Preparation and Characterization of Metal-Containing Bismaleimides from Divalent Metal Salts of *p*-Aminobenzoic Acid

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ABSTRACT: A series of novel metal-containing bismaleimides monomers BMI(M) (M = Ca, Sr, Ba, Pb, Co, Ni) were prepared by reacting maleic anhydride with diaminodiphenyl carboxylate to form bismaleamic acid precursors, and subsequently by imidizing them chemically or thermally to form bismaleimides. The samples were characterized by IR, ^{1}H-NMR, and TG-DTA. The results of thermal analysis show that the BMI(M) have high thermo-oxidiative stability and their temperatures of initial decomposition have a relationship with metals introduced and the imidization methods. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1827–1831, 1997

Key words: metal-containing bismaleimides; ^{1}H-NMR; IR; TG-DTA

INTRODUCTION

More and more attention has been paid to metal-containing polymers. Some work about metal-containing polyimide[1–3] and polyurea,[4] in which new approaches to metal-containing polymers were first put forward, was carried out by us. Polymers from bismaleimides have been widely used due to their excellent comprehensive properties, especially their high heat-resistance, low cost, and good tractability. Many thermal analysis studies have been reported elsewhere.[5–12] However, very little work on metal-containing bismaleimides has been investigated. In previous work, we reported on a series of metal-containing bismaleimides prepared from divalent metal salts of sulfanilic acid and some information was published.[13] In the present work, a series of metal-containing bismaleimides from divalent metal salts of *p*-aminobenzoic acid were prepared and characterized, and their thermal properties were also investigated.

EXPERIMENTAL

Materials and Instrumentation

Diaminodiphenyl carboxylates were prepared according to the method of Matsuda and Takechi.[14] The other reagents were of analytical grade, used

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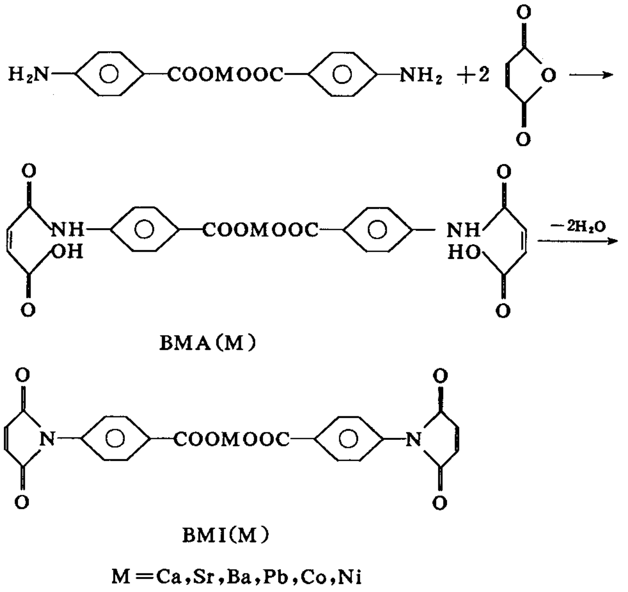
as received from Shanghai General Chemical Reagent Factory.

IR spectra were recorded with the 4100 spectrometer, KBr pellet; ^{1}H-NMR spectra were obtained by using the FT-80A spectrometer in DMSO-d_6 solvent; TG-DTA were investigated with the PCT-1 analyzer at the heating rate of 10°C/min in static air.

Preparation of Metal-Containing Bismaleimides

The metal-containing bismaleimides were prepared according to the following scheme:



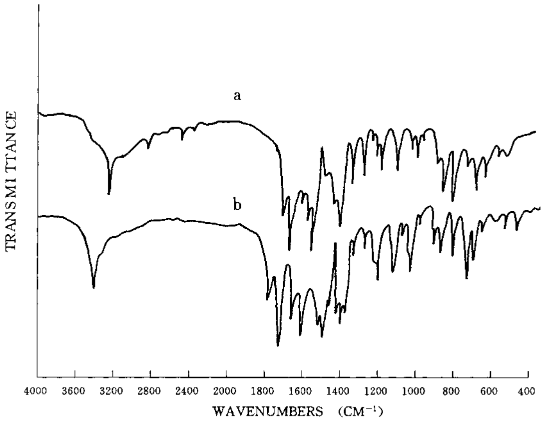


Figure 1 IR Spectra of (a) BMA(Ca) and (b) BMI(Ca)

Into a flask equipped with a mechanical stirrer thermometer and addition funnel 5.0 mmol of diaminodiphenyl carboxylate and 50 ml DMF were placed. Maleic anhydride (10.0 mmol), dissolved in 60 ml DMF, was added dropwise with constant stirring. The mixture was stirred at ambient temperature for 2 h and then at 60°C for an additional 2 h. The solution, which is homogeneous or heterogeneous, was poured into ethanol and the precipitate was collected, washed several times with ethanol, and dried *in vacuo* at 80°C. A DMF solution of BMA(M) was treated with acetic anhydride and soldium acetate (300 ml and 27 g, respectively, per mol of water condensed) and the mixture was heated at 90°C for 2.5 h. The dark brown solution that resulted was combined with ethanol to precipitate the product. The brown solid obtained was collected, washed with ethanol, and dried to afford the metal bismaleimide monomer by chemical imidization. BMA(M) powder was also imidized *in vacuo* within the thermal cycloclehydration temperature range T_1 listed in Table IV as follows: 1 h at the downward temperature, and then 4 h at the upward temperature. Thus, the metal-containing bismaleimides were obtained by thermal imidization. Together six kinds of BMA(M) (M = Ca, Sr, Ba, Pb, Co, Ni) were prepared and imidized thermally into BMI(M) (M = Ca, Sr, Ba, Pb, Co, Ni). And four kinds of BMI(M) (M = Ca, Sr, Ba, Pb) were synthesized from the corresponding BMA(M) composition by chemical imidization.

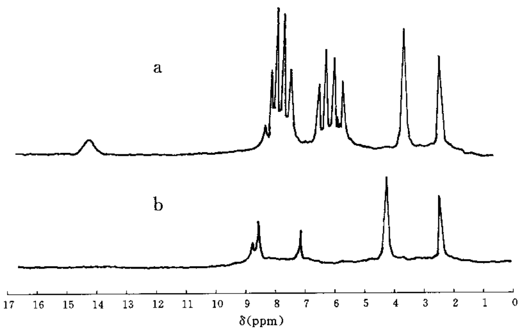


Figure 2 ^{1}H-NMR Spectra of (a) BMA(Ca) and (b) BMI(Ca)

Table I IR Date for BMA(M) (cm^{-1})

Samples	—COOH		—CONH—			—COO$^-$		Phenyl Ring	
BMA(Ca)	2900~2460	1660	3300	1560	1320	1550	1420	1610	1510
BMA(Sr)	2880~2550	1660	3360	1545	1330	1550	1430	1600	1500
BMA(Ba)	2900~2600	1660	3280	1560	1310	1540	1430	1600	1490
BMA(Pb)	2850~2600	1600	3400	1560	1310	1530	1430	1600	1510
BMA(Co)	2880~2620	1660	3360	1570	1310	1540	1420	1610	1490
BMA(Ni)	2900~2560	1660	3440	1560	1330	1540	1420	1600	1490

RESULTS AND DISCUSSION

IR and ^{1}H-NMR Analysis

Supposedly different imidization methods would lead to no difference in IR and ^{1}H-NMR spectra for each kind of BMI(M), which was proven by IR and ^{1}H-NMR analyses in the present work. Thus, the IR and ^{1}H-NMR spectra of BMI(M) obtained by chemical and thermal imidization were not discussed, respectively.

Figures 1 and 2 show the IR and ^{1}H-NMR spectra of BMA(Ca) and BMI(Ca). In Figure 1(a), the absorption bands at 2900 ~ 2460 cm^{-1}, 1710 cm^{-1} (—COOH), 3300 cm^{-1}, 1560 cm^{-1}, and 1320 cm^{-1} characterize the amic acid structure. The bands at 1550 cm^{-1} and 1420 cm^{-1} are assigned to $—CO_2^-$. This means that a static ionic bond between $—COOH^-$ and Ca^{2+} is formed. In Figure 2(a), the chemical shifts can be assigned as following: 14.51 ppm (—COOH), 8.31 ppm (—CONH—), (the two peaks above are exchangeable to D_2O), 8.00 ~ 7.57 ppm (double doublets, protons of phenyl ring), 6.33 ~ 5.71 ppm (double doublets, protons of —CH=CH— in bismaleimide acid structure). It can be concluded that the desired BMA(Ca) was obtained. In Figure 1(b), the characteristic bands of amic acid disappeared, meanwhile the characteristic bands of the imide ring at 1780 cm^{-1}, 1710 cm^{-1}, 1380 cm^{-1}, and 730 cm^{-1}, and the bands of olefinic bonds in the imide ring at 810 cm^{-1} and 685 cm^{-1}, appeared. In Figure 2(b), there is a broad peak at ~ 8.63 ppm corresponding to protons in the phenyl ring, and a singlet at 7.17 ppm corresponding to the olefinic protons in the bismaleimide ring. In addition, the spectrum lacked the peaks for of carboxylic protons and amide groups. So complete imidization can be confirmed from these changes.

Similar results have also been obtained for other samples and the IR results of BMA(M) and BMI(M) are listed in Tables I and II.

It was also found that BMA(M) and BMI(M) have good solubility in water. Furthermore, BMA(Ca), BMA(Ba), and MBA(Pb) can be dissolved in DMSO, and their chemical shifts of ^{1}H-NMR are listed in Table III. After imidization, the solubility of BMI(M) decreases, and only BMI(Ca), BMI(Ba), BMI(Pb), and BMI(Ni)

Table II IR Data for BMI(M) (cm^{-1})

Samples	Imide Structure					—COO$^-$		—CH=CH—		Phenyl Ring	
BMI(Ca)	1780	1710	1380	1120	730	1550	1470	810	685	1610	1500
BMI(Sr)	1780	1710	1380	1100	720	1550	1420	840	700	1600	1500
BMI(Ba)	1780	1710	1385	1110	710	1550	1410	830	690	1610	1500
BMI(Pb)	1780	1715	1380	1110	710	1550	1410	820	680	1810	1510
BMI(Co)	1780	1710	1380	1100	710	1550	1410	830	690	1600	1500
BMI(Ni)	1780	1715	1380	1110	710	1560	1415	830	660	1610	1490

Table III ^{1}H-NMR Chemical Shifts of BMA(M) (ppm)

Samples	—COOH	Phenyl Ring	—CH=CH—
BMA(Ca)	14.51	8.00~7.57	6.33~5.71
BMA(Sr)	14.96	7.94~7.55	6.28~5.66
BMA(Ba)	14.85	7.96~7.65	6.34~5.75
BMA(Pb)	12.84	7.95~7.59	6.33~5.96

BMA(Co) and BMA(Ni) can not be dissolved in DMSO.

have very little solubility in DMSO. There is only one broad peak in the ^{1}H-NMR spectra, and the chemical shifts are assigned as 9.04 ppm, 8.72 ppm, and 7.97 ppm for BMI(Ba), BMI(Pb), and BMI(Ni), respectively.

Thermal Analysis

Figure 3 shows the TG-DTA curves for BMA(Ca) and BMI(Ca), obtained by chemical imidization. In the TG curve of BMA(Ca), the slight weight loss at 122.0°C–251.2°C is due to evaporation of the remaining solvent and dehydration. After complete imidization, BMI(Ca) was formed and its weight loss at 366. 2°C is owing to the decomposition of the sample. The plateau observed above

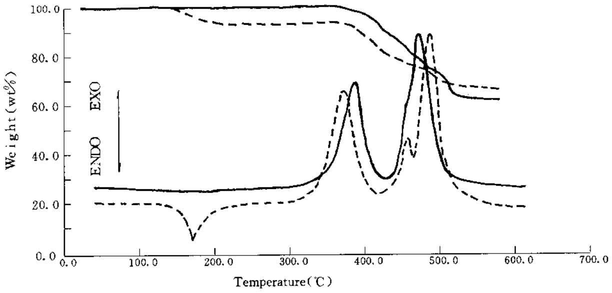


Figure 3 TG-DTA Curves of BMA(Ca) (--------) and BMI(Ca) (——) in air

531.8°C corresponds to the formation of $CaCO_3$ for BMI(Ca). Similarly, for some other BMI(M), the metal-oxide may also be formed. In the DTA curve of BMA(Ca), a small endothermic peak at 166.5°C is relative to the imidization of BMA(Ca), the exothermic peak at 367.8°C indicates the decomposition of the sample, and the exothermic peaks at 458.2°C and 484.8°C imply that complete docomposition of the sample has occurred. In the TG curve for BMI(Ca), there is no weight loss below 354.8°C. The loss above 354.8°C means that the thermal decomposition has occurred, and the plateau above 485°C is due to the formation of $CaCO_3$. Meanwhile, there are two exothermic peaks at 390.2°C and 473.0°C in the DTA curve.

Table IV Thermal Analysis Data for BMA(M) (°C)

	TG			DTA			
Samples	T_1[a]	T_2[b]	T_3[c]	T_4[d]	T_5[e]	T_6[f]	
BMA(Ca)	122.0~251.2	366.2	449.2	166.5	367.8	458.2	484.4
BMA(Sr)	104.2~262.6	354.8	426.0	209.2	366.8	473.0	485.2
BMA(Ba)	122.0~226.8	354.8	447.2	122.0	362.6	447.2	461.4
BMA(Pb)	159.2~234.0	307.0	409.0	196.8	319.0	409.8	
BMA(Co)	122.0~258.5	349.0	402.2	171.8	331.0	378.5	
BMA(Ni)	158.0~221.8	347.4	402.2	171.8	331.2	378.5	408.2

[a] T_1, the temperature range of BMA(M) imidization.
[b] T_2, the initial decomposition temperature of BMI(M).
[c] T_3, the temperature of the third weight loss.
[d] T_4, the temperature of slightly endothermic peak of BMA(M) in imidization.
[e] T_5, the temperature of exothermic peak of BMI(M) in decomposition.
[f] T_6, the temperature of exothermic peaks of BMI(M) complete decomposition.

Table V Thermal Analysis Data for BMI(M) by Thermal Imidization (°C)

Samples	T_d	T_{p_1}	T_{p_2}	
BMI(Ca)	354.8	376.2	484.8	
BMI(Sr)	349.6	367.2	449.8	473.0
BMI(Ba)	336.2	366.8	426.0	461.4
BMI(Pb)	294.8	319.4	414.0	
BMI(Co)	366.8	367.2	—	
BMI(Ni)	349.0	343.0	402.2	

T_d, the initial decomposition temperature of BMI(M) from TG curves.

T_{p_1}, the initial decomposition temperature of BMI(M) from DTA curves.

T_{p_2}, the final decomposition temperature of BMI(M) from DTA curves.

Table VI Thermal Analysis Data for BMI(M) by Chemical Imidization (°C)

Samples	T_d	T_{p_1}	T_{p_2}
BMI(Ca)	354.8	390.2	473.0
BMI(Sr)	331.2	360.8	449.0
BMI(Ba)	337.2	343.0	455.5
BMI(Pb)	294.8	378.5	461.5

T_d, T_{p_1}, and T_{p_2} have the same meanings as in Table V.

Other thermal analysis data are listed in Tables IV–VI. The results show that the thermooxidative stability of BMI(M) was excellent, affected not only by the metal incorporated but also by the imidization methods (chemical imidization and thermal imidization).

REFERENCES

1. W. Qiu, C. Li, W. Zeng, J. Liu, L. Lu, and X. Wang, *J. Appl. Polym. Sci.,* **56,** 1295 (1991).
2. W. Zeng, W. Qiu, J. Liu, X. Yang, L. Lu, X. Wang, and Q. Dain, *Polymer,* **36,** 3761 (1995).
3. X. Yang, W. Qiu, C. Li, W. Zeng, J. Liu, L. Lu, X. Wang, and B. C. Sanctuary, *Polymer,* **35,** 4300 (1994).
4. W. Qin, W. Zeng, X. Zhang, C. Li, L. Lu, X. Wang, X. Yang, and B. C. Sanctuary, *J. Appl. Polym. Sci.,* **49,** 405 (1993).
5. S. Jakeda, H. Aliyamd, and H. Kokiucki, *J. Appl. Polym. Sci.,* **35,** 1341 (1988).
6. M. J. Nanjan and K. Sivaraj, *J. Polym. Sci., Polym. Chem. Ed.,* **27,** 375 (1989).
7. A. P. Melissaris and John A. Mikroyannidis, *J. Appl. Polym. Sci.,* **34,** 2657 (1987).
8. J. A. Mikroyannidis. *J. Polym. Sci., Polym. Chem. Ed.,* **22,** 1717 (1984).
9. I. K. Varma and S. Sharma, *Polymer,* **26,** 1561 (1985).
10. John A. Mikroyannidis, *J. Polym. Sci., Polym. Chem.,* **28,** 679 (1990).
11. Jerry E. White, *J. Polym. Sci., Polym. Chem. Ed.,* **22,** 590 (1984).
12. K. Krishnan and K. N. Ninan, *Thermochimica Acta,* **189,** 241 (1991).
13. C. Li, W. Qiu, W. Hua, L. Lu, and X. Wang, *Thermochimica Acta,* **55,** 355 (1995).
14. H. Matsuda and S. Takechi, *J. Polym. Sci., Polym. Chem. Ed.,* **28,** 1895 (1990).