Synthesis and Thermal Behavior of Some Brominated Bismaleimides and Polyaspartimides

M. Sava

Department of Photochemistry, "Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41A-700487, Romania

ABSTRACT: Brominated bismaleimides were synthesized by the reaction of brominated bisphenols with 3- or 4-maleimidobenzoyl chloride. The reaction of these maleimides with various aromatic diamines yielded brominated polyaspartimides. The monomers and polymers were characterized by Fourier transformed infrared and proton nuclear magnetic resonance spectroscopy. Thermal behavior of these brominated polyaspartimides was studied and compared with that of related polyaspartimides having other substituents instead of bromine or other bridges in the bisphenolic segment. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1399–1406, 2009

Key words: brominated bismaleimides and poly-aspartimides; thermal properties; structure–properties relationship

INTRODUCTION

Bismaleimide resins are a class of polyimides obtained by polyaddition reactions of bismaleimide compounds having unsaturated end groups. These resins contain unsaturated double bonds that can be thermally polymerized without the formation of volatile byproducts (that can cause voids) and can be processed in a manner similar to the epoxies.

Polyaspartimides are of great interest because of their attractive properties such as high thermal stability, outstanding mechanical properties, excellent radiation and corrosion resistance, good flame resistance, low water susceptibility, excellent chemical behavior, and good retention of thermomechanical properties, even after long aging times at 250°C. All these make them attractive for various applications[1–14] such as high-performance composite matrices for multilayer printed circuit boards for large-scale computers, advanced composites for aerospace, electronic, nuclear industries, and structural adhesives. Major applications of these resins are printed circuit boards carbon-fiber composites for aero-engines and military aircraft.

However, bismaleimide resins have a number of disadvantages such as solvent retention, high melting, and curing temperature, as well as brittleness because of their high crosslink density, which limits their processability.[15–18] To reduce the brittleness of these compounds, a chain extension by Michael's addition reaction using aromatic diamines can be used. Another method is the insertion of atoms or groups of atoms in the backbone of monomers, which improves the processability and solubility without much loss of thermal stability.

This article presents a study of the influence of the brominated monomer structure on the properties of the synthesized polyaspartimides when compared with other related nonbrominated ones.

EXPERIMENTAL

Materials

2,2-Bis-(4-hydroxyphenyl)propan (Fluka, Buchs, Germany), maleic anhydride (Fluka, Buchs, Germany), 3(4)-aminobenzoic acid (Fluka, Buchs, Germany), acetic anhydride (Merck, Darmstadt, Germany), triehylamine (Fluka, Buchs, Germany), thionyl chloride (Fluka, Buchs, Germany), and bromine (Fluka, Buchs, Germany) are commercially available products and were used as received. The new synthesized monomers were purified by recrystallization. Commercial solvents such as acetone (Fluka, Buchs, Germany), 1,2-dichloroethane (Fluka, Buchs, Germany), chloroform (Fluka, Buchs, Germany), and *N*-methyl-pyrrolidone (NMP) (Riedel-Haen, Seelze, Germany) were dried and purified by standard methods.

The synthetic route to prepare brominated bismaleimides based on brominated bisphenol A (BMI-1, BMI-2, and BMI-3) is illustrated in Scheme 1.[19,20]

Bismaleimides BMI-4, BMI-5, and BMI-6, which do not contain bromine, were prepared in the same manner, but with other bisphenols.

General procedure for the preparation of bismaleimides BMI(1–6)

Monomers BMI(1–6) were synthesized following the literature, via the reaction of 3- or 4-

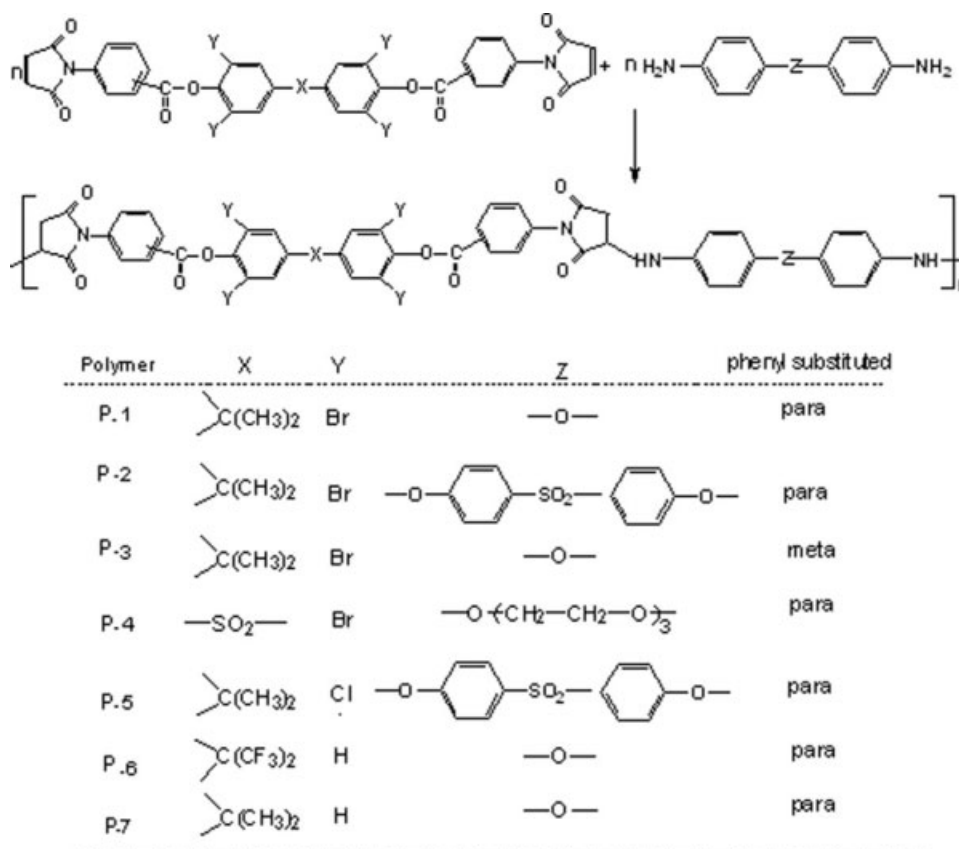*Correspondence to:* M. Sava (msava@icmpp.ro).
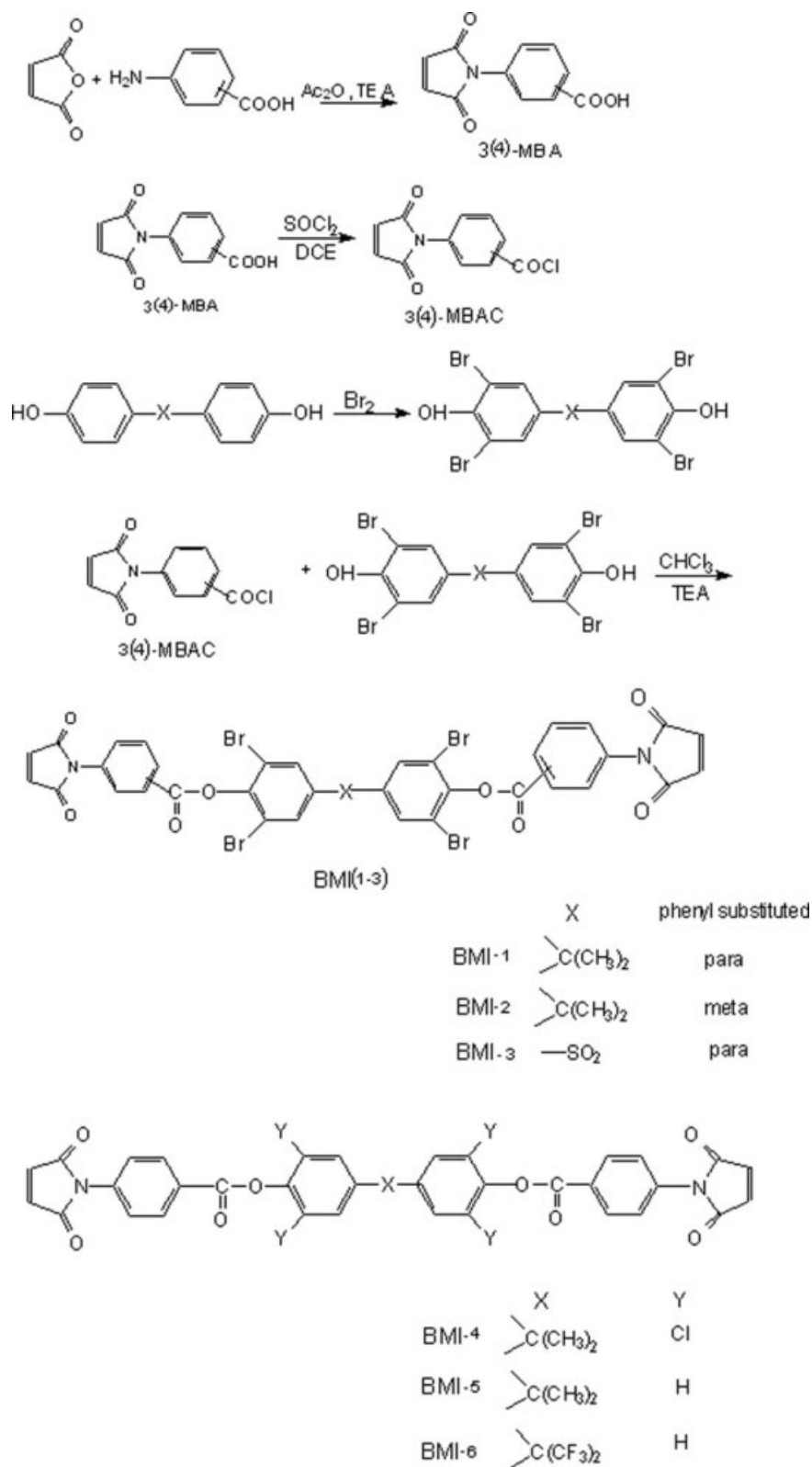
Scheme 1 Synthesis of bimaleimide monomers.

maleimidobenzoyl chloride with various diols, according to Scheme 1.

Bismaleimides were prepared by dissolving or suspending one equivalent of bisphenol in chloro-

form with two equivalents of triethylamine (TEA). The solution was chilled in an ice bath under stirring and two equivalent of 3- or 4-maleimidobenzoyl chloride were carefully added. The reaction mixture

Polymer	X	Y	Z	phenyl substituted
P.1	C(CH3)2	Br	—O—	para
P.2	C(CH3)2	Br	—O—⟨⟩—SO2—⟨⟩—O—	para
P.3	C(CH3)2	Br	—O—	meta
P.4	—SO2—	Br	—O(CH2—CH2—O)3—	para
P.5	C(CH3)2	Cl	—O—⟨⟩—SO2—⟨⟩—O—	para
P.6	C(CF3)2	H	—O—	para
P.7	C(CH3)2	H	—O—	para

Scheme 2 Polymers synthesis.

was stirred for 1–1.5 h and then precipitated in hexane. The product was filtered and treated with sodium carbonate solution (10%) and then thoroughly washed with water. Recrystallization from an appropriate solvent was followed by drying under vacuum at 75°C.

Brominated bisphenols were prepared as follows[21]: In a 250-mL flask, 0.04 mol of bisphenol were dissolved in 200 mL of acetic acid. To this solution, 0.14 mol of bromine were added slowly under stirring. The reaction was carried out at room temperature over a period of about 20 min. Then, the temperature was raised up to 60°C. Finally, the reaction temperature was maintained at 80–85°C for 1.5 h to ensure complete bromination. After cooling, the product was filtered and then washed with sodium bicarbonate solution to remove the excess of bromine. The final product was recrystallized from acetic acid.

Synthesis of polymers

Into a 50-mL three-necked flask fitted with mechanical stirrer, thermometer, and nitrogen inlet, 0.01 mol of bismaleimide, 0.01 mol of diamine, NMP as solvent (up to 15% of monomer concentration) and a small amount of acetic acid were charged. The reaction mixture was kept in a water bath at 90–95°C for different time intervals. The product was isolated by pouring the reaction mixture into methanol.

All resulting polymers were redissolved in fresh solvent, precipitated in a nonsolvent medium, and dried for 16 h in a vacuum oven at 80°C.[22] The synthetic pathway to prepare these polymers is illustrated in Scheme 2.

Some polymers possess film-forming ability. Their solutions in NMP having a concentration of about 8–10% were cast onto glass substrates and dried to yield thin reddish-brown films.

MEASUREMENTS

The Fourier transformed infrared (FTIR) spectra were recorded on a Bruker Vertex 70 spectrophotometer. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Bruker NMR spectrometer Avance DRX 400 MHz, using DMSO-d_6 as solvent and tetramethylsilane as internal standard. Differential scanning calorimetry (DSC) measurements were performed using a Mettler DSC 12E apparatus with a heating rate of 10°C/min in air. Melting points were determined with a Gallenkamp
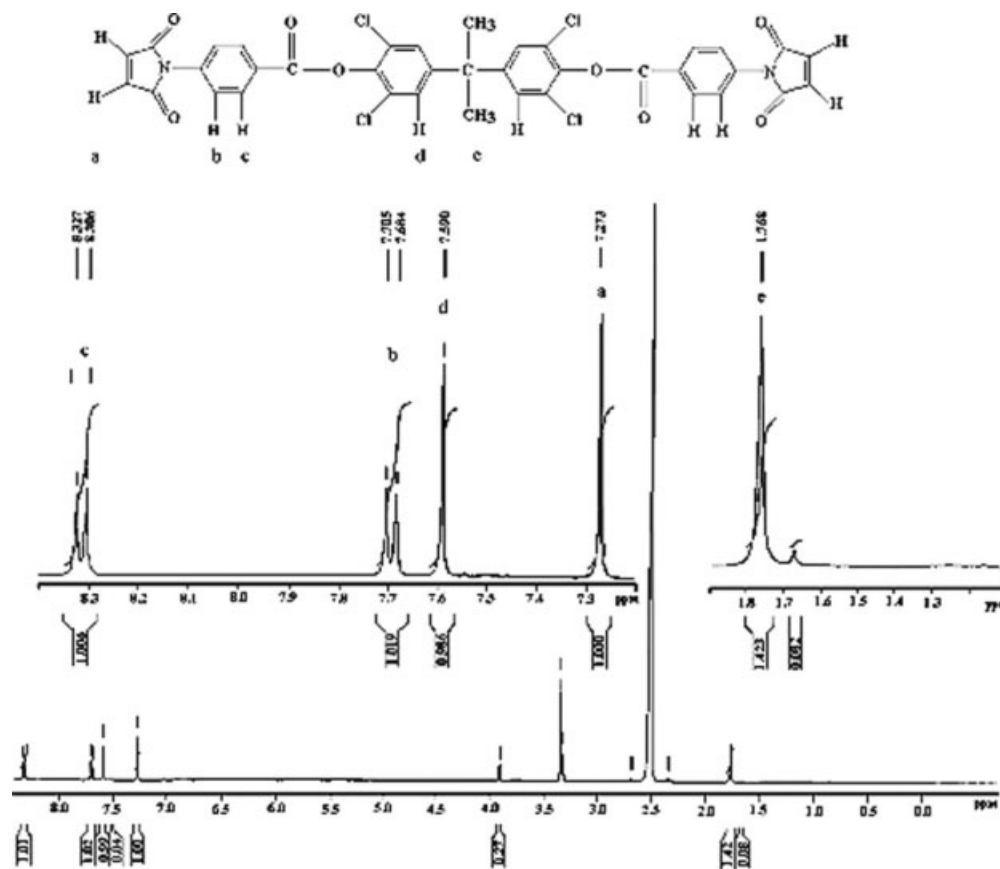
Figure 1 ^{1}H-NMR spectrum of bismaleimide BMI-4.

hot-block melting point apparatus. TGA was carried out in air, with a F. Paulik Derivatograph at a heating rate of 12°C/min. The inherent viscosities of polymer solutions in NMP (measured at a concentration of 0.5 g/dL) were determined at 25°C using an Ubbelohde suspended level viscometer. Gel permeation chromatography (GPC) analysis was carried out on a PL-EMD 950 Evaporative Light Scattering Detector instrument using dimethylformamide as eluent and standard polystyrene samples for calibration. The stress–strain properties of polymer films were measured at room temperature on an Instron Tensile Tester TIRA TEST-2161 (cross-head speed of 1 mm/min) using a E-MODUL AND DEHN GRENZEN program. All specimens having a thickness between 5 and 20 μm were cured at 150°C/1 h, 175°C/2 h, and 190°C/2 h.

RESULTS AND DISCUSSION

Monomer synthesis

The IR spectra of bismaleimide monomers bearing ester groups with or without bromine atoms showed the carbonyl doublet characteristic peak in the range of 1790–1780 and 1730–1720 cm^{-1} due to C=O from imide group. Bismaleimides BMI(1–5) showed an

absorption band at 3000–2890 cm^{-1} attributed to —C(CH$_3$)$_2$ groups, whereas BMI-6 exhibited a band between 1250 and 1175 cm^{-1} due to hexafluoroisopropylidene group. Also, an absorption band at 1755–1740 cm^{-1} appeared in all spectra due to ester groups. In addition, BMI-3 showed absorption bands at 1320 and 1160 cm^{-1} attributed to —SO$_2$ group.

The ^{1}H-NMR spectrum of BMI-4 (Fig. 1) confirmed its chemical structure as follows: aromatic protons of monomer BMI-4 appear as two separated doublets in the range of 8.327–8.306 ppm (Ar-H, *ortho* to —COO) and 7.705–7.684 ppm (Ar-H, *ortho* to maleimide). Other signals at 7.590 ppm correspond to the aromatic protons adjacent to isopropylidene group, whereas the singlet at 7.275 ppm is ascribed to the olefinic protons. The singlet at 1.768 ppm was attributed to isopropylidene group.

Some thermal data of these bismaleimides are shown in Table I.

The onset temperature for curing reaction, in the case of BMI-1 and BMI-4, was overshadowed by their melting endotherms. Concerning the onset temperature of curing, monomer BMI-3 have the lowest onset, whereas bismaleimide BMI-5 have the highest one, followed by monomer BMI-6 as a consequence of their structures. (BMI-5 and BMI-6 are unsubstituted monomers when compared with the others.)

TABLE I
Physical and Thermal Properties of the Prepared Bismaleimides BMI(1–6)

Monomer	MP (°C)	T_{end}[a] (°C)	T_{exo}[b] (°C)	T_p[c] (°C)	ΔH[d] (kJ/mol)	IDT[e] (°C)	Y_c[f] (%)
BMI-1	281–283	285	307	–	–	325	25
BMI-2	265–268	268	306	287	45	313	18
BMI-3	98–101	104	207	153	95	260	21
BMI-4	276–279	282	302	–	–	366	33
BMI-5	216–218	244	319	257	69	402	59
BMI-6	212–215	220	297	245	82	443	49

[a] Endotherm peak temperature by DSC.
[b] Exothermal peak temperature by DSC.
[c] Start of polymerization by DSC.
[d] Heat of polymerization by DSC.
[e] Onset degradation temperature by TGA.
[f] Char yield at 600°C.

It was observed that BMI-6 showed the highest IDT value, whereas BMI-3 had the lowest value of IDT.

Polymer synthesis

The polyaspartimides were synthesized by Michael addition of diamines, such as 4,4-diaminodiphenylether (DDE), 1,4-bis(2-aminophenoxy)diphenylsulfone (APDPS), and 1,2-bis[2-(4-aminophenoxy)ethoxy]ethane (APEE) to bismaleimide monomers in NMP at 90–95°C. The polymers were isolated by pouring the reaction mixture into methanol, followed by filtration and washing. Results are summarized in Table II. An optimization study on the reaction parameters (time, temperature, concentration) was carried out to achieve polymers with high molecular weights.

The structure of polymers was confirmed by elemental analysis (Table III) and FTIR spectroscopy.

The IR spectra showed that polymers are characterized by the same absorption bands as monomers, but they are wider. Figure 2 presents the FTIR spectrum of polymer P-4. A characteristic carbonyl band appeared at 1790 and 1720 cm^{-1}. Other characteristic bands were observed in the range 2968–2872 cm^{-1} because of the aliphatic groups, and the band at 1383 cm^{-1} was attributed to —SO$_2$ moiety. A band at 1749 cm^{-1} appeared in the spectrum due to ester groups. The disappearance of the band at 3124 cm^{-1} (=CH maleimidic) and at 1150 cm^{-1} (maleimide ring) and the appearance of the band at 1174 cm^{-1} (succinic ring) proving that the reaction did take place was observed.[23]

The inherent viscosities vary between 0.26 and 0.44 dL/g. The highest value was obtained for polymer P-3. The lowest result was obtained for P-1, which yield in a brittle film. The GPC curve indicated that the number-average relative molar mass (M_n) values of polymers varied between 7830 and 14,110 and the M_w/M_n ratio, as a measure of molecular weight distribution, had values between 1.92 and 2.75.[24] Flexible films were obtained by casting from NMP solutions of polymers P(2–4) and P(6–7).

The thermal stabilities of cured resins were evaluated by TGA (Fig. 3 and Table IV) and by isothermal gravimetric analysis (IGA) (Fig. 4).

The initial decomposition temperatures (IDT) of polymers are in the range 277–332°C and percentage char yield (Y_c) at 600°C is in the range 36–50%.[25] The highest value of IDT was obtained for polymer P-4 (based on brominated bismaleimide BMI-3 having a —SO$_2$ group and APEE amine component). The polymer P-5 (based on bismaleimide BMI-4 and APDPS) showed the lowest IDT. The polymers P-4 and P-6 showed similar decomposition patterns after 340°C, whereas polymers P(1–3) showed similar

TABLE II
Preparation and Properties of Polyaminobismaleimides P(1–7)

Polymer	Diamine	Temp. (°C)	Time (h)	Conc. (%)	η[a] (dL/g)	M_n	M_w/M_n	Films prop.
P-1	DDE	95	30	10	0.26	7830	2.43	Brittle
P-2	APDPS	90	25	15	0.38	–	–	Flexible
P-3	DDE	95	25	15	0.44	13525	2.11	Flexible
P-4	APEE	95	30	15	0.41	13.920	2.75	Flexible
P-5	APDPS	95	20	10	0.27	−14.110	–	Brittle
P-6	DDE	90	48	15	–		1.92	Flexible
P-7	DDE	95	25	10	0.42	12.425	2.49	Flexible

[a] Inherent viscosity measured at a concentration of 0.5 g/dL in NMP at 2°C.

TABLE III
Elemental Analysis of Polymers P(2–3) and P(5–6)

Polymer	Elemental analysis						
	C	H	N	Br	Cl	F	S
P-2							
Calcd	53.37	2.93	4.08	23.28	–	–	2.33
Found	52.89	3.11	4.21	23.07	–	–	2.46
P-3							
Calcd	51.60	2.82	4.91	28.02	–	–	–
Found	51.32	2.98	5.06	27.83	–	–	–
P-5							
Calcd	61.30	3.37	4.68	–	9.60	–	2.68
Found	61.55	3.49	4.47	–	9.74	–	2.51
P-6							
Calcd	63.09	3.23	6.00	–	–	12.22	–
Found	62.83	3.29	5.78	–	–	12.37	–

Figure 3 TGA thermograms of polymers P(1-7).

decomposition patterns after 425°C. Note that polymer P-1 showed a higher weight loss between 350 and 425°C when compared with polymers P-2 and P-3. Considering IDT as a thermostability criterion, the following order can be established:

$$P\text{-}4 > P\text{-}1, P\text{-}2 > P\text{-}6, P\text{-}7 > P\text{-}3 > P\text{-}5$$

It is noticeable that polymers P(1–6) showed a two-stage decomposition, whereas P-7 showed a three-stage decomposition because of the combination of different chemical segments in the polymer chain. In addition, Table IV summarizes temperatures $T_D{}^5$, $T_D{}^{10}$, and $T_D{}^{25}$, where 5, 10, and 25 are percentage weight loss observed.

The polymers P-4 and P(6–7) showed the highest values of char yield (Y_c) when compared with the other polymers because of the influence of bismaleimide and diamine components. The study of these thermograms indicated that brominated polymers P(1–3) are less stable than unbrominated ones (curve pattern above 340°C), whereas polymer P-4 is more
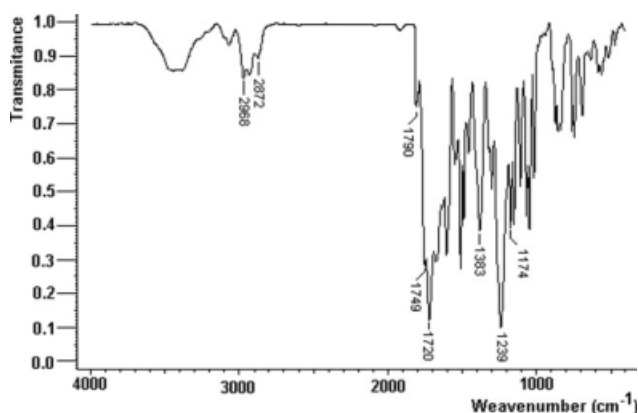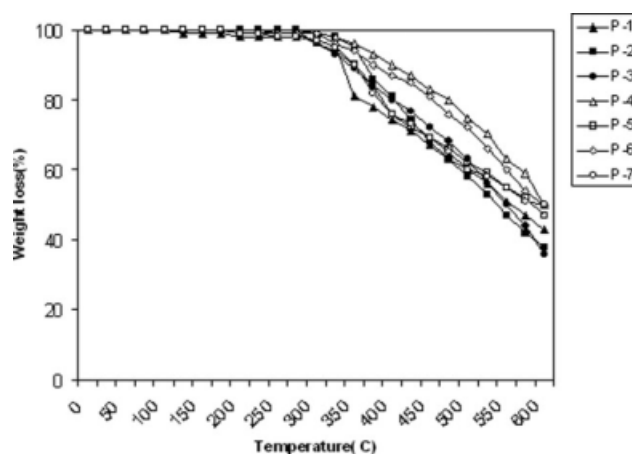
thermostable. The thermal stability of brominated or unbrominated aromatic polymers depends on the bridging groups between benzene units and substituents at the aromatic rings.

This investigation was expanded to include the evaluation of the thermooxidative stability of these polymers by IGA. Figure 4 presents the IGA traces of polymers and monomers.

After isothermal aging at 300°C for 20 h, polymers P-2, P(4–5), and P-7 lost 65.9, 44.6, 40.0, and 46.7% of their weight, respectively, whereas for BMI-3 and BMI-5 weight losses were 37.9 and 3%, respectively. The polymer P-2 showed the lowest thermostability, whereas P-5 had the highest thermostability.

In addition, a different behavior of monomers BMI-3 and BMI-5 was observed. Brominated BMI-3 showed a thermal behavior almost similar with that of polymers P(4–5) and P-7, whereas nonbrominated bismaleimide BMI-5 presented a very high thermostability. Even under the degradation conditions (20 h at 300°C), it looses only 3%. These differences may be attributed to the negative influence of bromine, as well as chlorine, atoms on the thermal stability of these halogenated compounds.

DSC investigation showed that polymers P(1–2), P-4, and P(6–7) had glass transition temperatures between 198 and 232°C, depending on their structures. Polymers P-3 and P-5 did not show any glass transition temperature when heated up to 350°C.

Table V lists the mechanical properties (tensile strength at break, tensile modulus, and elongation at break) values.

The polymer films have tensile strength of 47–52 MPa, elongation at break of 1.5–1.8%, and tensile modulus of 1850–2110 MPa.[26] The tensile strength value of polymer P-6 is the highest, most probably due to the influence of hexafluoroisopropylidene group.

Figure 2 FTIR spectrum of polymer P-4.

TABLE IV
Thermal Properties of Polyaminobismaleimides P(1–7)

Polymer	Color	T_g (°)	IDT (°C)	PDT$_{max}$ (°C)	T_5	T_{10}	T_{25}	Y_c (%)
P-1	Brown	214	320	330, 555	330	335	408	43
P-2	Cream	198	320	365, 410	345	366	421	38
P-3	Reddish-brown	–	300	325, 524	310	340	439	36
P-4	Cream	210	332	400, 500	355	402	501	50
P-5	Cream	–	277	385, 505	306	355	400	47
P-6	Reddish-brown	218	310	350, 565	345	384	480	50
P-7	Reddish-brown	232	310	367, 470, 565	320	346	407	50

T_g, glass transition temperature; IDT, initial decomposition temperature; PDT$_{max}$ = maximum decomposition temperature; T_5, T_{10}, T_{25}, temperature at which 5, 10, and 25% weight loss, respectively, was observed; Y_c, char yield at 600°C.

CONCLUSION

Bismaleimide monomers and polymers with different substituents at the aromatic ring (Br and Cl) or with hexafluoroisopropylidene group between benzene rings were synthesized and characterized by spectroscopy (FTIR and ^{1}H-NMR).

Thermal behavior of monomers and polymers showed important differences. Thus, in the case of new synthesized monomers, comparing the values of the IDT, it was found that monomers with bromine and chlorine substituents showed significant lower values than unhalogenated monomers. The same result was observed for char yield values. So, the presence of bromine or chlorine in the structure determines an alteration of the thermal stability of the corresponding monomers.

In the case of polymers P(1–7), IDT values are in a narrow range, but for char yield differences still appear. The polymers containing bromine showed

the lowest values of the initial decomposition temperature and char yield.

As a general conclusion, we can state that thermal stability depends first on the structure of the bismaleimide component (substituted or not) and second on the amine component.
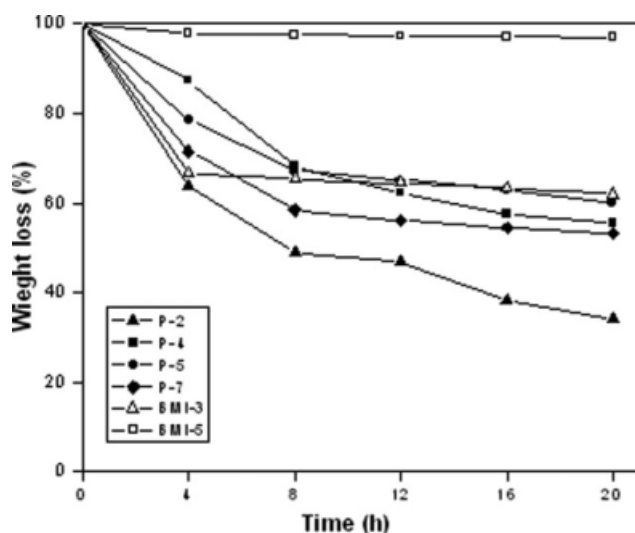
TABLE V
Mechanical Properties of Polymers P-2, P-4, and P-6

Polymer[a]	Tensile strength at break (MPa)	Tensile modulus (MPa)	Elongation at break (%)
P-2	49	1,920	1.7
P-4	47	1,850	1.5
P-6	52	2,110	1.8

[a] The sample size used for studying mechanical properties was 30 mm × 4 mm.

Figure 4 The isothermal weight loss in air at 300°C for 20 h of polymers P-2, P(4–5), P-7, and monomers BMI-3 and BMI-5.

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