrated sulfuric acid were recorded on a Carl-Zeiss u.v.-Specord. N.m.r. spectra of the polymers in DMSO-d_6 were recorded with a JEOL FX 90 Q FT n.m.r. spectrometer; chemical shifts in δ values were obtained using tetramethylsilane as internal standard. Mass

Table 1 Data on polymers from bisisoimides and diamines[a]

Isoimide	Diamine	Polymer	Yield	η_{inh}[b] (g dl^{-1})	Repeat unit		Percentage composition		
							C	H	N
BIMI	DABB	BBBM$_c$	95	0.33	$(C_{22}H_{20}N_4O_4)_n$	Exp.	65.48	4.91	13.99
						Calc.	65.35	4.95	13.86
BIMI	DBMDA	DBBM$_d$	86	0.33	$(C_{21}H_{16}n_4O_4Br_2)_n$	Exp.	46.01	2.97	9.89
						Calc.	45.98	2.92	10.22
MBIMI	DABB	BBMBM$_e$	93	0.42	$(C_{35}H_{30}N_4O_4)_n$	Exp.	73.73	5.24	9.91
						Calc.	73.68	5.26	9.82
MBIMI	DBMDA	DBMBM$_f$	83	0.31	$(C_{34}H_{26}N_4O_4Br_2)_n$	Exp.	58.02	3.53	7.91
						Calc.	57.14	3.64	7.84

[a] Polymerization was carried out at room temperature with 5 mmol of each monomer, at a monomer concentration of 20 wt% in NMP containing LiCl (4% w/v)
[b] Measured at a concentration of 0.5 g dl^{-1} in concentrated sulfuric acid at 25°C
[c] Poly{[N-4 (4'-aminophenethyl)]-{N'-maleamido]}maleamide
[d] Poly{[N-2-bromo-4 (4'-amino-3'-bromobenzyl)phenyl]-[N'-maleamido]-[N'-maleamidol]}maleamide
[e] Poly{[[N-4 (4'-aminophenethy)phenyl]-[N'-4 (4'-maleamidobenzyl)phenyl]}maleamide
[f] Poly{[N-2-bromo-4 (4'-amino-3'-bromobenzyl)phenyl]-[N'-4 (4'-maleamidobenzyl)phenyl]}maleamide
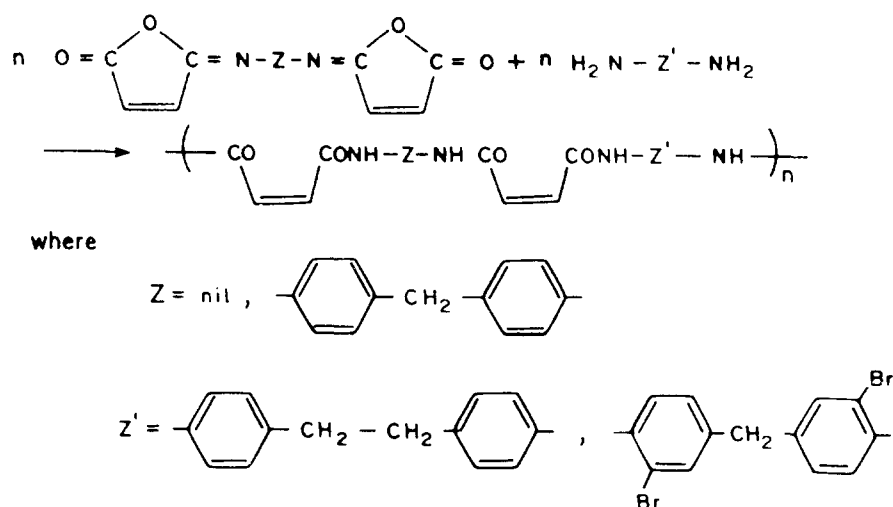
Scheme 2 Synthesis of polymaleamides

Table 2 Solubility of polymers in various solvents

Solvent/polymer	BBBM	DBBM	BBMBM	DBMBM
Concentrated sulfuric acid	+ +	− +	+ +	+ +
N-Methyl-2-pyrrolidinone	+ +	−	+ +	+
N,N-Dimethylacetamide	+ +	+	+ +	+
Dimethylsulfoxide	+	+	+ +	+
N,N-Dimethylformamide	±	+	±	+
Formic acid	−	−	−	−
m-Cresol	−	−	s	s
Tetrahydrofuran	−	±	±	±
Ethanol	−		−	−
Acetone	−	−		−

+ +, Soluble at room temperatrure; +. soluble on heating; ±, partially soluble; −, insoluble; s, swells

Table 3 Infra-red (KBr matrix) and ultraviolet–visible (conc. H_2SO_4) absorption spectral data

Sample	Infra-red. wave number (cm^{-1})			C H of *cis* C=C	U.v.–vis. λ_{max} (nm)
	NH stretching	CH_2 group	Amide I		
MC I	3320	− −	1600	695	197, 233, 320
BBBM	3240	2920, 2845	1650, 1600	645	194, 235, 386
DBBM	3360	2920, 2860	1665, 1620	675	199, 225, 365
MC II	3460	2920, 2850	1600	690	205, 288, 368
BBMBM	3315	2930, 2850	1605	640	222, 302, 376
DBMBM	3300	2900, 2840	1605	670	200, 220, 374

spectral analysis of the products obtained by vacuum pyrolysis of the polymers was carried out in a MAT 112 S instrument. The thermogravimetric studies were carried out using a Du Pont 1090 thermal analyser, in nitrogen, with a sample of 3–5 mg.
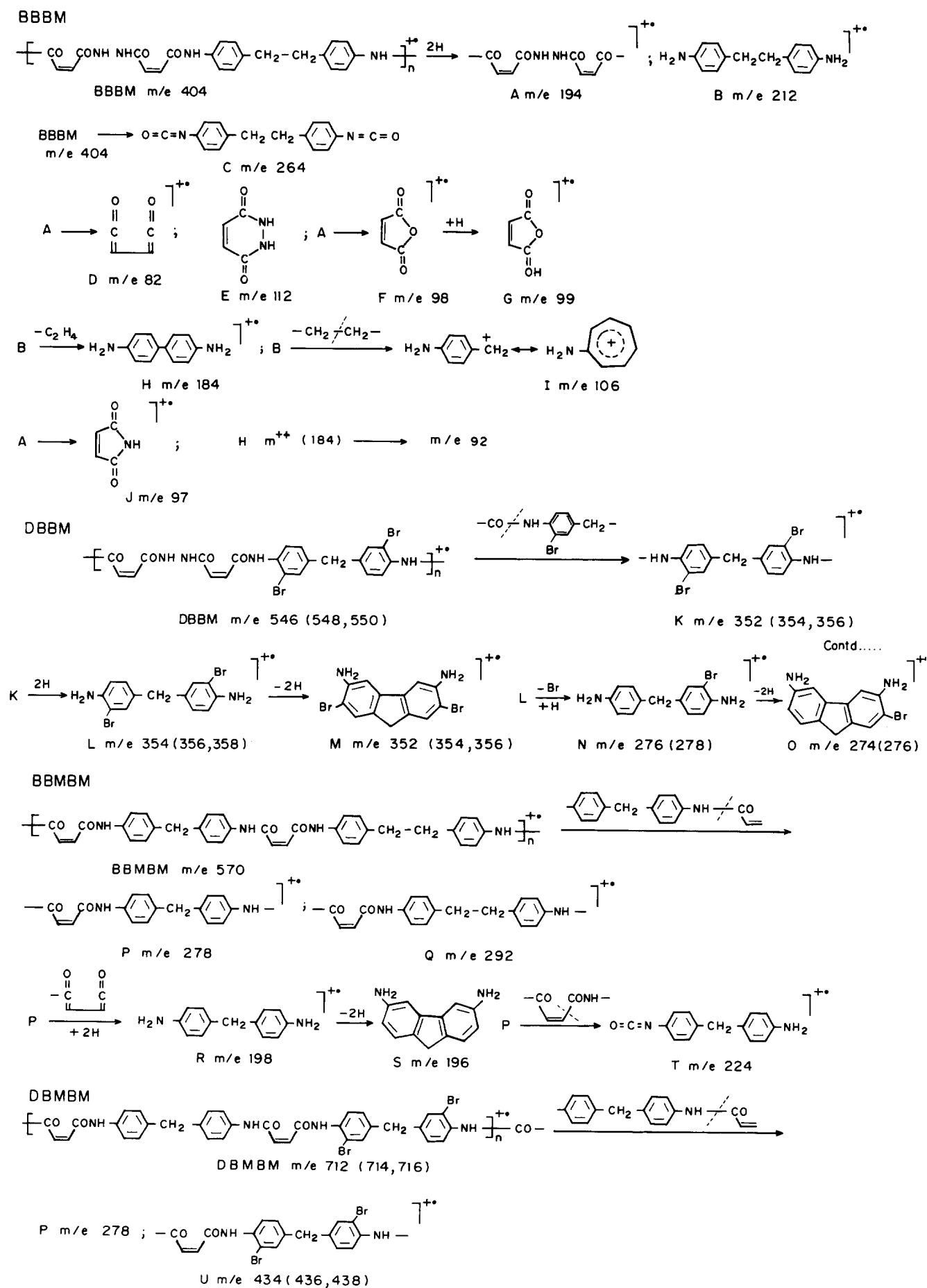
RESULTS AND DISCUSSION

In this polymerization, the diamines employed are almost soluble in the solvent (NMP + LiCl) on stirring, whilst the isoimide monomer was found to dissolve in the solvent slowly as the reaction proceeds. Added LiCl increases the solubility of the growing polymer, more

than in pure NMP, leading to a further extension of the polymer chain. The Cl^- and Li^+ ions may associate with polyamide and NMP, respectively; the positively charged solvent–Li species solvates the negatively charged chloride–polymer molecule and it is this neutral entity which is soluble in the solvent[18].

Nucleophilic attack by the diamines at the carbonyl-carbon lactonyl-oxygen bond of the isoimides produced an amide and an *in situ* tautomerizing imidol group.

The polymerization is carried out at room temperature owing to the fact that, at elevated temperatures the isoimides change into imides, which are less reactive towards diamines[17,19]. Potential side reactions include nucleophilic addition of diamine across the double

BBBM

BBBM m/e 404

A m/e 194

B m/e 212

BBBM m/e 404

C m/e 264

A

D m/e 82

E m/e 112

F m/e 98

G m/e 99

B

H m/e 184

I m/e 106

A

J m/e 97

H m^{++} (184) $\longrightarrow$ m/e 92

DBBM

DBBM m/e 546 (548,550)

K m/e 352 (354,356)

K

L m/e 354 (356,358)

M m/e 352 (354,356)

N m/e 276 (278)

O m/e 274 (276)

Contd.....

BBMBM

BBMBM m/e 570

P m/e 278

Q m/e 292

P

R m/e 198

S m/e 196

P

T m/e 224

DBMBM

DBMBM m/e 712 (714,716)

P m/e 278 ;

U m/e 434 (436,438)

Scheme 3 Fragmentation mechanism for the polymers BBBM, DBBM, BBMBM and DBMBM

Table 4 ¹H n.m.r. chemical shifts of the polymaleamides BBBM, DBBM, BBMBM and DBMBM in DMSO-d_6

| Polymer	Repeat unit	Types of protons	Chemical shifts δ
BBBM	*(structure)*	-CONH NH CO- -CONH Ar CH₂ CH₂ Ar NHCO- Aromatic protons (AB-quartet) Vinyl protons -Ar CH₂ CH₂	11.3 (2H) 9.2 (2H) 7.8 (4H, H_a); 7.1 (4H, H_b) 6.35 (4H) 2.4 (2H,*t*); 2.6 (2H,*t*)
DBBM	*(structure)*	-CO NH NH -CO NH Ar CH—2 Ar- Aromatic protons (*m*) Vinyl protons -Ar CH₂ Ar-	11.3 (2H) 10.2 (2H) 7.3–7.5 (6H, H–a and H_b) 6.45 (4H) 3.7 (2H)
BBMBM	*(structure)*	-CONH- Aromatic protons (*m*) Vinyl protons -Ar CH₂ Ar- and -ArCH₂ CH₂ Ar-	8.8 (4H) 8.77 (8H, H_a); 7.1 (8H, H_b) 6.45 (4H) 2.6–2.8 (6H,*t*)
DBMBM	*(structure)*	-CON$_a$H- -CON$_b$H Aromatic protons (A B-quartet) Aromatic protons (*m*) Vinyl protons	9.0 (2H) 8.8 (2H) 7.2–7.6 (8H, H_a' and H_b') 6.9 7.1 (6H, H_a and H_b) 6.5 (4H) 2.7 (2H,*s*) 2.45 (2H,*s*)
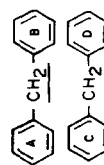
Table 5 Thermal stability of polymers in nitrogen

Polymer	Initial decomposition temperature (°C)	10% Weight-loss temperature (°C)	Maximum weight-loss temperature[a] (°C)	IPDT (°C)
BBBM[b]	275	310	355	482
DBBM	150	285	335	361
BBMBM	190	290	340	451
DBMBM	150	280	330	355

[a] Temperature at which the weight of the sample falls steeply
[b] Heating rate, 50°C min^{-1}, others, 20°C min^{-1}

bond[20,21] and trans-imidative cleavage at the hydrazide linkage[22]. The polymerization results are given in Table 1. The inherent viscosity values range from 0.30 to 0.41 g dl^{-1}. These polymers are insoluble in common organic solvents, but are soluble in concentrated sulfuric acid at room temperature. In amide-type solvents they are soluble only on heating (Table 2).

Significant i.r. and electronic spectral data are presented in Table 3. The i.r. spectra of the polymers show identical features. The absorption bands at 3400–3200 cm^{-1} (broad, NH stretching[23]) and 1600 cm^{-1} (C=C and C=O stretchings overlapped[24]) evidence ROPA. Moreover, the absence of bands at 1790 and 1680 cm^{-1} respectively, assigned to five-membered lactone ring and C=N group) characteristic of isoimide demonstrates the establishment of amide link in the polymers[12]. Of particular note is the peak at 730–665 cm^{-1}, assigned to C–H stretching of cis alkenic hydrogens; the absence of an absorption band in the region 980–960 cm^{-1} (for the trans isomer) corroborates the view that ROPA has taken place, retaining the cis geometry of the isoimide monomer. The presence of an additional amide I band in the cases MC I, BBBM and DBBM is due to the -CONHNHCO- unit[25]. The absorptions at 2920 and 2845 cm^{-1} are assigned to the C–H stretching of the -CH$_2$- groups[26].

The red shifts in the $\pi^* \leftarrow n$ transition in the cases of BBBM, DBBM and MC II compared to that of MC I and also the $\pi^* \leftarrow \pi$ transition of BBMBM compared to that of MC II are due to increase in the area of delocalization of the electrons. The blue shift observed in the case of DBMBM (cf. MC II and BBMBM) is due to the bulky bromine atom present at the ortho position to the amide group twisting it to a non-coplanar structure[27,28].

The chemical shift values (δ) of the polymaleamides are presented in Table 4. In view of the similarity of the structural features, the ^{1}H n.m.r. spectra of BBBM and BBMBM are bunched together while those of DBBM and DBMBM are discussed together[29,30]. The spectra of all the four polymers showed a common feature with regard to the vinyl protons, which appeared between 6.35 and 6.5. Likewise, the -CONH protons appeared as broad peaks between 11.3 (-CONHNHCO-) and 8.8–10.2 (-CONHAr). The aromatic protons presented a complex picture in general; however, when the ring was p-disubstituted, an AB-quartet was observed between 7.2 and 7.8; the presence of bromine in the ring caused a shift to higher fields and the protons appeared as multiplets.

The methylene groups linking the aromatic ring appeared between 2.4 and 3.7. In the cases of BBBM and BBMBM, they appear as closely spaced triplets. The ^{1}H n.m.r. spectra are consistent with the proposed structure for these polymers.

Mass spectral studies of the polymers BBM, DBBM, BBMBM and DBMBM were carried out. Identification of the major fragments provided sufficient information to postulate the fragmentation mechanism for the degradation of polyamides (Scheme 3). The mechanism is consistent with earlier reports[31–36]. The fragmentations are accounted for from the repeat units in the cases of BBBM, DBBM and BBMBM; however, in the case of DBMBM, an extended repeating unit is taken into consideration to account for the species P and U. For BBBM, a detailed fragmentation patern is furnished; for other polymers, characteristic fragmentations are given. In the case of DBBM, additional signals at m/e 82, 97, 98, 99, 106, 112 and 194 were also observed, as in BBBM. Similarly, BBMBM also shows additional signals at m/e 98, 99, 106, 210 and 212. DBMBM shows a characteristic signal at m/e 434; other signals for this polymer are seen to occur at m/e 98, 99, 106, 196, 198, 224, 278, 352 (354,356) and 354 (356,358), as observed with other polymers. The formation of a tropylium structure from a molecule with a toluene component has been reported in the literature[34]. In the present investigation, the species at m/e 106 is due to the tropylium species with a -NH$_2$ substituent (I). BBBM and DBBM give rise to the corresponding diamines (B and L) and bimaleic hydrazide (m/e 194) (A); (A), in turn, gives rise to a diketene (m/e 82) (D) and maleic hydrazide (m/e 112) (E). The formation of maleimide (cis-butenimide) (m/e 97) (J), from m/e 194 (A), could arise easily. In the cases of BBMBM and DBMBM, the species m/e 278 (P) produces the diamine with m/e 198 (R) with the elimination of diketene (m/e 82). Doubly charged species are postulated for the fragments (A), (B) and (H).

The thermogravimetry results are presented in Table 5. The initial decomposition temperature, 10% weight-loss temperature, maximum weight-loss temperature and integral-procedural-decomposition temperature (IPDT)[37] indicate the order of stability approximately as BBMB > BBMBM > DBBM > DBMBM. The introduction of a methylene group into the isoimide portion causes flexibility, thus reducing the stability of BBMBM relative to BBBM; this is evidenced by a blue shift ($\pi^* \leftarrow \pi$) in their electronic spectra. In the cases of DBBM and DBMBM the bulky bromine atoms reduce

the interchain hydrogen bonding, and lower the crystallinity of the polymers, thereby bringing down their thermal stability.

Thus, it has been possible to prepare polymaleamides with a *cis* geometrical disposition about C=C through ROPA of bisisoimide monomers retaining their geometry.

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