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Synthesis and characterization of polyimides from metal-containing (Ba, Sr, Pb, Zn) diamines

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Metal-containing polyimides with the metals in the main chain were prepared by firstly reacting pyromellitic dianhydride with a mixture of divalent metal salts of sulfanilic acid [ASA(M)] and 4,4′-diaminodiphenylmethane to form poly(amide acid) salts, the desired polyimides being obtained when the poly(amide acid) salts were separated from the solvent and heated under imidization conditions. The structures of the resulting polyimides were characterized by ^{1}H and ^{13}C nuclear magnetic resonance and infra-red spectroscopy, and their thermal properties by thermogravimetric analysis and dynamic thermal analysis. It was found that the inherent viscosity of the poly(amide acid) salt solutions decreased markedly with increasing metal content.

(Keywords: metal-containing polyimide; structure; characterization)

INTRODUCTION

Since the first formation of solid complexes between poly(ethylene oxide)[1] and metal salts, numerous investigations have been conducted on a variety of polymer–metal salt systems[2–7]. Metal-containing polyurethanes[8], poly(urethane urea)s[9] and polyureas[10,11] have been prepared. Attention has also been paid to metal-containing polyimides[12,13], prepared by adding inorganic salts or metal complexes, such as Al(acac)$_3$, AlCl$_3$, CaCl$_2$, EuCl$_3$ and CoAc$_2$ to the poly(amide acid), followed by thermal conversion. However, several experimental problems have arisen with this procedure, limiting the preparation of good quality films. These problems include: (1) the poor solubility of the metal complexes in most common organic solvents; (2) gel formation or crosslinking of the polymer may occur upon interaction with the metal; (3) poly(amide acid) precipitation takes place when the metal complex is added; and (4) the metal promotes thermo-oxidative degradation of the polymer film upon curing.

So far as the authors are aware, metal-containing polyimides with the metals in the main chain have not been prepared previously. In the present work, such metal-containing polyimides are manufactured by a two-step polycondensation reaction. The first step is the reaction of pyromellitic dianhydride with metal-containing diamines [ASA(M)] which are prepared and characterized as described in refs 14 and 15; the second step is thermal conversion to the desired polyimides. The properties of the metal-containing polyimides were investigated.

EXPERIMENTAL

Materials

Dimethylacetamide (DMAc) and 4,4′-diaminodiphenylmethane (MDA) were of analytical grade; pyromellitic dianhydride (PMDA) was a guaranteed reagent. The divalent metal salts of *p*-aniline sulfonic acid [ASA(M)] were synthesized according to refs 14 and 15.

Syntheses of metal-containing polyimides

Into a flask equipped with a mechanical stirrer, a thermometer and addition funnel were placed with 9.0 mmol diamines [ASA(M) + MDA] dissolved in DMAc. The solution was kept at 15°C, and 9.2 mmol PMDA powder was added gradually to the solution with stirring over a 20 min period. The reaction was allowed to proceed for 4 h and the resulting (solid) metal-containing poly(amic acid) salts were obtained by evaporation of the solvent. The poly(amic acid) salts were heated above 300°C *in vacuo* for 2.5 h to obtain the metal-containing polyimides (PI).

Measurements

Infra-red (i.r.) spectra were recorded with a 7400 instrument. ^{1}H nuclear magnetic resonance (n.m.r.) spectra were measured using an FT-80A spectrometer. ^{13}C n.m.r. was performed on a CMX-300 instrument. Viscosities were determined at 25°C with a SanSe

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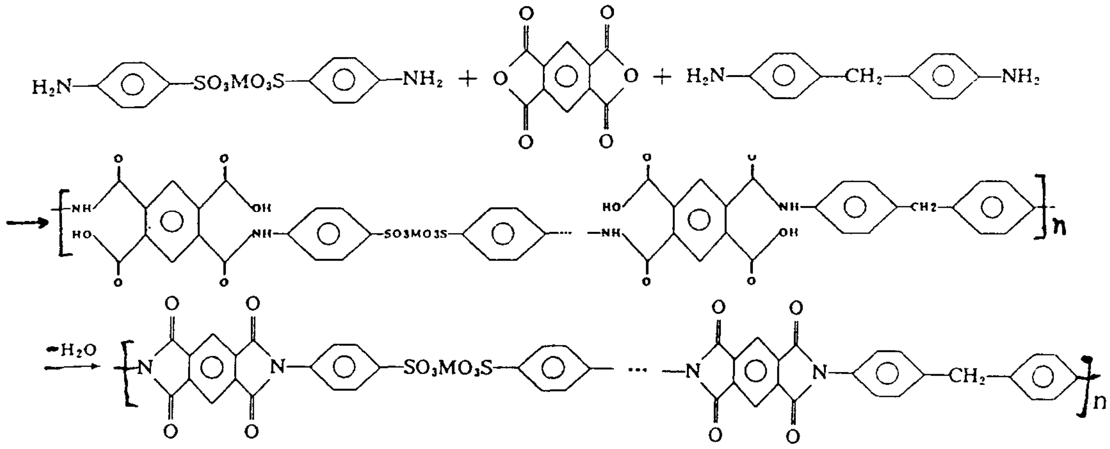


Scheme 1

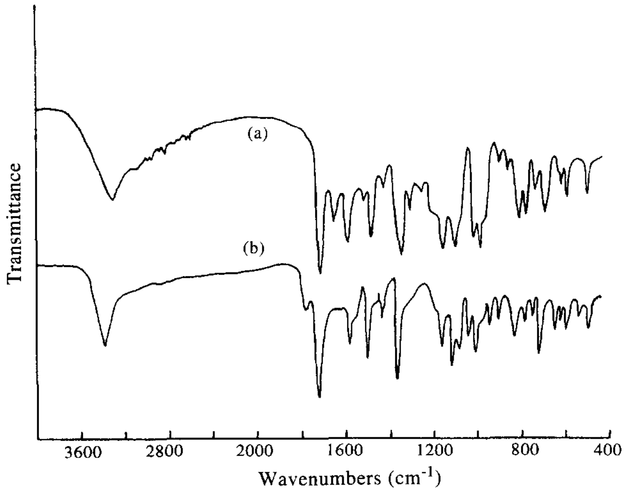


Figure 1 I.r. spectra of metal-containing (a), PAA and (b) PI; 50 mol% ASA(Pb) in feed diamines

viscometer. Thermogravimetric analysis (t.g.a.) and dynamic thermal analysis (d.t.a.) were performed using a PCT-1 analyser at a heating rate of 10°C min^{-1} in air.

RESULTS AND DISCUSSION

Syntheses of metal-containing polyimides

It is well known that polyimides have a high heat resistance and have been widely used. Typically, they are prepared by reacting an organic diamine with an aromatic dianhydride. Two processes which have been of particular interest are the 'melt polymerization' process and the 'solution polymerization' process, the latter being more popular. Solution polymerization is generally conducted by reacting an aromatic dianhydride and an organic diamine in an inert solvent. Firstly, poly(amic acid)s (PAAs) are obtained, and then the poly(amic acid)s are converted to the desired polyimides under imidization conditions.

In this paper, metal-containing polyimides are synthesized by reacting pyromellitic dianhydride with a mixture of metal-containing diamines, ASA(M) and MDA, according to *Scheme 1*, where M = Pb, Ba, Sr, Zn. For comparison, the parent poly(amic acid) and polyimide were also prepared from PMDA and MDA.

Table 1 I.r. data (wavenumber, cm^{-1}) of metal-containing PAAs

Product	ASA(M) in feed diamines (mol%)	–COOH		–CONH				–SO_2–O–			Phenyl ring	
PAA(O)		1700	3040–2500	1640	1540	1300	3360				1595	1500
PAA(Pb)	5	1710	3040–2500	1665	1540	1300	3400	1175	1035	690	1600	1510
	20	1710	3050–2520	1660	1525	1320	3400	1175	1035	700	1595	1510
	50	1710	3000–2600	1665	1525	1320	3360	1175	1035	700	1590	1510
	80	1710	3040–2640	1670	1525	1320	3400	1175	1035	700	1600	1500
	100	1710	3080–2700	1675	1530	1320	3400	1175	1035	700	1595	1495
PAA(Ba)	5	1710	3000–2600	1670	1550	1310	3400	1170	1030	695	1600	1500
	80	1710	3080–2680	1660	1545	1320	3400	1180	1040	700	1600	1495
PAA(Sr)	5	1710	3040–2600	1660	1550	1310	3400	1170	1030	695	1610	1510
	80	1710	3080–2680	1665	1545	1320	3400	1180	1040	695	1595	1500
	100	1710	3080–2680	1665	1545	1320	3400	1190	1050	695	1595	1500
PAA(Zn)	5	1710	3040–2640	1635	1550	1250	3400	1170	1030	695	1600	1510
	80	1710	3080–2600	163	1550	1260	3400	1180	1040	695	1595	1500
	100	1710	3080–2500	1630	1540	1300	3400	1180	1040	695	1595	1495

Table 2 I.r. data (wavenumber, cm^{-1}) of metal-containing PIs

Product	ASA(M) in feed diamines (mol%)	Imide structure			$-SO_2-O-$			Phenyl ring	
PI(O)		1775	1710	720				1600	1500
PI(Pb)	5	1775	1710	720	1175	1035	645	1600	1500
	20	1775	1720	720	1175	1035	645	1595	1510
	50	1775	1720	720	1175	1035	645	1590	1500
	80	1775	1720	720	1190	1040	645	1590	1495
	100	1780	1725	720	1195	1045	645	1595	1500
PI(Ba)	5	1775	1725	720	1190	1050	645	1610	1510
	80	1780	1725	720	1190	1050	645	1595	1500
	100	1780	1720	720	1190	1050	645	1595	1500
PI(Sr)	5	1775	1720	720	1190	1050	645	1610	1510
	80	1780	1720	720	1180	1050	645	1595	1500
	100	1780	1720	720	1180	1050	645	1595	1495
PI(Zn)	5	1775	1720	720	1195	1040	645	1610	1510
	80	1775	1720	720	1195	1040	645	1595	1500
	100	1780	1720	720	1195	1040	645	1595	1500

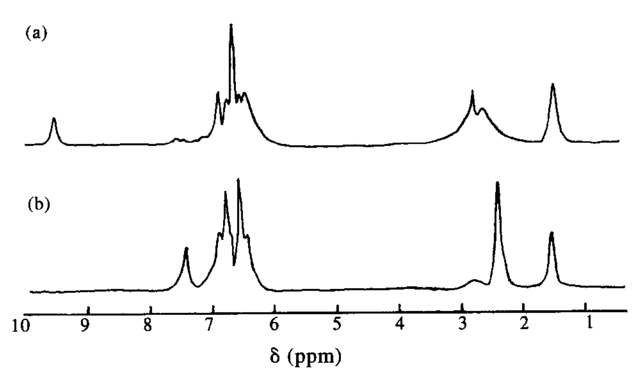


Figure 2 ^1H n.m.r. spectra of metal-containing (a), PAA and (b) PI; 50 mol% ASA(Pb) in feed diamines

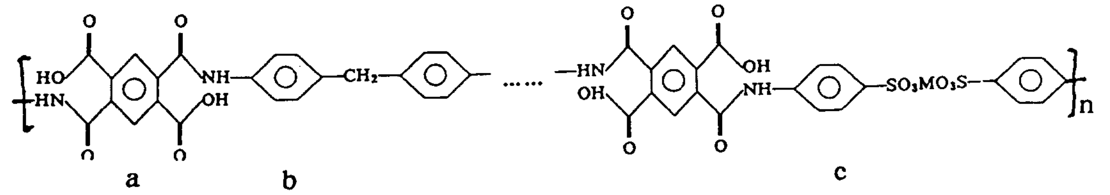
I.r. spectra of representative metal-containing PAA and metal-containing PI compounds, in which the molar ratio of ASA (Pb) is 50% in the feed diamines, are shown in *Figures 1a* and *b*, respectively. In *Figure 1a*, absorption bands characteristic of carboxylic acid are observed at 1710 and 3300–2600 cm^{-1}, while the bands at 1665, 1525, 1320 and 3360 cm^{-1}, are attributed to the absorption of amide. This suggests that the structure of amide–acid exists in the PAA.

From *Figure 1b*, it can be observed that the absorption bands at 3000–2600, 1665, 1525 and 1320 cm^{-1} disappear, and some new absorption bands appear at 1775, 1720, 1380 and 720 cm^{-1}. Apparently, these bands are the characteristic absorption of imide and the polyimide is obtained. The i.r. data for other metal-containing PAAs and PIs are listed in *Table 1* and *2*.

Figure 2 shows the ^1H n.m.r. spectra of the metal-containing PAA and PI in which the molar ratio of ASA(Pb) was 50% in the feed diamines. DMSO-d_6 solvent was used for the determination. *In Figure 2a*, protons of the –COOH groups give the singlet at 10.58 ppm and the protons of the amide groups, which can be exchanged by D_2O, are found at 8.51 and 8.13 ppm due to the *cis–trans* isomerism of such protons. The singlet at 7.96 ppm is attributed to the phenyl ring protons of the PMDA that has been amidized; however, the phenyl ring protons of the MDA that has been amidized give the multiplets at 7.73–7.43 ppm (not containing 7.63 ppm), and the singlet of aromatic protons for the ASA(M) appears at 7.63 ppm.

In *Figure 2b*, the singlet at 10.56 ppm attributed to –COOH and the peaks at 8.62 and 8.13 ppm assigned to the protons of amide groups disappear, suggesting that the structure of poly(amic acid) does not exist. A downfield shift to 8.37 ppm is observed for the phenyl ring protons of the PMDA that has been imidized. The

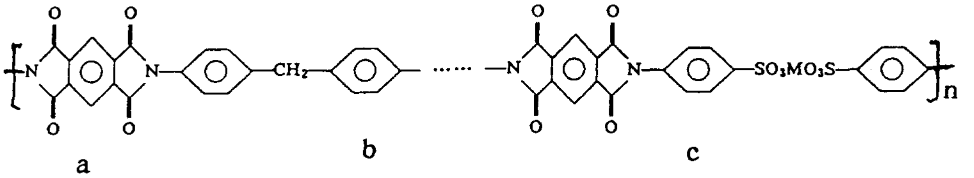
Table 3 ^1H n.m.r. chemical shifts (ppm) of metal-containing PAAs



Product	ASA(M) in feed diamines (mol%)	Phenyl ring a	Phenyl ring b	Phenyl ring c	–COOH	–CONH		$-CH_2-$	Peaks exchanged by D_2O		
PAA(O)		7.98(s)	7.07–7.16(f)	^{a}	10.69(s)	8.29	8.23(d)	3.86(s)	10.69	8.29	8.23
PAA(Pb)	5	7.98(s)	7.07–7.16(f)	^{b}	10.60(s)	8.33	8.29(d)	3.76(s)	10.60	8.33	8.29
	10	7.94(s)	7.73–7.43(f)	^{b}	10.62(s)	8.57	8.20(d)	3.63(s)	10.62	8.57	8.20
	50	7.96(s)	7.73–7.43(f)	7.63(s)	10.58(s)	8.51	8.13(d)	3.75(s)	10.58	8.51	8.13
	80	7.95(s)	^{c}	7.62(s)	10.58(s)	8.51	8.06(d)	^{d}	10.58	8.51	8.06
	100	7.98(s)	^{a}	7.65(s)	10.56(s)	8.62	8.13(d)	^{a}	10.56	8.62	8.13
PAA(Sr)	80	7.97(s)	^{c}	7.62(d)	10.58(s)	8.64	8.06(d)	^{d}	10.58	8.64	8.06
	100	7.97(s)	^{a}	7.65(d)	10.61(s)	8.64	8.09(d)	^{a}	10.61	8.64	8.09
PAA(Ba)	80	7.97(s)	^{c}	7.63(d)	10.62(s)	8.51	8.10(d)	^{d}	10.62	8.51	8.10
	100	7.98(s)	^{a}	7.65(d)	10.55(s)	8.50	8.18(d)	^{a}	10.55	8.50	8.18
PAA(Zn)	80	7.97(s)	^{c}	7.63(d)	10.56(s)	8.64	8.09(d)	^{d}	10.56	8.64	8.09
	100	8.00(s)	^{a}	7.64(d)	10.62(s)	8.64	8.10(d)	^{a}	10.62	8.64	8.10

[a] Phenyl ring b does not exist if ASA(M) is 100%.
[b] Peaks covered by that of phenyl ring b
[c] Peaks covered by that of phenyl ring c
[d] Peaks covered by that of H_2O
s, singlet; d, doublet; f, double doublets

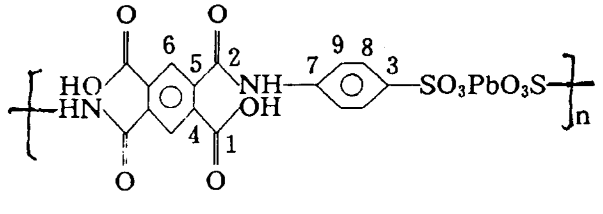
Table 4 ^{1}H n.m.r. chemical shifts (ppm) of metal-containing PIs (DMSO-d$_6$ solvent)



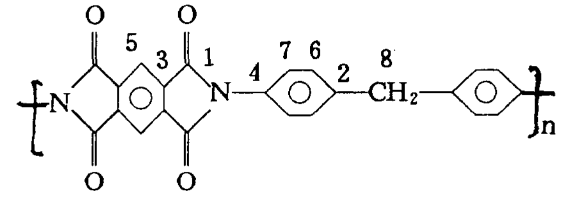
Products	ASA(M) in feed diamines (mol%)	Phenyl ring a	Phenyl ring b, c	-CH$_2$-
PI(Pb)	50	8.38(s)	7.85–7.43(f)	3.75(s)
	80	8.39(s)	7.87–7.45(f)	3.75(s)
	100	8.37(s)	7.86–7.44(f)	
PI(Sr)	80	8.42(s)	7.83–7.43(f)	[a]
	100	8.36(s)	7.81–7.36(f)	
PI(Zn)	80	8.38(s)	7.81–7.49(f)	[a]
	100	8.34(s)	7.83–7.40(f)	
PI(Ba)	80	8.37(s)	7.82–7.41(f)	[a]
	100	8.38(s)	7.84–7.38(f)	

s, singlet; f, double doublets.

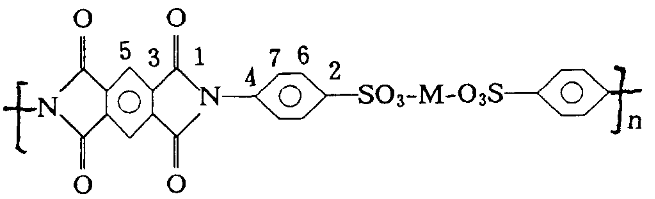
[a] Peaks covered by that of H_2O



Scheme 2



Scheme 3



Scheme 4

broader double doublets are due to the partial overlap of peaks given by the phenyl ring protons of MDA and ASA(Pb) that have been imidized. Thus we can conclude that the desired polyimide is obtained. The chemical shifts of other metal-containing poly(amic acid) salts and polyimides are summarized in *Tables 3* and *4*; note that metal-containing PIs in which the molar ratio of ASA(M) is in the feed diamines <50% are not charac-terized by ^{1}H n.m.r., due to their insolubility even in polar solvents.

The metal-containing poly(amic acid)s, the parent polyimide (i.e. that prepared from PMDA and MDA) and the metal-containing polyimides were also characterized by solid-state ^{13}C n.m.r. (1) The spectrum of PAA(Pb) [ASA(Pb) is 100% in feed diamines] may be assigned as follows (see *Scheme 2* for labelling sequence of C atoms): δ (ppm) 166.8 (C1), 166.0 (C2), 143.0 (C3), 139.6 (C4), 139.0 (C5), 132.5 (C6), 128.5 (C7), 126.3 (C8), 118.9 (C9). (2) For the parent polyimide (see *Scheme 3*): δ (ppm)166.0 (C1), 141.4 (shoulder) (C2), 137.8 (C3), 132.0 (C4), 130 (C5), 127 (shoulder) (C6), 119.5 (C7) 41.2 (C8). (3) For metal-containing polyimides in which ASA(M) is 100 mol% in the feed diamines (see *Scheme 4*), assignments (δ, ppm) can be made as follows.

M = Pb: 165.4 (C1), 145.1 (C2), 138.3 (C3), 133.0 (C4), 130.0 (C5), 127.9 (C6), 116.4 (C7);
M = Zn: 166.0 (C1), 145.1 (C2), 137.8 (C3), 133.1 (C4), 130.0 (C5), 127.4 (C6), 116.9 (C7);
M = Sr: 164.9 (C1), 143.5 (C2), 138.3 (C3), 133.1 (C4), 130.0 (C5), 127.9 (C6), 116.4 (C7).

Solution viscosity of metal-containing poly(amic acid)s

The viscosity of metal-containing PAAs in DMAc was investigated. *Figure 3* shows the relationship between the

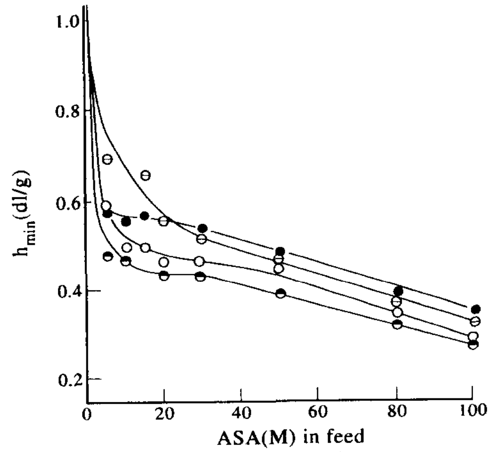


Figure 3 Plot of viscosity *versus* content of ASA(M): ●, PAA(Ba); ⊖, PAA(Zn); ○, PAA(Pb); ◓, PAA(Sr)

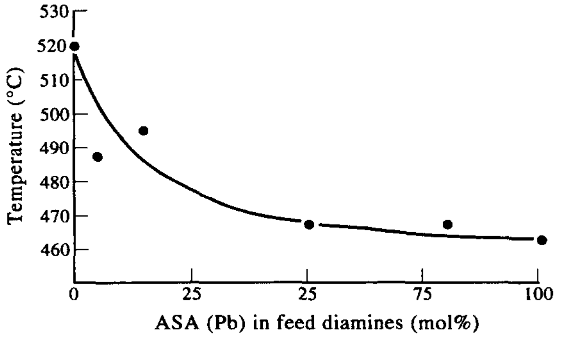


Figure 4 Initial decomposition temperature *versus* content of ASA(Pb) in feed diamines

inherent viscosity of the poly(amic acid) salts and metal content of the polymer, where it may be observed that the inherent viscosity decreases markedly even when very little metal is introduced. The inherent viscosity decreased greatly when the ASA(M) content in the feed diamines was increased, indicating that, in a typical polar solvent, the $-SO_3-M-O_3S-$ links (which have partial ionic links in the main chain of the polymer) dissociated into low molecular weight polymer that was terminated by sulfonate. In addition, the higher the content of ASA(M) in the feed diamines, the lower the polymer fragment molecular weight.

Thermal properties of polyimides

Compared with the parent polyimide, the t.g.a.–d.t.a. curves of all metal-containing polyimides show decreased thermo-oxidative stability. The t.g.a. curves indicate that the initial decomposition temperature decreases on introducing the metal into the polyimide. Similar behaviour can be seen from the d.t.a. curves, with an exothermic peak, which is considered to be due to degradation, occurring via oxidation.

Figure 4 shows the relationship between the initial decomposition temperature and the metal content of the polyimide. The initial decomposition temperature decreases markedly as the ASA(Pb) content increases, even when very little metal is introduced. The decrease is slower, however, when the ASA(Pb) content is >20 mol% in the feed diamines.

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