Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

New Polymaleamides from *N,N'*-Ethylenedianilinobisisomaleimide and Aromatic Diamines by Ring-Opening Polyaddition: Synthesis and Characterization

E. R. Nagarajan[a]; N. Rajeswari[b]; S. Viswanathan[a]
[a] Department of Printing, Technology Anna University, Madras, India [b] Department of Polymer, Science University of Madras, Madras, India

To cite this Article Nagarajan, E. R. , Rajeswari, N. and Viswanathan, S.(1997) 'New Polymaleamides from *N,N'*-Ethylenedianilinobisisomaleimide and Aromatic Diamines by Ring-Opening Polyaddition: Synthesis and Characterization', Journal of Macromolecular Science, Part A, 34: 6, 1055 — 1076

To link to this Article: DOI: 10.1080/10601329708015010

URL: http://dx.doi.org/10.1080/10601329708015010

J.M.S.—PURE APPL. CHEM., A34(6), pp. 1055–1076 (1997)

NEW POLYMALEAMIDES FROM *N,N′*-ETHYLENEDIANILINOBISISOMALEIMIDE AND AROMATIC DIAMINES BY RING-OPENING POLYADDITION: SYNTHESIS AND CHARACTERIZATION

E. R. NAGARAJAN and N. RAJESWARI

Department of Printing Technology
Anna University
Madras-600 025, India

S. VISWANATHAN*

Department of Polymer Science
University of Madras
Madras-600 025, India

ABSTRACT

Polymaleamides have been synthesized by the ring-opening polyaddition of *N,N′*-ethylenedianilinobisisomaleimide (EBIMI) with the aromatic diamines, 4,4′-diaminodiphenylmethane, 4,4′-diaminobibenzyl, 4,4′-diaminodiphenylsulfone, 1,5-diaminonaphthalene, and 2,4-diaminopyridine in 1-methyl-2-pyrrolidinone. The appropriate model compound was also prepared. The structures of EBIMI, the model compound, and the polymaleamides were confirmed by IR, UV-Vis, ^{1}H-NMR spectra, and elemental analyses. The IR spectra revealed the retention of *cis*-geometry about the C=C bonds in EBIMI and in the polymaleamides. The polymers were characterized by inherent viscosity, solubility, thermal stability, and DSC measurements. The polymaleamides were found to have inherent viscosities in the 0.06–0.13 dL/g range. The polymers were completely soluble in concentrated sulfuric acid and were found to be insoluble in organic solvents such as ethyl alcohol and acetone. The thermal degradation behaviors of the polymaleamides were studied by mass spectrometry; proposed fragmentation schemes for the polymaleamides are discussed.

INTRODUCTION

Ring-opening polyaddition (ROPA) of *N,N′*-arylenedisulfonylbissuccinimides with aromatic diamines in 1-methyl-2-pyrrolidinone at room temperature afforded polyacylsulfonamideamides [1]. ROPA of bisbutanolides (having ethylene and oxydiphenylene substituents between the 4 and 4′ positions) with hexamethylenediamine and *m*-xylylenediamine produced polyamides with hydroxyl groups attached to the polymer backbone [2, 3]. Diamines undergo ROPA with various reactive heterocyclic compounds such as 2,2′-disubstituted bis[5-(4*H*)-oxazolone] and 4,4′-*m*-phenylenedimethylidinebis(azalactones) to give polyamides [4–8]. A new series of thermosetting resins was prepared from the reaction of 4,4′-bismaleimidediphenylmethane with diaminomaleonitrile, and the resins had a complex network structure depending on their composition [9]. Also, bismaleimides were found to react with *N,N′*-cyano-substituted diamines of the general formula NCHN—Ar—NHCN, which are known as biscyanimides, resulting in the formation of heat-resistant polymers [10].

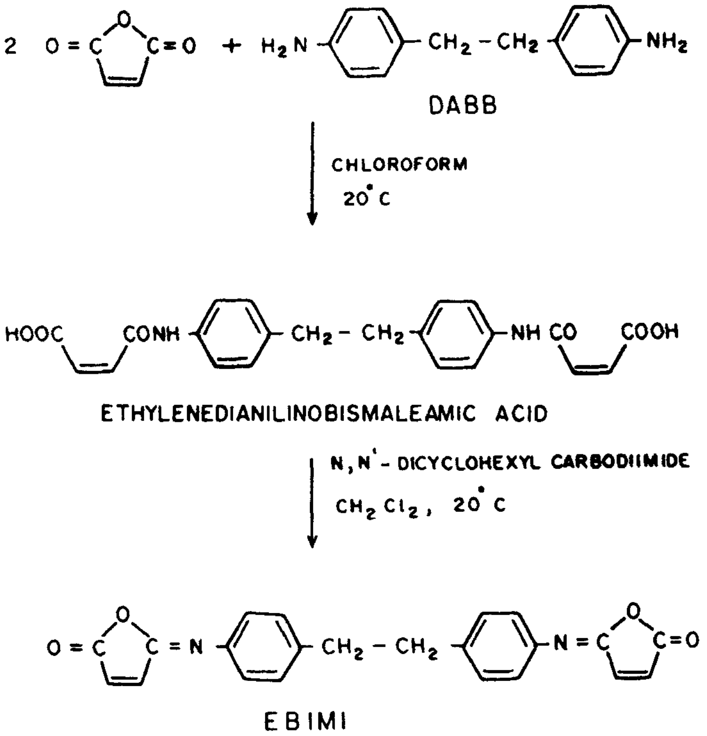
The melt polymerization methods were adopted for the production of aliphatic-aromatic polyamides; the polymers frequently became discolored, probably because of branched/network structures [11]. In solution and interfacial procedures using diacid chlorides, monoalkylamide and dialkylamide may be formed [12], thus retarding the growth of the polymer. These difficulties were circumvented by employing the ring-opening technique. Bisisoimides constitute an interesting class of potentially reactive compounds [13, 14]. Different polymaleamides have been synthesized by ROPA of *N,N′*-methanedianilinebisisomaleimide [15], *N,N′*-biphenylbismaleimide [16], and *N,N′*-biphenyletherbimaleimide [17] with aliphatic diamines. We recently reported the synthesis and characterization of polymaleamides from the bisisoimides, *N,N′*-ethanedianilinebisisomaleimide, *N,N′*-bisisomaleimide, and *N,N′*-methylenedianilinobisisomaleimide and some aromatic and aliphatic diamines [18–20].

The present work deals with the synthesis and characterization of polymaleamides by ROPA of *N,N′*-ethylenedianilinobisisomaleimide with various aromatic diamines in 1-methyl-2-pyrrolidinone. The following results are reported here: 1) Properties such as inherent viscosity and solubility, 2) electronic spectral characteristics, 3) evidence for the opening of the ring of the reactant during polymerization from IR and ^{1}H-NMR spectral studies, 4) thermochemical data from TGA and DSC, and 5) fragmentation mechanism for thermal degradation of the polymers from mass spectral studies.

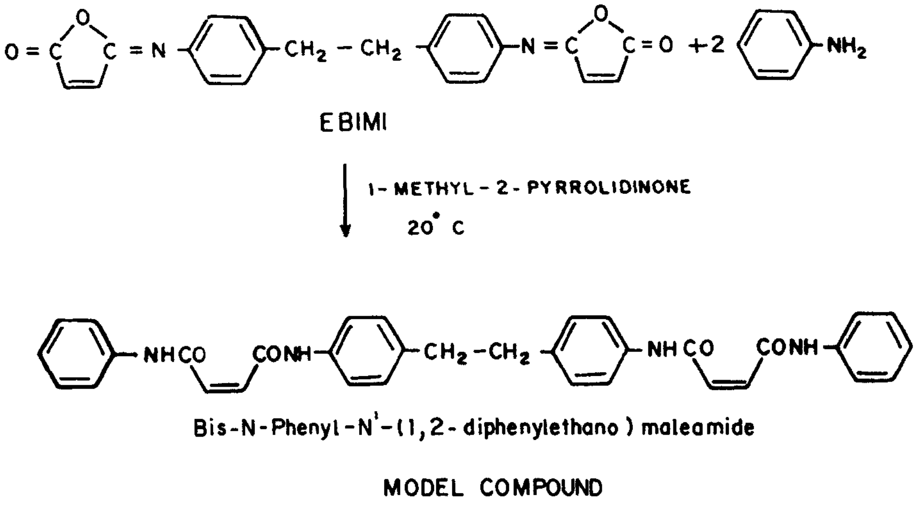
EXPERIMENTAL

Reagents and Materials

Maleic anhydride (BDH) was purified by Soxhlet extraction with chloroform, mp 56°C; 4,4′-diaminodiphenylmethane (methylenedianiline) (MDA) (Merck) was recrystallized from benzene using Norit, mp 91°C; 1,5-diaminonaphthalene (DAN)



SCHEME 1.



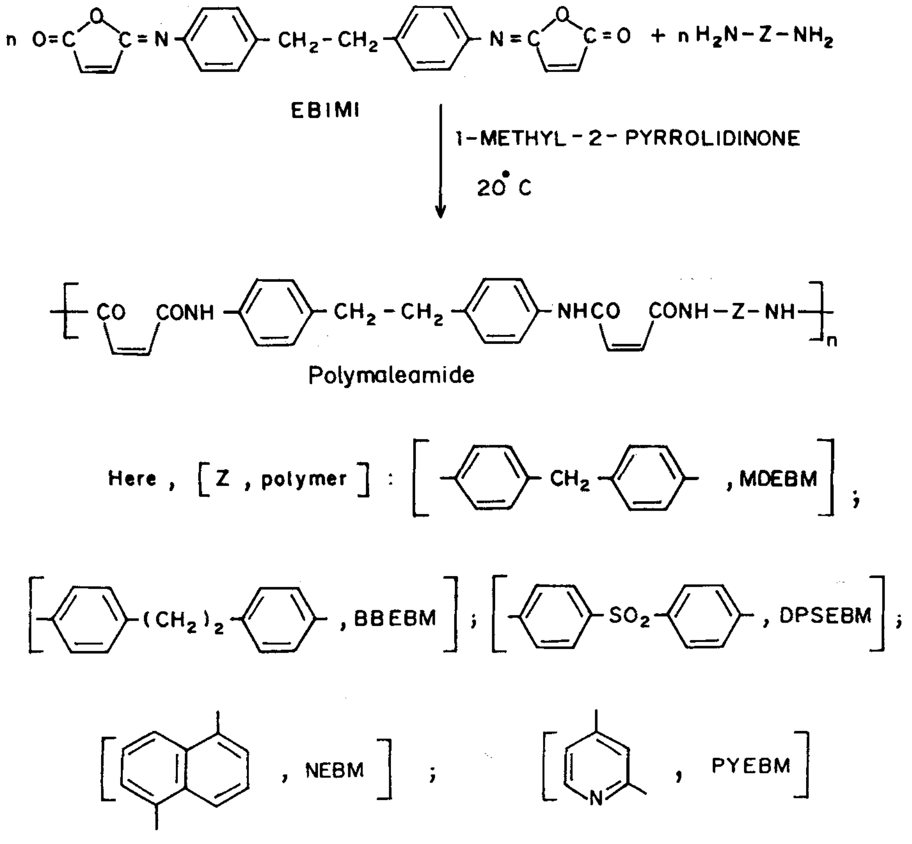
SCHEME 2.

(Purum, Fluka) was sublimed in vacuum to give white crystals, mp 190°C; and 2,4-diaminopyridine (DAPY) (Fluka) was recrystallized from water to give plates, mp 107°C [21]. 4,4′-Diaminobibenzyl (DABB) was synthesized from 4,4′-dinitrobibenzyl as described in the literature [22, 23] (mp 135°C; Ref. 23, 135–136°C). 4,4′-Diaminodiphenylsulfone (DADPS) was synthesized according to the literature [24, 25] (mp 174°C; Ref. 25, 174–176°C). The reagent *N,N′*-dicyclohexylcarbodiimide (DCC) (Fluka) was used as received. 1-Methyl-2pyrrolidinone, sulfuric acid, chloroform, and other solvents were commercial products appropriately purified before use.

Synthesis of *N,N′*-Ethylenedianilinobisisomaleimide (EBIMI)

Stage A

N,N′-Ethylenedianilinobismaleamic acid was prepared as follows [26]: To an ice-cooled solution of maleic anhydride (9.8 g, 0.1 mol) in chloroform (100 mL), 4,4′-diaminobibenzyl (10.6 g, 0.05 mol) in the same solvent was added with shaking under nitrogen; the mixture was allowed to stand overnight. The settled bismaleamic acid was filtered off and washed with chloroform. Purification was carried out by



SCHEME 3.

TABLE 1. Yield, Elemental Analysis, Viscosity, and Electronic Spectral Data for the Polymaleamides Investigated

				Elemental analysis found (calc)				
Diamine	Polymer	Yield %	Repeat unit	% C	% H	% N	η_{inh},[a] dL/g	λ_{max} (in conc H_2SO_4), nm
MDA	MDEBM[b]	96	$C_{35}H_{30}N_4O_4$	73.70 (73.69)	5.30 (5.26)	9.75 (9.82)	0.12	292,370
DABB	BBEBM[c]	95	$C_{36}H_{32}N_4O_4$	74.00 (73.97)	5.50 (5.48)	9.70 (9.59)	0.13	292,360
DADPS	DPSEBM[d]	92	$C_{34}H_{28}N_4O_6S$	66.00 (65.81)	4.60 (4.52)	9.10 (9.03)	0.06	286,368
DAN	NEBM[e]	92	$C_{32}H_{26}N_4O_4$	72.25 (72.45)	4.70 (4.90)	10.45 (10.57)	0.09	278,364
DAPY	PYEBM[f]	85	$C_{27}H_{23}N_5O_4$	67.48 (67.37)	4.99 (4.78)	15.12 (14.55)	0.08	295,350

[a] Measured in sulfuric acid at a concentration of 0.05 g/dL at 25 ± 0.1°C.

[b] Poly-[*N*-{4(4′-aminobenzyl)phenyl}-*N*′-(1,2-diphenylethano-4′-maleamido)] maleamide.

[c] Poly-[*N*-{4(4′-aminophenethyl)phenyl}-*N*′-(1,2-diphenylethano-4′-maleamido)] maleamide.

[d] Poly-[*N*-{4(4′-aminosulfonylphenyl)phenyl}-*N*′-(1,2-diphenylethano-4′-maleamido)] maleamide.

[e] Poly-[*N*-{1(5-aminonaphthyl)}-*N*′-(1,2-diphenylethano-4′-maleamido)] maleamide.

[f] Poly-[*N*-{4(2-aminopyridyl)}-*N*′-(1,2-diphenylethano-4′-maleamido)] maleamide.

dissolving it in $NaHCO_3$ solution and reprecipitating it by adding concentrated HCl. The solid mass was filtered off, washed with water to remove HCl, and then dried in vacuum (yield 95.5%).

Stage B

A solution of this bismaleamic acid (16.32 g, 0.04 mol) in dichloromethane (50 mL) was stirred during dropwise addition of DCC (16.48 g, 0.08 mol) in the same solvent. Stirring was continued for 3 hours, and the contents were filtered off to remove *N,N'*-dicyclohexyl urea; the product, EBIMI, was obtained by removing the solvent under reduced pressure. The product was recrystallized from a 1:1 benzene–ether mixture. Yield 83.06%, mp 168°C [27].

Analysis. Calculated for $C_{22}H_{16}N_2O_4$: C, 70.97; H, 4.30; N, 7.53%. Found: C, 71.00; H, 4.20; N, 7.55%. IR (KBr): the adsorption at 1730 cm^{-1} (imide) as well as the absence of a band at 1670 cm^{-1} (isoimide) indicate the formation of maleimide units in EBIMI.

Synthesis of Model Compound

The model compound was synthesized from EBIMI (0.744 g, 0.002 mol) and aniline (0.372 g, 0.004 mol) by employing 1-methyl-2-pyrrolidinone as the solvent under nitrogen and allowing the reaction to proceed for 24 hours. The resulting pale yellow solid was filtered off, washed with water, and dried in vacuum to give the model compound, yield 86%.

Analysis. Calculated for $C_{34}H_{30}N_4O_4$: C, 73.12; H, 5.38; N, 10.04%. Found: C, 73.00, H, 5.40; N, 10.15%.

Polymer Synthesis

A typical synthesis procedure for polymers from EBIMI and diamines is as follows. A 50-mL two-necked polymerization kettle with a side nitrogen inlet was fitted with an air-tight ground joint, mechanical glass stirrer with a glass paddle,

TABLE 2. Solubility of Polymaleamides[a]

	Polymer				
Test solvent	MDEBM	BBEBM	DPSEBM	NEBM	PYEBM
Concentrated sulfuric acid	+ +	+ +	+ +	+ +	+ +
1-Methyl-2-pyrrolidinone	+ +	±	+ +	+ +	±
Dimethylformamide	+ +	s	+ +	+	±
Dimethylacetamide	+ +	s	+ +	+ +	+
Dimethylsulfoxide	+ +	+	+ +	+ +	s
Tetrahydrofuran	±	±	±	±	–
Formic acid	+	+ +	–	+	±
m-Cresol	+	+	±	–	–
Ethyl alcohol	–	–	–	–	–
Acetone	–	–	–	–	–

[a](+ +) Soluble, (+) soluble on heating, (±) partially soluble, (s) swollen, (–) insoluble.

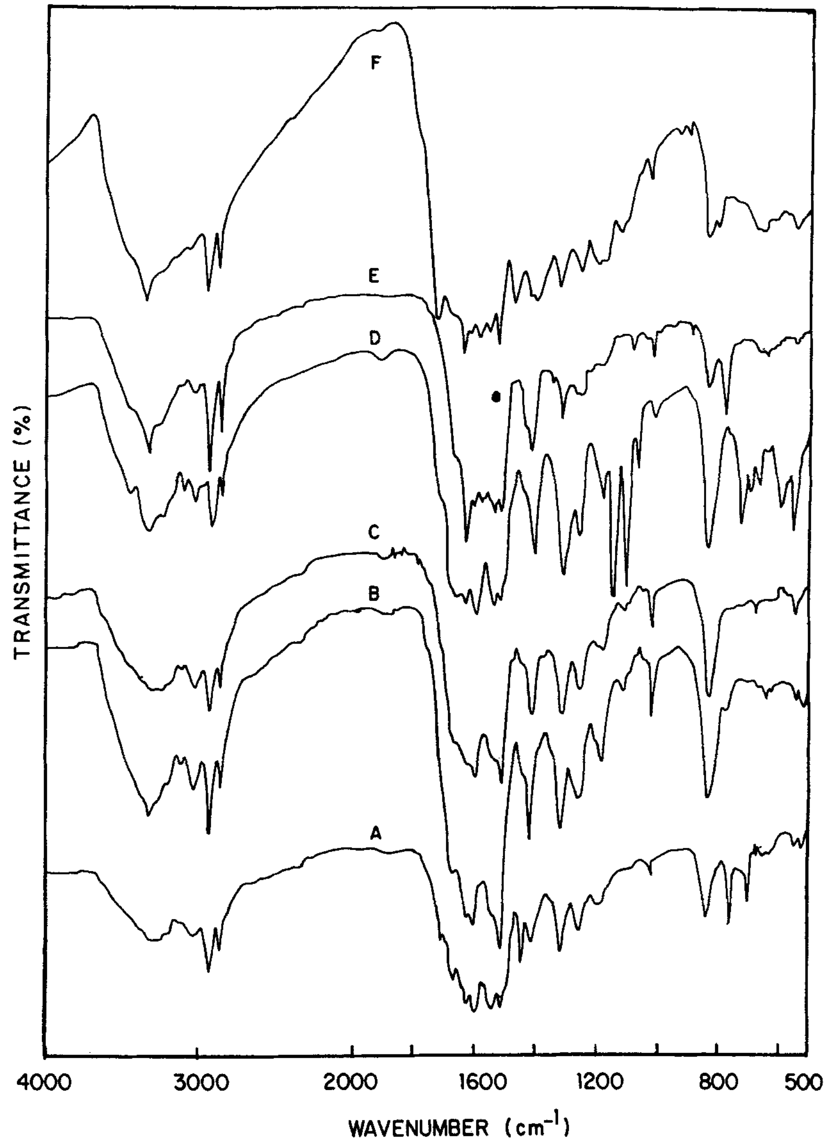
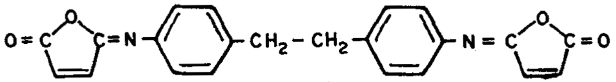


FIG. 1. The IR spectra of (A) model compound, (B) MDEBM, (C) BBEBM, (D) DPSEBM, (E) NEBM, and (F) PYEBM.

and a calcium chloride guard tube. The freshly purified 0.005 mol diamine was placed in the kettle and dissolved by stirring in 1-methyl-2-pyrrolidinone under dry nitrogen atmosphere. The kettle was cooled in an ice-water bath; 0.005 mol EBIMI was then added without disturbing the inert atmosphere. The mixture was stirred (3500 rpm) at 20°C for 24 hours. The polymer was precipitated with water, filtered off, washed successively with dilute HCl, dilute $NaHCO_3$, water, and ethyl alcohol, and vacuum dried at 65°C. The polymer yields were in the 85–96% range.



EBIMI

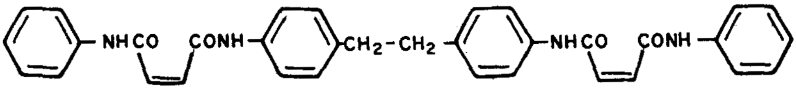
Total number of protons = 16

Types of protons :

Aromatic protons , 7.0-7.45 δ (m , 8H)

Ar$C\underline{H_2}$, 2.45 δ (broad and s , 4H)

Vinylic protons , 6.85 δ (s , 4H)



Bis-N-Phenyl-N'-(1,2-diphenylethano) maleamide

MODEL COMPOUND

Total number of protons = 30

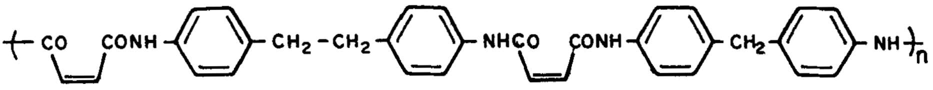
Types of protons :

$-\underset{\underset{O}{\|}}{C}-N\underline{H}-$, 8.6 δ (br., 4H)

Aromatic protons , 7.15-7.65 δ (m , 18H)

Ar$C\underline{H_2}$, 2.52 δ (s , 4H)

Vinylic protons, 6.55 δ (broad and s , 4H)



MDEBM

Total number of protons per repeat unit = 30

Types of protons :

$-\underset{\underset{O}{\|}}{C}-N\underline{H}-$, 8.35 δ (br., 4H)

Aromatic protons , 7.05-7.65 δ (m, 16H)

Ar$C\underline{H_2}$, 2.5-2.65 δ (t , 6H)

Vinylic protons , 6.65 δ (s , 4H)

FIG. 2. ^{1}H-NMR spectral chemical shift values for EBIMI, model compound, and the polymer MDEBM.

Characterization Methods

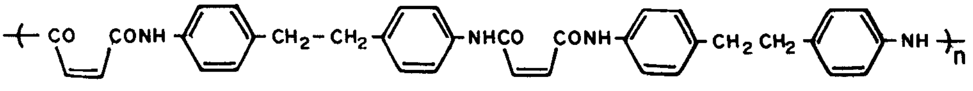
Elemental analyses of EBIMI, model compound, and polymeric samples were carried out on a C, H, O, N Elemental Analyzer (Perkin-Elmer 240 B Analyzer). The inherent viscosities of polymer solutions (0.05 g/dL) in sulfuric acid were determined at 25 ± 0.1°C by using an Ubbelohde suspended level viscometer. UV-Vis spectroscopy was carried out using a Carl-Zeiss UV-Vis Specord. The solubilities of polymers were examined using 0.01 g polymer in 1-2 mL solvent at ambient temperature. Infrared spectra (IR) were recorded by the KBr pellet method on a Perkin-Elmer Model 598 spectrophotometer. Proton NMR spectra were run on a Jeol FX90 QFT NMR spectrometer at room temperature in DMSO-d_6 using TMS as the internal reference. Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) data were collected using a Du Pont 1090 Thermal Analyzer at a heating rate of 10°C/min in N_2. Mass spectral analysis of the products obtained by the vacuum pyrolysis of the polymers was carried out in a MAT Model 112S instrument.

RESULTS AND DISCUSSION

N,N'-Ethylenedianilinobismaleamic acid was first prepared from maleic anhydride and DABB by ROPA. Employing the special dehydrating agent DCC, this bismaleamic acid was then cyclodehydrated to the isomaleimide, EBMIMI (Scheme 1). A model compound which describes well the chemical structure of the polymers was synthesized by ROPA of EBIMI with aniline in 1-methyl-2-pyrrolidinone at 20°C (Scheme 2). As can be seen, the elemental analysis data are acceptable. Polymaleamides were synthesized by ROPA of EBIMI with various aromatic diamines as shown in Scheme 3.

The yields of polymers, elemental analysis, inherent viscosity (η_{inh}), and electronic spectral data are summarized in Table 1. The elemental analysis data of polymers showed good agreement between calculated and estimated values. The small differences in C content for samples could be due to an incomplete purification of these polymers. The inherent viscosities of polymer solutions are in the 0.06–0.13 dL/g range. Polymer solubilities were determined for 10 common solvents at a concentration of 0.05 g/dL at 25 ± 0.1°C; the polymers were completely soluble in concentrated sulfuric acid but insoluble in organic solvents such as ethyl alcohol and acetone (Table 2).

The structures of the model compound and the polymaleamides were elucidated primarily by IR spectra (Fig. 1). The absorptions at 1780 and 1670 cm^{-1} are due to the presence of a five-membered lactone ring and a C=N— group, respectively. The absence of absorption for an imide group around 1720 cm^{-1} [28] also confirms the formation of only isoimide rings from bisamic acids through dehydration by DCC (Scheme 1). The IR spectra of the model compound and the polymaleamides reveal the disappearance of the characteristic absorption of the ring structure and the C=N— group and the appearance of the two new bands centered at 1600 and 3300 cm^{-1}, indicating respectively the C=O and N—H stretching vibrations of the newly created amide unit [29]. The absorptions at 2900 and 2850 cm^{-1}



BBEBM

Total number of protons per repeat unit = 32

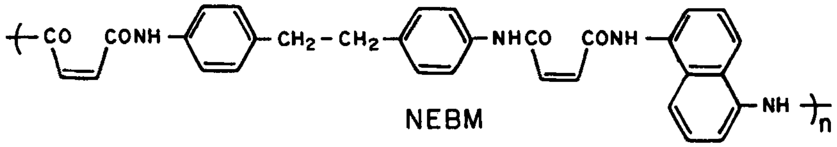
Types of protons :

$-\underset{\underset{O}{\|}}{C}-N\underline{H}-$, 8.8 δ (br.,4H)

Aromatic protons , 7.30–7.75 δ (m ,16H)

Ar$\underline{CH_2}$, 2.6 δ (t, 8H)

Vinylic protons , 6.45 δ (s ,4H)



NEBM

Total number of protons per repeat unit = 26

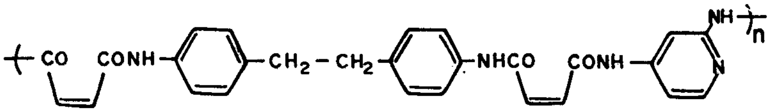
Types of protons :

$-\underset{\underset{O}{\|}}{C}-N\underline{H}-$,8.35 δ (br.,4H)

Aromatic and naphthalene ring protons , 7.0–8.1 δ (m ,14H)

Ar $\underline{CH_2}$, 2.4 δ (t ,4H)

Vinylic protons , 6.75 δ (s ,4H)



PYEBM

Total number of protons per repeat unit = 23

Types of protons :

$-\underset{\underset{O}{\|}}{C}-N\underline{H}-$, 8.35 δ (br., 4H)

Aromatic and pyridine ring protons , 6.95–7.85 δ (m, 11H)

Ar$\underline{CH_2}$, 2.35 δ (t , 4H)

Vinylic protons , 6.6 δ (s ,4H)

FIG. 3. ^{1}H-NMR spectral chemical shift values for the polymers BBEBM, NEBM, and PYEBM.

are assigned to the presence of C—H stretching vibration of the methylene group [30]. The absorption at 1570 cm^{-1} in the case of BBEBM is due to the presence of an amide II type band. DPSEBM shows strong absorptions at 1315 and 1150 cm^{-1}, corresponding to the symmetric and asymmetric stretching vibrations of the sulfone group. The N—H stretching vibration in the pyridine unit of PYEBM appears at 3035 cm^{-1}; the deformations due to ring C—H of the pyridine group of the polymaleamide appear along with amide III bands.

The UV-Visible absorption spectra of the model compound and the polymaleamides (Table 1) were recorded in concentrated sulfuric acid. The model compound has absorbances at 364 and 300 nm corresponding to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The extent of the shift toward red in MDEBM (370 nm) compared with the model compound (364 nm) is very small, even though the extension due to conjugation through the benzene ring is present. The slight blue shift in the case of DPSEBM (368 nm) may be due to the electron-withdrawing nature of the sulfone group. The introduction of an $-CH_2-CH_2-$ moiety in BBEBM between the benzene ring causes a shift toward blue (360 nm). The shift toward blue in the case of PYEBM (350 nm) is due to the lower resonance stabilization.

The ^{1}H-NMR chemical shift values of EBIMI, the model compound, and the polymaleamides MDEBM, BBEBM, NEBM, and PYEBM are presented in Figs. 2 and 3. The spectra of all four polymers showed a common feature with regard to the vinyl protons which appeared between 6.45-6.75δ. The fact that isomaleimide ring-opening has occurred is strongly evidenced by the appearance of —CONH protons in the model compound and polymaleamides, accounting for four —CONH protons in each polymer. Comparison of the polymaleamides with the model compound showed several similarities with regard to the chemical shifts of the —CONH (amide) protons (8.35-8.80δ) and aromatic protons (6.95-8.10δ). The aromatic protons presented a complex picture in general. The methylene groups linking the aromatic rings appeared between 2.35-265δ [31-34].

The thermal stabilities of polymers were evaluated by TGA in N_2 at a heating rate of 10°C/min. The TGA curves of the polymers are given in Fig. 4, and the thermogravimetry results are presented in Table 3. The initial decomposition temperature (IDT), the temperature at 10% polymer weight loss (T_{10}), and the integral procedural decomposition temperature (IPDT) [35] indicate the order of stability to be approximately NEBM > BBEBM > MDEBM > PYEBM ≃ DPSEBM. The presence of a condensed ring system in NEBM imparts a good thermal stability to the polymaleamide. The polymaleamides MDEBM, BBEBM, and DPSEBM, possessing two aromatic rings with the inclusion, in between the rings, of flexible groups $-CH_2-$, $-CH_2-CH_2-$, and $-SO_2-$, respectively, have a lower stability than NEBM [36-41]. As can be seen, only polymer NEBM is completely stable up to about 200°C while the other polymers are lost in the range of 2.5-3.5%, 125-150°C. The higher stability for the polymer NEBM could be due to the presence of the naphthalenic units in the polymer backbone.

The DSC curves (first heating, Fig. 5) show an endotherm below 200°C for the polymaleamides BBEBM and DPSEBM. The thermal stability for TGA curves is reflected by the occurrence of an exothermal peak. The higher the stability in the 2.5-3.5% range, the higher the temperature onset for the exothermal peak. The T_{10}

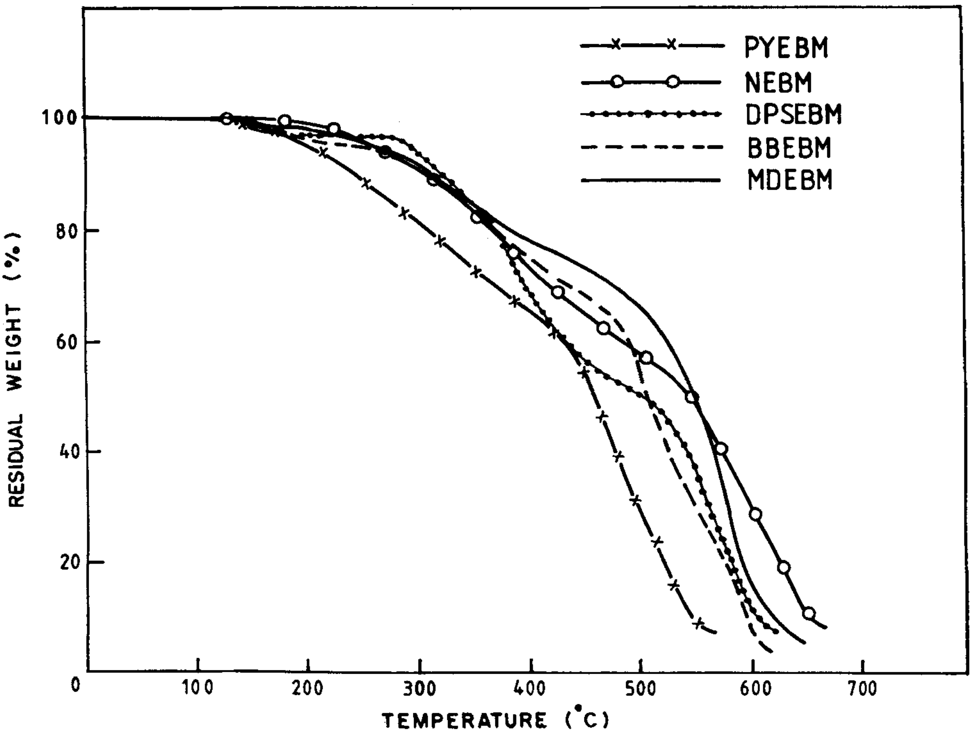


FIG. 4. The TGA thermograms of polymaleamides measured at a heating rate of 10°C·min^{-1}.

value for the polymaleamide DPSEBM (320°C) agrees remarkably with its exothermic transition temperature.

Mass spectral studies of the polymers MDEBM, BBEBM, and DPSEBM were carried out. Their mass spectra are given in Figs. 6–8. Identification of the major fragments provided sufficient information to postulate a fragmentation mechanism for the degradation of the polymaleamides (Schemes 4–6) in line with earlier reports

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

Polymer	IDT	T_{10}	IPDT
MDEBM	140	315	287
BBEBM	150	315	343
DPSEBM	125	320	260
NEBM	200	370	363
PYEBM	125	245	261

[a] In nitrogen (heating rate, 10°C/min).

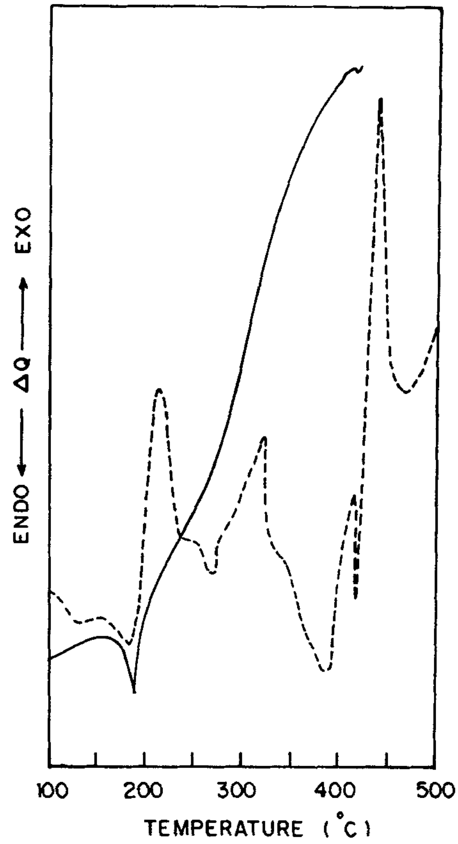


FIG. 5. The DSC curves for the polymaleamides: BBEBM (——) and DPSEBM (- - -).

[42-48]. The fragmentations are accounted for from the repeat unit in the case of DPSEBM (Scheme 6); however, in the cases of MDEBM and BBEBM, extended repeating units are taken into consideration to account 1) for species A and B (Scheme 4) and 2) for species A (Scheme 5), respectively. The formation of a tropylium structure from a molecule with a toluene component has been reported in the literature [46]. In Schemes 4-6, *m/e* 106 is due to a tropylium species $[C_7H_8N]^+$ with a $-NH_2$ substituent; the mass spectra of BBEBM show a very intense fragmentation peak with *m/e* 106 at higher temperature. In all three cases, namely MDEBM, BBEBM, and DPSEBM, the doubly-charged diaminodiphenylethane species is seen at *m/e* 212. In addition, in the case of DPSEBM, diaminodiphenylsulfone is seen at *m/e* 248; in the case of MDEBM, diaminodiphenylmethane is seen at *m/e* 198. In all cases the maleimide part as a diketene fragment at *m/e* 82 or maleimide at *m/e* 98 or maleic anhydride at *m/e* 99 was observed. The maleimide moiety in fragments A and C of MDEBM, in fragments D and G of BBEBM, and in fragments A and B of DPSEBM can be easily obtained from the polymers.

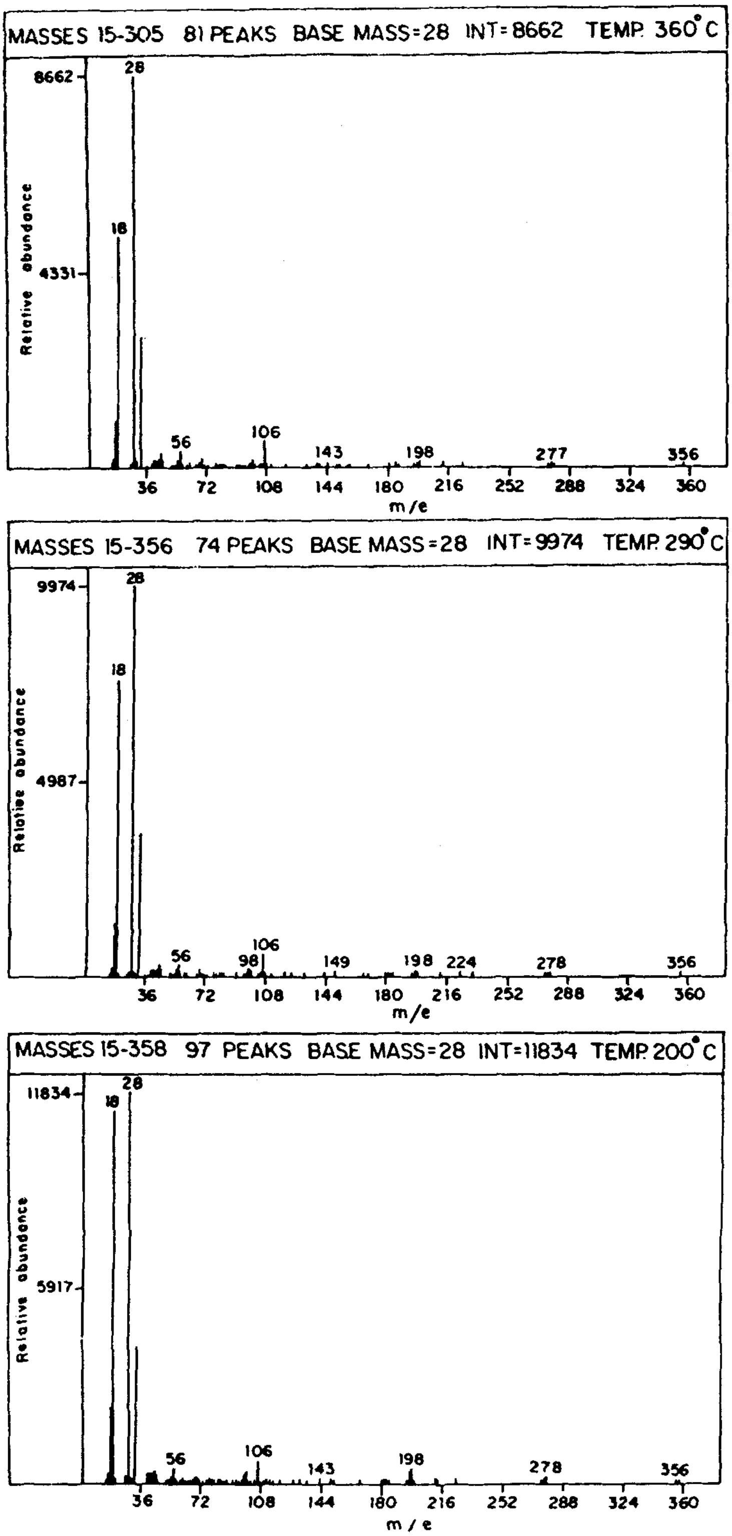


FIG. 6. The mass spectra of pyrolysate MDEBM at 200, 290, and 360°C (Scheme 4).

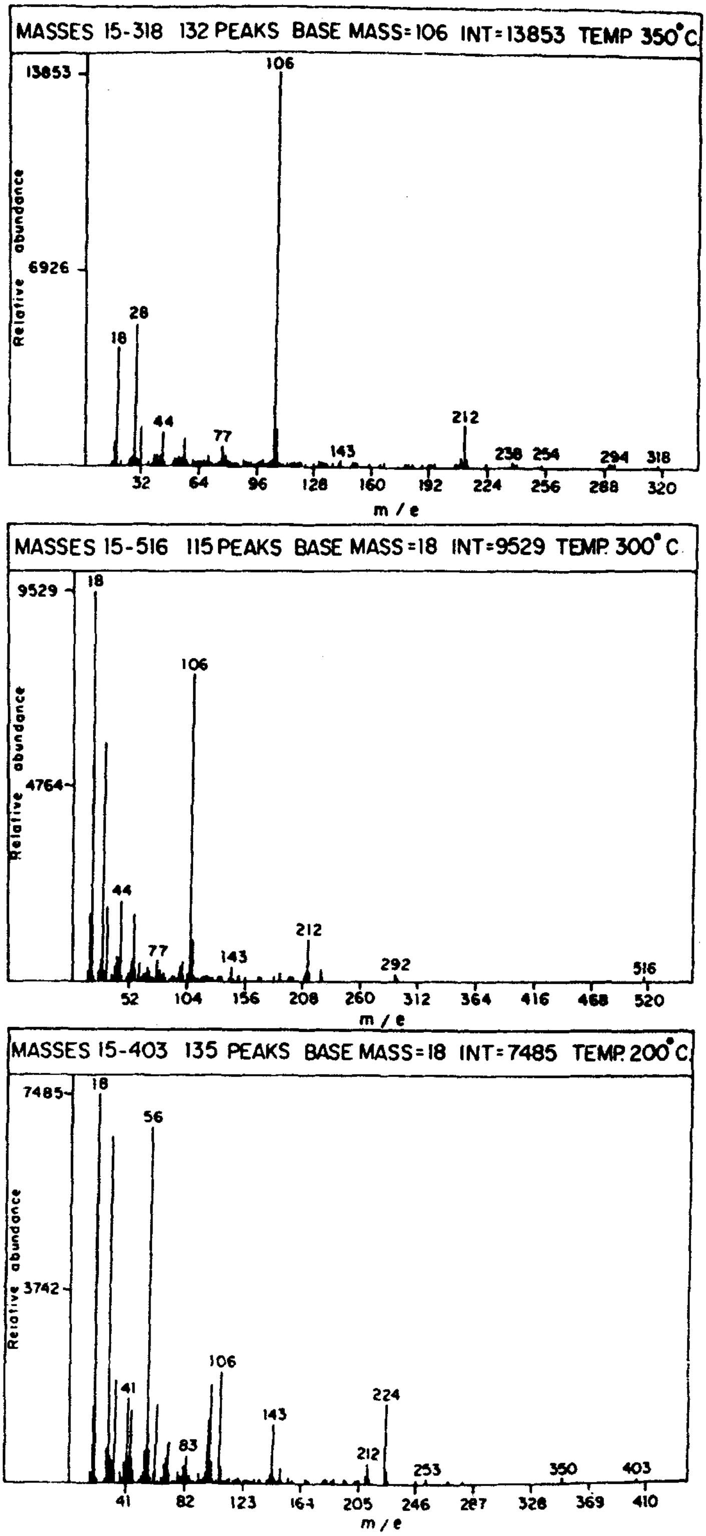


FIG. 7. The mass spectra of pyrolysate BBEBM at 200, 300, and 350°C (Scheme 5).

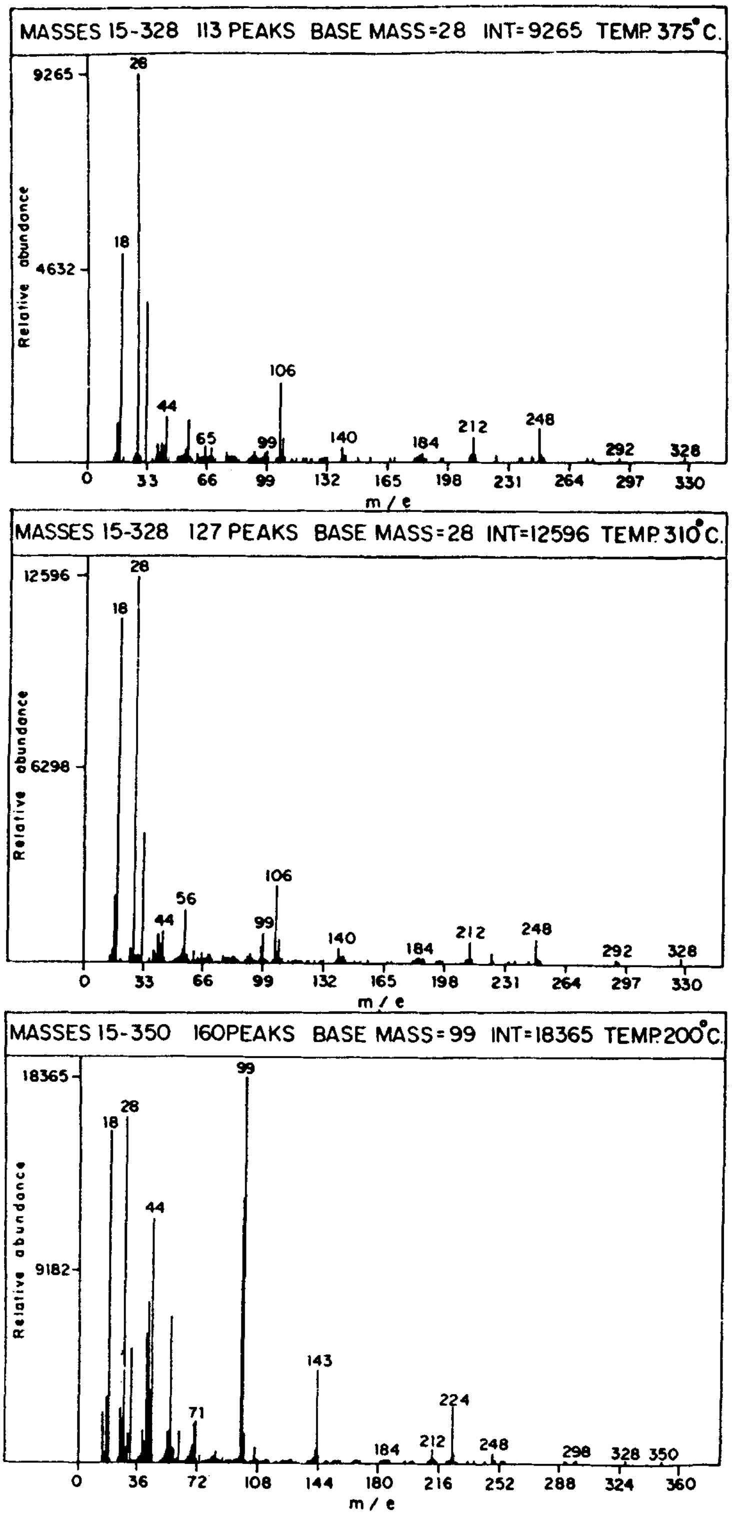
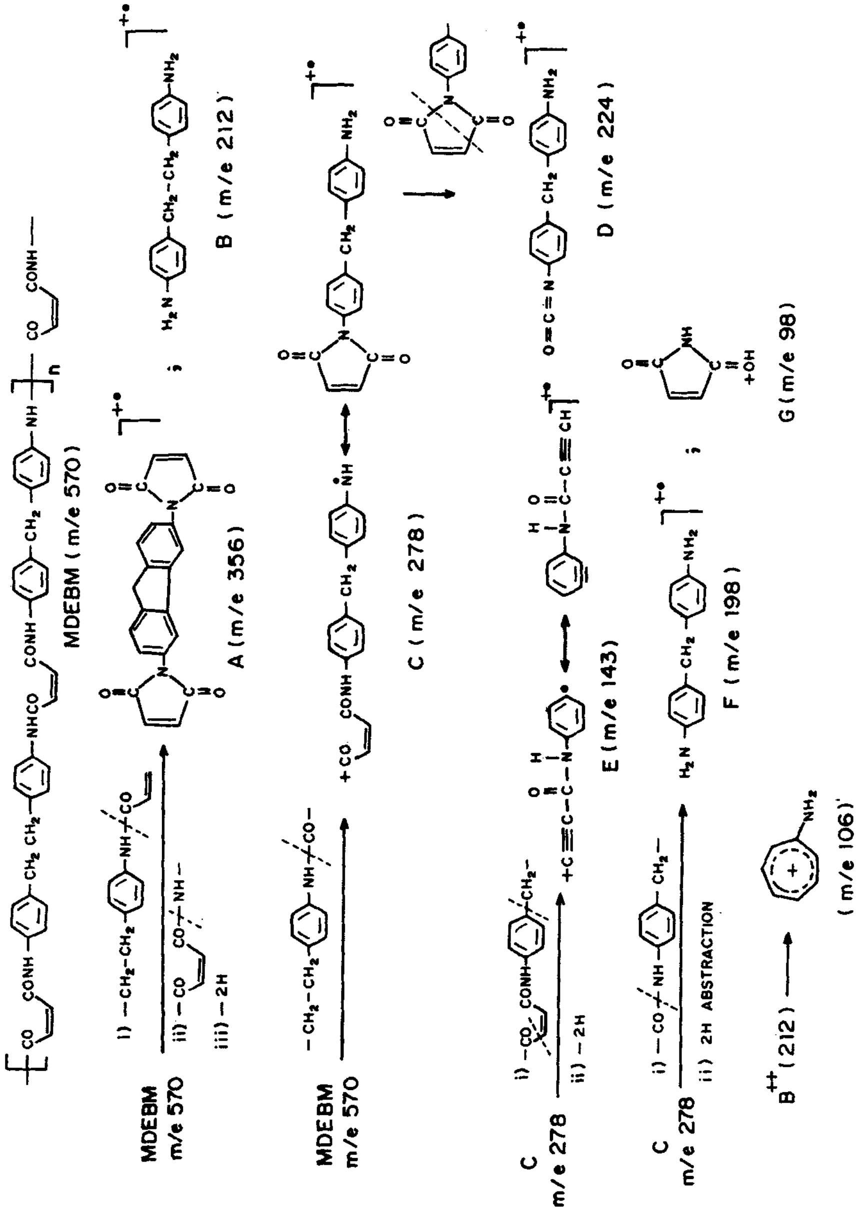
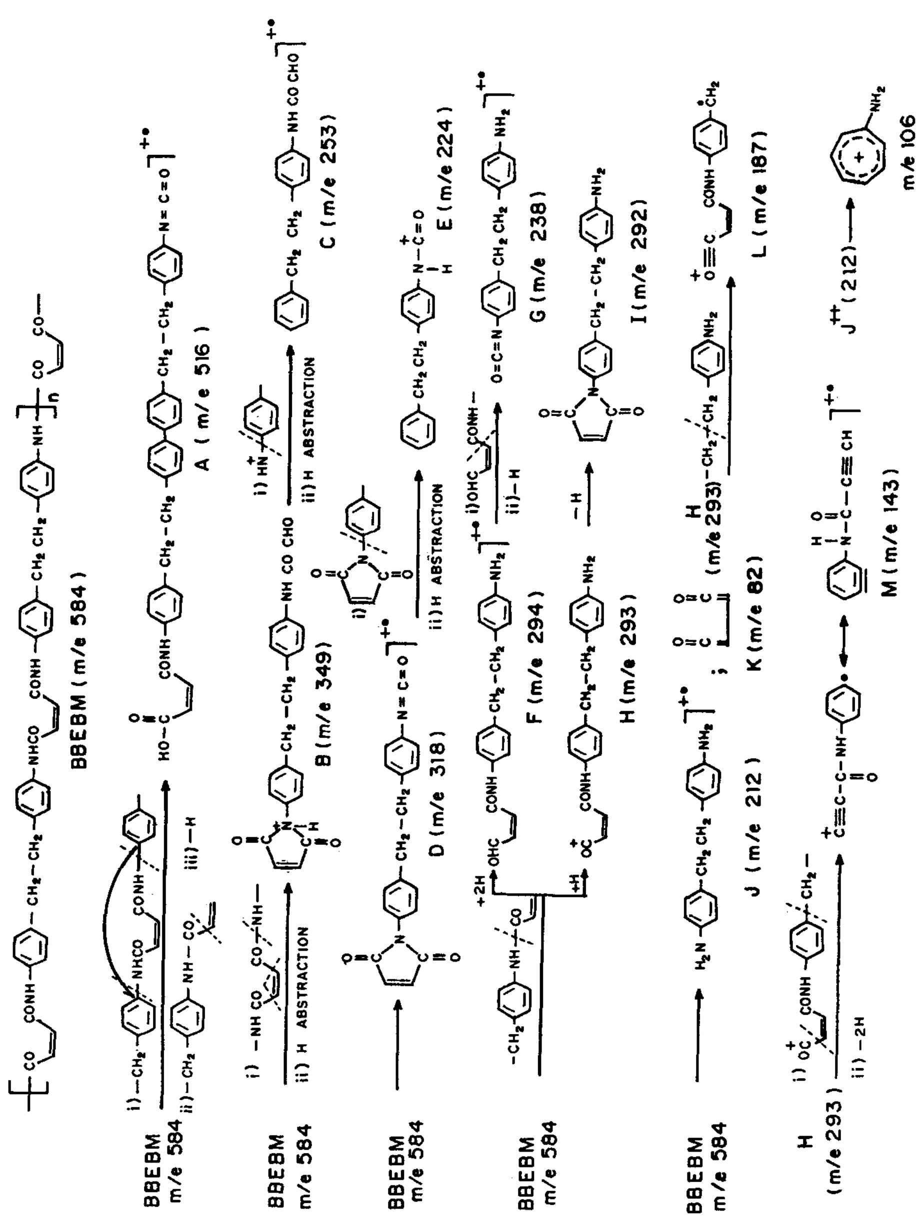


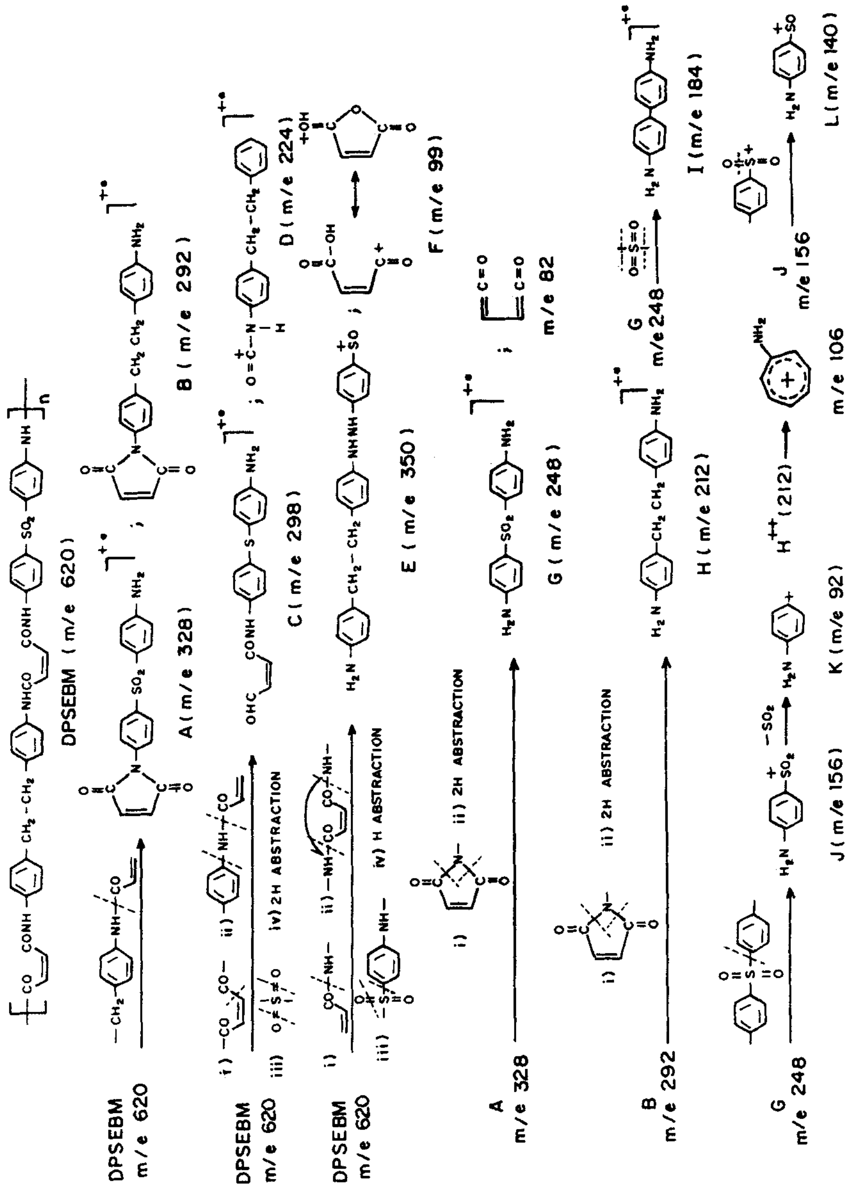
FIG. 8. The mass spectra of pyrolysate DPSEBM at 200, 310, and 375°C (Scheme 6).


MDEBM (m/e 570)
MDEBM m/e 570
i) —CH2-CH2—
ii) —CO
iii) —2H
A (m/e 356)
B (m/e 212)
C (m/e 278)
D (m/e 224)
C m/e 278
i) —CO
ii) —2H
E (m/e 143)
F (m/e 198)
G (m/e 98)
i) —CO
ii) 2H ABSTRACTION
B++ (212)
(m/e 106)

SCHEME 4.


BBEBM (m/e 584)
BBEBM m/e 584
A (m/e 516)
B (m/e 349)
C (m/e 253)
D (m/e 318)
E (m/e 224)
F (m/e 294)
G (m/e 238)
H (m/e 293)
I (m/e 292)
J (m/e 212)
K (m/e 82)
L (m/e 187)
M (m/e 143)
m/e 106
J++ (212)
ii) H ABSTRACTION

SCHEME 5.


DPSEBM (m/e 620)
DPSEBM m/e 620
A (m/e 328)
B (m/e 292)
C (m/e 298)
D (m/e 224)
E (m/e 350)
F (m/e 99)
m/e 82
G (m/e 248)
H (m/e 212)
I (m/e 184)
J (m/e 156)
K (m/e 92)
L (m/e 140)
m/e 106
H⁺⁺ (212)
−SO₂
i) ii) iii) iv) 2H ABSTRACTION
iv) H ABSTRACTION
ii) 2H ABSTRACTION
A m/e 328
B m/e 292
G m/e 248
J m/e 156

SCHEME 6.

CONCLUSION

A detailed study of synthesis and characterization of polymaleamides from *N,N'*-ethylenedianilinobisisomaleimide and five aromatic diamines has been performed. The ^{1}H-NMR spectra are in good accord with the proposed structure for these polymers. TGA reveals the polymer NEBM to have higher stability compared to others due to the presence of naphthalenic units in its repeat unit structure. All the polymaleamides, MDEBM, BBEBM, and DPSEBM, formed doubly-charged diaminobibenzyl species at m/e 212 and the maleimide part as diketene fragment at m/e 82 or maleimide at m/e 98 or maleic anhydride at m/e 99.

ACKNOWLEDGMENT

The authors are indebted to Dr. K. Rajagopalan, Professor and Head, Department of Organic Chemistry, University of Madras, for useful discussions.

REFERENCES

[1] Y. Imai, M. Ueda, and K. Okuyama, *J. Polym. Sci., Polym. Chem. Ed., 17,* 1901 (1979).

[2] M. Ueda, M. Yabuuchi, and Y. Imai, *Ibid., 15,* 323 (1977).

[3] I. Hayashi, S. Takahashi, and Y. Hachihama, *Kogyo Kagaku Zasshi, 60,* 646 (1957).

[4] C. S. Cleaver and B. C. Pratt, *J. Am. Chem. Soc., 77,* 1541 (1955).

[5] N. Ogata, K. Sanui, and K. Konishi, *Kobunshi Kagaku, 30,* 202 (1973).

[6] M. Ueda, K. Kino, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed., 13,* 659 (1975).

[7] M. Ueda, M. Yabuuchi, and Y. Imai, *Ibid., 15,* 2641 (1977) and references therein.

[8] M. Ueda, K, Kino, K. Yamaki, and Y. Imai, *Ibid., 16,* 155 (1978).

[9] C. D. Diakoumakos, J. A. Mikroyannidis, C. A. Krontiras, M. N. Pisanias, and S. N. Georga, *Eur. Polym. J., 31,* 1057 (1995).

[10] A. Takahashi, M. Suzuki, and W. Wajima, *J. Appl. Polym. Sci., 43,* 943 (1991).

[11] D. A. Holmer, O. A. Pickett, and J. H. Saunders, *J. Polym. Sci., Polym. Chem. Ed., 10,* 1547 (1972).

[12] T. C. Pletcher and P. W. Morgan, *Ibid., 18,* 643 (1980).

[13] R. Nagarathinam and S. Viswanathan, *Polym. Bull., 16,* 147 (1986).

[14] R. Nagarathinam and S. Viswanathan, *Polym. J., 18,* 865 (1986).

[15] N. Rajeswari, S. Viswanathan, and H. Kothandaraman, *Indian J. Chem., 28A,* 965 (1989).

[16] N. Rajeswari, R. Nagarathinam, S. Viswanathan, H. Kothandaraman, and E. Ponnusamy, *J. Macromol. Sci.—Chem., A26,* 1585 (1989).

[17] N. Rajeswari, G. Roshan Deen, and S. Viswanathan, *Indian J. Chem., 33B,* 1170 (1994).

[18] E. R. Nagarajan, N. Rajeswari, R. Nagarathinam, S. Viswanathan, and V. T. Ramakrishnan, *Polym. Int.*, *39*, 141 (1996).

[19] E. R. Nagarajan, N. Rajeswari, R. Nagarathinam, and S. Viswanathan, *Eur. Polym. J.*, In Press.

[20] S. Viswanathan, R. Nagarathinam, and N. Rajeswari, *Polymer*, In Press.

[21] *CRC Handbook of Chemistry and Physics*, 56th ed., CRC Press, London, 1975.

[22] H. O. House, *Org. Synth.*, *34*, 35 (1954).

[23] H. Minlon, *J. Am. Chem. Soc.*, *70*, 2802 (1948).

[24] Yu. Lichi and Jo-Yung, *Mol. Ke Hsuch Tung Pao, 2*, 50 (1957); *Chem. Abstr.*, *53*, 18896i (1959).

[25] R. E. Buckles, *J. Chem. Educ.*, *31*, 36 (1954).

[26] C. D. Hurd, A. S. Roe, and J. W. Williams, *J. Org. Chem.*, *2*, 314 (1938).

[27] R. J. Cottor, C. K. Sauers, and J. M. Whelan, *Ibid.*, *26*, 10 (1961).

[28] I. K. Varma, Sangita, and D. S. Varma, *J. Polym. Sci., Polym. Chem. Ed.*, *22*, 1419 (1984).

[29] M. G. Gherasim and L. Zugravescu, *Eur. Polym. J.*, *14*, 985 (1978).

[30] A. D. Cross, *Introduction to Practical Infrared Spectroscopy*, 2nd ed., Butterworths, London, 1964.

[31] I. Ya. Slonim and A. N. Lyubimov, *The NMR of Polymers*, Plenum Press, New York, NY, 1970.

[32] P. A. Mirau, *Polymer Characterization—NMR Characterization of Polymers* (B. J. Hunt and M. I. James, Eds.), Blackie Academic & Professional, London, 1993, Chap. 3.

[33] L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed., Pergamon, New York, NY, 1969.

[34] C. H. Yoder and C. D. Schaeffer Jr., *Introduction to Multinuclear NMR—Theory and Application*, Benjamin/Cummings, California, 1987.

[35] C. D. Doyle, *Anal. Chem.*, *33*, 77 (1961).

[36] D. D. Coffman, G. F. Berchet, W. R. Peterson, and E. W. Spanagel, *J. Polym. Sci.*, *2*, 306 (1947).

[37] S. L. Kwolek and P. W. Morgan, *J. Polym. Sci., Part A*, *2*, 2693 (1964).

[38] F. M. Silver and F. Dobinson, *J. Polym. Sci., Polym. Chem. Ed.*, *15*, 2535 (1977).

[39] R. S. Lenk, J. F. Fellers, and J. L. White, *Polym. J.*, *9*, 9 (1977).

[40] I. K. Varma, V. S. Sundari, and D. S. Varma, *J. Appl. Polym. Sci.*, *22*, 2857 (1978).

[41] J. J. Maguire and R. S. Lenk, *Ibid.*, *30*, 3283 (1985).

[42] R. Davis and M. Frearson, *Mass Spectrometry—Analytical Chemistry by Open Learning* (F. E. Prichard, Ed.), Wiley, New York, NY, 1989.

[43] Y. P. Khanna, E. M. Pearce, J. S. Smith, D. T. Burkitt, H. Njuguna, D. M. Hindenlang, and B. D. Forman, *J. Polym. Sci., Polym. Chem. Ed.*, *19*, 2817 (1981).

[44] G. F. L. Ehlers, K. R. Fisch, and W. R. Powell, *J. Polym. Sci., Part A-1*, *8*, 3511 (1970).

[45] D. A. Chatfield, I. N. Einhorn, R. W. Mickelson, and J. H. Futrell, *J. Polym. Sci., Polym. Chem. Ed.*, *17*, 1367 (1979).

[46] F. W. McLafferty, *Interpretation of Mass Spectra*, 2nd ed., Benjamin/Cummings, Massachusetts, 1978.

[47] H. Budzikiewiez, C. Djerassi, and D. H. Williams, *Interpretation of Mass Spectra of Organic Compounds*, Holden-Day, San Francisco, CA, 1964, p. 174.

[48] H. Budzikiewiez, C. Djerassi, and D. H. Williams, *Mass Spectrometry of Organic Compounds*, Holden-Day, San Francisco, CA, 1967, p. 558.

Received April 1, 1996
Revision received October 5, 1996