

Preparation and Polymerization of Bismaleimide Compounds

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ABSTRACT: Bismaleimides with main chains of different structures were prepared by the reaction between maleic anhydride and various diamines and by the reaction between 4-maleimidobenzoylchloride and 3,5-dihydroxybenzoic acid. The monomers were characterized with IR and $^1\text{H-NMR}$ spectroscopy. Polymers based on these compounds were prepared through the Michael addition of diamines to bis-

maleimides. The thermal characterization of the monomers and polymers was performed with differential scanning calorimetry and dynamic thermogravimetric analysis. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2185–2191, 2007

Key word: synthesis; structure-property relations; thermal properties; infrared spectroscopy; NMR

INTRODUCTION

Bismaleimide (BMI) polymers constitute an addition polyimide class obtained from BMIs with various structures and contain unsaturated end groups, which can be thermally polymerized without the formation of volatile byproducts. This provides considerable advantages in processing over conventional condensation-type polyimides.^{1–12}

These polyaminobismaleimide (PABM) resins are a subject of interest because of their attractive properties, such as high thermal stability, outstanding mechanical properties, good flame resistance, excellent chemical and corrosive resistance, low water susceptibility, high glass-transition temperatures, excellent radiation resistance, and good retention of thermomechanical properties even after long times of aging at 250°C.¹³

PABM resins are widely used as high-performance polymers because of their attractive combination of physical, chemical, and mechanical properties.

They have higher radiation and fire resistance than epoxy resins. Their excellent thermal behavior at high temperatures allows them to be used for multilayer printed circuit boards, large-scale computers, advanced composites for the aerospace industry, and structural adhesives.^{14,15}

However, these compounds present some unfavorable features, such as low solubility in common solvents, high melting and curing temperatures, and brittleness of the final polymer due to the high cross-

linking density of the network polymers, that restrict their practical applications.^{16–19} To use thermosetting resins as high-performance structural composite materials, the fracture toughness must be improved without other important properties being sacrificed. Further attempts have been made to improve the processability and properties of BMI resins through the introduction of various substituents to the aromatic rings in the main chain. This article presents the influence of the monomer structure on the solubility, melting point, reactivity, and thermal properties of the polymers.

EXPERIMENTAL

General procedure for the preparation of the BMIs

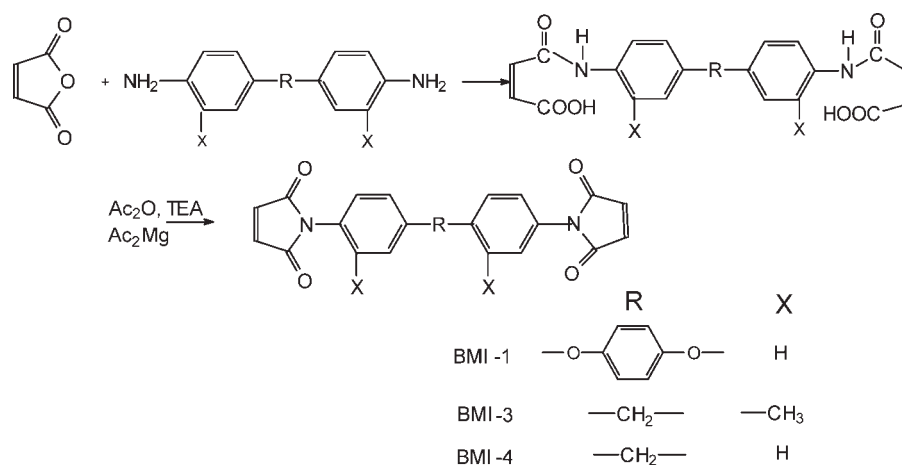
BMI-1, BMI-3, and BMI-4 were synthesized according to the literature^{20,21} (Scheme 1). The monomer used in the reaction was prepared from aromatic diamines (0.25 mol) with maleic anhydride (0.55 mol) in dry acetone. Intermediate bismaleamic acid was cyclodehydrated *in situ* with acetic anhydride and triethylamine (TEA) with magnesium acetate as a catalyst. The final product was recrystallized and dried under a vacuum.

Monomer BMI-2 with ester groups was synthesized via the reaction of 4-maleimidobenzoyl chloride (4-MBAC) with 3,5-dihydroxybenzoic acid according to the literature^{22,23} (Scheme 2).

4-Maleimidobenzoyl chloride (4-MBA) was obtained as previously described in the literature²³ (mp = 225–228°C).

4-MBAC was prepared as described in the literature²⁴ (mp = 169–171°C).

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Scheme 1

4-MBAC (0.2 mol) in 200 mL of chloroform (CHCl₃) was stirred and cooled in an ice bath. TEA (0.2 mol) as an acid acceptor and a solution of 3,5-dihydroxybenzoic acid (0.1 mol) in 100 mL of CHCl₃ were added. After stirring for 1.0 h, the mixture was filtered and precipitated in *n*-hexane. The product was filtered and then thoroughly washed with water (four times). The filtered precipitated monomer was recrystallized from dioxane/ethanol.

BMI-1

The monomer was recrystallized from ethanol (yield = 72%).

mp: 233–236°C. IR (KBr, cm⁻¹): 1780 and 1720 (C=O imide), 1250 (—O—). ANAL. Calcd for C₂₆H₁₆N₂O₆: C, 69.00%; H, 3.52%; N, 6.19%. Found: C, 68.43%; H, 3.71%; N, 6.56%.

BMI-3

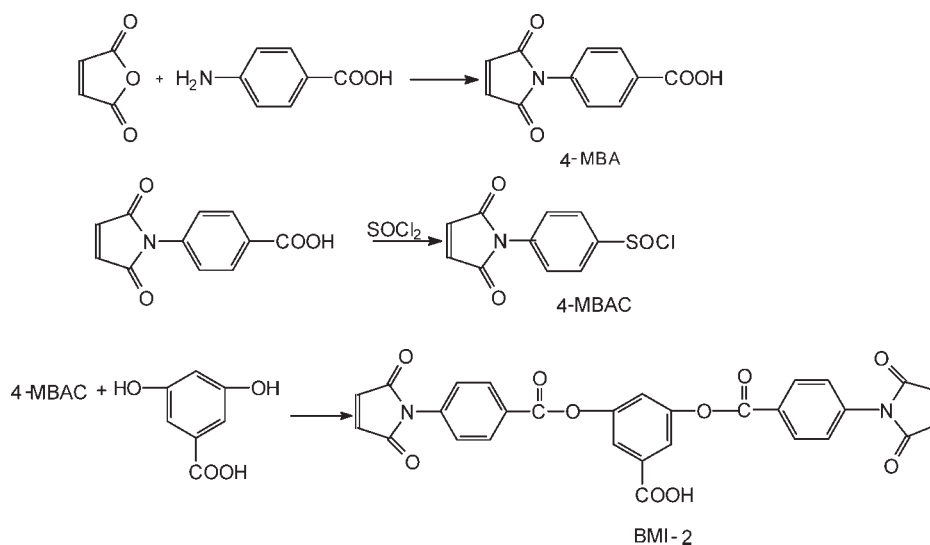
The compound was recrystallized from ethanol (yield = 69%).

mp: 197°C. IR (KBr, cm⁻¹): 1780 and 1720 (C=O imide), 2970–2860 (—CH₃). ANAL. Calcd for C₂₃H₁₈N₂O₄: C, 71.49%; H, 4.69%; N, 7.24%. Found: C, 71.65%; H, 4.63%; N, 7.43%.

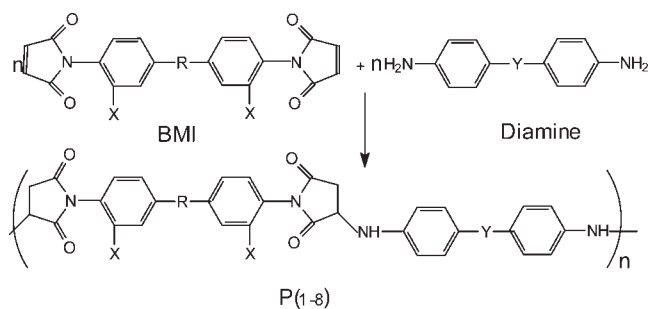
BMI-4

The product was recrystallized from toluene (yield = 73%).

mp: 147°C. IR (KBr, cm⁻¹): 1785 and 1710 (C=O imide), 3100 (=C—H). ANAL. Calcd for C₂₁H₁₄N₂O₄: C, 70.38%; H, 7.81%; N, 3.96%. Found: C, 69.91%; H, 7.58%; N, 4.08%.



Scheme 2



BMI-2

The monomer was recrystallized from a mixture of dioxane and ethanol (yield = 67%).

mp: 175°C. IR (KBr, cm^{-1}): 1780 and 1725 ($\text{C}=\text{O}$ imide), 1740 ($\text{C}=\text{O}$ ester). ANAL. Calcd for $\text{C}_{29}\text{H}_{16}\text{N}_2\text{O}_{10}$ C, 63.04%; H, 2.91%; N, 5.07%. Found: C, 62.81%; H, 2.76%; N, 5.32%.

Synthesis of the polymers

The polymers were prepared as described in the literature (Scheme 3).²⁵ Into a 100-mL, three-necked flask fitted with a mechanical stirrer, thermometer, and nitrogen inlet, 0.02 mol of BMI, 0.02 mol of diamines, and *N*-methylpyrrolidine-2-one (NMP) as a solvent (with a 10–15% monomer concentration) were charged. Small amounts of acetic acid were added. The polymers were isolated by the pouring of the reaction mixture into methanol to yield powder polymers. The products were filtered and washed thoroughly. The reaction parameters (time, concentration, and temperature) were varied to achieve polymers with different characteristics. The influence of the reaction conditions on the properties of the polymers was studied.

Measurements

The IR spectra were recorded on a Carl Zeiss Jena Specord M90 spectrophotometer (Jena, Germany) with the KBr pellet technique. $^1\text{H-NMR}$ spectra were recorded on a Bruker Avance DRX 400-MHz NMR spectrometer (Rheinstetten, Germany) with dimethyl sulfoxide- d_6 as a solvent and tetramethylsilane as an internal standard. Differential scanning calorimetry (DSC) measurements were performed with a Mettler TA Instrument DSC 12E (Greifensee, Switzerland) at a heating rate of 10°C/min in air. Thermogravimetric analysis (TGA) was carried out in air with an F. Paulik derivatograph (Budapest, Hungary) at a heating rate of 12°C/min. The inherent viscosities of the polymer solutions were measured at a concentration of 0.5 g/dL in NMP and were determined at 25°C with an Ubbelohde suspended-level viscometer. The melting point of BMI-1 was determined with a Linkam TP92 hot-stage appa-

ratus (Tokyo, Japan) at a heating rate of 50°C/min in air.

RESULTS AND DISCUSSION

The IR spectra of the obtained monomers showed characteristic carbonyl doublets in the range of 1785–1710 cm^{-1} . BMI-2 showed an absorption band at 1740 cm^{-1} due to ester groups. The absorption peak at 1250 cm^{-1} (BMI-1) corresponded to the ether groups. Figure 1 presents the IR spectrum of BMI-1.

The $^1\text{H-NMR}$ spectrum of monomer BMI-3 confirmed its chemical structure. Figure 2 shows that the aromatic protons of BMI-3 appeared as a singlet at 7.264 ppm (attributed to aromatic protons ortho to *N*-maleimide), two doublets in the ranges of 7.196–7.192 and 7.176–7.172 ppm (due to aromatic protons ortho to $-\text{CH}_2$), and a doublet in the range of 7.132–7.112 ppm (attributed to aromatic protons ortho to $-\text{CH}_3$). The absorption at 7.148 ppm, observed in the spectrum, confirmed the presence of the olefin protons in the terminal maleimide ring.

Other signals at 3.963 ppm corresponded to the protons from the $-\text{CH}_2$ group, and signals at 2.029 ppm corresponded to the $-\text{CH}_3$ group.

The monomers were analyzed with DSC (Fig. 3). The DSC curves for all BMIs were characterized by a sharp melting endotherm in the range of 160–230°C due to the melting of these compounds (Table I).

The reactivities of these BMIs were in the temperature range of 178–251°C (except for BMI-3, for which the onset temperature for the curing reaction was overshadowed by the melting endotherm). The reactivity of the BMIs was influenced by the chemical nature of the moiety between the maleimide groups. Some literature data¹ certify that an electron-donating group, such as an alkyl moiety, reduces the reactivity of BMIs when they are bonded to a phenylene ring bearing a maleimide group. On the other hand, electron-attracting groups such as $\text{C}=\text{O}$ and SO_2 have the

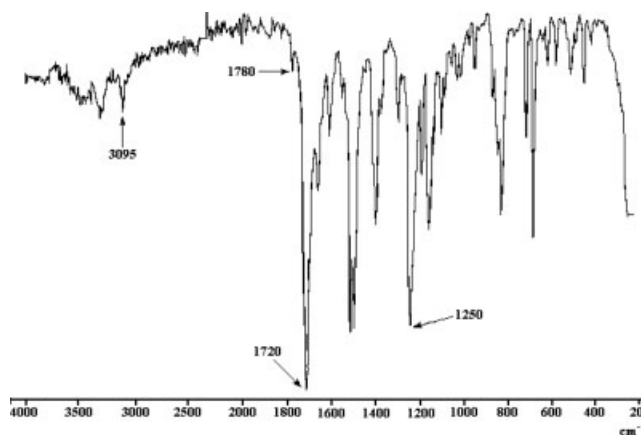


Figure 1 IR spectrum of BMI-1.

TABLE I
Physical and Thermal Properties of the Prepared Monomers

Monomer	Color	DSC					TG		
		Melting point (°C)	T_{end} (°C) ^a	T_{exo} (°C) ^b	T_p (°C) ^c	ΔH (kJ/mol) ^d	IDT (°C)	PDT_{max} (°C) ^e	Y_c (%) ^f
BMI-1	Light yellow	233–236 ^g	230	310	251	60	390	432, 530	58
BMI-2	Light yellow	175	187	254	210	43	305	466	44
BMI-3	Light yellow	197	212	264	—	—	313	365, 441	54
BMI-4	Yellow	147	160	237	178	63	460	500	62

^a Melting endotherm.

^b Exotherm.

^c Onset temperature for the curing reaction.

^d Heat of polymerization measured by DSC.

^e Temperature of maximum decomposition.

^f Char yield at 600°C.

^g Determined visually in a capillary-tube melting-point apparatus.

appearance of the band at 1180 cm^{-1} (succinic ring) showed that a reaction took place.²⁷

The polymers dissolved in polar amidic solvents such as dimethylformamide, dimethyl acetamide, and NMP. This good solubility was due to the relatively high flexibility of the macromolecular chains, which was obtained by the introduction of ether linkages into the structure of the polymers.

Model molecules of polymers P-1 and P-5 are shown in Figure 5. The disturbed packing of the macromolecular chain facilitated the diffusion of small molecules of solvents between the polymer chain, and this led to improved solubility.

The inherent viscosities, measured in NMP solutions, were in the range of 0.21–0.46 (Table II). The best value was obtained for polymer P-5. The poorest results were obtained for P-2, which had the lowest viscosity. Flexible films were obtained via solution casting with NMP for polymers P-3, P-4, P-5, and P-6.

The thermal behavior of the PABMs was evaluated with thermogravimetry (TG) and DSC (glass-transition temperature) analysis. The TGA curves of polymers P-2, P-3, P-4, P-5, and P-6 are shown in Figure 6, and the data for the IDT and char yield at 600°C are

listed in Table III. The IDTs of the polymers were in the range of 305–356°C.

The IDT was higher for polymer P-5 and was followed by that of P-3, whereas P-2 showed the lowest IDT (being obtained from a BMI derived from 3,5-dihydroxybenzoic acid).

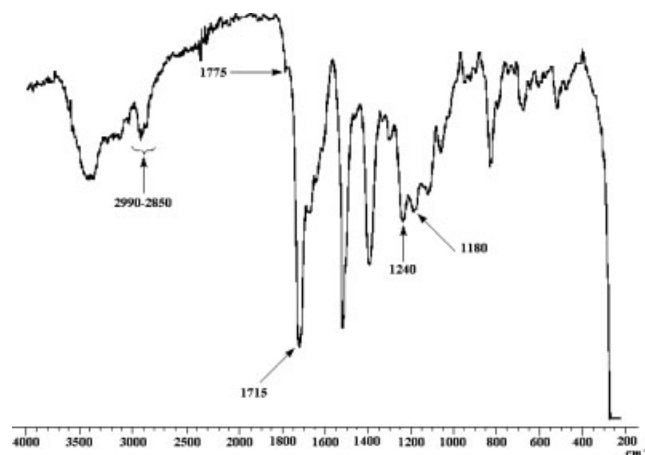


Figure 4 IR spectrum of polymer P-5.

TABLE II
Reaction Between BMIs and Diamines

Polymer	R	X	Y	Temperature (°C)	Time (h)	Concentration (%)
P-1		H	—O—	90	35	10
P-2		H	—O—	90	25	15
P-3	—CH ₂ —	CH ₃	—O—	95	20	15
P-4	—CH ₂ —	H	—O—	95	20	15
P-5	—CH ₂ —	CH ₃	—SO ₂	95	25	15
P-6	—CH ₂ —	H	$\text{o}-(\text{CH}_2-\text{CH}_2-\text{O})_3$	90	20	15
P-7		H	—SO ₂	90	30	10
P-8		H	$\text{o}-(\text{CH}_2-\text{CH}_2-\text{O})_3$	90	25	15

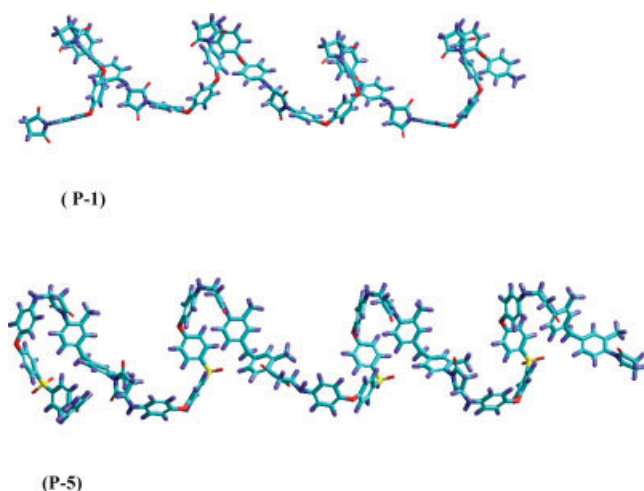


Figure 5 Models of fragments of polymers P-1 and P-5. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

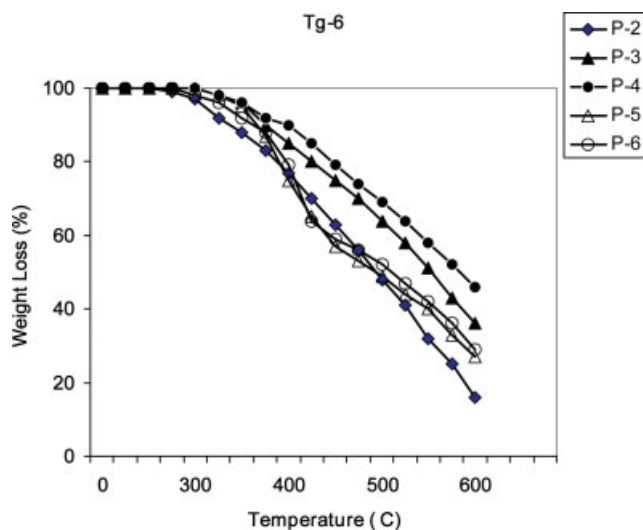


Figure 6 TGA thermograms of polymers P-2, P-3, P-4, P-5, and P-6.

TABLE IV
Electrical Volume Resistivity and Dielectric Constants of the Polymers

Polymer ^a	Volume resistivity (Ω cm) ^b	Dielectric constant ^c
P-2	1.1×10^{16}	4.1
P-3	3.4×10^{16}	4.0
P-4	2.5×10^{17}	3.6
P-5	4.3×10^{16}	3.4
P-6	3.7×10^{17}	3.9

^a Each film was prepared with NMP at an initial concentration of 15 wt %. The cure cycle was 2 h at 150°C, 2 h at 190°C, and 2 h at 220°C.

^b Measured with a Straton Teralin III electrometer.

^c Measured with an EO711 digital RLC meter at 1 kHz. R, resistance; L, inductance; C, capacitance.

With IDT used as a thermostability criterion, the following order could be established: P-5 > P-3 > P-6 > P-4 > P-2.

All the resins gave under aerobic conditions char yields of 16–46%, and this indicated that the char yield was seriously affected by the structure of the BMI and diamine used. Polymer P-4 showed the highest value of the char yield, and it was followed by P-3; P-5 and P-6 showed close values, whereas polymer P-2 showed the lowest value.

The glass-transition temperatures of polymers P-3, P-4, and P-5 were in the range of 221–247°C, being highly dependent on the BMI and diamine component structure. Polymers P-2 and P-6 did not show any glass-transition temperature up to 350°C.

The electrical insulation properties of the polymers were evaluated on the basis of their dielectric constants and electrical volume resistivity. The dielectric constants of polymers P-2, P-3, P-4, P-5, and P-6 varied between 3.4 and 4.1, and the electrical volume resistivity ranged from 1.13×10^{16} to 3.73×10^{17} (Table IV). These results show that the magnitude of the dielectric constant decreased from P-2 to P-5.

The volume resistivity of the polymers increased in the order of P-2 < P-3 < P-5 < P-4 < P-6. The volume

TABLE III
Some Characterization Data of the Prepared Polymers

Polymer	Color	Inherent viscosity ^a	Glass-transition temperature (°C) ^b	Film property	TG		
					IDT (°C)	PDT _{max} (°C) ^c	Y _c (%) ^d
P-2	Brown	0.21	—	Brittle	305	—	16
P-3	Brown	0.43	234	Flexible	335	385	36
P-4	Cream	0.37	247	Flexible	316	445	46
P-5	Reddish-brown	0.46	221	Flexible	356	408	27
P-6	Reddish-brown	0.38	—	Flexible	410	410	29

^a Measured at a concentration of 0.5 g/dL in NMP at 25°C.

^b Determined by DSC at a heating rate of 10°C/min.

^c Temperature of maximum decomposition.

^d Char yield at 600°C.

resistivity of polymer P-6 was higher, and P-2 showed the lowest value.

CONCLUSIONS

A series of BMI monomers and PABMs with different structures were synthesized and characterized with spectroscopy (IR and $^1\text{H-NMR}$). The thermal behavior of these monomers and polymers was evaluated with DSC and TGA. The results of our study are conclusive and substantiate that the monomer structures and regime parameters affect the structure–property relationship of the synthesized polymers.

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