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## A study of the thermal stability of metal bismaleimides and the thermal cyclodehydration of their precursors

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### Abstract

A series of novel metal (Ca, Sr, Ba, Zn, Co, Ni, Pb) bismaleimide monomers [BMI(M)] was prepared by reaction of maleic anhydride and metal diamines. The thermal cyclodehydration of the precursors of the bismaleimides was studied by TG–DTA, IR and  $^1\text{H}$  NMR spectrometry. It was found that the thermal stability of BMI(M) is dependent on the nature of the metal, and has the following order in air as indicated by  $T_d$  (the temperature of initial decomposition from the TG curves): BMI(Sr) > BMI(Ba) > BMI(Co) > BMI(Pb) > BMI(Zn) > BMI(Ca) > BMI(Ni).

*Keywords:* Bismaleimide; Cyclodehydration; DTA; Monomer; Stability; TG

### 1. Introduction

Polyimides have a variety of uses in many areas. The polymers derived from bismaleimide, which are known as addition-type polyimides, are industrially important because of their high heat resistance and low cost. There are many reports on thermal analysis of the common bismaleimides [1–8] but little work has been reported on metal bismaleimides. Matsuda and co-workers used divalent metal salts of *p*-aminobenzoic acid to prepare polyureas containing ionic linkages in the main chain [9–11]. Recently, we reported the preparation and characterization of polyureas derived from divalent metal salts of sulfanilic acid [12] in order to show the influence of the metal on the thermal properties of the polyimide. In the present

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work, a series of metal bismaleimides has been synthesized and characterized in which a variety of metals are incorporated in the main polymer chain. Special attention is paid to the thermal cyclodehydration of the precursors, and the thermal stability of the bismaleimides has also been studied.

## 2. Experimental

### 2.1. Materials

Maleic anhydride was of chemically pure grade and the solvents used were of analytically pure grade; all were obtained from the Shanghai chemical factory. The diamines were prepared according to the method of Qiu et al. [12].

#### 2.1.1. Preparation of samples

Into a flask equipped with a mechanical stirrer, a thermometer and an addition funnel were placed 6.0 mmol of the diamine and 50 ml of dimethylformamide (DMF), and the diamine was allowed to dissolve; 12.04 mmol of maleic anhydride dissolved in 80 ml of DMF was then added, dropwise, with constant stirring. The reaction mixture was stirred at 25°C for 4 h, during which it changed to a yellow transparent solution. Next, 100 ml of acetone was added and the solution was allowed to stand for 8 h. The precipitate was filtered off, washed several times with acetone, and dried in vacuo at 80°C for 5 h and subsequently at 120°C for an additional 2 h. The bismaleamide acid precursor [BMA(M)] was obtained thus. The BMA(M) powder was heated in vacuo at the thermal cyclodehydration temperature determined by TG–DTA to prepare the bismaleimide [BMI(M)].

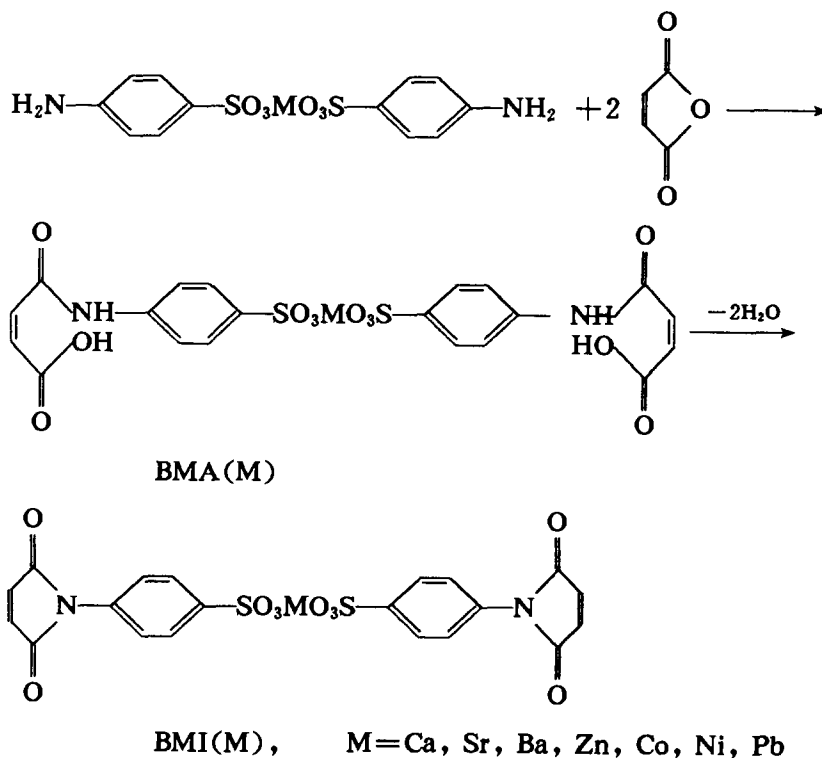
### 2.2. Instrumentation

The IR spectra of samples were recorded over the range 400–4000  $\text{cm}^{-1}$  with a Shanghai-4100 spectrometer using the KBr pellet technique. The  $^1\text{H}$  NMR spectra were obtained with a Varian FT-80A spectrometer, DMSO- $d_6$  being used as solvent. The TG–DTA experiments were carried out with a Beijing PCT-1 thermal analyser at a heating rate of 10°C  $\text{min}^{-1}$  in static air over the range 20–600°C. The DTA reference was  $\text{Al}_2\text{O}_3$ . For elemental analyses, C, H and N contents were determined using a 204C elemental analysis instrument. The metals were determined by atomic absorption spectrophotometry (WFX-1C) following heating of samples at 600°C.

## 3. Results and discussion

### 3.1. Preparation of bismaleimides

The preparation of the novel metal bismaleimides may be described by the following reactions [12,13].



The yields and the results of elemental analysis are listed in Table 1.

### 3.2. IR and $^1\text{H}$ NMR spectral studies

The IR and  $^1\text{H}$  NMR spectra of BMA(Ba) are shown in Figs. 1 and 2. In Fig. 1, curve a, the absorption bands at  $3000\text{--}2600\text{ cm}^{-1}$ ,  $1710\text{ cm}^{-1}$  ( $-\text{COOH}$ ),  $3450\text{ cm}^{-1}$ ,  $1630\text{ cm}^{-1}$ ,  $1557\text{ cm}^{-1}$  and  $1310\text{ cm}^{-1}$  characterize the amic acid structure. The bands at  $1175$ ,  $1025$  and  $700\text{ cm}^{-1}$  can be assigned to  $-\text{SO}_2-\text{O}-$  and the bands at  $1600$  and  $1500\text{ cm}^{-1}$  are the absorption bands of the phenyl ring. In Fig. 2, curve a, the chemical shifts can be assigned as follows:  $10.56\text{ ppm}$ ,  $-\text{COOH}$ ;  $6.69\text{--}6.10\text{ ppm}$ , double doublets  $-\text{CH}=\text{CH}-$ ;  $7.89\text{ ppm}$ ,  $-\text{CONH}-$ ;  $7.61\text{ ppm}$ , phenyl protons. It is concluded that the desired Ba bismaleamide has been obtained.

The bismaleimide BMI(Ba) was obtained from BMA(Ba) by the reaction of dehydrocyclization, for which the imidization conditions were studied by TG-DTA, IR and  $^1\text{H}$  NMR. It was found that the imidization reaction can be carried out more efficiently and conveniently by thermal methods as compared with chemical methods. BMA(Ba) was heated at  $140^\circ\text{C}$  for 1 h, then at  $200^\circ\text{C}$  for 1 h, and subsequently at  $260^\circ\text{C}$  for 4 h in vacuo. The IR and  $^1\text{H}$  NMR spectra were

Table 1  
Elemental analysis data for BMI(M)

BMI(M)	Yield/%		M	C	H	N
BMI(Ca)	90.2	Calc.	7.35	44.12	2.21	5.15
		Found	7.32	44.20	2.53	5.41
BMI(Sr)	53.8	Calc.	14.81	40.57	2.03	4.73
		Found	14.78	40.50	2.40	4.61
BMI(Ba)	52.7	Calc.	21.41	37.42	1.87	4.34
		Found	21.33	37.50	2.01	4.41
BMI(Zn)	66.2	Calc.	11.48	42.15	2.11	4.92
		Found	11.44	42.09	2.43	4.71
BMI(Co)	90.1	Calc.	10.47	42.63	2.13	4.97
		Found	10.36	42.81	2.30	5.08
BMI(Ni)	96.7	Calc.	10.43	42.65	2.13	4.98
		Found	10.45	42.81	2.49	5.12
BMI(Pb)	75.8	Calc.	29.13	33.74	1.69	3.94
		Found	29.08	33.65	1.81	3.75

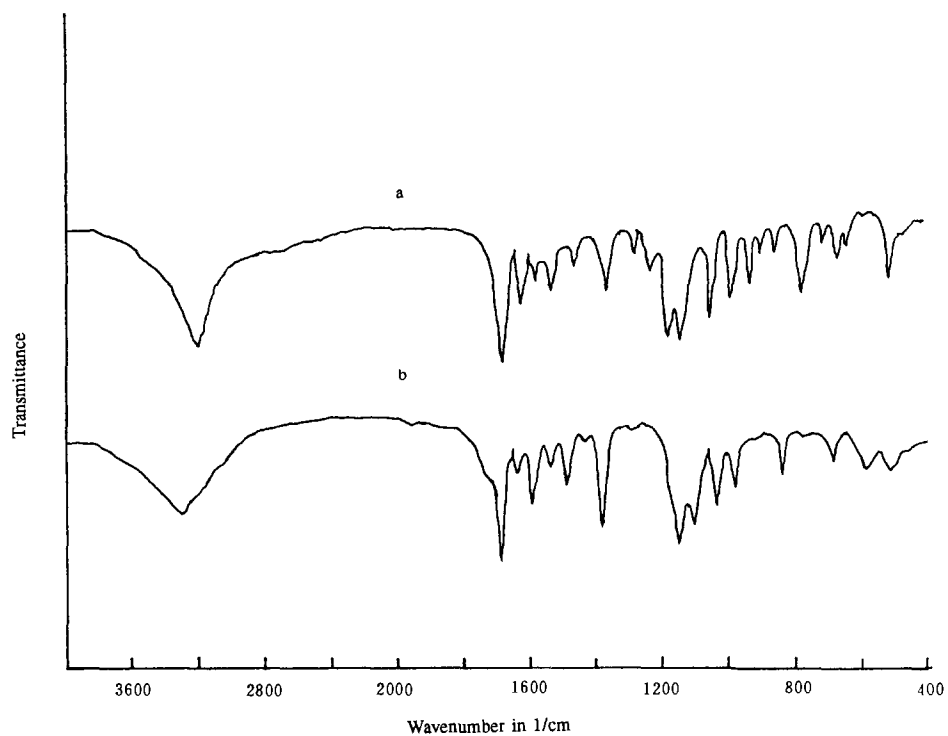


Fig. 1. IR spectra of Ba samples: (curve a) BMA(Ba); (curve b) BMI(Ba).

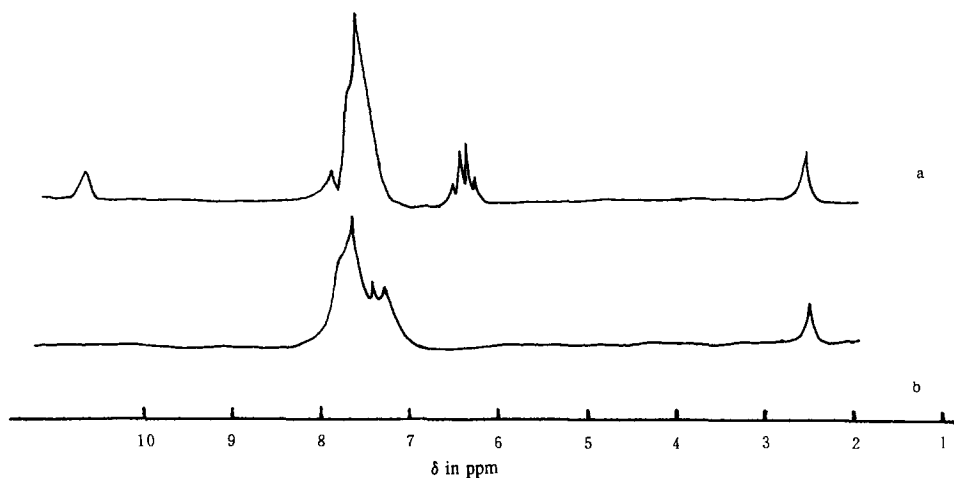


Fig. 2.  $^1\text{H}$  NMR spectra of the Ba samples: (curve a) BMA(Ba), (curve b) BMI(Ba).

used to record the degree of imidization every 30 min until there was no further change in the spectra. The dehydrocyclization reaction leading to the imide structure was found to be complete. After complete imidization, an additional 0.5 h of heating was supplied to assure the completion of the reaction. The IR and  $^1\text{H}$  NMR spectra of BMI(Ba) are given in Fig. 1, curve b and Fig. 2, curve b. In Fig. 1, curve b, it is evident that the characteristic bands of the amic acid have disappeared and new strong absorption bands appear at 1775, 1720 and  $720\text{ cm}^{-1}$ , indicating that

Table 2  
IR data for BMA(M)  $\text{cm}^{-1}$

BMA(M)	-COOH	-CONH	-SO <sub>2</sub> -O-	Phenyl ring
BMA(Ca)	1700, 3040–2600	1640, 1570 1320, 3400	1175, 1030 700	1600, 1500
BMA(Sr)	1700, 3030–2600	1630, 1575 1310, 3020	1175, 1030 700	1600, 1550
BMA(Ba)	1710, 3000–2600	1630, 1575 1310, 3460	1175, 1025 700	1600, 1500
BMA(Zn)	1710, 3000–2700	1630, 1570 1315, 3400	1175, 1030 700	1600, 1500
BMA(Co)	1690, 3050–2500	1600, 1500 1315, 3400	1180, 1040 700	1600, 1500
BMA(Ni)	1720, 3040–2500	1625, 1570 1310, 3400	1175, 1025 700	1600, 1500
BMA(Pb)	1700, 3050–2500	1630, 1570 1315, 3400	1175, 1030 700	1600, 1500

Table 3  
IR data for BMI(M) in  $\text{cm}^{-1}$

BMI(M)	Imide structure	$-\text{SO}_2-\text{O}-$	Phenyl ring
BMI(Ca)	1775, 1710, 710	1175, 1035, 640	1600, 1500
BMI(Sr)	1775, 1710, 730	1175, 1035, 670	1600, 1500
BMI(Ba)	1775, 1720, 720	1175, 1030, 655	1595, 1500
BMI(Zn)	1775, 1710, 710	1170, 1030, 650	1600, 1500
BMI(Co)	1775, 1720, 720	1160, 1025, 640	1595, 1500
BMI(Ni)	1775, 1710, 730	1170, 1030, 630	1600, 1500
BMI(Pb)	1775, 1710, 720	1170, 1030, 670	1600, 1500

Table 4  
 $^1\text{H}$  NMR chemical shifts for BMA(M) in ppm

BMA(M)	$-\text{COOH}$	$-\text{CONH}$	$-\text{CH}=\text{CH}-$	Phenyl ring
BMA(Ca)	10.90	7.92	6.52, 6.36, 6.30, 6.15	7.59
BMA(Sr)	10.78	7.85	6.54, 6.38, 6.30, 6.13	7.59
BMA(Ba)	10.56	7.89	6.69, 6.43, 6.31, 6.10	7.61
BMA(Zn)	10.64	7.90	6.61, 6.46, 6.37, 6.16	7.60
BMA(Co)	10.80	7.90	6.81, 6.66	7.44
BMA(Ni)	10.58	7.90	6.59, 6.42, 6.30, 6.13	7.59
BMA(Pb)	10.84	7.93	6.49, 6.35, 6.27, 6.09	7.57

Table 5  
 $^1\text{H}$  NMR chemical shifts for BMI(M) in ppm

BMI(M)	$-\text{CH}=\text{CH}-$	Phenyl ring
BMI(Ca)	7.15	7.82, 7.72
BMI(Sr)	7.15	7.33, 7.66
BMI(Ba)	7.14	7.74, 7.68
BMI(Co)	7.15	7.58
BMI(Ni)	7.15	7.54
BMI(Pb)	7.11	7.61

the imide has been formed. In Fig. 2, curve b, the chemical shifts can be assigned as follows: 7.14 ppm, singlet,  $-\text{CH}=\text{CH}-$  in the imide ring; 7.74 and 7.68 ppm, phenyl ring. From Fig. 1, curve b, and Fig. 2, curve b, it is concluded that the imidization reaction has occurred and the desired Ba-containing bismaleimide has resulted.

Similar results have also been obtained for other samples, and the IR results for BMA(M) and BMI(M) are listed in Tables 2 and 3; the  $^1\text{H}$  NMR chemical shifts of BAM(M) and BMI(M) are listed in Tables 4 and 5.

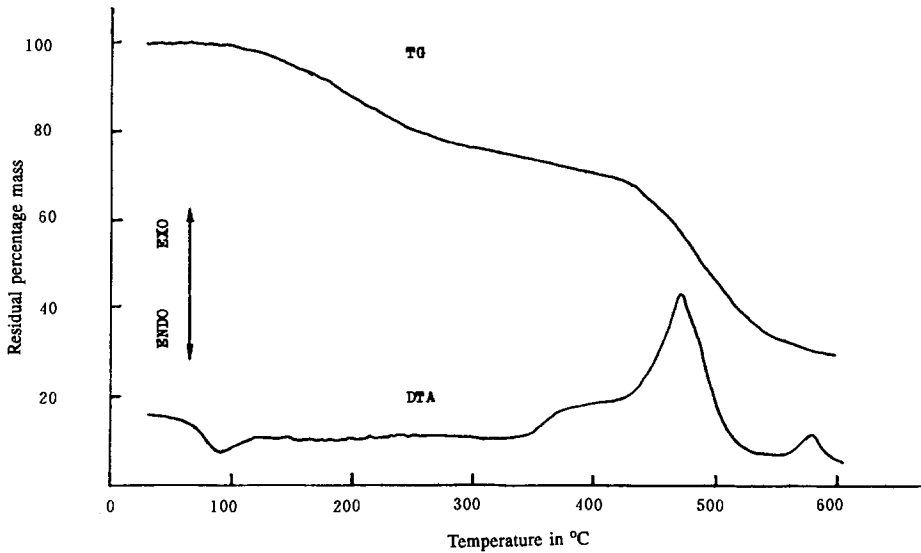


Fig. 3. TG–DTA curves for BMA(Ba) in air.

### 3.3. Thermal analyses

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) curves of BMA(Ba) in air are shown in Fig. 3, and the related temperature data for BMA(M) are listed in Table 6. In Fig. 3, TG shows that the first stage temperature is  $\approx 73.6^\circ\text{C}$ , the main loss resulting from moisture evaporation, and the range of the imidization (cyclodehydration) temperature is  $\approx 181.8\text{--}253.8^\circ\text{C}$ ; at this stage the main loss is due to the evaporation of the remaining solvent and the dehydration of

Table 6  
Thermal analysis data for BMA(M)

BMA(M)	TG			DTA		
	$T_1/^\circ\text{C}$	$T_2/^\circ\text{C}$	$T_3/^\circ\text{C}$	$T_4/^\circ\text{C}$	$T_p/^\circ\text{C}$	
BMA(Ca)	93.6	150–256.8	342.2	97.0–240.8 (endo)	491.8	500.2
BMA(Sr)	86.7	191.2–269.8	450.5	90.2–270.2 (endo)	510.4	563.7
BMA(Ba)	73.6	181–253.8	437.4	73.8–253.8 (endo)	490.2	583.5
BMA(Zn)	100.8	160.6–248.8	400.2	102.8–250.6 (endo)	489.5	509.8
BMA(Co)	103.5	140.4–238.8	423.5	102.8–230.8 (endo)	449.8	503.5
BMA(Ni)	97.4	135.6–235.2	337.8	103.1–240.5 (endo)	437.8	496.5
BMA(Pb)	–	151.7–250.5	433.2	–	456.8	–

Key:  $T_1$ , temperature of moisture evaporation (from TG curves);  $T_2$ , temperature range of BMA(M) imidization (from TG curves);  $T_3$ , temperature of BMA(M) decomposition (from TG curves);  $T_4$ , temperature range of evaporation of entrapped solvent and dehydration of BMA(M) (from DTA curves);  $T_p$ , temperature of the BMA(M) maximum and complete decomposition (from DTA curves).

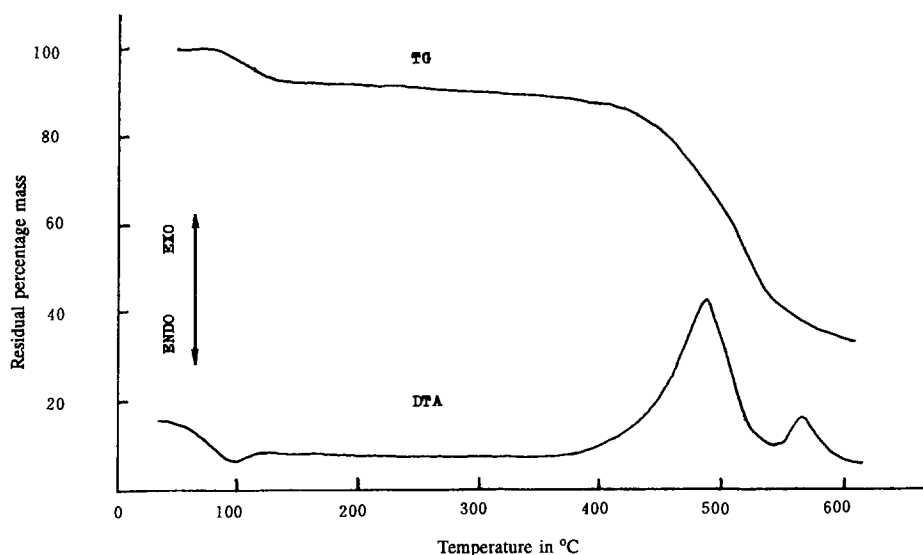


Fig. 4. TG–DTA curves for BMI(Ba) in air.

BMA(Ba). After complete imidization, BMI(Ba) is formed and the peaks of decomposition of BMI(Ba) appear at  $\approx 437.4^\circ\text{C}$ . The endothermic peaks in the range  $73.8\text{--}253.8^\circ\text{C}$  in the DTA curve are due to the evaporation of the entrapped solvent and the dehydration of BMA(Ba). The two exothermic peaks at  $\approx 490.2$  and  $583.5^\circ\text{C}$  imply that complete decomposition of the sample has occurred.

The TG and DTA curves of BMI(Ba) in air are shown in Fig. 4 and the related temperature data are listed in Table 7. TG shows that the initial main loss temperature of BMI(BA) is  $\approx 97.5^\circ\text{C}$ , corresponding to the release of moisture, and

Table 7  
Thermal analysis data for BMI(M)

BMI(M)	TG		DTA
	$T_1/^\circ\text{C}$	$T_d/^\circ\text{C}$	$T_p/^\circ\text{C}$
BMI(Ca)	97.6	346.1	508.1
BMI(Sr)	107.0	456.2	514, 556.2
BMI(Ba)	97.5	430.0	484.9, 566.2
BMI(Zn)	–	383.8	496.1, 508.2
BMI(Co)	–	418.6	463.6, 508.2
BMI(Ni)	101.7	337.2	445.9, 449.5, 526.8
BMI(Pb)	102.0	408.6	428.8

Key:  $T_1$ , temperature of moisture evaporation (from TG curves);  $T_d$ , temperature of the initial decomposition of BMI(M) (from TG curves);  $T_p$ , temperature of the BMI(M) maximum and complete decomposition (from DTA curves).



the decomposition occurs at  $\approx 430.0^\circ\text{C}$ . The DTA curve of BMI(Ba) shows one endothermic peak at  $97.5^\circ\text{C}$  and two exothermic peaks at  $\approx 484.9$  and  $566.2^\circ\text{C}$ . From Table 7, it is concluded that the thermal stability of the BMI(M) decreases in the following order in air: BMI(Sr) > BMI(Ba) > BMI(Co) > BMI(Pb) > BMI(Zn) > BMI(Ca) > BMI(Ni). Thus, the thermal stability of BMI(M) is dependent on the nature of the metal.

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