

# Syntheses of Bismaleimides with Ester Units and Their Polymerization with Diamines

M. SAVA

"Petru Poni" Institute of Macromolecular Chemistry, 41 A Grigore Ghica Voda, Iasi Ro—6600, Romania

Received 27 April 2001; accepted 28 July 2001

**ABSTRACT:** Five structurally different bismaleimides were synthesized by reaction between 3(4)-maleimidobenzylchloride with various diphenols. They were characterized by infrared (IR) and proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ) spectroscopy. Thermal characterization of monomers and their polymers was accomplished by differential scanning calorimetry (DSC) and dynamic thermogravimetric analysis (TGA). Polyaminobismaleimides having inherent viscosities of 0.1–0.4 dL/g were prepared by Michael addition of diamines to bismaleimides. The polymers are soluble in solvents as DMF, NMP, and DMSO, and afforded film from their solutions. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 750–757, 2002; DOI 10.1002/app.10294

**Key words:** bismaleimides; polyaminobismaleimides; thermal properties; mechanical properties; solubility

## INTRODUCTION

Bismaleimide resins are a generation of matrix resins having better thermal stability, better fire resistance than epoxy resins, and excellent mechanical properties.<sup>1–6</sup> A wide variety of polyimides with end-capped reactive maleimide have been developed in the last 30 years with the aim of improving the processability without altering their thermal behavior and mechanical strength. However, the applications are restricted by solvent retention in the prepregs, brittleness of polymers due to high crosslink density, and the high temperatures used for curing.<sup>7–9</sup>

Brittleness of polymers has been overcome by chain-extended bismaleimide prepolymer molecules modification, which was prepared by Michael addition reaction of bismaleimides with diamines.

This paper continues our work in order to develop some improved heat- and fire-resistant bismaleimide resins with reduced brittleness. We

presently report on the synthesis of bismaleimides containing ester units and resins obtained from these (Scheme 1). We postulated that the resins containing hexafluoroisopropylidene units, and oxyethylene units or ether groups, will increase physical and mechanical performances.

## EXPERIMENTAL

### Synthesis

#### *3-Maleimido Benzoic Acid (3-MBA) and 4-Maleimido Benzoic Acid (4-MBA)*

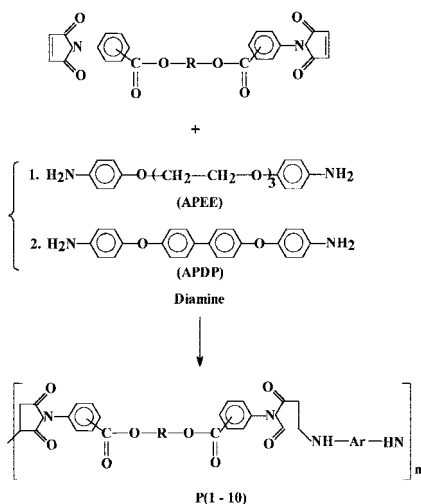
The products were obtained as described<sup>10</sup>; mp 3-MBA: 238–240°C; mp 4-MBA: 225–229°C. Reference 11: mp 239–241 and 225–228°C, respectively.

#### *3-Maleimido Benzoic Acid Chloride (3-MBAC) and 4-Maleimido Benzoic Acid Chloride (4-MBAC)*

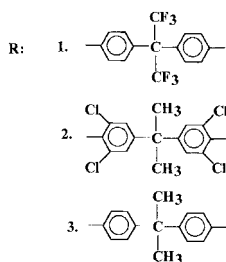
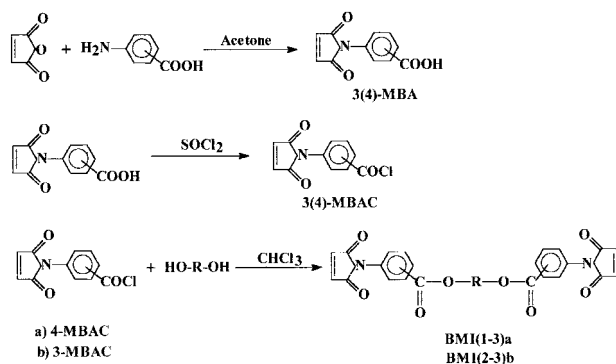
The products were prepared as described in literature<sup>12</sup>; mp 3-MBAC: 125–128°C; mp 4-MBAC: 169–171°C. Reference 13: mp 4-MBAC 170°C.

Correspondence to: M. Sava (ftanasa@ichpp.tuiasi.ro).

*Journal of Applied Polymer Science*, Vol. 84, 750–757 (2002)  
© 2002 John Wiley & Sons, Inc.



Polymer	BMI	Diamine
P-1	BMI-1a	APEE
P-2	BMI-1a	APDP
P-3	BMI-2a	APEE
P-4	BMI-2a	APDP
P-5	BMI-3a	APEE
P-6	BMI-3a	APDP
P-7	BMI-2b	APEE
P-8	BMI-2b	APDP
P-9	BMI-3b	APEE
P-10	BMI-3b	APDP



Scheme 1

### General Procedure for the Preparation of Bismaleimides BMI(1-3)a and BMI(2-3)b

Bismaleimides were synthesized following the literature.<sup>14</sup>

3-MBAC or 4-MBAC (0.05 mol) in 50 mL  $\text{CHCl}_3$  was cooled in an ice bath. Triethylamine

(0.027 mol) as acid acceptor and a solution of diphenol (0.025 mol) in 50 mL  $\text{CHCl}_3$  were added. After stirring for 1 h, the mixture was filtered and precipitated in n-heptane. The product was filtered and treated with sodium bicarbonate solution, and then thoroughly washed (3 times) with water. The filtered precipitated product was recrystallized.

### Bismaleimide 1a (BMI 1a)

The product was recrystallized from dichloroethane/ethanol. Yield 68%; mp 212–215°C.

IR (KBr)  $\text{cm}^{-1}$ , 1780 and 1730 (C=O imide), 1750 (C=O ester).

Anal. calcd. for  $\text{C}_{37}\text{H}_{20}\text{F}_6\text{N}_2\text{O}_8$  (%): C, 60.49; H, 2.74; F, 15.51; N, 3.81. Found: C, 60.13; H, 2.95; F, 15.31; N, 3.73.

### Bismaleimide 2a (BMI 2a)

The bismaleimide was recrystallized from dichloroethane/ethanol. Yield 73%; mp 276–279°C.

IR (KBr)  $\text{cm}^{-1}$ , 1780 and 1730 (C=O imide), 1755 (C=O ester).

Anal. calcd. for  $\text{C}_{37}\text{H}_{22}\text{Cl}_4\text{N}_2\text{O}_8$  (%): C, 58.15; H, 2.90; Cl, 18.55; N, 3.66. Found: C, 57.83; H, 3.11; Cl, 18.63; N, 3.78.

### Bismaleimide 3a (BMI 3a)

The product was recrystallized from  $\text{CHCl}_3$ . Yield 71%; mp 214–216°C.

IR (KBr)  $\text{cm}^{-1}$ , 1790 and 1725 (C=O imide), 1745 (C=O ester).

Anal. calcd. for  $\text{C}_{37}\text{H}_{26}\text{N}_2\text{O}_6$  (%): C, 70.92; H, 4.15; N, 4.47. Found: C, 71.15; H, 4.29; N, 4.31.

### Bismaleimide 2b (BMI 2b)

The monomer was recrystallized from n-heptane/dichloroethane. Yield 76%; mp 240–243°C.

IR (KBr)  $\text{cm}^{-1}$ , 1720 (C=O imide), 1760 (C=O ester).

Anal. calcd. for  $\text{C}_{37}\text{H}_{22}\text{Cl}_4\text{N}_2\text{O}_8$  (%): C, 58.15; H, 2.90; Cl, 18.55; N, 3.66. Found: C, 57.91; H, 2.77; Cl, 18.73; N, 3.79.

### Bismaleimide 3b (BMI 3b)

The bismaleimide was recrystallized from dichloroethane/ethanol. Yield 73%; mp 167–170°C.

IR (KBr)  $\text{cm}^{-1}$ , 3000–2900 (C— $\text{CH}_3$ ), 1740 (C=O ester), 1720 (C=O imide).

Anal. calcd. for  $\text{C}_{37}\text{H}_{22}\text{Cl}_4\text{N}_2\text{O}_8$  (%): C, 58.15; H, 2.90; Cl, 18.55; N, 3.66. Found: C, 57.91; H, 2.77; Cl, 18.73; N, 3.79.

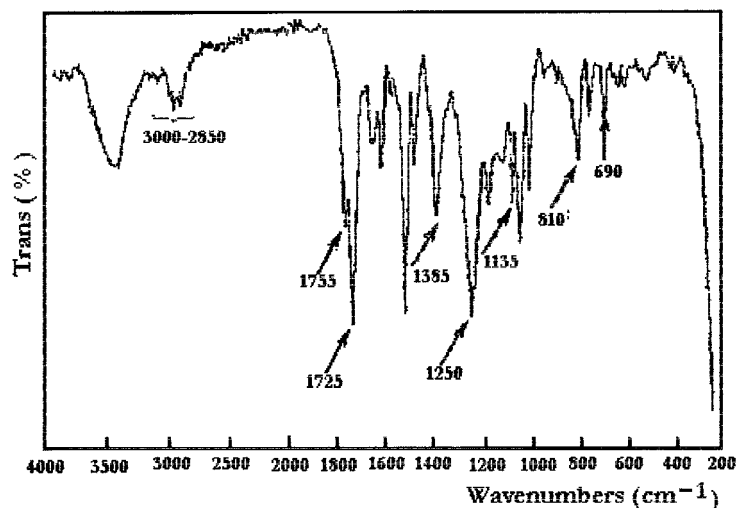


Figure 1 IR spectra of monomer BMI 2a.

### Synthesis of Polymers

The polymers were prepared as described in literature.<sup>15</sup>

Into 50 mL three-necked flask fitted with mechanical stirrer, thermometer, and nitrogen inlet were charged 0.01 moles BMI, 0.01 moles diamine, *m*-cresol, or *N*-methylpyrrolidone-2-one (NMP) as solvent (up to 10–15% monomer concentration), and a small amount of acetic acid when NMP was used as solvent. The reaction mixture was kept in a water bath at 95°C. The polymers were isolated by pouring the mixture into methanol to give brown powder polymers. The products were filtered off, and washed thoroughly. In order to obtain higher molecular weight polymers, the reaction conditions (time, solvent, concentration) were varied.

### MEASUREMENTS

The IR spectra were recorded on a Specord M90 Carl Zeiss Jena Spectrophotometer using the KBr pellet technique. <sup>1</sup>H-NMR spectra were run on a JEOL 60MHz, NMR spectrometer at 60°C in DMSO-*d*<sub>6</sub> using tetramethylsilane (TMS) as internal reference. Differential scanning calorimetry (DSC) measurements were done by using a Mettler TA, instrument DSC 12E with a heating rate of 10°C/min in nitrogen. Thermal gravimetric analysis (TGA) was carried out in air with an F. Paulik Derivatograph at a heating rate of 12°C/min. The inherent viscosities of polymer solutions measured at concentration of 0.5 g/dL in NMP were determined at 25°C using an Ubbelohde sus-

pending level viscometer. Volume resistivity was measured by using a TERALIN Straton Electrometer. The dielectric constant was measured using a Digital RLC Meter E 0711 at 1 kHz. The stress-strain properties of polymer films were measured at room temperature, at a cross-head speed of 20 mm/min on an Instron Tensile Tester TIRA TEST-2161 using a E-MODUL AND DEHNGRENZEN program.

## RESULTS AND DISCUSSION

### Monomer Synthesis

The IR spectra of obtained bismaleimides showed characteristic carbonyl doublet in the range 1780–1720  $\text{cm}^{-1}$ . Characteristic bands of imide groups were observed in the range 1395–1385  $\text{cm}^{-1}$  (imide II), 1145–1135  $\text{cm}^{-1}$  (imide III), and 705–695  $\text{cm}^{-1}$  (imide IV). The absorption peaks around 1760–1740  $\text{cm}^{-1}$  correspond to the ester groups. Bismaleimides (2–3)a and (2–3)b showed an absorption band at 3000–2850  $\text{cm}^{-1}$  due to aliphatic groups. In addition, the characteristic absorption of per fluoromethyl group of monomer BMI 1a appeared in the range 1215–1190  $\text{cm}^{-1}$ . Figure 1 presents the infrared (IR) spectra of bismaleimide BMI 2a.

The <sup>1</sup>H-NMR spectra of bismaleimide BMI 1a confirmed its chemical structure.

From Figure 2, it can be seen that the aromatic protons of monomer BMI 1a appear as two separated doublet in the range 8.18–8.04 (Ar-H, *ortho* to —COO), and 7.58–7.42 (Ar-H, *ortho* to maleimide). The bismaleimide BMI 1a showed a sin-

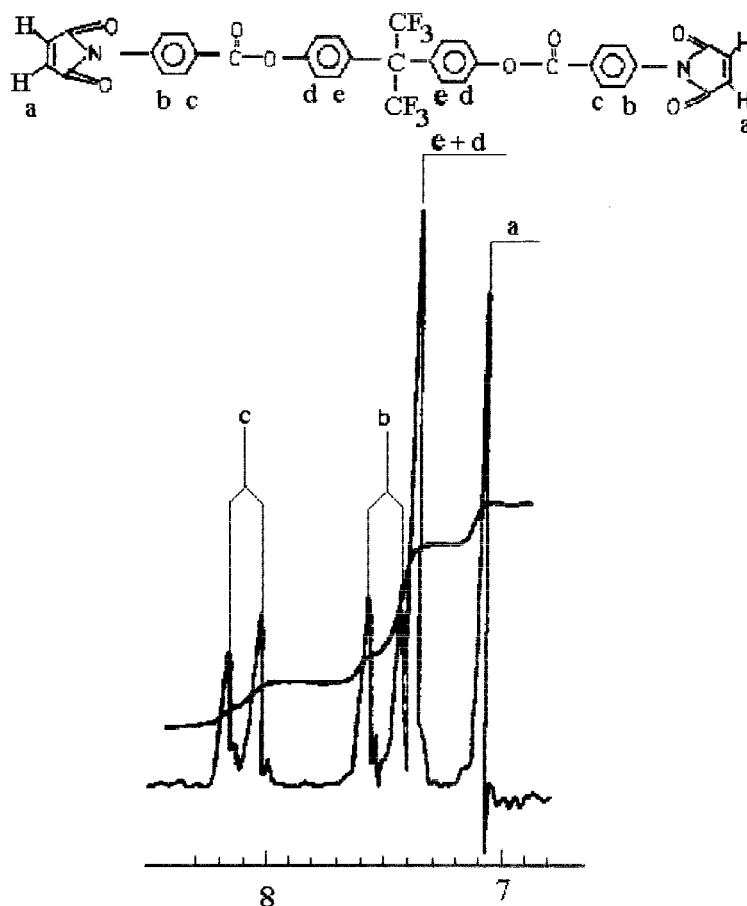


Figure 2  $^1\text{H-NMR}$  spectra of monomer BMI 1a.

glet at 7.37 [Ar-H, *ortho* to OCO and Ar-H, *ortho* to  $-\text{C}(\text{CF}_3)$ ] and another singlet at 7.06 due to olefinic protons.

All monomers were analyzed by DSC—Figure 3.

The DSC curves for the bismaleimides were characterized by a sharp melting endotherm in the temperature range 188–290°C and it is due to the melting of these monomers. The monomers exhibited an exothermic transition associated with thermal curing at 292–319°C. The onset temperature for curing reaction, in the case of bismaleimides BMI 2a and BMI 2d, was overshadowed by melting endotherm. The higher onset of cure of BMI 1a may be due to the high electron-withdrawing capacity of the perfluoromethyl group.

### Polymer Synthesis

The polyaminobismaleimides with ester units were synthesized by Michael addition of 1,2-bis-[2-(4-aminophenoxy)ethoxy]ethane (APEE) and

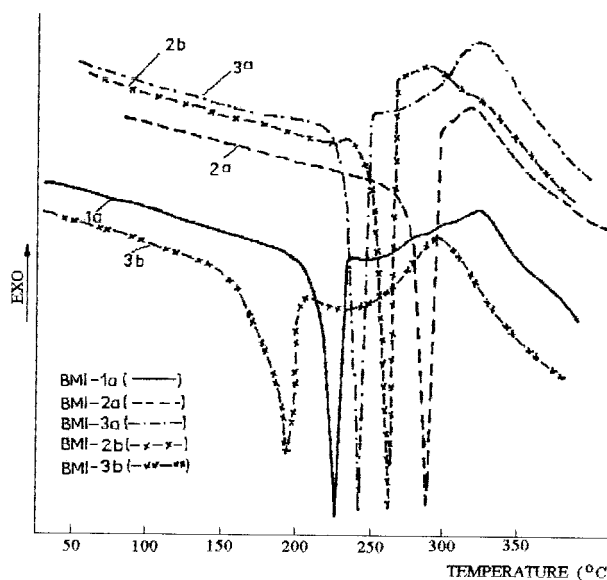


Figure 3 DSC scans of bismaleimides BMI(1–3)a and BMI(2–3)b in nitrogen atmosphere at heating rate of 10°C/min.

**Table I Reaction Between Bismaleimides and Diamines<sup>a</sup>**

No.	Bismaleimide	Diamine <sup>c</sup>	Solvent	Temp. (°C)	Time (h)	Conc. (%)	$\eta_{inh}^b$ (dL/g)	Films Prop.	Elemental Analysis					
									Calcd.	Found	C%	H%	N%	Cl%
1	BMI 1a	APEE	NMP	95	8	15	0.17	—	Calcd.	62.03	3.97	5.26	—	10.70
									Found	61.71	3.83	5.23	—	10.41
2	BMI 1a	APEE	NMP	95	20	15	0.34	Flexible	Calcd.	62.03	3.97	5.26	—	10.70
									Found	60.94	4.21	5.09	—	10.22
3	BMI 1a	APDP	NMP	95	10	10	0.30	Flexible	Calcd.	66.42	3.65	5.08	—	10.33
									Found	65.61	4.01	4.83	—	9.89
4	BMI 2a	APEE	Cresol	95	4	10	0.22	Brittle	Calcd.	60.23	4.22	5.11	12.92	—
									Found	61.42	4.63	4.75	12.47	—
5	BMI 2a	APEE	NMP	95	4	10	0.25	Flexible	Calcd.	60.23	6.22	5.11	12.92	—
									Found	60.94	3.82	5.41	12.36	—
6	BMI 2a	APDP	NMP	95	15	15	0.096	Very brittle	Calcd.	64.67	3.74	4.94	12.52	—
									Found	63.84	4.07	5.51	12.81	—
7	BMI 3a	APEE	Cresol	95	4	10	0.40	Flexible	Calcd.	68.88	5.25	5.84	—	—
									Found	69.13	4.89	6.05	—	—
8	BMI 2b	APEE	Cresol	95	4	10	0.27	—	Calcd.	60.23	4.22	5.11	12.92	—
									Found	59.85	4.03	5.07	12.88	—
9	BMI 2b	APEE	NMP	95	12	15	—	Brittle	Calcd.	60.23	4.22	5.11	11.92	—
									Found	61.45	3.87	5.44	12.15	—
10	BMI 3b	APEE	NMP	95	20	15	0.16	—	Calcd.	68.88	5.25	5.84	—	—
									Found	69.76	5.46	5.38	—	—

<sup>a</sup> Reactions between bismaleimides and diamines were carried out by mixing and heating equimolar mixtures of reagents dissolved in NMP or m-cresol.

<sup>b</sup> Inherent viscosity measured at a concentration of 0.5 g/dL in NMP at 25°C.

<sup>c</sup> APEE, 1,2-bis-[2-(4-aminophenoxy)ethoxy]ethane; APDP, 4,4'-bis(4-aminophenoxy)diphenyl.

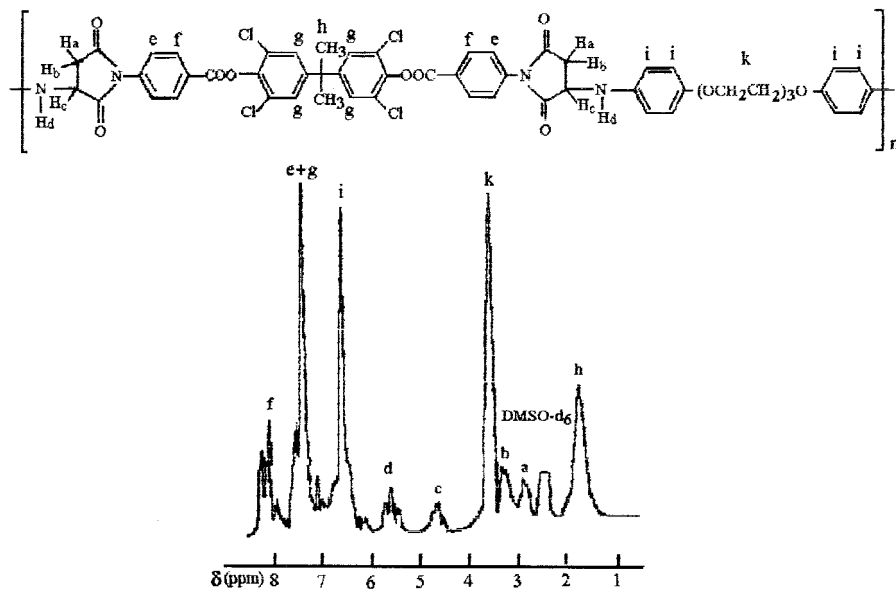


Figure 4  $^1\text{H-NMR}$  spectra of polymer P-3.

4,4'-bis(4-aminophenoxy)diphenyl (APDP) to bismaleimides in NMP or *m*-cresol at  $95^\circ\text{C}$ . The polymers were isolated by pouring the reaction mixture into methanol to give brown powder polymers. Results are summarized in Table I.

The structures of the polymers were confirmed by IR and  $^1\text{H-NMR}$  spectra, and by elemental analysis. The IR spectra showed that polymers are characterized by the same absorption bands as the monomers, but they are wider. The  $^1\text{H-NMR}$  spectrum of polymer P-3 displays signals at 8.24–8.09 (d, *ortho* to  $-\text{COO}$ ), at 7.56–7.39—which are attributed to aromatic protons *ortho* to maleimide—and *ortho* to  $-\text{C}(\text{CH}_3)_2$  (Fig. 4).

The aromatic protons of the diamine compound resonated around 6.74–6.47 ppm, and the proton

of  $-\text{NH}$  appeared at 5.72–5.50 ppm. The  $^1\text{H-NMR}$  spectrum showed a multiplet between 4.75 and 4.62 ppm due to hydrogen  $\text{H}_c$  (succinic ring), and signals between 3.37–3.25 and 2.95–2.80 ppm which are attributed to aliphatic protons  $\text{H}_b$  and  $\text{H}_a$ , respectively. The polymer exhibited a singlet at 3.62 ppm due to aliphatic protons ( $-\text{CH}_2-\text{CH}_2-$ ) and another singlet at 1.78 ppm attributed to aliphatic protons ( $\text{CH}_3-\text{C}-\text{CH}_3$ ).

Elemental analysis data for C, H, N, Cl, and F are in good agreement with the calculated values.

The reaction was conducted at different times as seen in Table I.

The viscosities vary between 0.096 and 0.41. The best one was obtained at the same tempera-

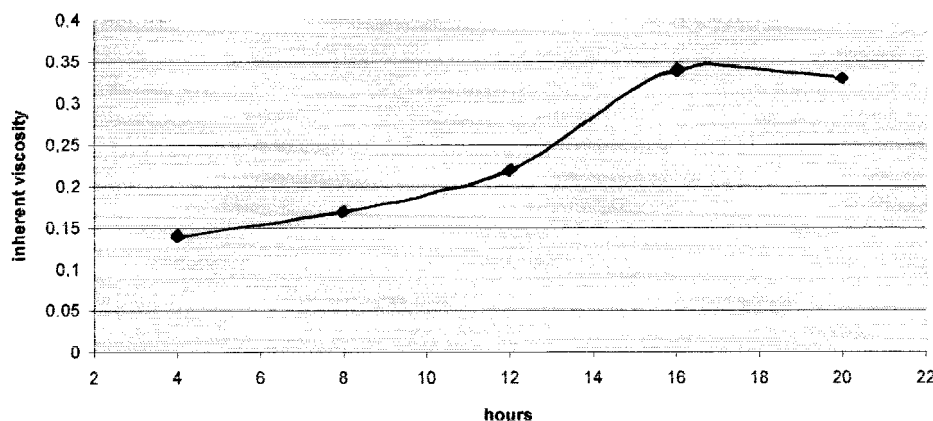


Figure 5 Dependence of inherent viscosity on the reaction duration for polymer P-1.

**Table II Thermal Properties of Polymers**

No.	Polymer	IDT <sup>a</sup> (°C)	PDT <sub>max</sub> <sup>b</sup> (°C)	Y <sub>c</sub> <sup>c</sup> (%)	Temp. for Weight Loss (°C)		T <sub>g</sub> <sup>d</sup> (°C)
					10%	20%	
1	P-1	310	350; 484 <sup>e</sup>	26	335	359	135
2	P-2	318	350	40	348	374	—
3	P-3	305	340	22	327	351	152
4	P-4	310	354	32	352	393	155
5	P-5	324	355	34	354	381	—
6	P-6	332	400	48	409	470	—
7	P-7	298	348	20	319	343	140
8	P-9	314	342	24	340	385	180

<sup>a</sup> Initial decomposition temperature.

<sup>b</sup> Maximum polymer decomposition temperature.

<sup>c</sup> Char yield at 600°C.

<sup>d</sup> Determined by DSC at a heating rate of 10°C/min.

<sup>e</sup> The polymer P-1 showed two-stage decomposition.

ture (95°C) for P-7. The poorest results was obtained from the reaction performed for 15 h (P-4), which gave the lowest viscosity.

Flexible films were obtained from solution casting from NMP for polymers P-2, P-3, P-5, and P-7.

Figure 5 presents the dependence of the inherent viscosity of polymer P-1 on the reaction duration. The viscosity values increase from 0.17 to 0.34, and then decrease to 0.33.

The thermal behavior of polymers was evaluated by means of DTA, TG, and DSC. Table II summarizes the thermal properties of polyaminobismaleimide.

The polymers (P-3, P-4, P-7, P-9) had glass transition temperatures between 140 and 180 °C depending on diamine and bismaleimide component structures. The polymers P-1, P-2, P-5, P-6 showed no  $T_g$ s up to 250°C. The initial decomposition temperatures (IDT) of polymers is in the range 298–318°C. The polymers had aerobic char yield of 20–48% at 600°C. It was observed that IDT are higher for polymers P-5 and P-6 (bismaleimide based on bisphenol A), while polymer P-3 has the lowest IDT (bismaleimide with chlorine atoms). The polymers P-2 and P-6 showed the highest values of Y<sub>c</sub> compared with polymers P-1 and P-5 (influence of diamine component). Polymer P-1 (Fig. 6) showed two-stage decomposition. The multistage decomposition observed for polymer P-1 is due to the combination of chemical different segments in polymer chain.

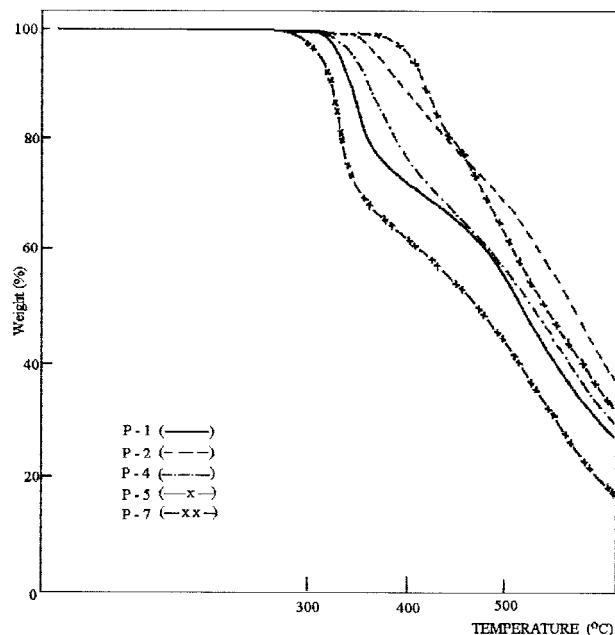
The solubility of polymers was evaluated qualitatively and results are presented in Table III.

All polymers prepared are soluble in polar solvents such as NMP, DMF, and DMSO at room

temperature, but are insoluble in CHCl<sub>3</sub>, dichloroethane, and toluene. So, all synthesized polymers show the same solubility for the same solvent. Still, it is easy to notice that polymer P-5 shows a lower solubility due to its high viscosity, as expected.

Table IV list the mechanical properties of polymer films.

The films have tensile strength of 42–69 MPa, elongation at break of 1.4–2.3 %, and tensile modulus of 1831–2350 MPa. The tensile strength

**Figure 6** TGA thermograms of polymer P-1.

**Table III Solubilities of the Polymers<sup>a</sup>**

No.	Polymer	NMP	DMF	CHCl <sub>3</sub>	DMSO	DCE	Toluene
1	P-1	+	+	-	+	-	-
2	P-2	+	+	-	+	-	-
3	P-3	+	+	-	+	-	-
4	P-4	+	+	-	+	-	-
5	P-5	+	+	-	+	-	-
6	P-6	+	+	-	+	-	-
7	P-7	+	+	-	+	-	-
8	P-9	+	+	-	+	-	-

<sup>a</sup> Solubility: (+)—soluble; (—)—insoluble.

value for polymer P-1 is highest due, probably, to contribution of the hexafluoroisopropylidene group in polymer molecules.

The films obtained by us were characterized by electric measurements such as dielectric constant and volume resistivity (values presented in Table V).

It can be seen from the above results that the dielectric constant increases from 2.23 to 4.26 and volume resistivity increases from  $1.51 \times 10^{11}$  to  $1.15 \times 10^{17}$ . It is noticeable that polymer P-1 has the lowest value of dielectric constant.

## CONCLUSIONS

A series of bismaleimides and polyaminobismaleimides with different structures were synthesized and characterized by IR and <sup>1</sup>H-NMR spectra, and DSC measurements.

Thermal, mechanical, and electric properties of these polymers were studied, and are influenced by the structures of bismaleimides, and diamines involved, and the reaction conditions as well.

**Table IV Mechanical Properties of the Polymer Films**

No.	Polymer	Tensile Strength at Break (MPa)	Tensile Modulus (MPa)	Elongation at Break (%)
1	P-1	69	2275	2.2
2	P-3	57	2350	2.3
3	P-5	58	2083	1.6
4	P-6	43	1831	1.9
5	P-9	42	1930	1.4

**Table V Electrical Properties of the Polyaminobismaleimides**

No.	Polymer <sup>a</sup>	$\rho^b$ ( $\Omega$ cm)	$\epsilon_r^c$
1	P-1	$2.39 \times 10^{16}$	2.23
2	P-2	$6.22 \times 10^{16}$	2.60
3	P-3	$1.15 \times 10^{17}$	3.76
4	P-4	$3.69 \times 10^{15}$	2.70
5	P-5	$1.51 \times 10^{11}$	4.12
6	P-7	$4.41 \times 10^{16}$	4.26

<sup>a</sup> Films prepared from NMP with initial concentration of 15%. Cure cycle: 2 h/100°C, 2 h/150°C, and 2 h/200°C.

<sup>b</sup> Volume resistivity; it was measured using a TERALIN III Straton Electrometer.

<sup>c</sup> Dielectric constant. The dielectric constant were measured using a Digital RLC Meter EO 711 at 1 MHz.

It is remarkable that polymer P-1 has the highest tensile strength at break, and the lowest dielectric constant, which confirms the beneficial influence of fluorinated compounds on polymer properties.

## REFERENCES

- Rakoutz, M.; Balme, M., *Polym J* 1987, 19, 173–184.
- Stenzenberger, H. D.; Herzog, M.; Röner, W.; Scheiblich R.; Reeves, N. J. *Br Polym J* 1983, 15, 2.
- Goldfarb, I. J.; Feld, W. A.; Saikumar, J. *Polymer* 1993, 34(4).
- White, J. E.; Scaia, M. D.; Snider, D. A. *J Polym Sci, Polym Chem Ed* 1984, 22, 589.
- Stenzenberger, H. D. *Adv Polym Sci* 1994, 117, 165–220.
- Sava, M.; Gaina, C.; Gaina, V.; Chiriac, C. I.; Stoleriu, A. *J Macromol Sci—Pure Appl Chem* 1997, A34(8), 1505.
- Chandra R.; Rajabi, L.; *JMS—Rev Macromol Chem Phys* 1997, C37(1), 61–96.
- Nanjan, M. J.; Sivary, K. *J Polym Sci Part A Polym Chem* 1989, 27, 375–388.
- Melissaris, A. P.; Mikroyannidis, J. A. *J Polym Sci Part A, Polym Chem* 1989, 27, 245–262.
- Park, J. O.; Jang, S. H. *J Polym Sci Part A, Polym Chem* 1992, 30, 723–729.
- Liu, F. J.; Munukutia, S.; Levent, K.; Tesoro, G. *J Polym Sci Part A, Polym Chem* 1992, 30, 157–162.
- Mikroyannidis, J. A. *J Polym Sci Part A, Polym Chem* 1990, 8, 679–691.
- Hoyt, A. E.; Benicewicz, B. C. *J Polym Sci Part A, Polym Chem* 1990, 28, 3403–3415.
- Hoyt, A. E.; Benicewicz, B. C. *J Polym Sci Part A, Polym Chem* 1990, 28, 3417–3427.
- Itoya, K.; Kumagai, Y.; Kanamaru, M.; Sawada, H.; Kakimoto, M.; Imai, Y. *Polym J* 1993, 25, 883–890.