

Preparation and Characterization of Metal-Containing Aromatic Polyimides

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ABSTRACT: A series of novel metal-containing aromatic polyimides were synthesized from divalent metal oxide/hydroxide (MO/M(OH)₂) (M = Ba, Sr, Ca, Mg, Zn, Cd, Co, Ni, Pb, Cu), *p*-aniline sulfonic acid (ASA), and 3,3'-4,4'-benzophenonetetracarboxylic dianhydride (BTDA). The C, H, N, and S contents were determined by elemental analysis, their structures were characterized by proton nuclear magnetic resonance (¹H-NMR) and Fourier transform infrared (FT-IR) spectroscopy, and the thermal properties of the polymers were also studied by TG-DTA. It is found that metal-containing polyimides have a higher thermal stability. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2363–2369, 2000

Key words: preparation; characterization; metal-containing aromatic polyimides

INTRODUCTION

Since polyimides were first prepared by Bogert and Renshaw¹ in 1908, they have been widely used and rapidly developed because of their excellent mechanical and chemical properties.^{2–5} In our earlier studies, we reported on the preparation and characterization of metal-containing polyureas⁶ and bismaleimides⁷ from divalent metal salts. We demonstrated that introducing metals into polyurea improved the thermal stability and the metal-containing bismaleimides had high thermooxidative stability and their tem-

peratures of initial decomposition showed a relationship with metals introduced and imidization methods. In this work, we present the synthesis and characterization of metal-containing aromatic polyimides [PBI(M)]. The structures of the polymers were investigated by FTIR and NMR spectroscopy, and their thermal stability was also characterized by TG-DTA.

EXPERIMENTAL

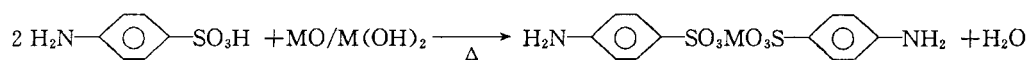
Materials

Sulfanilic acid [*p*-aniline sulfonic acid (ASA)], 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), DMF, and other solvents used were of analytical grade; metal oxide/hydroxide and acetic anhydride were of laboratory pure grade.

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(M = Mg, Ca, Sr, Ba, Co, Ni, Cu, Zn, Cd, Pb)

Scheme 1

Measurements

Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were measured using an FT-80A NMR spectrometer in $\text{DMSO-}d_6$. Infrared spectra were recorded with a Bruker Vector 22 instrument. For elemental analyses, the C, H, N, and S contents were determined using a Perkin-Elmer 240C elemental analysis instrument. TG-DTA was carried out with a Beijing Optical Instrument Factory PCT-1 analyzer at a heating rate of $10^\circ\text{C min}^{-1}$ in air.

Syntheses of ASA(M)

ASA(M) was synthesized according to Scheme 1 using the procedures described previously.⁸ The synthesized samples with metal M are listed in Table I.

Preparation of Metal-Containing Polymers

The synthetic path could be described as shown in Scheme 2.

A flask equipped with a magnetic stirrer, thermometer, and addition funnel was filled with a solution containing 0.02 mol of ASA(M) in 15 mL DMF. To the vigorously stirred solution, 0.01 mol BTDA dissolved in 25 mL DMF was added drop-

wise in 1.5 h. Stirring of the mixture lasted for 3 h at ambient temperature.

An aliquot of the reaction solution was poured into water and a deposit appeared. The solid was filtered, washed three times with water, and dried *in vacuo* at 60°C for 3 h to yield the metal-containing polyamic acid [PBA(M)]. Three milliliters of acetic anhydride and 0.27 g of sodium acetate were added to the remaining solution. The mixture was boiled under reflux for 2 h and subsequently poured into a large amount of water. The solid obtained was filtered, washed three times with water, and then dried *in vacuo* at 60°C for 3 h. The metal-containing polyimide PBI(M) was thus obtained.

RESULTS AND DISCUSSION

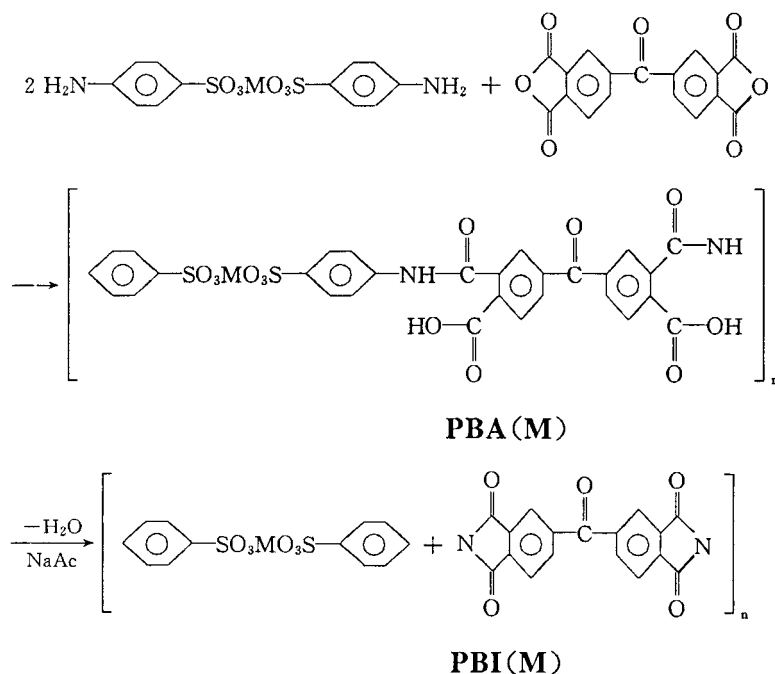
Characterization of ASA(M)

Elemental Analysis

The results of elemental analysis of ASA(M) are shown in Table II. The values from elemental analysis agreed well with the calculated values.

Table I Synthesized Samples for ASA(M)

Samples	MO/M(OH) ₂	Temperature (°C)	Precipitant	Color
ASA(Mg)	MgO	60	Acetone	White
ASA(Ca)	CaO	60	<i>tert</i> -Butanol	White
ASA(Sr)	Sr(OH) ₂	60	Acetone	White
ASA(Ba)	Ba(OH) ₂ · 8H ₂ O	60	<i>tert</i> -Butanol	Yellow
ASA(Co)	Co(OH) ₂	70	Acetone	Pink
ASA(Ni)	Ni(OH) ₂	80	<i>tert</i> -Butanol	Green
ASA(Cu)	CuO	80	Acetone	Yellow
ASA(Zn)	ZnO	70	<i>tert</i> -Butanol	White
ASA(Cd)	CdO	80	Acetone	White
ASA(Pb)	PbO	80	Acetone	White

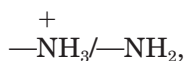


(M = Mg, Ca, Sr, Ba, Co, Ni, Cu, Zn, Cd, Pb)

Scheme 2

¹H-NMR

The ¹H-NMR spectrum data of ASA are shown in Table III. The broad peak at about 6.85 ppm corresponds to



which can be exchanged by D₂O. The peaks with chemical shifts at 7.21, 7.32, 7.64, and 7.74 ppm are referred to as protons of the phenyl ring. Figure 1 shows the ¹H-NMR spectrum of

ASA(Ba), as compared with ASA; the resonance peaks at 3.35 and 5.22 ppm are associated with protons of HDO/H₂O and —NH₂, respectively. However, the chemical shifts of the phenyl ring shifted upfield, corresponding to 6.41, 6.50, 7.25, and 7.36 ppm, resulting from shieldings of the phenyl ring while bonding to the metal atom. The other ¹H-NMR data of ASA(M) are listed in Table III.

Figure 2 presents the spectrum of metal-containing polyamic acid [PBA(M)]. As compared with the ¹H-NMR data of BTDA, the peaks of the

Table II Elemental Analysis Data of ASA(M) (Calcd) (%)

Sample	C (%)	H (%)	N (%)	S (%)
ASA(Mg)	38.87 (39.08)	3.19 (3.26)	7.39 (7.60)	16.88 (17.42)
ASA(Sr)	32.81 (33.35)	2.62 (2.78)	6.51 (6.48)	14.32 (14.87)
ASA(Ba)	29.78 (29.91)	2.47 (2.49)	5.75 (5.82)	13.45 (13.33)
ASA(Ni)	36.12 (35.74)	3.03 (2.98)	6.83 (6.95)	16.35 (15.93)
ASA(Cu)	35.61 (35.32)	3.05 (2.94)	6.84 (6.87)	15.87 (15.75)
ASA(Zn)	35.25 (35.16)	3.01 (2.93)	6.88 (6.84)	15.77 (15.67)
ASA(Cd)	32.84 (31.54)	2.58 (2.63)	6.48 (6.13)	14.59 (14.06)
ASA(Pb)	26.31 (26.12)	2.24 (2.18)	5.01 (5.08)	11.82 (11.64)

Table III $^1\text{H-NMR}$ Spectral Data of ASA(M) (ppm)

Sample	a		b		$-\text{NH}_3^+/\text{NH}_2/\text{H}_2\text{O}$	HDO/ NH_2	NH_2	HDO	DMSO- d_6
ASA	7.21	7.32	7.64	7.74	6.85 (bs)*				2.50
ASA(Mg)	6.80	6.91	7.43	7.53		5.11			2.50
ASA(Ca)	6.66	6.77	7.38	7.49		5.50			2.50
ASA(Sr)	6.89	7.00	7.49	7.60		5.32			2.50
ASA(Ba)	6.41	6.51	7.25	7.36			5.22	3.35	2.50
ASA(Co)	6.55		7.12						2.50
ASA(Ni)	6.12		7.18				4.75	3.26	2.50
ASA(Cu)	6.78		7.60						2.50
ASA(Zn)	6.43	6.52	7.24	7.33			5.24	3.35	2.50
ASA(Cd)	6.57	6.67	7.31	7.41		4.21			2.50
ASA(Pb)	6.41	6.52	7.25	7.36			5.25	3.35	2.50

bs: broad single peak.

phenyl ring protons for BTDA shift upfield, which means that the electronic distribution of the phenyl ring is directly affected when the BTDA is linked by ASA(Ba). In contrast, downfield shifts are observed for the phenyl ring protons of ASA(Ba), and the two-spin system *AB* remained unchanged. The other peaks can be assigned as

follows: The proton of $-\text{OH}$ in carboxylic acid gave a singlet at a chemical shift of $\delta = 10.78$ ppm, the proton in $-\text{NH}_2$ showed one peak at $\delta = 4.72$ ppm (exchanged by D_2O), and the peak at $\delta = 2.50$ ppm refers to DMSO- d_6 . The $^1\text{H-NMR}$ data for other metal-containing polymeric acids PBA(M) are summarized in Table IV.

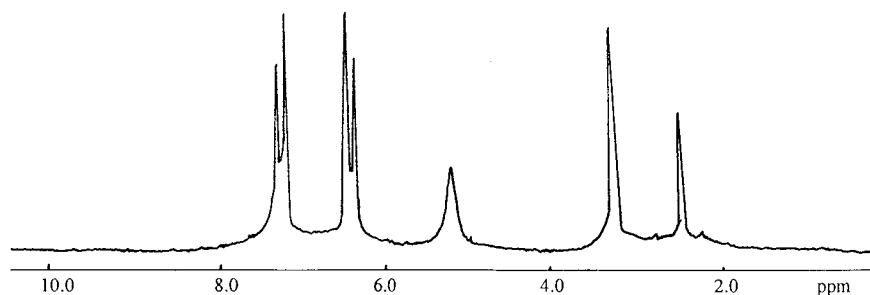
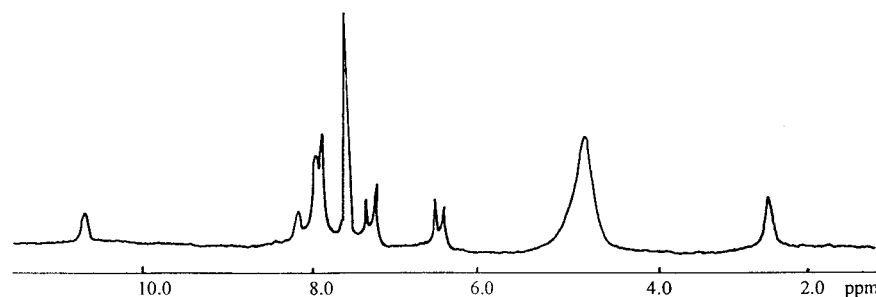
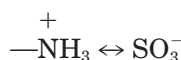
**Figure 1** $^1\text{H-NMR}$ spectrum of ASA(Ba).**Figure 2** $^1\text{H-NMR}$ spectrum of PBA(Ba).

Table IV $^1\text{H-NMR}$ Data of Metal-Containing Polymeric Acid (ppm)

Sample	DMSO- d_6	HDO/H $_2$ O/-NH $_2$			-COOH
BTDA	2.50		7.86–8.28		
PBA(Mg)	2.50	6.00	7.21–7.72	7.74–8.15	10.04
PBA(Sr)	2.50	4.32	6.45–7.77	7.78–8.22	10.64
PBA(Ba)	2.50	4.72	6.45–7.40	7.65–8.23	10.78
PBA(Co)	2.50	3.71	7.36–7.78	7.46–8.14	9.95
PBA(Zn)	2.50	3.55	7.38–7.82	7.96–8.37	10.57
PBA(Pb)	2.50	4.37	6.42–7.32	7.67–8.21	10.74

IR Spectra

Table V shows the IR spectra data of ASA and ASA(Ba). In Table V for ASA, the absorption bands at 1602, 1499, and 834 cm^{-1} are assigned to the phenyl ring, while the bands at 1159, 1036, and 686 cm^{-1} are attributed to the absorption of SO_3^- . C—N gives an absorption band at 1319.3 cm^{-1} , and the $-\text{NH}_2$ group exhibits absorption bands at 3363 and 1631 cm^{-1} . The characteristic absorption of $-\overset{+}{\text{NH}}_3$ appears at 2881, 2648, 1578, and 1548 cm^{-1} . In Table V, for ASA(Ba), the absorption bands at 2881, 2648, 1578, and 1548 cm^{-1} disappeared. We can thus conclude that ASA existed as



in solution. The IR data for other ASA(M) (M = Mg, Ca, Sr, Ba, Co, Ni, Cu, Zn, Cd, Pb) are listed in Table V.

Shown in Figure 3 are the IR spectra of (a) the metal-containing polyamic acid [PBA(Ba)] and (b) the responsive polyimide [PBI(Ba)]. In Figure 3(a), $-\text{NH}_2$ gives absorption bands at 3500–3200 and 1392 cm^{-1} , $-\text{COOH}$ exhibits absorption bands at 2900–2700 and 1718 cm^{-1} , and the bands at 1598 and 1503 cm^{-1} are attributed to the structure of the phenyl ring. From Figure 3(b), it can be observed that the characteristic absorption bands of amic acid disappear and some new absorption bands appear at 1783, 1720, 1400, 1134, and 733 cm^{-1} . These bands are the characteristic absorption bands of imide.⁹ The characteristic absorption and assignments for other

Table V IR Wavenumbers of ASA(M) (cm^{-1})

Sample	Phenyl Ring	$-\text{SO}_2-\text{O}-$	C—N	$-\text{NH}_2$	$-\text{NH}_3^+$
ASA	1602 1499 834	1159 1036 686	1319	3363 1631	2881 2648 1548 1578
ASA(Mg)	1602 1501 825	1164 1036 689	1423	3310 1684	
ASA(Ca)	1600 503 829	1197 1065 700	1428	3398 1631	
ASA(Sr)	1602 1500 828	1176 1038 688	1423	3364 1625	
ASA(Ba)	1602 1502 829	1126 1035 696	1301	3387 1635	
ASA(Co)	1603 1500 834	1160 1038 688	1426	3325 1631	
ASA(Ni)	1604 1501 833	1181 1034 694	1430	3386	
ASA(Cu)	1603 1501 838	1160 1035 687	1425	3302 1632	
ASA(Zn)	1603 1501 837	1156 1037 687	1431	3306	
ASA(Cd)	1602 1501 835	1165 1037 688	1430	3311 3253	
ASA(Pb)	1598 1502 831	1196 1030 687	1430	3348	

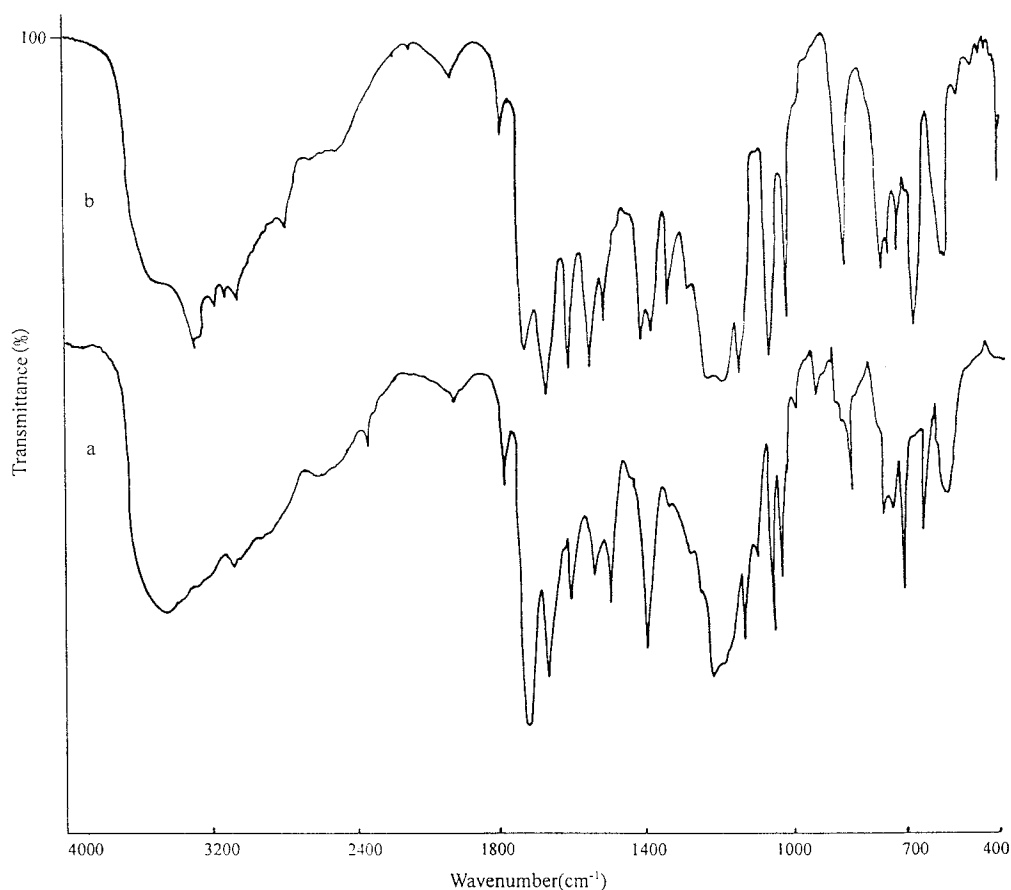


Figure 3 IR spectra of (a) PBA(Ba) and (b) PBI(Ba).

polyamic acids and polyimides are listed in Tables VI and VII, respectively.

Thermal Properties

The TG-DAT data of the metal-containing polyimides [PBI(M)] are listed in Table VIII. It was

found that all metal-containing polyimides have a higher thermal stability, and the thermal stability of the PBI(M) decreases in the following order in air: PBI(Sr) > PBI(Ba) > PBI(Zn) > PBI(Mg) > PBI(Co) > PBI(Pb) > PBI(Cu). Thus, the thermal stability of PBI(M) is dependent on the na-

Table VI IR Wavenumbers of Metal-Containing Polyamic Acid (cm^{-1})

Sample	—C—N	—NH ₂	—NH— $\overset{\text{O}}{\parallel}$ —C—	$\overset{\text{O}}{\parallel}$ —C—OH	Phenyl Ring
PBA(Sr)	1338	3486	3486 1655 1520	2900–2700 1719	1597 1500
PBA(Ba)	1392	3489	3489 1656 1520	2900–2720 1718	1598 1503
PBA(Zn)	1345	3488	3488 1654 1521	2900–2720 1719	1600 1496
PBA(Pb)	1304	3491	3491 1655 1542	2900–2720 1718	1600 1493

Table VII IR Wavenumbers of Metal-Containing Polyimides (cm⁻¹)

Sample	—C—N	—NH ₂	$\begin{array}{c} \text{O} \quad \quad \quad \text{O} \\ \parallel \quad \quad \quad \quad \quad \quad \parallel \\ \text{—C—N—C—} \end{array}$	Phenyl Ring
PBI(Sr)	1320	3400–3200	1783 1719 1397 1134 713	1601 1532
PBI(Ba)	1322	3400–3200	1783 1720 1400 1134 733	1600 1539
PBI(Zn)	1302	3400–3200	1783 1721 1401 1135 710	1600 1501
PBI(Pb)	1304	3400–3200	1783 1719 1393 1135 715	1600 1493

ture of the metal and the polymer aggregation. From the TG–DTA curve data, it can be seen that all PBI(M)s have much higher thermal stability than that of the polyimides.⁵

Table VIII TG–DTA Data of ASA(M) and PBI(M) (°C)

Sample	Decomposition Temperature ^a	
	Initial	Peak
PBI(Mg)	529	550 584
PBI(Sr)	556	612
PBI(Ba)	531	573 604
PBI(Co)	488	535
PMI(Cu)	424	462
PBI(Zn)	513	587
PMI(Pb)	465	519

^a Initial and peak temperatures are from TG and DTA curves, respectively.

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