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M. Sava^a; C. V. Grigoras^a

^a "P. Poni" Institute of Macromolecular Chemistry, Romania

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Bismaleimide Monomers and Polymers with Ester and Ether Units. Synthesis and Properties

M. SAVA AND C. V. GRIGORAS

“P. Poni” Institute of Macromolecular Chemistry, Romania

A series of bismaleimide monomers were used to prepare poly(aminobismaleimide)s in an attempt to achieve polymers with improved properties. Structurally different bismaleimides with ester units were synthesized by reaction between 3(4)-maleimidobenzoylchloride with various diphenols. Bismaleimides BMI-3 and BMI-4 were synthesized by reaction of maleic anhydride with diamines respectively. Polymers based on these bismaleimides were prepared by the Michael addition of diamines to bismaleimides. The monomers and polymers were characterized by infrared (IR) and proton nuclear resonance (¹H-NMR) spectroscopy. Thermal characterization of monomers and polymers was accomplished by differential scanning calorimetry (DSC) and dynamic thermogravimetric analysis (ATG).

Keywords bismaleimide, polyaminobismaleimides, synthesis, thermal properties and characterization

Introduction

Polybismaleimides are an addition polyimides class obtained from bismaleimide and contain unsaturated end groups. These resins are widely used as high performance composite matrices for their high temperature resistance, multi-layer printed circuit boards for large-scale computers, advanced composites for aerospace industries structural adhesives. Polybismaleimide resins possess many desirable properties, which make them very attractive for various applications. These properties include high tensile strength and modulus, excellent chemical radiation and corrosion resistance, good retention of thermo-mechanical properties even after long ageing times at 250°C (1–13).

Bismaleimide resins can be processed in a manner similar to the epoxies and their curing evolves without volatiles. Unfortunately, these resins have a number of disadvantages, such as brittleness (due to their high crosslink density), a high melting temperature and curing temperature (14–17). To use thermosetting resins as high-performance structural composite materials, the fracture toughness must be improved without sacrificing other important properties. Further attempts have been made to improve the processability and properties of BMI resins, by the introduction of various substituents to the aromatic rings in the main chain. In this study, we examined the influence of monomer structure on the properties of bismaleimide resins.

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Address correspondence to M. Sava, “P. Poni” Institute of Macromolecular Chemistry, 41A Gr. Ghica Voda Alley Iasi, RO-700487, Romania. E-mail: msava@icmpp.tuiasi.ro

Experimental

Synthesis of Monomers

3(4)-Maleimido Benzoic Acid (3(4)-MBA). The products were obtained as described (18). m.p. 3-MBA: 236–240°C toluene; m.p. 4-MBA: 225–230 toluene. Reference (19), 239–241°C and 225–228°C, respectively.

3(4)-Maleimido Benzoic Acid Chloride (3(4)-MBAC). The products were prepared as described in literature (20), m.p. 3-MBAC; 125–128°C dichloroethane; m.p. 4-MBAC; 169–171°C. Reference (21), m.p. 4-MBAC; 170°C.

General Procedure for the Preparation of Bismaleimides

Bismaleimides BMI (1-2)a and BMI(1-2)b were synthesized following the literature (21) (Scheme 1).

3(4)-MBAC (0.1 mol) in 100 mL chloroform (CHCl_3) was cooled in an ice bath. TEA (0.1 mol) (as acid acceptor) and a solution of diphenol (0.05 mol) in 100 mL CHCl_3 were added. After stirring for 1–1.5 h, the mixture was filtered and precipitated in petroleum ether. The product was filtered and treated with sodium bicarbonate solution and then thoroughly washed with water. The filtered precipitated product was recrystallized.

Bismaleimide 3–4 was synthesized following the literature (22). The bismaleimides used in the reaction were prepared from aromatic diamines (0.1 mol) with maleic anhydride (0.22 mol) in dry acetone at reflux temperature according to the described method. Intermediate bismaleamic acid was cyclodehydrated *in situ* with acetic anhydride and triethylamine, using magnesium acetate as a catalyst. The final product was recrystallized and dried under vacuum.

Bismaleimide 1a (BMI-1a). The product was recrystallized from ethanol (yield = 70%; m.p. = 121°C); IR (KBr) cm^{-1} : 1790 and 1720 (C=O imide), 1750 (C=O ester), 1225–1180 (hexafluoroisopropylidene group).

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, 60.08; H, 2.93; F, 15.21; N, 4.03.

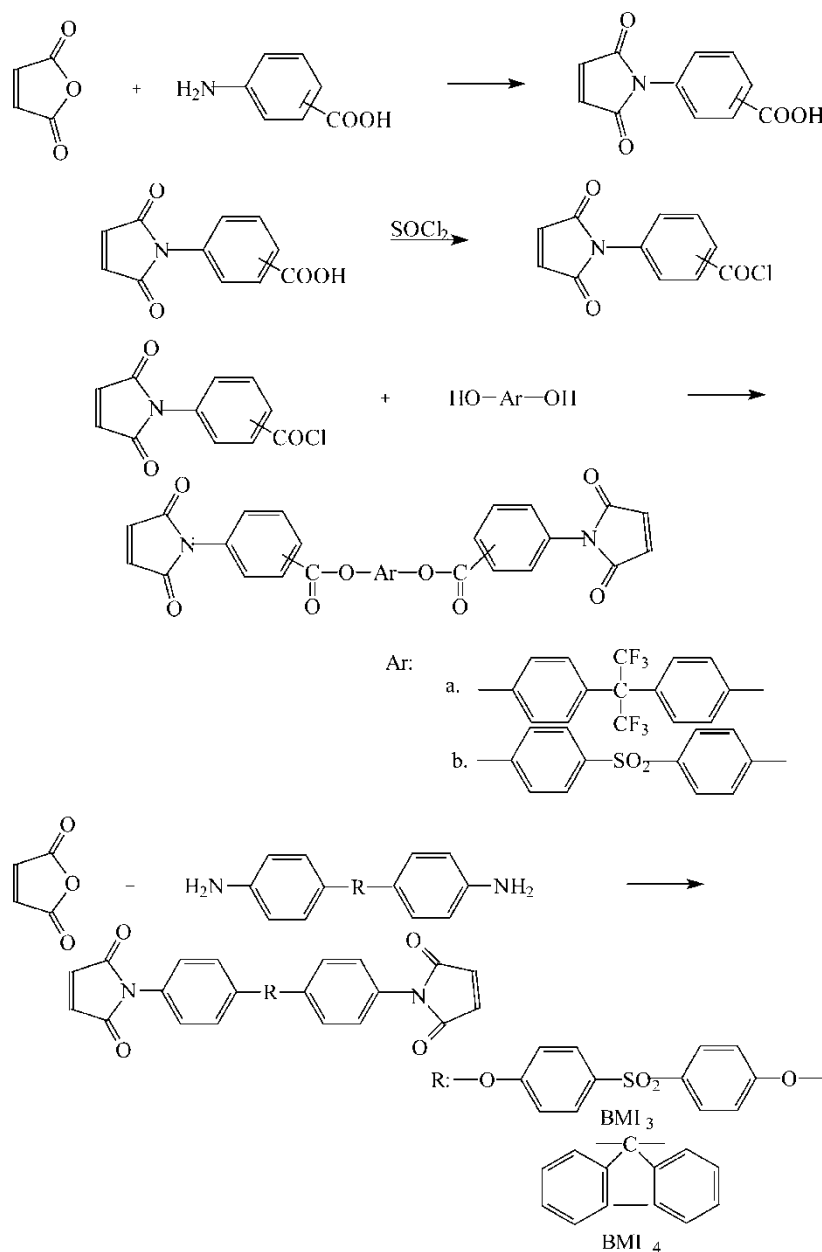
Bismaleimide 2a (BMI-2a). The monomer was recrystallized from dichloroethane (DCE)/ethanol (yield = 68%; m.p. = 212–215°C). IR (KBr) cm^{-1} : 1780 and 1730 (C=O imide), 1750 (C=O ester), 1215–1190 (hexafluoroisopropylidene group).

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, 15.15; N, 3.81. Found: C, 60.24; H, 2.87; F, 15.26; N, 3.67.

Bismaleimide 1b (BMI-1b). The product was recrystallized from DCE (yield = 67%; m.p. = 91°C). IR (KBr) cm^{-1} : 1780 and 1715 (C=O imide), 1745 (C=O ester), 1320 and 1150 ($-\text{SO}_2$).

Anal. Calcd. for $\text{C}_{37}\text{H}_{20}\text{N}_2\text{O}_{10}\text{S}$ (%): C, 62.96; H, 3.10; N, 4.31; S, 4.94. Found: C, 63.13; H, 2.87; N, 4.52; S, 4.73.

Bismaleimide 2b (BMI-2b). The monomer was recrystallized from DCE/ethanol (yield = 69%; m.p. = 236–240°C). IR (KBr) cm^{-1} : 1785 and 1725 (C=O imide), 1755 (C=O ester), 1330 and 1160 ($-\text{SO}_2$).



Scheme 1.

Anal. Calcd. for $C_{37}H_{20}N_2O_{10}S$ (%); C, 62.96; H, 3.10; N, 4.13; S, 4.94. Found: C, 62.43; H, 2.85; N, 4.52; S, 4.83.

Bismaleimide 3 (BMI-3). The product was recrystallized from toluene (yield = 71%, m.p. = 190–194°C). IR (KBr) cm^{-1} ; 1790 and 1715 (C=O imide), 1340 and 1165 ($-SO_2$), 1265 ($-O-$).

Anal. Calcd. for $C_{37}H_{20}N_2O_8S$ (%): C, 64.86; H, 3.40; N, 4.72; S, 5.41. Found: C, 64.53; H, 3.58; N, 4.89; S, 5.62.

Bismaleimide 4 (BMI-4). The monomer was recrystallized from dioxane/water (yield = 67%, m.p. = 315–318°C. IR (KBr) cm^{-1} ; 1790 and 1710 (C=O imide). Anal. Calcd. for $C_{35}H_{20}N_2O_4$ (%): C, 77.94; H, 3.96; N, 5.50. Found: C, 77.59; H, 4.13; N, 5.47.

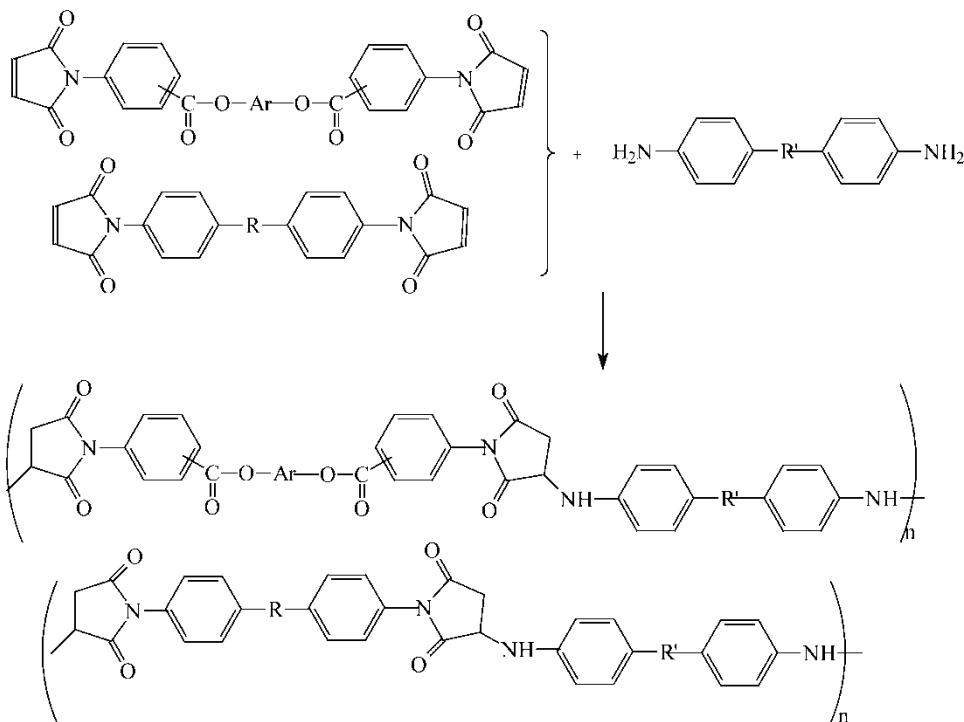
Synthesis of Polymers

The polymers were prepared as described in literature (23) (Scheme 2).

Into 100 mL three-necked flask fitted with mechanical stirrer, thermometer and nitrogen inlet, 0.02 moles of BMI, 0.02 moles diamines, N-methylpyrrolidine-2-one (NMP) as solvent (up to 15% of monomer concentration), were charged. Small amounts of acetic acid at various reaction time intervals were added. The polymers were isolated by pouring the reaction mixture into methanol to give powder polymers. The products were filtered and washed thoroughly. An optimization study on reaction parameters (time, temperature, concentration) was carried out, in order to achieve polymers with higher molecular weights.

Measurements

The IR spectra were recorded on a Specord M90 Carl Zeiss Jena Spectrophotometer using the KBr pellet technique. 1H -NMR spectra were run on a JEOL 60 MHz, NMR Spect-



Scheme 2.

ometer at 60°C in DMSO- d_6 using TMS as an internal reference. Differential scanning calorimetry (DSC) measurements were done by using a Mettler TA instrument DSC 12E, with heating rate of 10°C/min in nitrogen. 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 were measured at a concentration of 0.5 g/dL in NMP and were determined at 25°C using an Ubbelohde suspended level viscometer. Gel permeation chromatographic (GPC) analysis was carried out on a PL-EMD 950 Evaporative Light Scattering Detector instrument using dimethylformamide (DMF) as eluent and standard polystyrene samples for calibration. The melting point of BMI-4 was determined with Hot Stage Type Linkam TP 92 apparatus at a heating rate of 50°C/min in air.

Results and Discussion

Monomer Synthesis

The IR spectra of obtained bismaleimides showed characteristic carbonyl doublet in the range 1790–1710 cm^{-1} . Bismaleimides BMI (1-2)a and BMI (1-2)b showed an absorption band at 1755–1745 cm^{-1} due to ester groups. The absorption peaks around 1215–1180 cm^{-1} (BMI (1-2)a) correspond to the hexafluoroisopropylidene groups. Compounds BMI (1-2)b showed an absorption band at 1340–1160 cm^{-1} due to the $-\text{SO}_2$ group. In addition, the characteristic absorption of ether units (BMI-3) appeared at 1265 cm^{-1} . Figure 1 presents the infrared (IR) spectrum of BMI-3.

The $^1\text{H-NMR}$ spectrum of monomer BMI-3 confirmed its chemical structure. From Figure 2 it can be seen that aromatic protons of bismaleimide BMI-3 appear as a

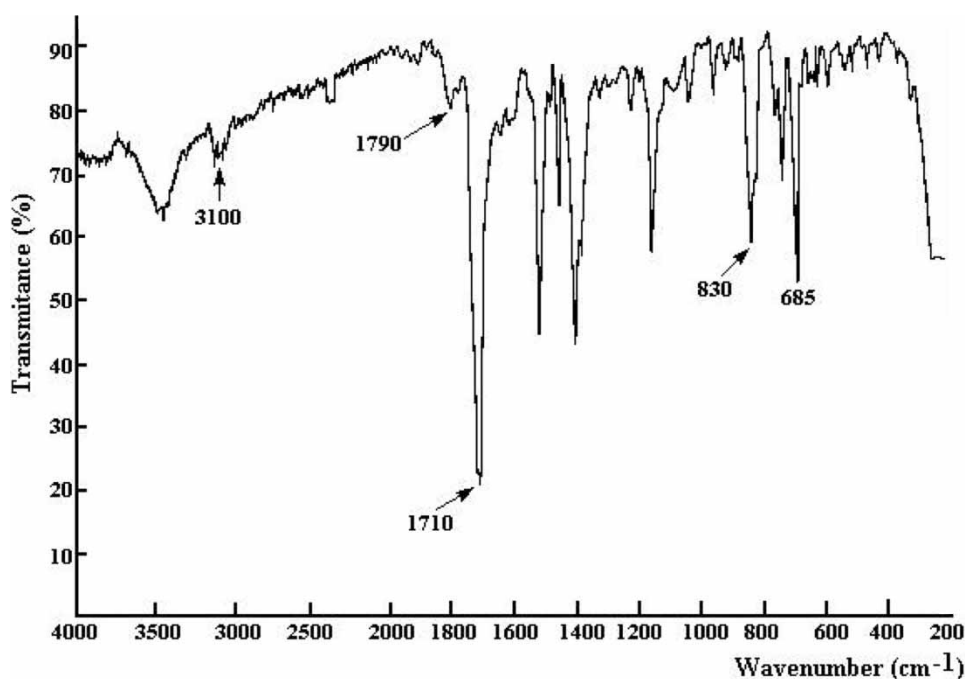


Figure 1. IR spectra of monomer BMI-4.

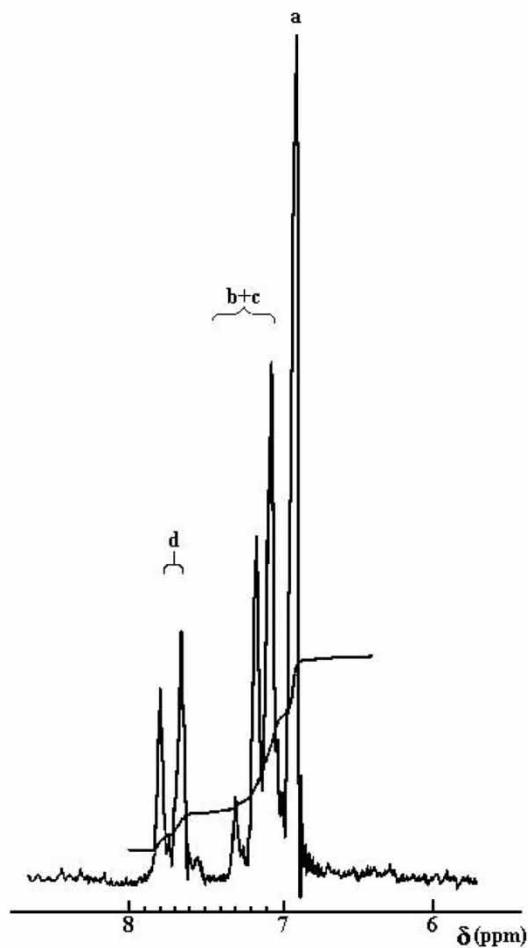
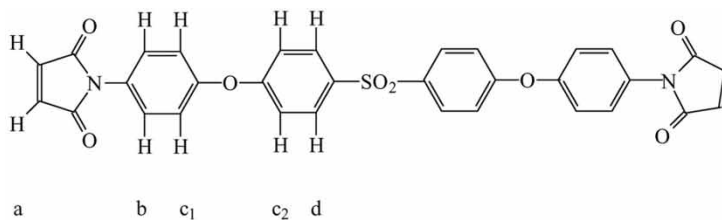


Figure 2. ¹H-NMR spectra of monomer BMI-3.

doublet in the range 7.80–7.66 ppm (attributed to aromatic protons ortho to $-\text{SO}_2$) and a multiplet in the range 7.30–7.06 ppm (due to aromatic protons ortho to maleimide and ortho to $-\text{O}-$). The ¹H-NMR spectrum showed a singlet at 6.95 ppm attributed to olefinic protons.

The monomers were analyzed by differential scanning calorimetry (DSC) (Figure 3). DSC curves for all bismaleimides (except BMI-4) were characterized by a sharp melting

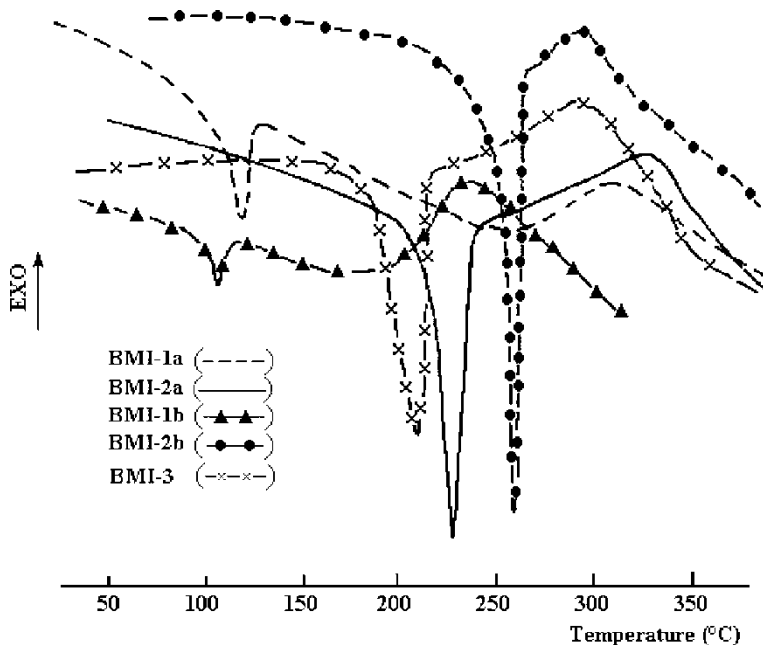


Figure 3. DSC scans of BMI (1-2)a, BMI (1-2)b and BMI-3.

endotherm in the temperature range 100–257°C due to the melting of these monomers (Table 1). Melting point of bismaleimide BMI-4 could not be recorded by DSC, when sample was heated from room temperature up to 350°C. This may be due to the crosslinking phenomenon along with the gradual heating. When bismaleimide BMI-4 was heated with a higher rate (50°C/min), the sample melted at 315–318°C. The bismaleimides BMI (1-2)a,

Table 1
Physical and thermal properties of the obtained monomers

Monomer	General appearance	M. P. ^a (°C)	T _{end} ^b (°C)	T _{exo} ^c (°C)	T _p ^d (°C)	IDT ^e (°C)	Y _c ^f (%)
BMI-1a	Light-yellow	121 ^g	123	313	235	422	48
BMI-2a	Light-yellow	212–215	220	297	245	443	49
BMI-1b	Cream	91 ^g	100	222	191	335	42
BMI-2b	White	235–240	257	289	272	390	35
BMI-3	Orange	204–208	207	298	232	435	57
BMI-4	Yellow	315–318 ^h	—	—	—	394	65

^aMelting point determined visually in a capillary tube melting point apparatus.

^bEndotherm peak temperature by DSC.

^cExothermal peak temperature by DSC.

^dStart of polymerization as measured by DSC.

^eOnset degradation temperature.

^fChar yield at 600°C.

^gMelting point as measured by DSC.

^hMelting point was determined with Hot Stage Type Linkam TP92.

BMI (1-2)b and BMI-3 exhibited an exothermic transition associated to thermal curing at 222–313°C. The onset temperatures for a curing reaction, in the case of bismaleimides BMI (1-2)a, BMI (1-2)b and BMI-3 are in the 191–272°C range. It is easy to notice that for BMI-1a and BMI-2a, these temperatures do not have very different values compared to temperature values for BMI-1b and BMI-2b, where the differences are significant.

Thermal stabilities of bismaleimide compounds were evaluated by TGA. The data of the onset of initial decomposition temperature (IDT), temperature of maximum decomposition and percent char yield at 600°C ($Y_c\%$) are listed in Table 1. The initial decomposition temperature of the compounds is in the 335–435°C range. BMI-2a showed the highest thermostability, whereas BMI-1b has the lowest thermostability. Ether units (BMI-3) and hexafluoroisopropylidene groups (BMI (1-2)a) has a beneficial influence. Considering as thermostability criterion the char yield at 600°C, BMI-4 is the monomer with the highest thermostability, and BMI-2b is the monomer having the lowest one. One can notice the influence of the ether group on the thermostability of BMI-3, which is also high. In conclusion, BMI-3 and BMI-4 proved very good thermostability due to the fact that these two monomers do not contain ester units. Among the bismaleimides having ester units in their structure, those with hexafluoroisopropylidene moieties have the higher thermostability.

Polymer Synthesis

The polyaminobismaleimides with ester and/or ether units were synthesized by the Michael addition of diamines, namely: (1,2-bis(2-aminophenoxy)ethoxy)etane (APEE), 1,4-bis(4-aminophenoxy)benzene (APB), 4,4-bis(4-aminophenoxy)diphenyl-sulfone (AP-DPS) and 9,9-bis(4-aminophenoxy)fluorene (APF), to bismaleimides in NMP at 90–95°C. The polymers were isolated by pouring the reaction mixture into methanol to give brown powder polymers. Results are summarized in Table 2. The structure of the polymers were confirmed by spectroscopy (IR and $^1\text{H-NMR}$), and by elemental analysis. The IR spectra showed that polymers are characterized by the same absorption bands as the monomers, but they are wider. Figure 4 presents the infrared (IR) spectrum of polymer P-1. The bands at 2950 and 2870 cm^{-1} ($\gamma\text{-CH}_2\text{-}$) and 1170 cm^{-1} ($\gamma\text{(C-N-C)}$) of the polymer are due to the formation of succinimide rings during the polyaddition reaction (24).

$^1\text{H-NMR}$ spectrum of polymer P-3 is presented in Figure 5. The multiplet at 7.87–6.73 ppm is associated with protons of aromatic rings (peaks broader than those in spectrum of monomer BMI-3). However, the spectrum of P-3 shows features different from the spectrum of monomer BMI-3. The peaks at 5.82–5.60 ppm are attributed to the -NH group. The multiplet between 4.84–4.62 ppm, is due to hydrogen H_c from succinic ring. The signals between 3.18–2.96 and 2.84–2.65 ppm are determined by aliphatic protons H_b and H_a , respectively.

Elemental analysis data for the polymers are listed in Table 3 and proved a good concordance between calculated and experimental values. The viscosities vary between 0.28–0.43. The best value was obtained at 95°C for P-3. The poorest results were obtained for P-2, which have the lowest viscosity.

The GPC curve indicated that number-average relative molar mass (M_n) values of polymers varied between 7500 and 15520 and the M_w/M_n ratio as a measure of molecular weight distribution was between 1.2 and 1.75. Flexible films were obtained from solution casting using NMP for polymers P-1, P-3, P-5, P-7 and P-8.

Table 2
Reaction between bismaleimides and diamines

Polymer	Bismaleimide	Diamine	Temp. (°C)	Time (h)	Conc. (%)	η^a (dL/g)	M_n	M_w/M_n	Films prop.
P-1	BMI-1a	APB	90	15	10	0.32	9,850	1.47	Flexible
P-2	BMI-2b	APF	90	15	15	0.28	—	—	Brittle
P-3	BMI-3	APB	95	20	15	0.43	15,520	1.36	Flexible
P-4	BMI-4	APEE	95	25	10	0.30	8,600	1.75	Brittle
P-5	BMI-1b	APEE	90	16	12	—	14,310	1.5	Flexible
P-6	BMI-1b	APF	95	10	12	0.31	—	—	Brittle
P-7	BMI-2a	APDPS	95	15	12	0.41	14,900	1.2	Flexible
P-8	BMI-2a	APDPS	95	40	10	0.39	—	—	Flexible
P-9	BMI-2a	APF	90	40	10	0.29	7,480	1.3	Brittle

^aInherent viscosity, measured at a concentration of 0.5 g/dL in NMP at 25°C.

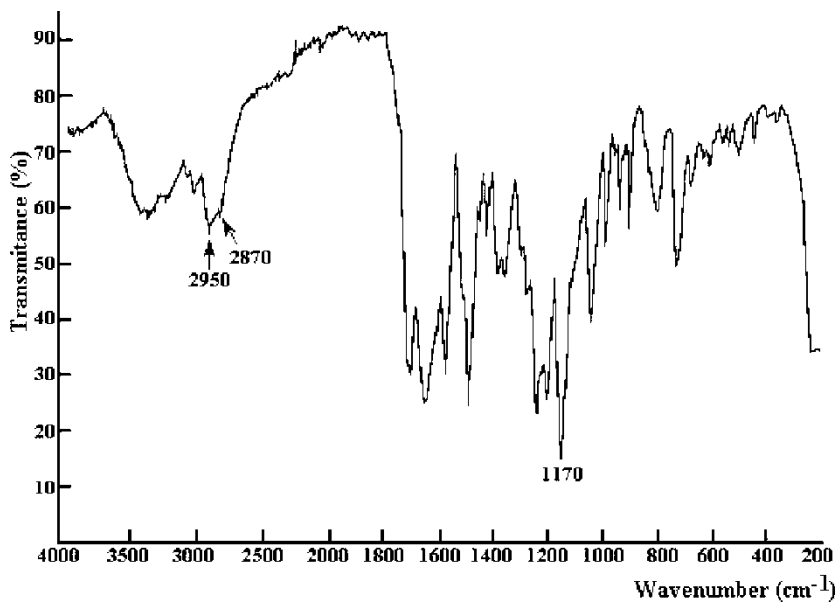


Figure 4. IR spectra of polymer P-1.

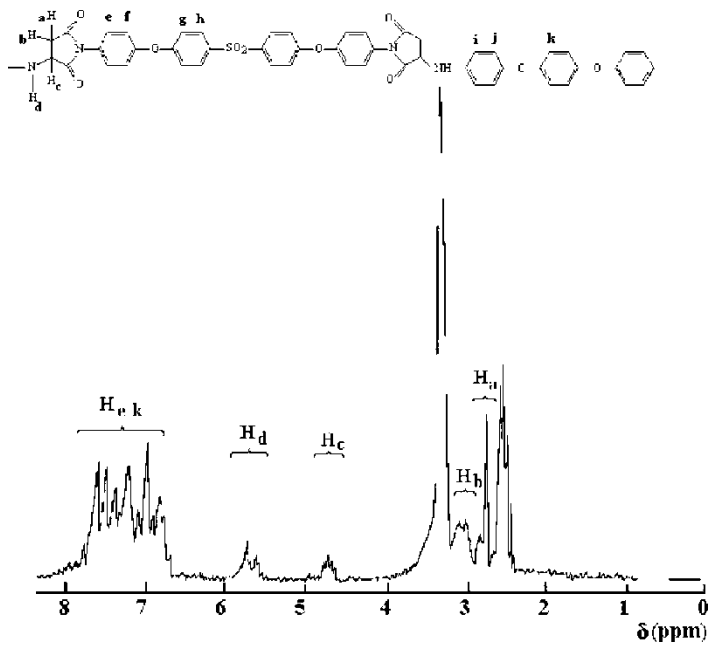


Figure 5. ¹H-NMR spectra of polymer P-3.

Table 3
Elemental analysis of the polymers

Polymer	Elemental analysis				
	C%	H%	N%	F%	S%
P-1					
Calcd	64.45	3.34	5.46	11.12	—
Found.	63.71	3.89	5.12	10.73	—
P-2					
Calcd.	73.01	5.04	6.67	—	—
Found	74.53	4.65	6.13	—	—
P-6					
Calcd.	71.21	3.84	5.63	—	3.22
Found.	70.15	4.07	5.19	—	—
P-7					
Calcd.	62.88	3.28	4.80	9.78	2.75
Found.	63.44	2.89	5.15	10.12	3.04
P-9					
Calcd.	68.88	3.54	5.18	10.54	—
Found.	69.16	3.21	4.85	10.22	—

The thermal behavior of polyaminobismaleimides was evaluated by means of TG, DSC (T_g) and isothermal gravimetric analysis (IGA) (Table 3). The thermogravimetric (TGA) curves of the polymers P (1–4), P-6 and P(8, 9) are shown in Figure 6 and data of the onset of initial decomposition temperature (IDT) and percentage char yield at 600°C are listed in Table 4. The initial decomposition temperatures of the polymers are in the range 250–338°C. It was observed that IDT are higher for polymers P-7 and P-9 (based on bismaleimides having hexafluoroisopropylidene groups and various amine components). As observed, the polymer P-3 shows the lowest IDT (being obtained from bismaleimide with –SO₂ groups). Considering IDT as a thermostability criterion, the

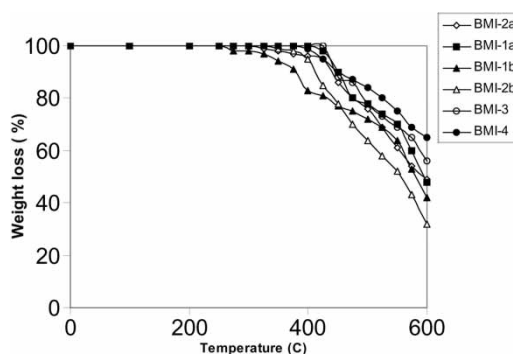


Figure 6. TGA thermograms of polymers P (1–4), P-6 and P (8–9), heating rate: 12°C/min.

Table 4
Some characterization data of prepared polymers

Polymer	Color	T_g^a (°C)	TG		
			IDT ^b (°C)	PDT ^c max (°C)	Y_c (%) ^d
P-1	Reddish-brown	158	272	382	43
P-2	Reddish-brown	—	250	382	53
P-3	Light-brown	178	295	432	44
P-4	Brown	166	291	348, 553	48
P-5	Reddish-brown	162	294	384, 542	44
P-6	Light-brown	—	282	382, 568	50
P-7	Reddish-brown	200	338	400	54
P-8	Reddish-brown	166	300	385, 558	55
P-9	Brown	—	332	540	50

^aThe glass transition temperatures, determined by DSC at a heating rate of 10°C/min.

^bOnset degradation temperature.

^cMaximum decomposition temperature.

^dChar yield at 600°C.

following order can be established:

$$P-7 > P-9 > P-8 > P-3 > P-5; \quad P-6 > P-1 > P-2$$

The polymers P-2, P-7 and P-8 showed the highest values of Y_c , compared to polymers P-1, P-3 and P-5 (due to the influence of bismaleimide and diamine components). The polymers P-4, P-5, P-6 and P-8 showed two-stage decomposition, due to the combination of chemical different segments in the polymer chain.

The glass transition temperatures of the polymers P-1, P (3–5), P (7, 8) were in the 158–200°C range, being highly dependent on the bismaleimide and diamine component structures. Polymers P-2, P-6 and P-9 do not show any glass transition temp-

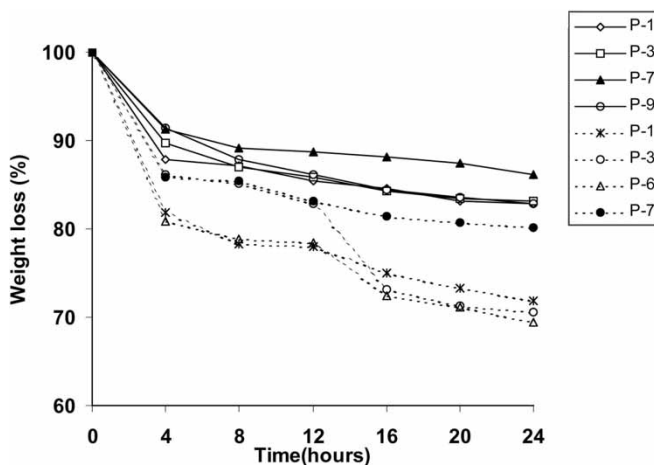


Figure 7. The isothermal weight loss in air at 275°C for 24 h (—) and at 325°C for 24 h (----).

Table 5
Mechanical properties of the polymers films

Polymer	Tensile strength at break (MPa)	Tensile modulus (MPa)	Elongation at break (%)
P-1	45	1920	1.8
P-3	80	2375	2.7
P-5	39	1875	1.5
P-7	72	2110	2.3
P-8	68	2450	2.1

erature up to 350°C. It can be seen that there is a large interval between glass transition and decomposition temperatures for all these polymers, a characteristic that can be advantageous for their processability.

The present investigation was expanded in order to include evaluation of thermo-oxidative stability of these polymers by IGA. The weight loss after 24 h at 275°C, in air, for polymers P (1–9) varied in the range of 13.0–29.5%. For polymers P-1, P-3, P-6 and P-7, after 24 h at 325°C, the weight loss was in the range 19.8–34%. Figure 7 presents the IGA traces of polymers P-1, P-3, P-7 and P-9 at 275°C and of polymers P-1, P-3, P-6 and P-7 at 325°C.

The mechanical properties of polymer films are listed in Table 5. The films have tensile strength values of 51–73 MPa, elongation at break of 2.1–3.4%, and tensile modulus of 1795–2430 MPa. The tensile strength value of polymer P-3 is the highest, this polymer having bismaleimide component with ether moieties (Table 5).

Conclusions

A series of bismaleimides and polyaminobismaleimides with different structures (ester, ether units, hexafluoroisopropylidene, sulphonyl and fluorene groups) were synthesized and characterized by spectroscopy (IR and ¹H-NMR) and elemental analysis. Thermal behavior of these compounds was evaluated by DSC, TGA and IGA. Mechanical properties of these polymers were also studied. This research was meant to establish the influence of the monomer structures and regime parameters on the properties of the synthesized polymers.

References

1. Goldfarb, I.J., Feld, W.A., and Saikumar, J. (1993) Synthesis and structure-property relationships of bismaleimides containing oxyalkylene linkages. *Polymer*, 34 (4): 813–818.
2. Sava, M., Gaina, C., Gaina, V., Chiriac, C., and Stoleriu, A. (1997) Synthesis, characterization and stability of bismaleimides containing ester groups in the backbone. *J. Macromol. Sci-Pure Appl. Chem.*, A34 (8): 1505–1514.
3. Mikroyannidis, J.A. (1992) Synthesis and diels-alder polymerization of furfurylidene and furfuryl-substituted maleamic acids. *J. Polym. Sci., Part A: Polym. Chem.*, 30: 125–132.
4. Stenzenberger, H.D. (1994) Addition polyimides. *Adv. Polym. Sci.*, 117: 165–220.
5. Dix, L.R., Ebdon, I.R., Flint, N.J., Hodge, P., and O'Dell, R. (1995) Chain extension and cross-linking of telechelic oligomers-i. michael addition of bisamines to bismaleimides and bis(acetylene ketone)s. *Eur. Polym. J.*, 31 (7): 647–652.

6. Fan, J., Hu, X., and Yue, C.Y. (2003) Static and dynamic mechanical properties of modified and cyanate ester interpenetrating polymer networks. *J. Appl. Polym. Sci.*, 88: 2000–2006.
7. Yan, Y., Shi, X., Liu, J., Zhao, T., and Yu, Y. (2002) Thermosetting resin system based on novolac and bismaleimide for resin-transfer molding. *J. Appl. Polym. Sci.*, 83: 1651–1657.
8. Hu, X., Shi, X., Liu, J., Zhao, T., and Yu, Y. (2001) Rheological study of crosslinking and gelation in bismaleimide/cyanate ester interpenetrating polymer network. *J. Appl. Polym. Sci.*, 80: 2437–2445.
9. Wang, C.S. and Hwang, H.J. (1996) Investigation of bismaleimide containing naphthalene unit. II. Thermal behavior and properties of polymer. *J. Polym. Sci., Part A: Polymer Chemistry*, 34: 1493–1500.
10. Liao, D.C. and Hsieh, K.H. (1994) Synthesis and characterization of bismaleimides derived from polyurethanes. *J. Polym. Sci. Part A: Polymer Chemistry*, 32: 1665–1672.
11. Hu, X., Zhang, J., Yue, Y.C., and Zhao, Q. (2000) Thermal and morphological properties of polyetherimide modified bismaleimide resins. *High Perform. Polym.*, 12: 419–428.
12. Gouri, C., Reghunadhan Nair, C.P., and Ramaswamy, R. (2000) Adhesive characteristics of alderene adduct of diallyl bisphenol a novolac and bisphenol a bismaleimide. *High Perform. Polym.*, 12: 497–514.
13. Hopewell, J.L., George, G.A., and Hill, D.J.T. (2000) Quantitative analysis of bismaleimide diamine thermosets using near infrared spectroscopy. *Polymer*, 41: 8221–8229.
14. Takeda, S., Akiyama, H., and Kakiuchi, H. (1998) Synthesis and properties of bismaleimides resins containing ether bonds. *J. Appl. Polym. Sci.*, 35: 1341–1350.
15. Dao, B., Hodkin, D.G., Jackson, M.B., and Morton, T.C. (1996) Preparation and characterization of some bismaleimide monomers and polymers based on diaminobisimides. *High Perform. Polym.*, 8: 245–252.
16. Hu, X., Fan, J., Yue, C.Y., and Liang, G.Z.J. (1999) Enhancement of the processibility of bismaleimide resins via copolymerization with allyl organo-boro compounds. *Mater Process Tech.*, 544: 89–90.
17. Wang, X., Chen, D., Ma, W., Yang, X., and Lu, L. (1999) Polymerization of bismaleimide and maleimide catalyzed by nanocrystalline titania. *J. Appl. Polym. Sci.*, 71: 665–669.
18. Park, J.O. and Jang, S.H. (1992) Synthesis and characterization of bismaleimides from epoxy resin. *J. Polym. Sci. Part A, Polym. Chem.*, 3: 723–729.
19. Liu, F.J., Munukutia, S., Levent, K., and Tesoro, G. (1992) Synthesis and characterization of some imide end-capped amide-imides. *J. Polym. Sci. Part A, Polym. Chem.*, 30: 157–162.
20. Mikroyannidis, J.A. (1990) Thermostable laminating resins based on aromatic diketone bis- and tetramaleimides. *J. Polym. Sci., Part A: Polym. Chem.*, 28: 679–691.
21. Hoyt, A.E. and Benicewicz, B.C. (1990) Rigid rod molecules as liquid crystal thermosets. ii. Rigid rod esters. *J. Polym. Sci., Part A: Polym. Chem.*, 28: 3417–3427.
22. Dix, L.R., Ebdon, J.R., Flint, N.J., Hodge, P., and O'Dell, R. (1995) Chain extension and crosslinking of telechelic oligomers-II. Michael addition of bistiols to bismaleimides, bismaleates and bis(acetylene ketone)s to give linear and crosslinked polymers. *Eur. Polym. J.*, 31 (7): 653–658.
23. Itoya, K., Kumagai, Y., Kanamuru, M., Sawada, H., Kakimoto, M., and Imai, Y. (1993) New high pressure polymerization and simultaneous processing for polyaminoimide from aromatic diamine and bismaleimide. *Polym. J.*, 25: 883–890.
24. Wu, W., Wang, D., and Ye, C. (1998) Preparation and characterization of bismaleimide-diamine prepolymers and their thermal-curing behavior. *J. Appl. Polym. Sci.*, 70: 2471–2477.