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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Synthesis and Characterization of Some Novel Polymaleamides from *N,N*-Biphenylbismaleimide and Aliphatic Diamines

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To cite this Article Rajeswari, N. , Nagarathinam, R. , Viswanathan, S. , Kothandaraman, H. and Ponnusamy, E.(1989) 'Synthesis and Characterization of Some Novel Polymaleamides from *N,N*-Biphenylbismaleimide and Aliphatic Diamines', *Journal of Macromolecular Science, Part A*, 26: 12, 1585 – 1610

To link to this Article: DOI: 10.1080/00222338908052075

URL: <http://dx.doi.org/10.1080/00222338908052075>

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SYNTHESIS AND CHARACTERIZATION OF SOME NOVEL POLYMALEAMIDES FROM N,N' -BIPHENYLBISMALEIMIDE AND ALIPHATIC DIAMINES

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ABSTRACT

New polymaleamides were synthesized by ring-opening polyaddition of N,N' -biphenylbismaleimide (BPBMI) to the aliphatic diamines 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane, piperazine, and 2,5-dimethylpiperazine in *m*-cresol. The appropriate model compound was also prepared. These polymers are completely soluble in concentrated sulfuric acid as well as in *m*-cresol and are found to be insoluble in common organic solvents. The identities of BPBMI, the model compound, and the polymaleamides were confirmed by elemental analysis and IR spectroscopy. These polymaleamides were found to have inherent viscosities in the range 0.10-0.14 dL/g. Their IR spectra reveal the retention of *cis*-geometry about the C=C bonds in BPBMI and in the polymaleamides. The thermal degradation behavior of the polymaleamides was studied by thermogravimetric analysis, differential scanning

calorimetry, and mass spectrometry. Fragmentation schemes for the polymaleamides are proposed.

INTRODUCTION

Ring-opening polymerization was first introduced by Wurtz [1] by the discovery of acid- and base-catalyzed polymerizations of oxirane. On ring-opening polymerization, ϵ -caprolactam gives a linear polyamide [2]. Fiber-forming polyamides are also patented [3-5]. N,N' -Hexamethylenebisphthalisoimide and N,N' -oxydi-*p*-phenylenebisphthalisoimide undergo ring-opening polymerization with aliphatic and aromatic diamines in polar solvents to give the corresponding polyamides [6]. N,N' -Bisomaleimide and N,N' -substituted bisomaleimides undergo ring-opening polyaddition with diamines, dihydrazines, and dihydrazides at room temperature in polar solvents, giving a new class of polyamides [7-12]. We prepared polyester-maleamides by ring-opening polyaddition of bisomaleimide, *p*-aminophenol, and isophthaloyl chloride/terephthaloyl chloride [13]. With aromatic diamines, bimaleimides undergo Michael addition, giving polyamides [14-16]; however, with aliphatic diamines they undergo ring-opening addition [17]. In this paper we report the synthesis, by ring-opening polyaddition of BPBMI with aliphatic diamines, of some linear polymaleamides and their characterization.

EXPERIMENTAL

Maleic anhydride (BDH) was purified by Soxhlet extraction with chloroform; mp 56°C. 1,6-Diaminohexane (DAH) (Koch-Light) was purified by vacuum distillation. 1,4-Diaminobutane (DAB) and 1,8-diaminooctane (DAO) (Fluka-AG) were used as received. 4,4'-Diaminobiphenyl (DABP) (Loba), piperazine (PPZ) (Wilson), and 2,5-dimethylpiperazine (DMPZ) (Fluka-AG) were purified by recrystallization from water, ethanol, and benzene, respectively. Anhydrous sodium acetate (BDH) was obtained by fusion. The solvents acetone, acetic anhydride, chloroform, *m*-cresol, and methanol were commercial products appropriately purified before use.

Molecular compositions were determined with a Perkin-Elmer 240B elemental analyzer. The solubilities of the polymers in various solvents were determined. Inherent viscosities (η_{inh}) were obtained from 0.5 dL/g polymer solutions in concentrated sulfuric acid at $25 \pm 0.1^\circ\text{C}$ with a modified form of the Ubbelohde viscometer. IR spectra were taken on a Perkin-Elmer IR spec-

trophotometer Model 598, using KBr pellets. TGA and DSC measurements were made with a Du Pont Model 1090 thermal analyzer at a heating rate of 10°C/min in nitrogen. Pyrolytic studies were made by using a MAT Model 112S mass spectrometer.

RESULTS AND DISCUSSION

Synthesis of *N,N'*-Biphenylbismaleimide (BPBMI) [18]

4,4'-Diaminobiphenyl (0.025 mol) in acetone was placed in a three-necked flask fitted with a mechanical stirrer and a nitrogen inlet. The flask was cooled in an ice-water bath. Maleic anhydride (0.055 mol) was added to the flask while the outside temperature was maintained at 20°C; the contents were vigorously stirred for 30 min. Acetic anhydride (20 mL) and fused sodium acetate (~2 g) were added to the bismaleamic acid produced, and the mixture was refluxed for 3 h to ensure complete cyclodehydration. The solution was then poured onto crushed ice and filtered. After washing with distilled water until the washings became neutral, the brown solid (BPBMI) was recrystallized from carbon tetrachloride and dried in vacuum (Scheme 1). Yield 7.5 g (87%); mp 185°C.

Analysis. Calculated for C₂₀H₁₂N₂O₄: C, 69.76; H, 3.49; N, 8.14%. Found: C, 70.00; H, 3.35; N, 8.25%.

The absorption at 1730 cm⁻¹ (imide) (see Fig. 1), as well as the absence of a band at 1670 cm⁻¹ (isoimide), indicates the formation of maleimide units in BPBMI.

Preparation of the Model Compound

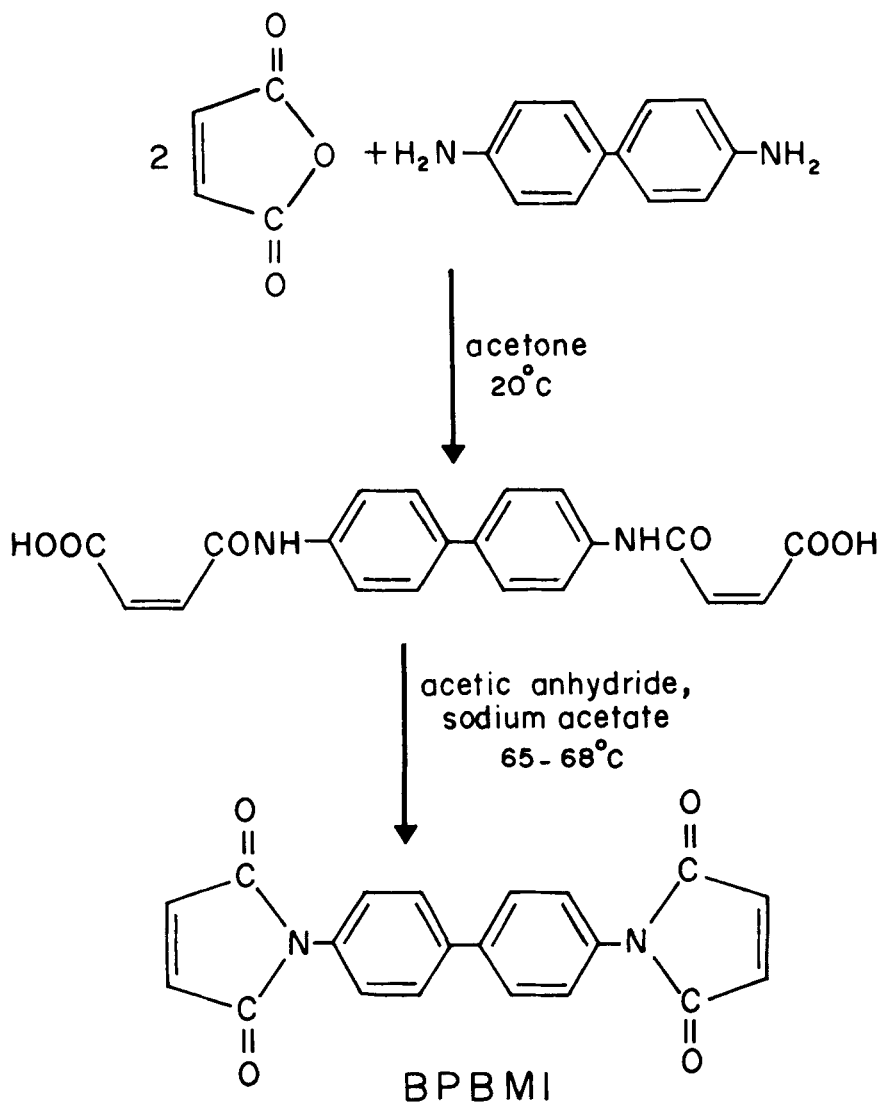
The model compound was prepared by ring-opening addition of *n*-butylamine to biphenylbismaleimide in *m*-cresol [17] (Scheme 2).

Analysis. Calculated for C₂₈H₃₄N₄O₄: C, 68.57; H, 6.94; N, 11.43%. Found: C, 69.58; H, 6.48; N, 11.62%.

The model compound was found to be freely soluble in concentrated sulfuric acid and in *m*-cresol. The most characteristic absorption bands appeared at 3315 cm⁻¹ (N–H stretching) and 1610 cm⁻¹ (carbonyl stretching).

Polymerization

A series of polymaleamides was prepared by ring-opening polymerization (Scheme 3) in *m*-cresol at 65–68°C. BPBMI (0.005 mol), aliphatic diamine



SCHEME 1. Synthesis of BPBMI.

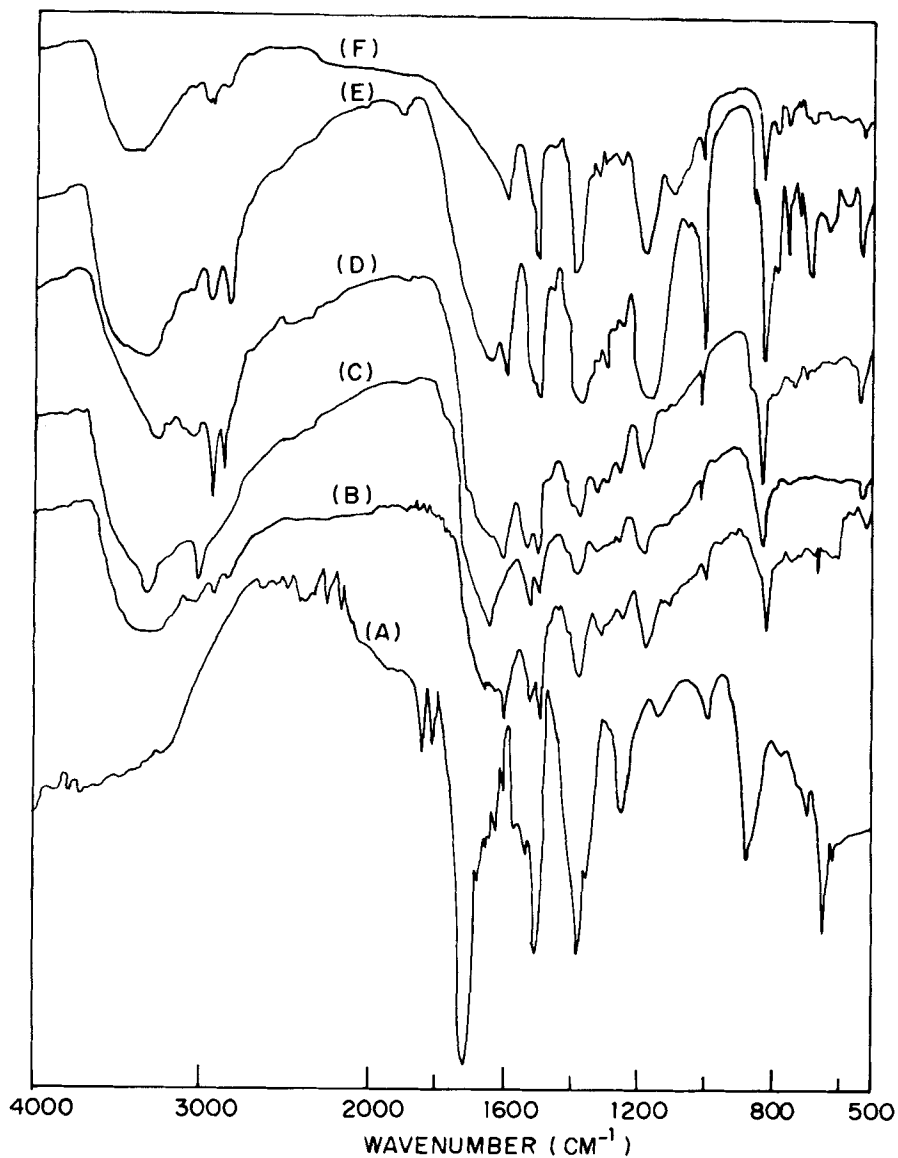
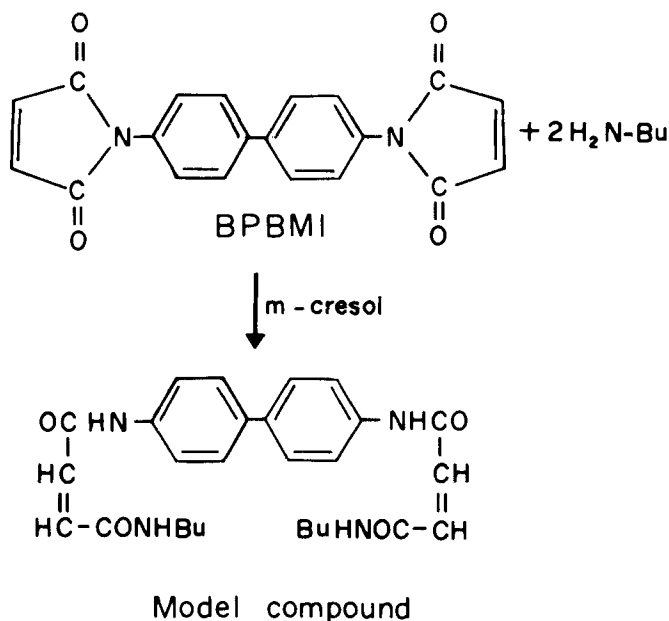


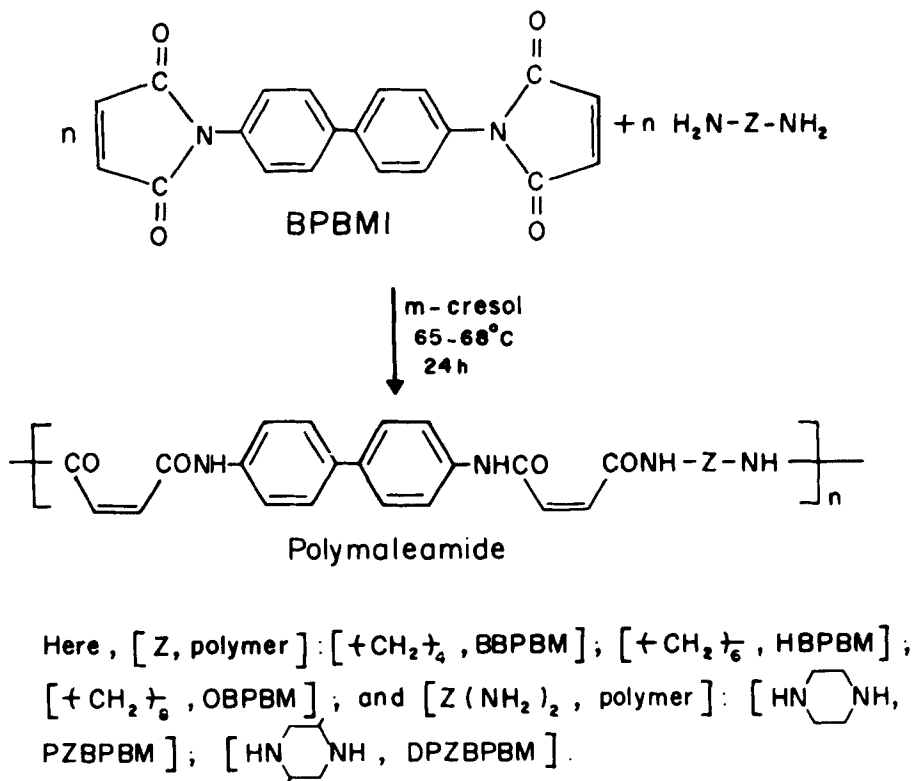
FIG. 1. IR spectra of (A) BPBMI, (B) BBPBM, (C) HBPBM, (D) OBPBM, (E) PZBPBM, and (F) DPZBPBM.



Scheme 2. Preparation of model compound.

(0.005 mol), and the solvent were placed in a polymerization kettle. The reaction mixture was refluxed under stirring (3500 rpm) for 24 h at 65–68°C under a blanket of pure, dry nitrogen. The polymer was precipitated by pouring the viscous reaction mixture into methanol. It was then filtered off, washed thoroughly with methanol, and dried in vacuum at 65°C for 48 h.

The yield of polymers, inherent viscosity (η_{inh}), and elemental analysis are summarized in Table 1; the η_{inh} values of the polymaleamides range from 0.52 to 0.69. The structures of the polymaleamides were determined by IR spectroscopy. IR spectra of the polymers (Fig. 1) were similar to those of the model compound. Characteristic bands appeared at $\sim 3300 \text{ cm}^{-1}$ for NH– and at $1640\text{--}1600 \text{ cm}^{-1}$ for amide I (due to conjugation between C=O and C=C groups) [19, 20]. These polymaleamides also showed two characteristic absorption bands, one at $1425\text{--}1405 \text{ cm}^{-1}$ and the other at $730\text{--}665 \text{ cm}^{-1}$ for the C–H in-plane and out-of-plane deformations, respectively. Further, the absence of absorption at $980\text{--}960 \text{ cm}^{-1}$ due to *trans* C=C confirms the retention of the *cis* geometry in the polymaleamide [21, 22].



SCHEME 3. Synthesis of polymaleamides.

Properties of the Polymaleamides

The solubility behavior of polymaleamides was determined for powdery samples in excess solvent at room temperature (Table 2). All the polymers were soluble in concentrated sulfuric acid and in *m*-cresol but undergo swelling in amide-type solvents such as DMF, DMAc, DMSO, NMP, and THF. However, they are insoluble in common organic solvents such as acetone, formic acid, and ethanol.

The thermal stability of these polymaleamides was evaluated by thermogravimetric analysis (TGA). The TGA curves of these polymers are shown in Fig. 2, and the thermal stability data are listed in Table 3. The initial de-

TABLE 1. Yield, Analytical, and Viscosity Data for the Polymaleamides Investigated

Polymer	Yield, %	Repeat unit	Analytical data found (calc)			η_{inh}^a dL/g
			% C	% H	% N	
BBPBM	84	$C_{24}H_{24}N_4O_4$	66.75 (66.67)	5.55 (5.56)	10.30 (12.98)	0.60
HBPBM	92	$C_{26}H_{28}N_4O_4$	67.90 (67.83)	6.00 (6.09)	12.30 (12.17)	0.59
OBPBM	95	$C_{28}H_{32}N_4O_4$	68.90 (68.85)	6.60 (6.56)	11.50 (11.48)	0.52
PZBPBM	89	$C_{24}H_{22}N_4O_4$	67.00 (66.98)	5.30 (5.12)	13.05 (13.02)	0.69
DPZBPBM	88	$C_{26}H_{26}N_4O_4$	68.20 (68.12)	5.75 (5.68)	12.30 (12.23)	0.53

^aMeasured at a concentration of 0.5 g/dL in sulfuric acid at $25 \pm 0.1^\circ\text{C}$.

composition temperature (IDT) and the temperature at 10% polymer weight loss (T_{10}) were selected as a measure of thermal stability. BBPBM, HBPBM, and OBPBM (having flexible polymethylene units) were found to be thermally less stable than PZBPBM, which has a cyclic ring in its backbone. PZBPBM had IDT at 220°C and T_{10} at 315°C , whereas DPZBPBM derived from dimethylpiperazine showed IDT at 185°C and T_{10} at 245°C . The difference in the thermal stability values is probably due to the structural differences affecting the intermolecular interactions. The introduction of methyl substituents into piperazine causes DPZBPBM to possess lower stability than PZBPBM. This may be attributed to the fact that the steric effect of the methyl substituent leads the polymer to possess a less closely packed structure.

The integral procedural decomposition temperature (IPDT) values of polymaleamides were also calculated [23]. Table 3 indicates that PZBPBM (IPDT, 370°C) is the most stable of the five polymers studied. These results suggest that the polymaleamide having piperazine units is thermally more

TABLE 2. Solubility of the Polymaleamides^a

Polymer	Solvent										
	H ₂ SO ₄	<i>m</i> -Cresol	DMF	DMAc	DMSO	NMP	THF	Acetone	HCOOH	EtOH	
BBPBM	++	++	+	+	+	s	s	-	-	-	
HBPBM	++	++	+	s	+	s	s	-	-	-	
OBPBM	++	++	+	+	+	s	s	-	-	-	
PZBPBM	++	++	+	s	+	s	+	-	-	-	
DPZBPBM	++	++	+	+	s	++	s	-	-	-	

^a(++) Soluble, (+) soluble on heating, (s) swelling, (-) insoluble.

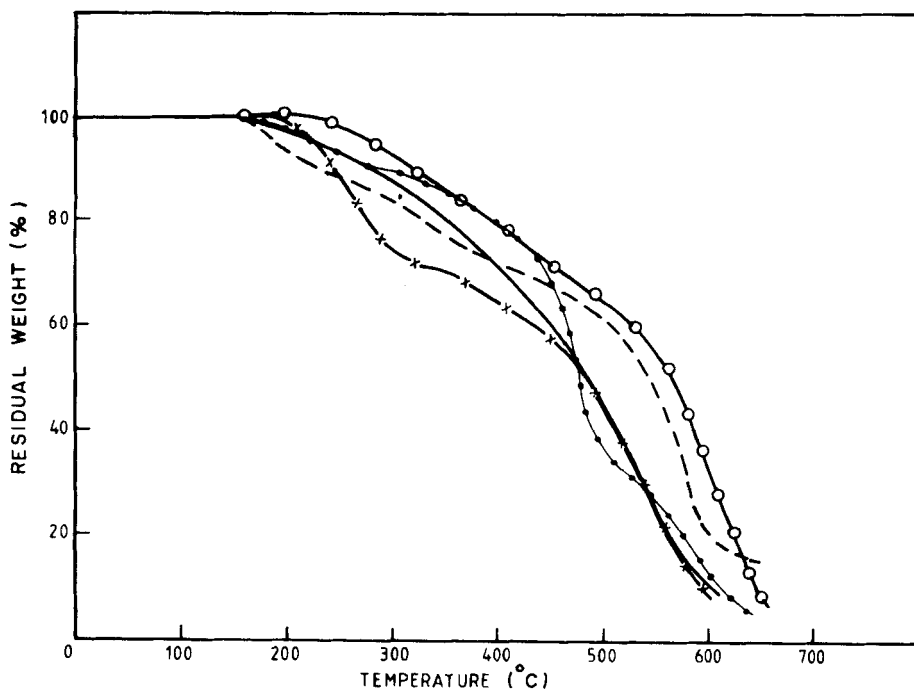


FIG. 2. TGA curves for the polymaleamides: BBPBM (●), HBPBM (---), OBPBM (—), PZBPBM (○), and DPZBPBM (X).

TABLE 3. Thermal Data (°C) of Polymaleamides^a

Polymer	IDT	T_{10}	IPDT
BBPBM	160	285	282
HBPBM	155	225	335
OBPBM	175	290	279
PZBPBM	220	315	370
DPZBPBM	185	245	285

^aIn nitrogen (heating rate, 10°C/min).

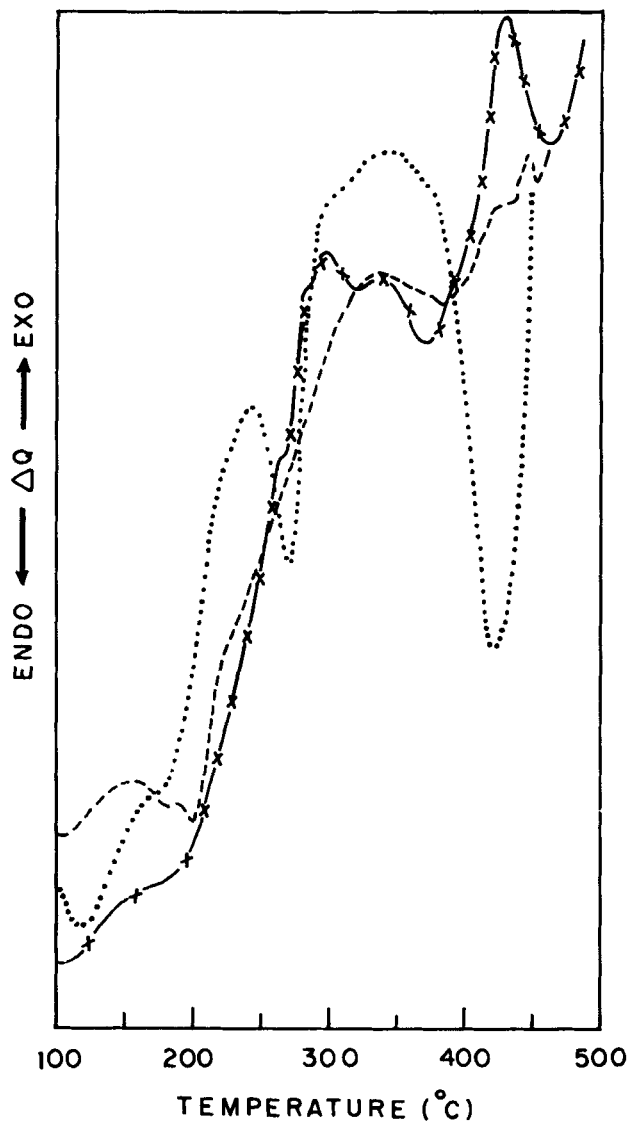


FIG. 3. DSC curves for the polymaleamides: OBPBM (---), PZBPBM (X), and DPZBPBM (· · ·).

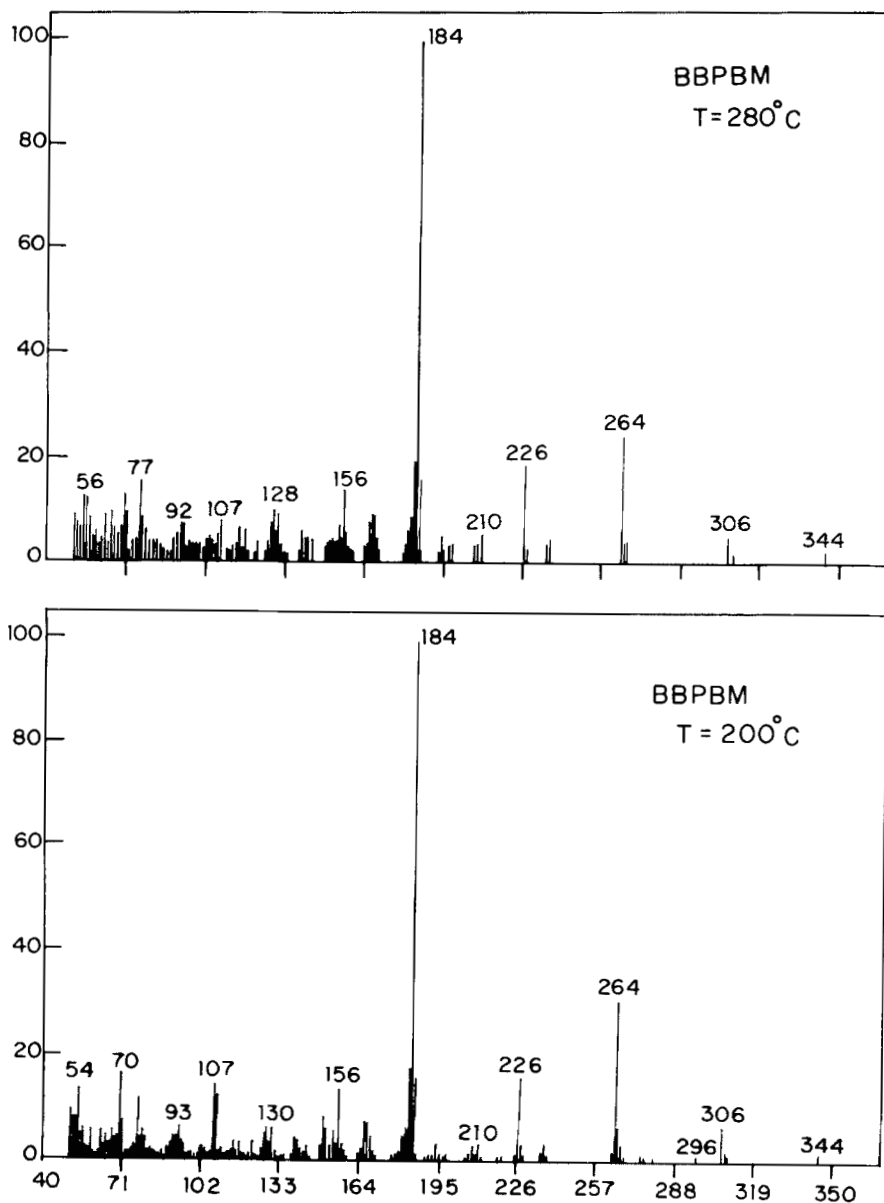


FIG. 4. Mass spectra of BBPBM at 200 and 280°C (Scheme 4).

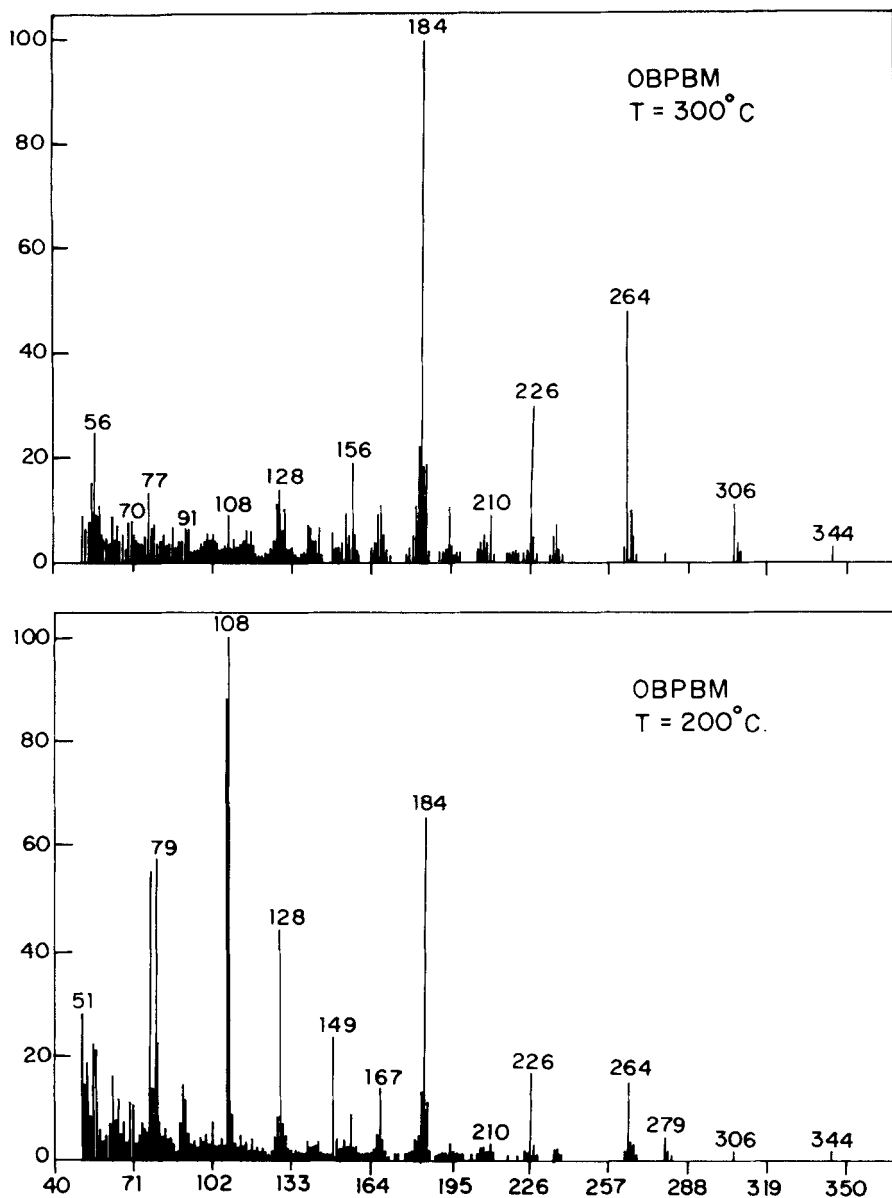


FIG. 5. Mass spectra of OBPBM at 200 and 300°C (Scheme 5).

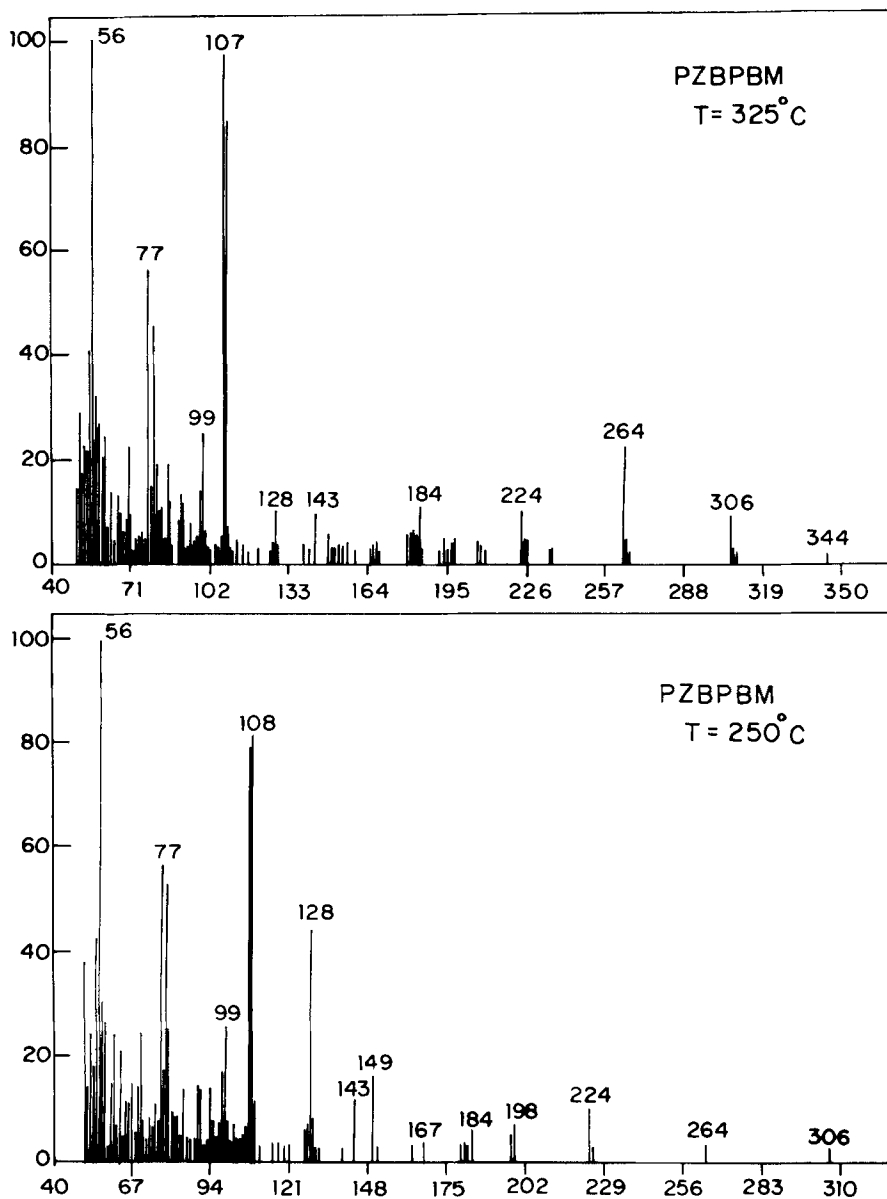
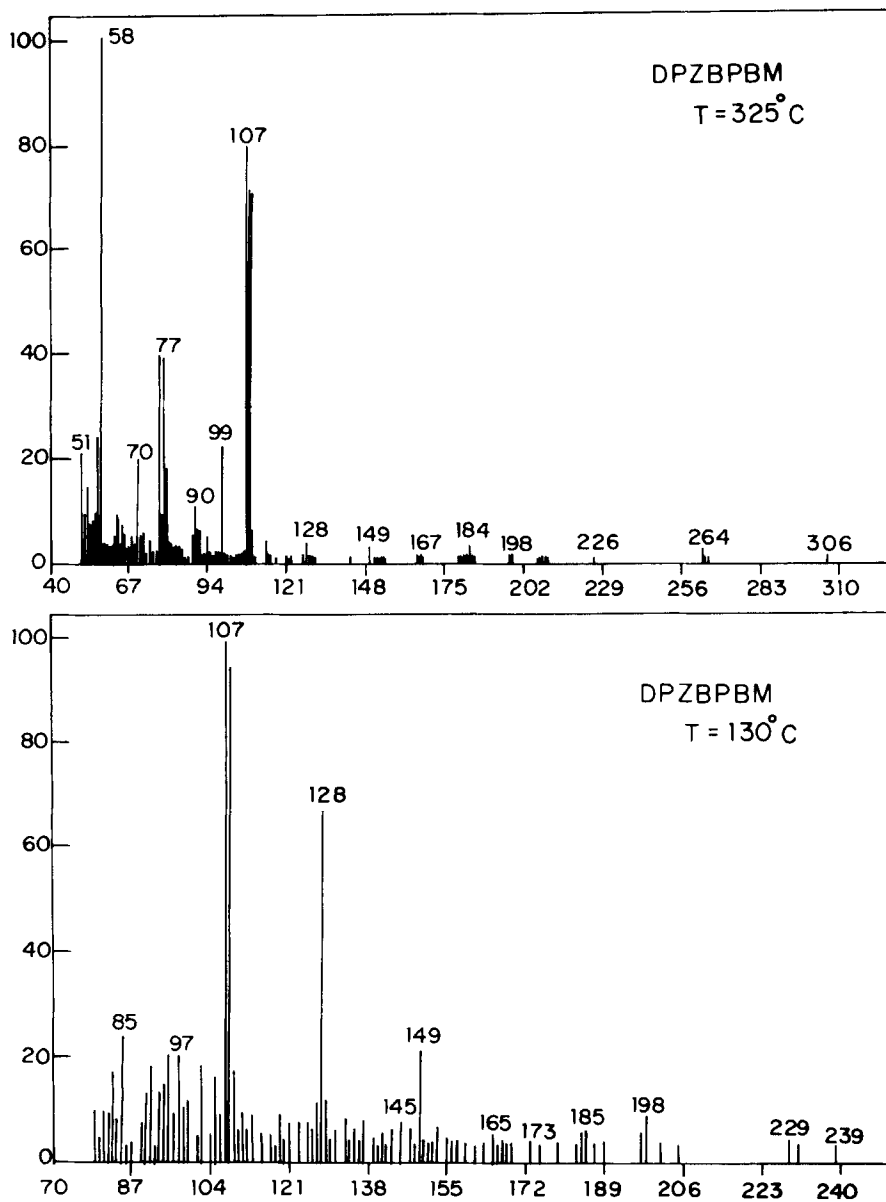
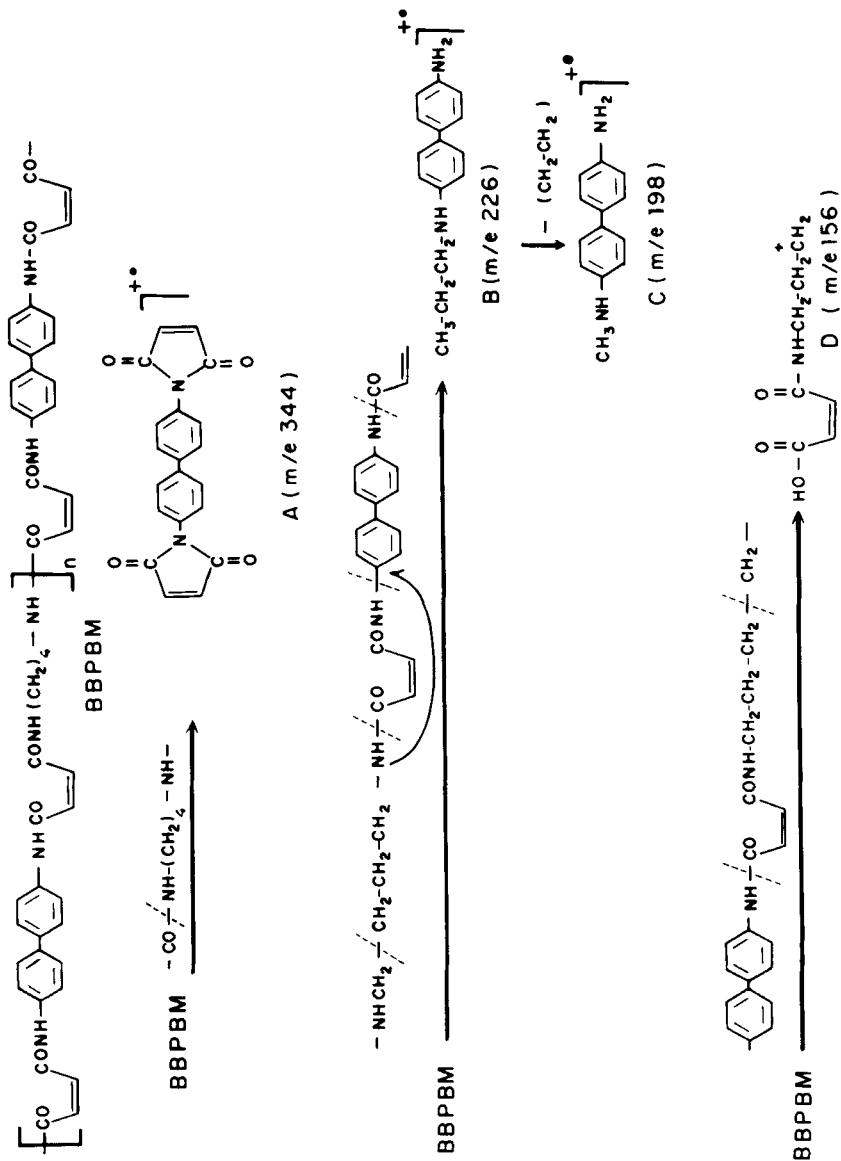
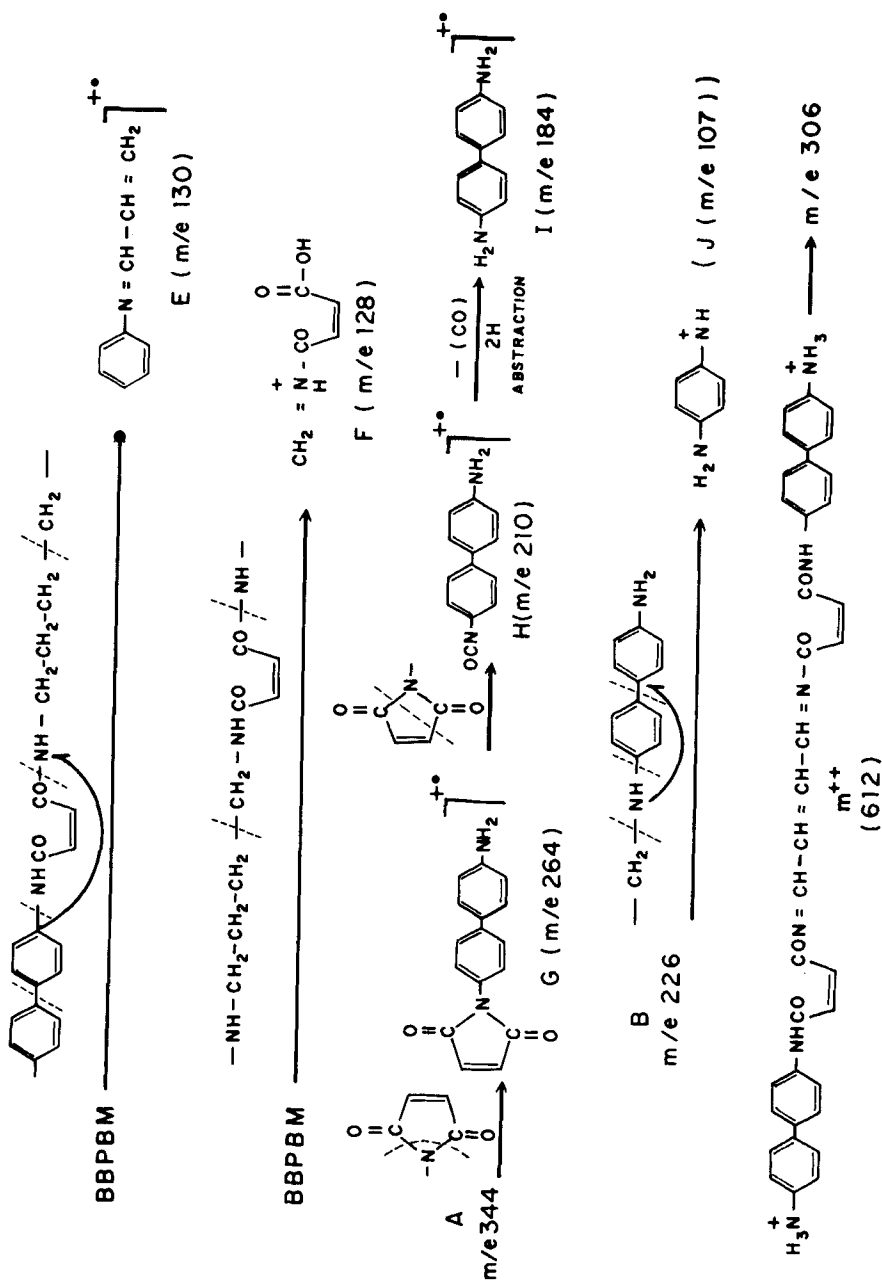


FIG. 6. Mass spectra of PZBPBM at 250 and 325°C (Scheme 6).

FIG. 7. Mass spectra of DPZBPBM at 130 and 325°C (Scheme 7).

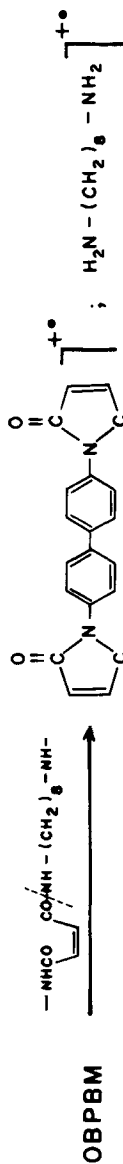
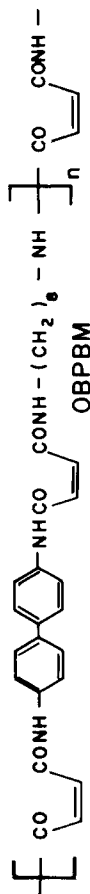
BBPBM : MOLECULAR WEIGHT OF THE REPEATING UNIT, 432



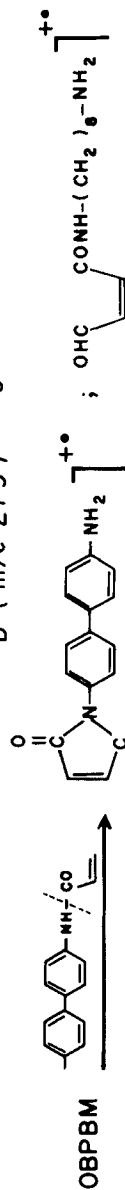
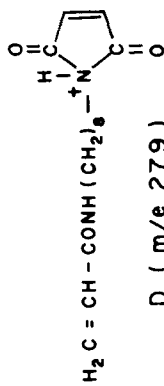
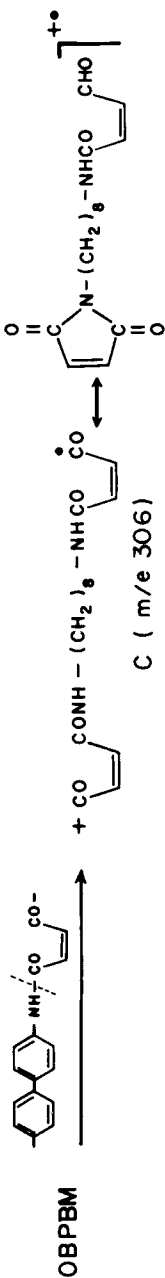


SCHEME 4. Fragmentation mechanism for BBPBM (Fig. 4).

OBPBM: MOLECULAR WEIGHT OF THE REPEATING UNIT, 488

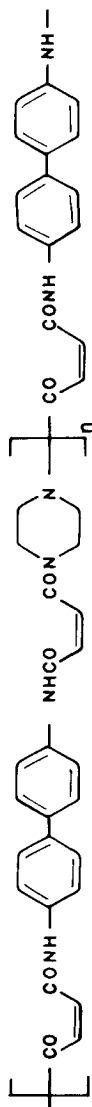


B (m/e 144)

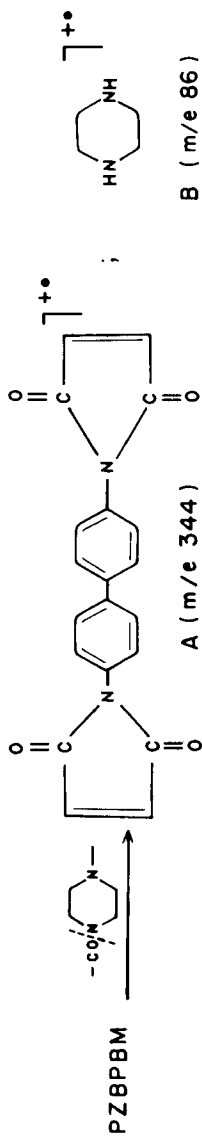


F (m/e 226)

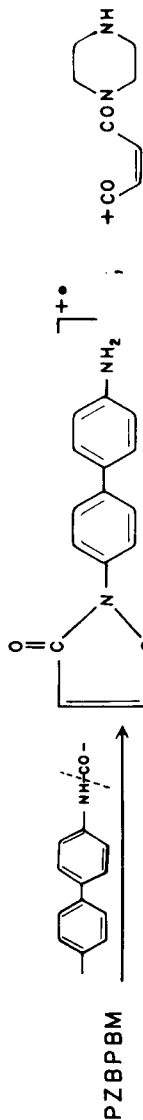
PZBPBM : MOLECULAR WEIGHT OF THE REPEATING UNIT , 430



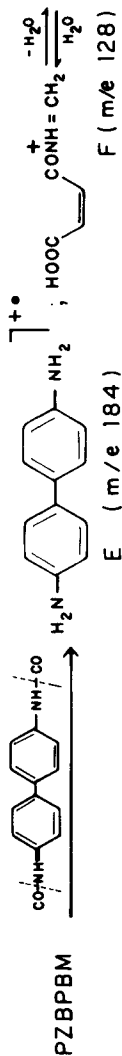
PZBPBM



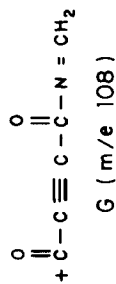
B (m/e 86)



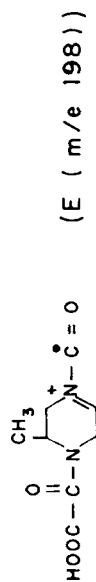
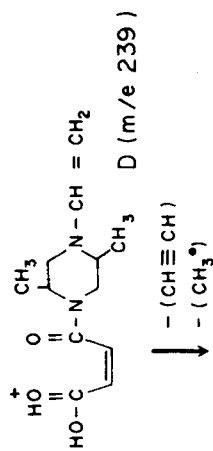
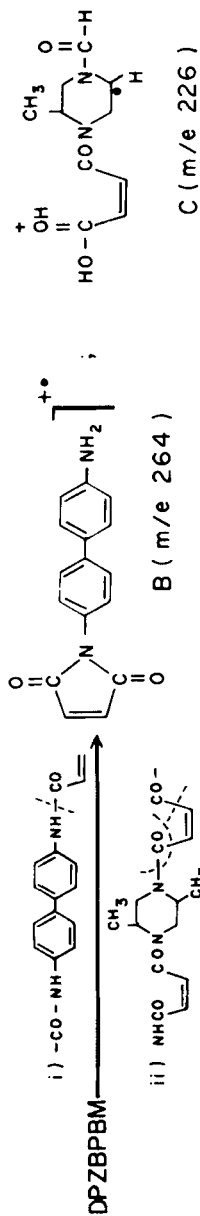
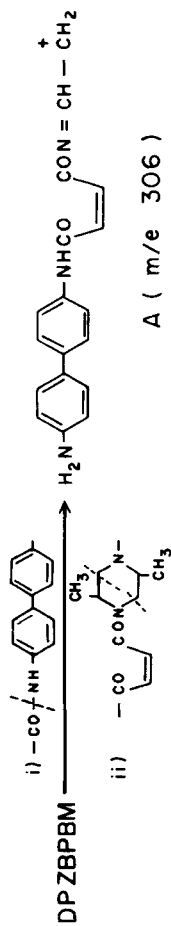
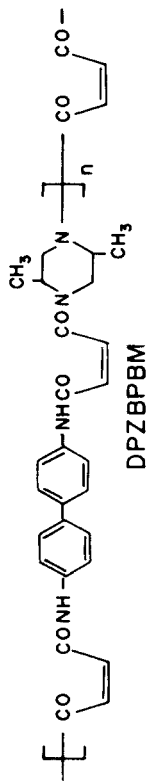
D (m/e 167)



F (m/e 128)



DPZBPBM : MOLECULAR WEIGHT OF THE REPEATING UNIT, 468



stable than that having methyl-substituted piperazine units or linear chain linkages.

DSC studies indicate that the decomposition reactions of the polymers are endothermic. Some typical DSC thermograms are shown in Fig. 3. OBPBM shows an endothermic peak at 180°C, in close agreement with the IDT, 175°C (Fig. 2).

The polymer samples **BBPBM**, **OBPBM**, **PZBPBM**, and **DPZBPBM** were subjected to pyrolysis study under vacuum at 130-325°C. Their mass spectra are given in Figs. 4-7.

Polymer degradations are usually complex in nature and are not discernible by a single well-defined mechanism. Identification of major volatile products, however, usually provides sufficient information to postulate a possible predominating breakdown mechanism for the degradation of polyamides by both homolytic and heterolytic cleavages [24].

During pyrolysis, polymers generally undergo a variety of reactions such as dehydration, hydrolysis, cyclization, aromatization, elimination, ring expansion, ring contraction, and deoxygenation. Fragments such as carbon monoxide, carbon dioxide, benzene, hydrogen cyanide, alkyne, -isocyanates, -amines, -carboxylic acids, five-, six-, seven-membered rings, maleic anhydride, maleimide, diketene, -aldehyde, -imine, -imide, -amine, -sulfoxide, -sulfide, tropylium species, aldehyde-amine, keto-aldehyde, and amic acids are formed [25-32]. Based on the m/e ratio, a doubly charged species with a particular mass (m^{++}) and a singly charged species with half this mass would be detectable at the same position in mass spectra.

In the light of the above facts, probable fragmentation schemes for the polymaleamides **BBPBM**, **OBPBM**, **PZBPBM**, and **DPZBPBM** are proposed (see Schemes 4-7).

ACKNOWLEDGMENT

N.R. is grateful to the Government of Tamil Nadu, India, for the award of a Research Fellowship.

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Received September 19, 1988