

Bismaleimide Monomers with Amide Units: Synthesis and Properties

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ABSTRACT: A series of bismaleimide monomers with amide groups were prepared and characterized. Structurally different bismaleimides (with amide units) were synthesized by a reaction between 4-maleimidobenzoyl chloride and various diamines. The monomers were characterized by infrared spectroscopy, proton nuclear magnetic resonance spectroscopy, and elemental analysis. The thermal charac-

terization of the bismaleimides was accomplished with differential scanning calorimetry and dynamic thermogravimetric analysis. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 567–572, 2006

Key words: synthesis; solubility; thermal properties

INTRODUCTION

Bismaleimide (BMI) resins are an addition-type polyimide class of macromolecular compounds produced from bismaleimide monomers and contain unsaturated end groups. They are used as high-performance composite matrices because of their high temperature resistance, high glass-transition temperature, high tensile strength and modulus, excellent chemical, radiative, and corrosive resistance, and good retention of thermomechanical properties even after long aging intervals at 250°C and because of their attractive combination of physical, chemical, and mechanical properties.^{1–9}

A wide variety of polyimides bearing end-capped reactive maleimides have been developed in the last 40 years to improve their processability without any alteration of their thermal behavior and mechanical strength. BMI monomers can be thermally polymerized without the formation of volatile byproducts, offering considerable advantages in processing over conventional condensation-type polyimides.

Unfortunately, these resins have a number of disadvantages, such as brittleness (because of their high crosslink density), high melting and curing temperatures, and poor solubility in ordinary solvents.^{10–12}

Further attempts have been made to improve the processability and properties of these resins with monomers with different structures. We were interested in preparing materials based on this concept and in investigating in their properties. In this study, we

examined the influence of the monomer structure (BMI with amide groups) on the solubility, reactivity, and thermal properties of these products.

EXPERIMENTAL

Synthesis of the monomers

4-Maleimidobenzoic acid

The product was obtained as described in the literature¹³ (mp = 224–227°C after crystallization from toluene, reference mp¹⁴ = 224–228°C after recrystallization from ethyl acetate/n-hexane solution).

4-Maleimidobenzoic acid chloride

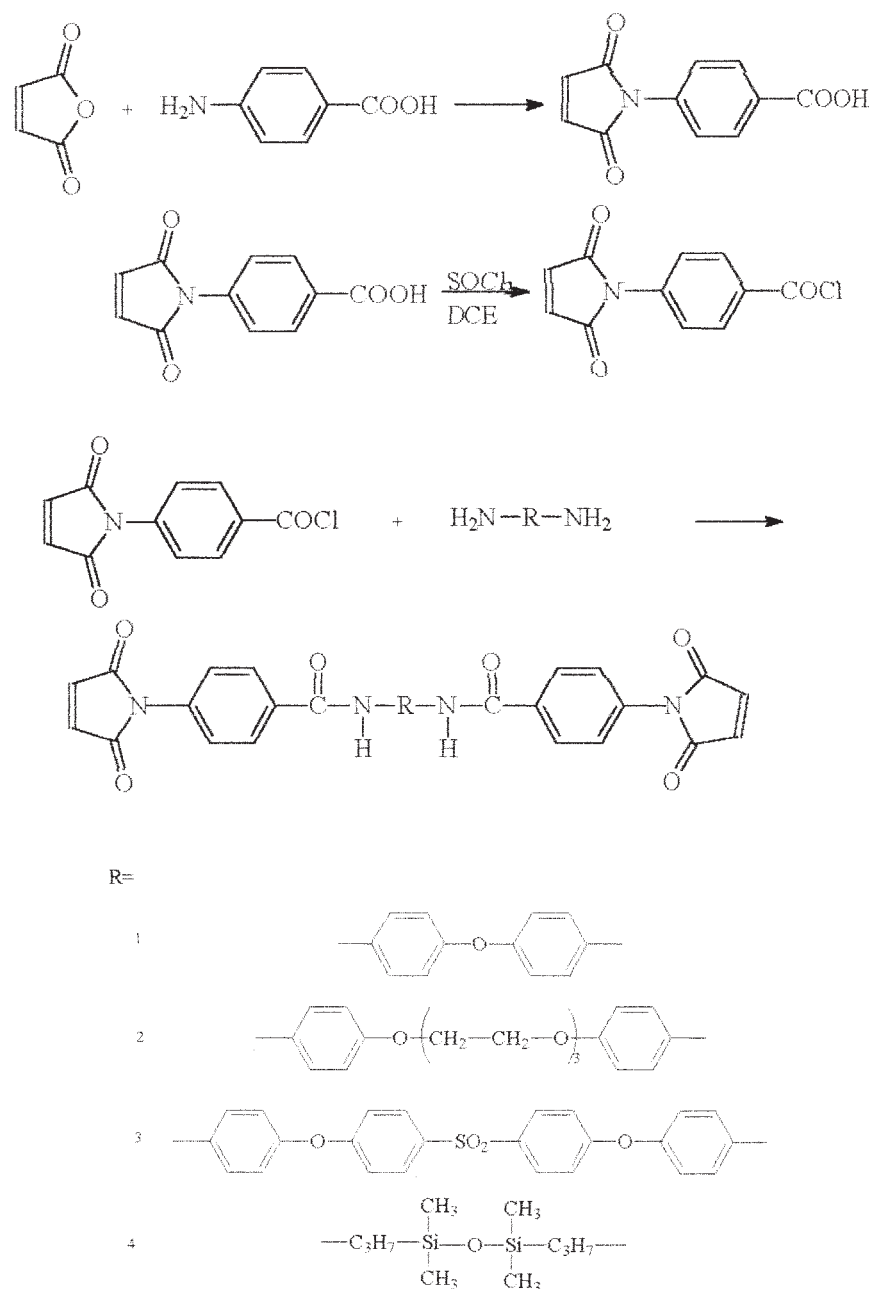
The product was prepared as described,¹⁵ as illustrated in Scheme 1.

In a 250-mL, round-bottom flask, maleimidobenzoic acid (0.1 mol) was suspended in 100 mL of dichloroethane (DCE) under nitrogen with stirring. To this, redistilled thionyl chloride (30 mL) was carefully added. Then, the reaction mixture was heated slowly to refluxing and maintained for 3–4 h. The hot solution was filtered, and the excess of thionyl chloride and DCE was distilled off under reduced pressure. The product was recrystallized from toluene (mp = 169–171°C, reference mp¹³ = 170°C).

Preparation of BMIs

Bismaleimide **1** (BMI-1), bismaleimide **2** (BMI-2), bismaleimide **3** (BMI-3), and bismaleimide **4** (BMI-4) were synthesized according to the literature.¹⁷

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Scheme 1

A diamine solution (0.05 mol) in 125 mL of CHCl_3 was cooled in an ice bath. Triethylamine (TEA) (0.1 mol) as an acid acceptor and a solution of 4-maleimidobenzoic acid chloride (0.1 mol) in 100 mL of CHCl_3 were added. After 1 h of stirring, the mixture was filtered and precipitated in hexane. The product was filtered and treated with a sodium carbonate solution (10%) and then thoroughly washed with water. The filtered and precipitated product was recrystallized.

BMI-1

The product was recrystallized from dimethylformamide (DMF)/ H_2O .

Yield: 71%. mp: 324–327°C. Infrared (IR; KBr, cm^{-1}): 3400 (—NH), 3100 (=C—H), 1775 and 1710 (C=O imide), 1665 and 1510 (C=O amide), 1250 (—O—). ANAL. Calcd for $\text{C}_{34}\text{H}_{22}\text{N}_4\text{O}_7$: C, 68.22%; H, 3.70%; N, 9.36%. Found: C, 68.46%; H, 3.42%; N, 8.94%.

BMI-2

The monomer was recrystallized from DMF.

Yield: 67%. mp: 232–236°C. IR (KBr, cm^{-1}): 3330 (—NH), 3100 (=C—H), 2960–2880 (—CH₂), 1775 and 1710 (C=O imide), 1640 and 1510 (C=O amide), 1235

(—O—). ANAL. Calcd for $C_{40}H_{34}N_4O_{10}$: C, 65.74%; H, 4.68%; N, 7.66%. Found: C, 65.29%; H, 4.79%; N, 7.91%.

BMI-3

The product was recrystallized from DMF/ H_2O .

Yield: 69%. mp: 237–240°C. IR (KBr, cm^{-1}): 3340 (—NH), 3100 (=C—H), 1775 and 1715 (C=O imide), 1610 and 1505 (C=O amide), 1320 and 1195 (—SO₂). ANAL. Calcd for $C_{46}H_{30}N_4O_{10}S$: C, 66.50%; H, 3.63%; N, 6.74%; S, 3.85%. Found: C, 66.23%; H, 3.95%; N, 6.53%; S, 4.08%.

BMI-4

The monomer was recrystallized from ethanol.

Yield: 72%. mp: 102–107°C. IR (KBr, cm^{-1}): 3370 (—NH), 3110 (=C—H), 2960–2880 (—CH₂—), 1780 and 1720 (C=O imide), 1640 and 1505 (C=O amide), 1390 and 1255 (Si—CH₃), 1090 (Si—O—Si). ANAL. Calcd for $C_{32}H_{38}N_4O_7Si_2$: C, 59.23%; H, 6.21%; N, 8.63%; Si, 8.65%. Found: C, 58.87%; H, 6.43%; N, 8.86%; Si, 8.32%.

Measurements

The IR spectra were recorded on a Carl Zeiss Jena Specord M90 spectrophotometer (Jena, Germany) with the KBr pellet technique. Proton nuclear magnetic resonance (¹H-NMR) spectra were recorded on a Bruker Avance DRX 400-MHz NMR spectrometer (Karlsruhe, Germany) with dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) as a solvent and tetramethylsilane as an internal standard. Differential scanning calorimetry (DSC) measurements were performed with a Mettler TA DSC 12E instrument (Greifensee, Switzerland) at a heating rate of 10°C/min in nitrogen. Thermogravimetric analysis (TGA) was carried out in air with an F. Paulic derivatograph (Budapest, Hungary) at a heating rate of 12°C/min. Melting points were determined with a Gallenkamp (UK) hot-block melting-point apparatus.

RESULTS AND DISCUSSION

The IR spectra of the obtained BMIs showed an absorption band at 3400–3370 cm^{-1} due to the —NH group. The monomers (BMI-1 to BMI-4) showed a characteristic carbonyl doublet in the ranges of 1780–1775 and 1720–1710 cm^{-1} due to C=O imide units and a doublet in the ranges of 1665–1640 and 1510–1505 cm^{-1} due to C=O amide groups. In addition, the characteristic absorption of the —SO₂ group appeared at 1320 and 1195 cm^{-1} (BMI-3). Also, there were absorption bands at 1390 and 1255 cm^{-1} (H₃C—Si) and

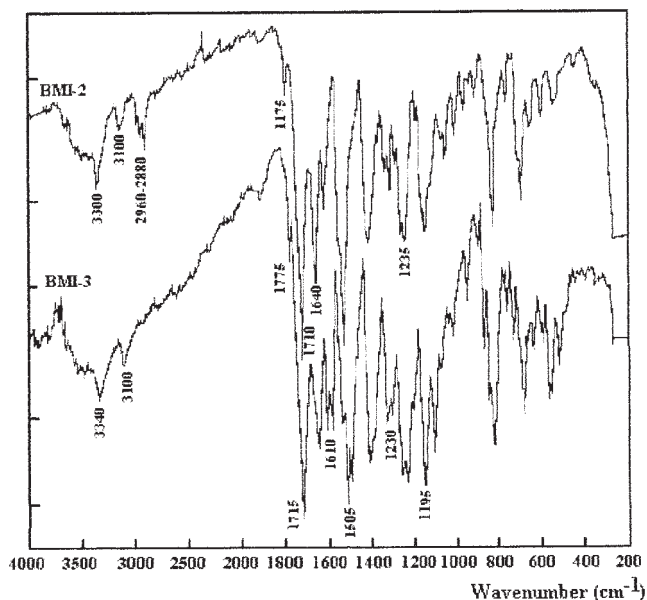


Figure 1 IR spectra of monomers BMI-2 and BMI-3.

1090 cm^{-1} (Si—O—Si; BMI-4). Figure 1 presents the IR spectra of BMI-2 and BMI-3.

The ¹H-NMR spectra of monomer BMI-1 confirmed its chemical structure (Fig. 2). The aromatic protons of BMI-1 appeared as four separated doublets in the ranges of 8.086–8.065 (Ar—H, ortho to —COO), 7.823–7.801 (Ar—H, ortho to maleimide), 7.541–7.521 (Ar—H, ortho to —NH), and 7.062–7.040 (Ar—H, ortho to —O—). The monomer BMI-1 showed a singlet at 10.370 (due to —NH) and another singlet at 7.190 due to olefinic protons.

The elemental analysis data for carbon, hydrogen, nitrogen, sulfur, and silicon were in good agreement with the calculated values.

The solubility of the monomers was evaluated in various solvents (Table I). All BMIs exhibited solubility in *N*-methylpyrrolidone (NMP) and DMF, except for BMI-2 (soluble in DMF upon heating).

Still, a small difference in the solubility of the monomers in these two solvents was observed as follows. The monomer BMI-3 was dissolved quickly in DMF and NMP, whereas BMI-1 and BMI-4 had better solubility in DMF than in NMP. BMI-2 showed good solubility only in warm DMF. As for the monomers' solubility in other solvents, only BMI-4 showed better behavior. However, the solubility of BMIs with amide units was lower than that of BMI monomers with ester groups.¹⁸

The thermal behavior of the BMI monomers was evaluated with a capillary melting apparatus, DSC, and TGA. Compounds BMI-2 and BMI-4 displayed melting behavior at slow heating rates. When BMI-1 and BMI-3 were heated in a capillary melting-point apparatus, they did not melt below 340°C. When the

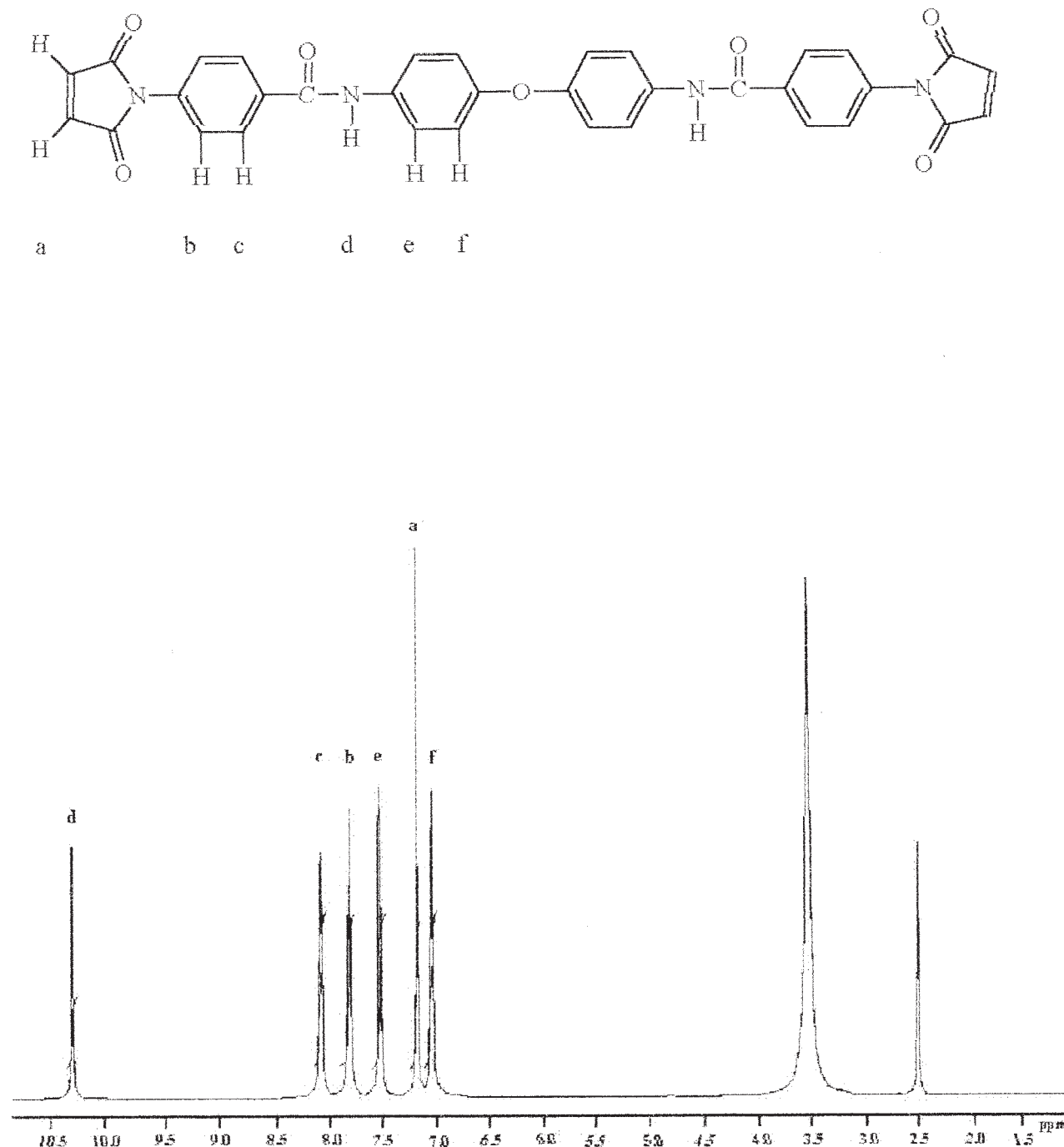


Figure 2 $^1\text{H-NMR}$ spectrum of BMI-1.

capillary apparatus was preheated to 310°C before the insertion of the sample, monomer BMI-1 first melted and then underwent polymerization. This was due to the fact that crosslinking occurred almost instantly after melting; this behavior was observed for BMI-1 when the heating rate was high enough to preclude extensive crosslinking of the sample during the heating process.

The same conclusion resulted from the DSC curve of BMI-1 (Fig. 3). This exhibited a sharp endotherm at

TABLE I
Solubility of the BMI Monomers

Monomer	Solvent					
	DMF	NMP	DMSO	CHCl_3	Toluene	Acetone
BMI-1	++	++	±	-	-	-
BMI-2	+	++	-	-	-	-
BMI-3	++	++	-	-	-	-
BMI-4	++	++	-	+	±	+

Solubility: ++ = soluble at room temperature; + = soluble on heating; ± = partially soluble on heating; - = insoluble.

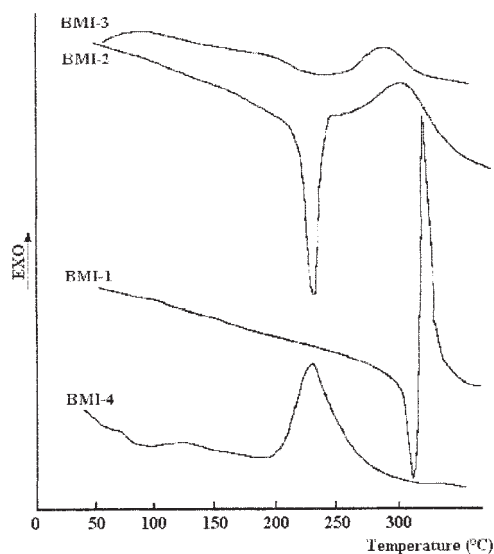


Figure 3 DSC scans of BMI-1 to BMI-4.

312°C, followed immediately by an exotherm at 317°C. The onset temperature for the curing reaction in the case of BMI-1 was overshadowed by the melting endotherm. Some of the DSC results for BMI-1 to BMI-4 are listed in Table II. The endotherm peak of BMI-2 was at 229°C. BMI-3 and BMI-4 exhibited a poor and broad endotherm in the regions of 195–260 and 85–115°C, respectively. Compounds BMI-2 to BMI-4 showed exothermic peaks characteristic of the curing process in the region of 229–300°C.

The TGA curves of the BMIs are shown in Figure 4. Data for the onset of the initial decomposition temperature (IDT) and percentage char yield at 600°C are listed in Table II. The IDTs of the monomers were in the range of 285–344°C. IDT was higher for BMI-1 with ether units. In comparison, BMI-4 with siloxane segments in the main chain showed the lowest IDT (because of the influence of aliphatic segments).

TABLE II
Physical and Thermal Properties of the Monomers

Monomer	General appearance	mp (°C)	T_{end} (°) ^a	T_{exo} (°) ^b	T_p (°) ^c	IDT (°)	Y_c (%) ^d
BMI-1	Yellow	324–327	312	317	—	344	35
BMI-2	Cream	232–236	229	300	249	325	24
BMI-3	Cream	237–240	235	286	—	332	25
BMI-4	Light yellow	109–113	80–120	229	203	285	42

^a Endotherm peak temperature by DSC.

^b Exotherm peak temperature by DSC.

^c Start of polymerization as measured by DSC.

^d Char yield at 600°C

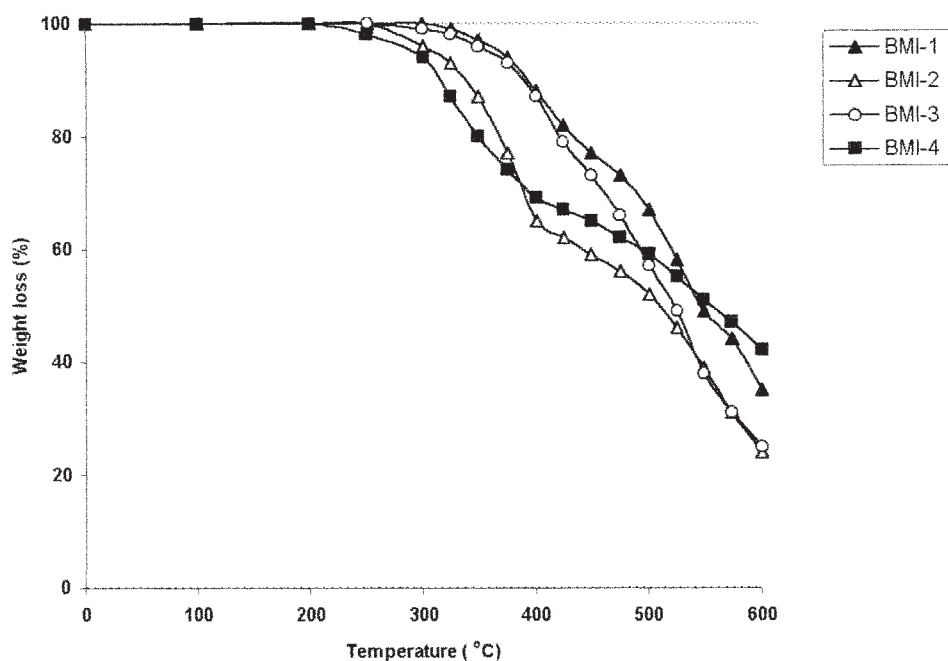


Figure 4 TGA thermograms of BMI-1 to BMI-4.

The monomer BMI-4 exhibited the highest char yield at 600°C, whereas compound BMI-2 showed the lowest value.

CONCLUSIONS

A series of BMIs with amide groups and different structures (ether, SO₂, oxyethylene, and silicone segments) were synthesized and characterized with IR and ¹H-NMR spectra and elemental analysis.

The thermal characterization of these compounds was accomplished with DSC and TGA. The structures of the monomers strongly influenced the properties of the final compounds.

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