Synthesis and Properties of Brominate Bismaleimide Monomers

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Received 25 January 2006; accepted 24 March 2006
DOI 10.1002/app.24526

ABSTRACT: Brominated bismaleimides were prepared by reacting 3(4)-maleimidobenzoylchloride with various bisphenols, using chloroform as solvent and triethylamine as acid acceptor. These monomers were characterized by elemental analysis, infrared (IR), and proton nuclear resonance (^{1}H-NMR) spectroscopy. Thermal properties of monomers were accomplished by differential scanning calorimetry (DSC) and dynamic thermogravimetric analysis (ATG). The properties of these compounds were compared with those of monomers derived from bisphenol A and bisphenol A chlorinated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3881–3885, 2006

Key words: brominated bismaleimide monomers; synthesis; thermal properties

INTRODUCTION

Polyimides are an important and widely studied class of materials because of their excellent thermal and adhesive properties. Condensation type polyimides, which have remarkable high temperature resistance and good mechanical and electrical properties, suffer from processing problems because of their infusibility, insolubility, and evolution of volatiles during the ring formation. Bismaleimides (addition-type polyimide) containing unsaturated end groups can polymerize without volatiles as by-products. The polybismaleimides exhibit chemical stability, radiative resistance. high decomposition temperatures, and good mechanical and electrical performance over a wide range of temperature and are superior to the most epoxy resins. Bismaleimide compounds are suitable for use in a wide range of composite materials for applications in aerospace, electronic, and nuclear industries.[1–7]

However, most of the cured BMIs have limitations because of brittleness due to high crosslinking density and their poor processability (poor solubility in ordinary solvents, a high melting and curing temperature).[8–10]

To obtain polymers with improved mechanical properties, thermal resistance, and processability, bismaleimide monomers that have various structures have been synthesized.

This article reports on preparation of the bromominated bismaleimides and evolution of their solubility, reactivity, and thermal properties. A comparative study on monomers derived from bisphenol A and bisphenol A chlorinate was performed to assess the level of performance of the new synthesized monomers.

EXPERIMENTAL

Synthesis of monomers

3(4)-Maleimido benzoic acid (3(4)-MBA)

The compounds were obtained as described in literature.[11–12] Mp 3-MBA, 236–240°C toluene; mp 4-MBA, 225–230°C toluene; Ref. 11 239–241°C 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 the literature.[13] Mp 3-MBAC, 125–128°C dichlorethane; mp 4-MBAC, 167–169°C; Ref. 12 mp 4-MBAC 170°C.

Tetrabromobisphenols

Brominated bisphenols were prepared as follows.[14] In a 250 mL flask, 0.04 mol of bisphenol S (bisphenol A) was dissolved in 200 mL of glacial acetic acid. To this solution, 0.14 mol of bromine was added slowly under stirring. The reaction was carried out at room temperature, over a period of about 15 min, and then the temperature was raised up to 60°C when the reaction medium appeared turbid. 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 a few drops of sodium bicarbonate solution for removing bromine.

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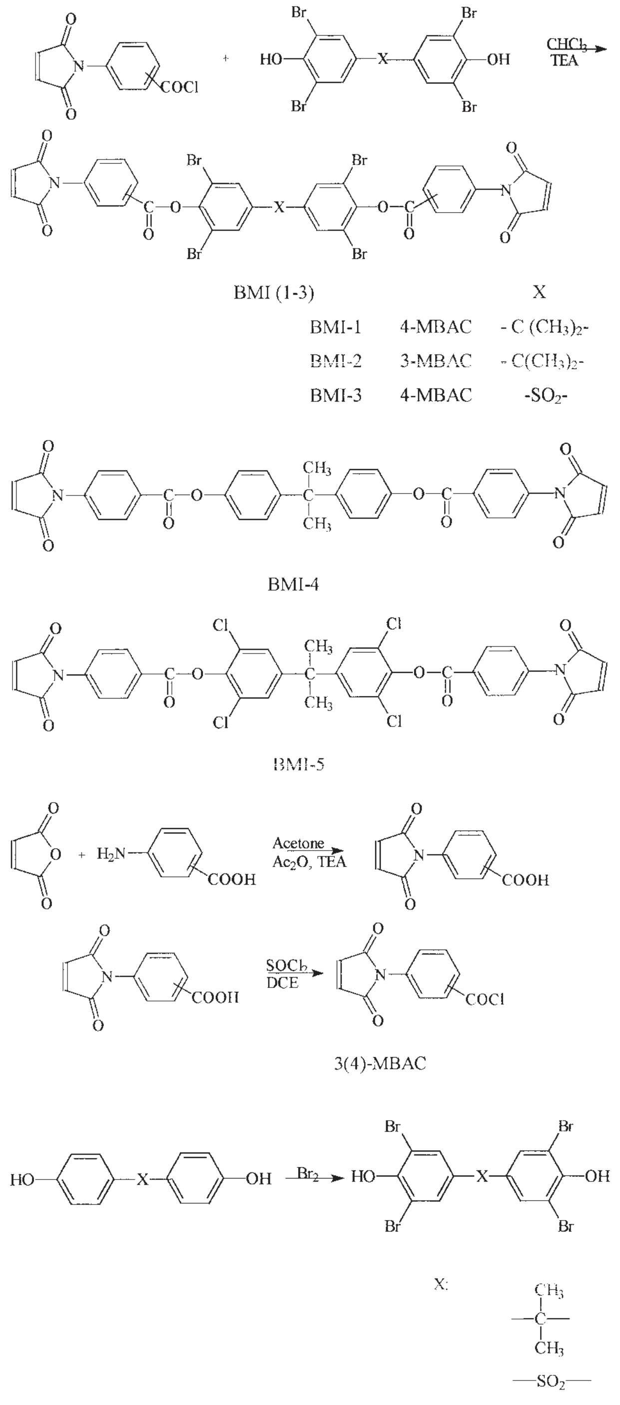
Journal of Applied Polymer Science, Vol. 101, 3881–3885 (2006)



Scheme 1

The product was recrystallized from acetic acid solution (15%). The yield was 71 and 69%, respectively.

Preparation of bismaleimides BMI(1–3)

Monomers BMI(1–3) were synthesized, as presented in Scheme 1, following the literature.[12] Bisphenol solution (0.01 mol) in 40 mL $CHCl_3$ was cooled in an ice bath. TEA (0.2 mol), as acid acceptor, and a solution of 3(4)-MBAC (0.2 mol) in 125 mL $CHCl_3$ were added. After stirring for 1.5 h, the mixture was filtered and precipitated in hexane. The product was filtered and treated with sodium carbonate solution (10%) and then thoroughly washed with water. The final product was then recrystallized. Bismaleimide BMI(4–5) was prepared from their corresponding bisphenols by the same aforementioned method.

Bismaleimide BMI-1

The monomer was recrystallized from DCE/Ethanol. Yield 67%, mp 281–283°C. IR (KBr) cm^{-1}: 1780 and 1720 (C═O imide), 1745 (C═O ester), 740 (C—Br).

Anal. calcd. for $C_{37}H_{22}Br_4N_2O_8$ (%): C, 47.16; H, 2.35; Br, 33.92; N, 2.97. Found: C, 47.71; H, 2.56; Br, 34.16; N, 2.83.

Bismaleimide BMI-2

The product was recrystallized from DCE. Yield 70%, mp 265–268°C. IR (BKBr) cm^{-1}: 1750 (C═O ester), 1720 (C═O imide), 1745 (C—Br).

Anal. calcd. for $C_{37}H_{22}Br_4N_2O_8$ (%): C, 47.16; H, 2.35; Br, 33.92; N, 2.97. Found: C, 47.39; H, 2.51; Br, 33.70; N, 2.74.

Bismaleimide BMI-3

The monomer was recrystallized from DCE/Ethanol. Yield 69%, mp 135–138°C. IR (KBr) cm^{-1}: 1750 (C═O ester), 1725 (C═O imide), 1320 and 1160 (—SO_2), 740 (C—Br).

Anal. calcd. for $C_{34}H_{16}Br_4N_2O_{10}S$ (%): C, 42.35; H, 1.67; Br, 33.14; N, 2.90; S, 3.32. Found: C, 41.93; H, 2.01; Br, 33.79; N, 3.28; S, 3.09.

Bismaleimide BMI-4

The product was recrystallized from $CHCl_3$. Yield 73%, mp 214–216°C. IR (KBr) cm^{-1}: 1790 and 1720 (C═O imide), 1740 (C═O ester).

Anal. calcd. for $C_{37}H_{26}N_2O_8$ (%): C, 70.92; H, 4.15; N, 4.47. Found: C, 71.37; H, 3.93; N, 4.62.

Bismaleimide BMI-5

The monomer was recrystallized from DCE/Ethanol. Yield 73%, mp 276–279°C. IR (KBr) cm^{-1} 1780 and 1730 (C═O imide), 1755 (C═O ester).

Anal. calcd. for $C_{37}H_{22}Cl_4N_2O_8$ (%): C, 58.15; H, 2.90; Cl, 18.55; N, 3.66. Found: C, 57.79; H, 3.03; Cl, 18.78; N, 3.67.

MEASUREMENTS

The IR spectra were recorded on a Specord M90 Carl Zeiss Jena Spectrophotometer, using the KBr pellet

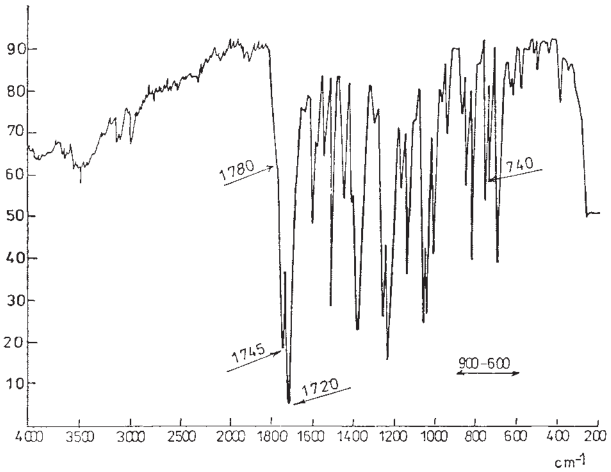


Figure 1 IR spectrum of monomer BMI-1.

TABLE I
Solubility of Bismaleimides BMI(1–5)

Monomer	DMF	NMP	DCE	$CHCl_3$	Toluene	Acetone
BMI-1	++	++	++	++	−	−
BMI-2	++	++	++	++	−	−
BMI-3	++	++	++	++	−	−
BMI-4	++	++	++	++	−	±
BMI-5	++	++	++	++	−	±

Solubility: ++, soluble at room temperature; +, soluble on heating; ±, partially soluble on heating; −, insoluble.

technique. ^{1}H-NMR spectra were recorded on a Bruker NMR spectrometer Avance DRX 400 MHz, using DMSO-d_6 as solvent and tetramethylenesilane as an internal standard. Differential scanning calorimetry (DSC) measurements were done by using a Meter TA instrument DSC 12F with a heating rate of 10°C/min in air. Melting points were determined with a Gallenkamp hot-block melting point apparatus and by DSC.

RESULTS AND DISCUSSION

The monomers BMI(1–5) showed carbonyl doublet in the range 1790–1780 and 1730–1720 cm^{-1} attributed to C=O imide units and a band at 1755–1740 cm^{-1} due to ester groups. In addition, the characteristic absorption of —SO_2 groups (BMI-3) appeared at 1320 and 1160 cm^{-1}. Also an absorption band at 745–740 cm^{-1} appeared due to C—Br bond. Figure 1 presents the infrared spectrum of BMI-1.

The ^{1}H-NMR spectrum of bismaleimide BMI-1 confirmed its chemical structure (Fig. 2). The aromatic protons of monomer BMI-1 appears as a doublet in the range 8.330–8.309 ppm (Ar-H, ortho to —COO) and a triplet in the range 7.716–7.682 ppm (Ar-H, ortho to —C—N—C and ortho to $C(CH_3)_2$). The compound BMI-1 showed a singlet at 7.268 ppm attributed to olefinic protons and a singlet at 1.755 due to —$C(CH_3)_2$ group.

The elemental analysis data for carbon, hydrogen,, nitrogen, chlorine, bromine, and sulfur are in good agreement with the calculated values.

The solubility of the monomers was evaluated in various solvents (Table I). All monomers exhibited solubility in *N*-methylpyrolidone (NMP), dimethylfor-

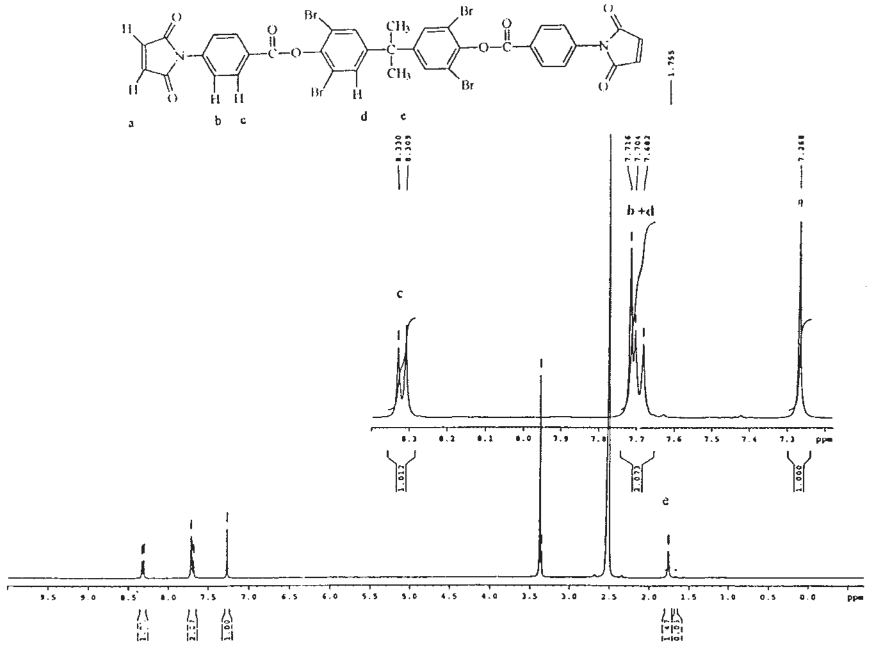


Figure 2 ^{1}H-NMR spectrum of bismaleimide BMI-1.

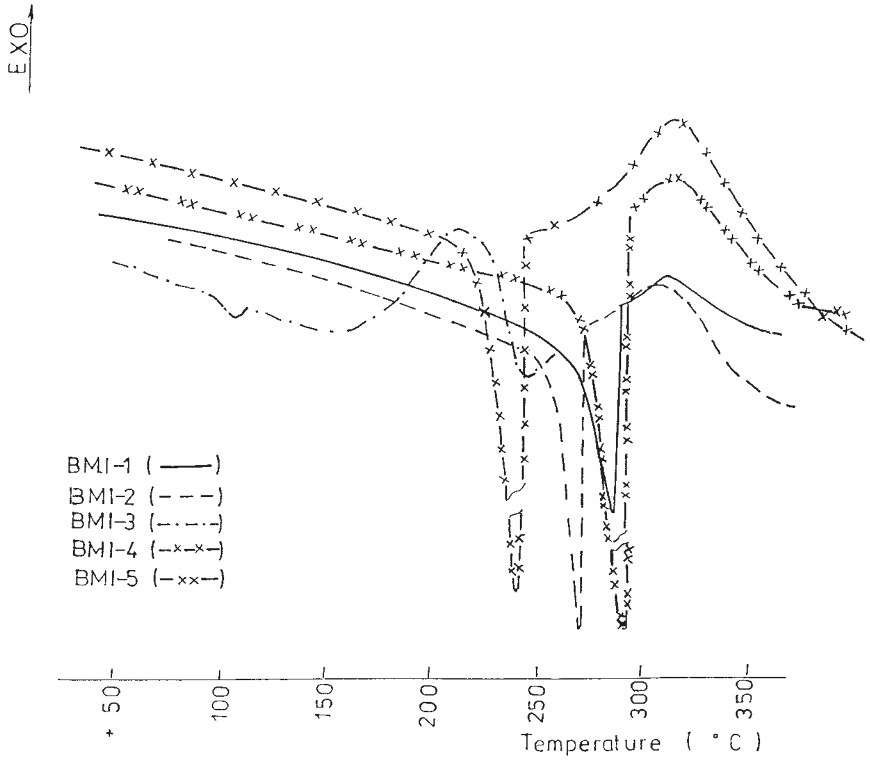


Figure 3 DSC scans of BMI(1–5).

mamide (DMF), dichlorethane (DCE) and chloroform ($CHCl_3$). Still, a small difference of solubility of the monomers in these four solvents was observed as follows. The monomer BMI-3 get dissolved quickly in all tested solvents while BMI-1 and BMI-2 have a lower solubility. All monomers BMI(1–5) are insoluble in toluene. Bismaleimide BMI-3 is insoluble in acetone while BMI-2 and BMI-2 are insoluble. The Table I compound BMI-5 is soluble only in warm acetone, but BMI-4 exhibited a partial solubility on heating. It was observed that the solubility of bismaleimide depends on monomers structures. It is interesting to notice that, considering those 3 monomers containing bromine atoms, the monomer with the highest solubility is BMI-3, even monomer BMI-2 is bearing a substituent in meta position. It is observed that the solubility of those 3 monomers with bromine atoms is influenced by the grouping situated between benzene rings (SO_2 and —$C(CH_3)_2$).

The thermal behavior of monomers was evaluated by using differential scanning calorimetry (DSC) and thermogravimetric analysis. The bismaleimides BMI-(1–5) were analyzed by DSC (Fig. 3). DSC curves for all monomers were characterized by a sharp melting endotherm (T_{end}) in the range 244–290°C (except for BMI-3, which have an endotherm less sharper at 104°C), because of the melting of these compounds (Table II). It is noticeable that BMI-3, bearing SO_2 groups and substituents in para position, has a lower endotherm (104°C) while monomer BMI-4, which contains chlorine atoms, has the endotherm at the highest temperatures (290°C).

The reactivities of these compounds(T_p) are in the temperature range of 153–278°C (except for BMI-1 and BMI-4, for which the onset temperature for curing

TABLE II
Physical and Thermal Properties of the Prepared Bismaleimides

Monomer	General appearance	mp[a] (°C)	T_{end} (°C)	T_{exo} (°C)	T_p (°C)	ΔH (kJ/mol)	IDT (°C)	Y_c (%)
BMI-1	White	281–283	285	307	–	–	325	25
BMI-2	Cream	265–268	268	306	278	45	313	18
BMI-3	Light-yellow	98–101	104	207	153	95	260	21
BMI-4	Yellow	276–279	290	318	–	–	382	28
BMI-5	Pale-yellow	225–228	244	319	257	70	375	38

[a] Melting point determined in a capillary tube melting point apparatus.

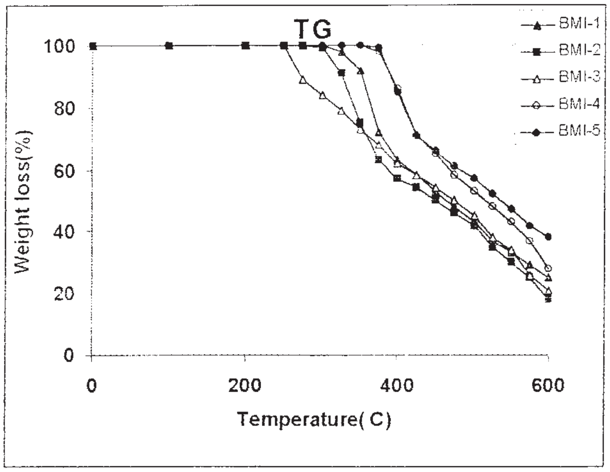


Figure 4 TGA thermograms of bismaleimides BMI(1–5).

reaction was over-shadowed by the melting endotherm). Table II The crosslinking reaction was responsible for the exothermic peak (T_{exo}) in the temperature range of 207–319°C, with a heat of polymerization (ΔH) of 45–95 kJ/mol. It is notice that for BMI(1–2) and BMI(4–5) the exothermic temperatures have nearly the same values, while for BMI-3 the temperature difference is significant.

The thermal stability of monomers BMI(1–5) was evaluated by dynamic TGA. Figure 4 presents TGA traces of these compounds in air. Certain TGA data are listed in Table II. The initial decomposition temperatures(IDT) of bismaleimides are in the range 260–382°C and the rapid weight loss occurs in the region 275–516°C in air. It was observed that IDT is higher for BMI-4 and BMI-5 (compounds with and without substituents). Bismaleimides with bromine atoms BMI(1–3) show smaller values of IDT. The curves corresponding to those 3 brominated monomers are showing different values of IDT (the lowest value for BMI-3) and various patterns between 250 and 400°C. After this temperature, all curves seem to be alike, up to 600°C. As for compounds BMI-1 and BMI-2, which have close IDT values, the TGA curves are overlapped up to ~435°C and afterwards they differentiate.

The compounds had an aerobic char yield (Y_c) of 18–38% at 600°C. It was observed that the substitution of bromine in monomers leads to the decrease of the amount of residue in air.

CONCLUSIONS

A series of BMIs with bromine atoms was prepared through the reaction of 3(4)-maleimidobenzoylchloride with two brominated bisphenols. Note that the solubility of monomer BMI-3 is higher, while the solubility of compounds BMI(1–2) is poorer than that of BMI.(4–5). Thermal properties of monomers BMI(1–5) were evaluated. A comparison of the initial decomposition temperature of BMI(1–3) with that of BMI(4–5) reveals that the former is lower by 50–115°C. The TGA showed that BMI(4–5) had higher thermal stability than that of BMI(1–3). The physical and thermal properties indicate a high degree of dependence of type of substituents and their positions. The incorporation of bromine in the monomer backbone caused a decrease of thermal stability.

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