Synthesis and Characterization of Polyimides from Divalent Metal Salts of p-Aminobenzoic Acid

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SYNOPSIS

Some 50 metal-containing polyimides with the metallic elements (Mg, Ca, Sr, Ba, Pb, Co, Ni) in the main chain were prepared first by reacting pyromellitic dianhydride (PMDA) with the mixture of divalent metal salts of p-aminobenzoic acid [ABA(M)] and 4, 4'-diaminodiphenylmethane (MDA) to form polyamic acid salts, and then the desired polyimides were obtained in high yield by separating the polyamic acid salts from the solvent and heating them under the imidization conditions. The structures of the samples were characterized by ^{1}H-NMR and IR, and the thermal properties of polyimides were measured by TG–DTA. It was found that the thermooxidative stability of polyimides decreased as a small amount of a metal element was introduced, and the stability of polymer varied slightly or tends to constancy as the metal content increased to a certain degree. In addition, the inherent viscosity of the polyamic acid salt solutions also decreased markedly with the increase of the metal content. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Metal-containing polyimides[1–3] have been investigated, and these polymers were generally prepared by the addition of inorganic salts or metal complexes, such as Al(acac)$_3$, AlCl$_3$, CaCl$_2$, EuCl$_3$, and CoAc$_2$, to the polyamic acid, followed by thermal conversion. The polymers prepared using divalent metal salts of p-aminobenzoic acid [ABA(M)] have not been reported so far as the authors are aware. The ABA(M) salts which contain an ionic bond formed between —COO$^-$ and M^{2+} and two terminal amino groups have been proposed to be used as additives[4,5] for rubbers and as sunscreen materials.[6] Also, polyureas[7,8] prepared by using ABA(M) were investigated by Matsuda and Takechi.

To study the application of ABA(M) in the synthesis of polyimide and to determine the effect of metal elements on the structure, viscosity, and thermal properties of a polymer, a series of novel metal-containing polyimides with the metallic elements in the main chain were prepared by reacting ABA(M) salts with dianhydride according to a two-step polycondensation reaction: The first step is to react pyromellitic dianhydride with the mixture of ABA(M) and MDA to form polyamic acid salts, and the second step is to thermally convert them to the desired polyimides. The polymers were characterized and their properties were investigated.

EXPERIMENTAL

Materials and Instruments

N,N'-Dimethyl formamide (DMF) and 4,4'-diaminodiphenyl-methane (MDA) were of analytical grade. Pyromellitic dianhydride (PMDA) was a guarantee reagent. The divalent metal salts of p-aminobenzoic acids [ABA(M)] were synthesized by the author as described elsewhere.[7]

Infrared spectra were recorded with a 7400 instrument. ^{1}H-NMR spectra were measured by using an FT-80A spectrometer. Viscosities were deter-

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mined at 25°C with a SanSe viscometer. TG–DTA were determined by a PCT-1 analyzer at a heating rate of 10°C min^{-1} in air.

Synthesis of Metal-containing Polyimides

Into a flask equipped with a mechanical stirrer, thermometer, and addition funnel, 9.0 mmol diamines [ABA(M) + MDA] dissolved in DMF were placed. The solution was kept at ambient temperature and 9.2 mmol PMDA powder was gradually added to the solution with stirring three times during 30 min. After the reaction lasting 4 h, the resulting metal-containing polyamic acid salts were obtained. After an aliquot of the reaction solution was volatilized at room temperature for 10 h and then at 100°C *in vacuo* for 3 h, the polyamic acid salts film was obtained. The film was heated *in vacuo* at 180, 220, and 250°C for 30 min, respectively, and then at 300°C for 2.5 h to dehydrate and the metal-containing polyimide film was obtained. The remaining solution was precipitated by adding ethanol and a water solution (by volume 1 : 1). After the precipitation was washed with ethanol and the water solution, dried at 60°C *in vacuo*, and then ground into powder, the polyamic acid powder was obtained. The powder was imidized in the imidization conditions as described above and the polyimide powder was obtained.

RESULTS AND DISCUSSION

Synthesis of Metal-containing Polyimides

Polyimides have been widely used due to their many excellent properties, especially their high heat resistance, and their modification has been investigated. Typically, polyimides are industrially prepared according to a "solution polymerization" process which is generally conducted by reacting an aromatic dianhydride with an organic diamine in an inert solvent. First, polyamic acid salts (PAA) are obtained, and then the polyamic acid salts are converted into the desired polyimides (PI) under imidization conditions. In the present work, a series of novel polymers, metal-containing polyimides containing ionic links in the main chain based on ABA(M), were synthesized according to the following schemes:

PAA(M)

PI(M)

M = Mg, Ca, Sr, Ba, Pb, Co, Ni
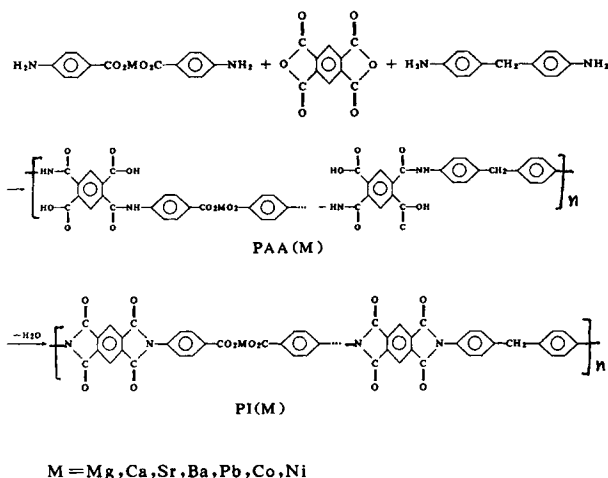
The polyamic acid solution obtained with an ABA(M) content of 0.5, 10, 15, 20, 25, 30, 35, 40, and 50 mol % in feed diamines was homogeneous in DMF. However, with increase of the content of ABA(M) in the feed diamines, the polyamic acid solution obtained became heterogeneous. Therefore, polymers with higher ABA(M) content were not synthesized, and only some 50 polymers were prepared.

Table I summarizes the wavenumbers of the IR spectra of the representative of metal-containing polymers and the parent polymers. The spectra of the polyamic acids show bands at 1710 and 3000–2700 cm^{-1} (—COOH), and the bands at 3360 cm^{-1} (ν_{NH}), 1640 cm^{-1} (C=O of the amide), 1540 cm^{-1} (ν_{C-N} and δ_{NH}), and 1310 cm^{-1} (ν_{C-N}) are consistent with the expected structure of polyamic acid salts. Also, the bands at 1560 and 1420 cm^{-1} are the characteristic bands of the carboxylate group. After imidization, the samples gave similar spectra, in which the absorption bands of carboxyl disappeared, and at the same time, the strong absorption bands which appeared at 1780 cm^{-1} (imide I, symmetric carbonyl stretching), 1720 cm^{-1} (asymmetric imide carbonyl stretching), 1380 cm^{-1} (imide II, imide ring vibration, axial), 1110 cm^{-1} (imide III, imide ring vibration, transverse), and 720 cm^{-1} (imide IV, imide ring vibration, out-of-plane) establish the present of imide rings in the structure of the polymer synthesized. This suggests that polyimides were obtained. Meanwhile, the bonds at 1560 and 1420 cm^{-1}, which are the characteristic bands of the carboxylate group, suggest that a static ionic bond between —COO$^-$ and M^{2+} exists. In addition, very little variation with different metals in the spectra can be found. However, the intensity of bands of the carboxylate group at about 1550 and 1420 cm^{-1} increases with increasing ABA(M) content in the feed diamines. According

Table I   Wavenumbers of IR of PAA(M) (cm^{-1})

| Sample	a	—COOH			—CONH—			—CO$_2^-$		Phenyl Ring	
PAA(0)	0	1700	3080–2700	1640	1540	1300	3360	—	—	1595	1500
PAA(Ca)	10	1710	3060–2460	1660	1515	1320	3400	1550	1420	1610	1510
PAA(Ca)	15	1710	3040–2520	1680	1520	1330	3300	1560	1420	1595	1510
PAA(Ca)	17	1710	3100–2540	1680	1535	1320	3360	1550	1420	1610	1510
PAA(Ca)	19	1710	3040–2700	1680	1520	1325	3300	1550	1420	1610	1510
PAA(Ca)	20	1710	3000–2520	1680	1520	1320	3340	1550	1425	1610	1510
PAA(Ca)	22	1710	3050–2460	1670	1520	1320	3340	1560	1415	1610	1510
PAA(Ca)	24	1710	3000–2520	1660	1530	1320	3460	1560	1415	1610	1510
PAA(Ca)	27	1710	2980–2460	1650	1540	1325	3460	1560	1430	1600	1510
PAA(Ca)	30	1710	2960–2500	1650	1545	1325	3460	1560	1420	1600	1510
PAA(Ca)	50	1710	2860–2480	1660	1520	1320	3420	1560	1420	1610	1510
PAA(Mg)	10	1710	2800–2520	1650	1530	1310	3340	1550	1410	1600	1510
PAA(Mg)	50	1710	2860–2640	1650	1540	1325	3320	1560	1420	1600	1510
PAA(Mg)	85	1710	2860–2680	1650	1540	1320	3350	1560	1410	1600	1500
PAA(Sr)	10	1710	3000–2700	1650	1535	1320	3250	1560	1425	1610	1490
PAA(Sr)	50	1710	2960–2620	1650	1530	1330	3300	1560	1420	1610	1510
PAA(Ba)	10	1710	2960–2620	1650	1535	1320	3300	1550	1430	1600	1510
PAA(Ba)	50	1710	2880–2640	1660	1530	1330	3400	1560	1430	1610	1510
PAA(Pb)	10	1710	2900–2660	1650	1530	1320	3340	1550	1410	1600	1510
PAA(Pb)	30	1710	2960–2560	1650	1530	1315	3300	1560	1410	1600	1510
PAA(Co)	10	1710	2860–2480	1650	1530	1320	3340	1550	1420	1600	1510
PAA(Co)	30	1710	2840–2500	1650	1535	1320	3320	1560	1410	1600	1510
PAA(Ni)	10	1710	2940–2620	1650	1530	1315	3320	1550	1410	1600	1510
PAA(Ni)	30	1710	2960–2600	1650	1530	1320	3340	1560	1410	1600	1510

ª ABA (M) in feed diamines (mol %).

to the results, it can be concluded that the metal-containing polyamic acid salts and polyimides with a metallic element in the main chain were obtained.

Table II gives the ^{1}H-NMR spectra of the parent polyamic acid and the representative of metal-containing polyamic acids. DMSO-d_6 was used as the solvent. As can be seen in Table II, the protons of the —COOH give the peak at about 10.85–10.20 ppm; the protons of the amide groups give the tetrad at 8.90–8.20 ppm; the singlet at 7.97–7.92 ppm is attributed to the phenyl ring protons of the PMDA that has been amidized; the protons of the phenyl ring
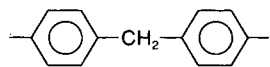
give double doublets at 7.68–7.12 ppm; the aromatic protons of
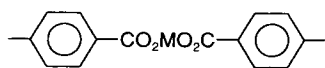
show the singlet at 7.90–7.80 ppm, which may be covered as the ABA(M) content is less than 50 mol

%; the broad peaks at about 4.0 ppm are due to H$_2$O and amide groups; and the protons of —CH$_2$— show a peak at 3.72 ppm. It also can be found that the ^{1}H-NMR spectra of polyamic acids have little difference in shape, but the chemical shifts variate to a certain extent. As expected, the ^{1}H-NMR spectra of Ni-containing and Co-containing polyamic acids (PAA-Ni and PAA-Co) show two broad peaks when ABA(M) (M = Ni, Co) content is over 25 mol % in feed diamines due to their cis-magnetizability. Owing to the insolubility, polyimides could not be determined by ^{1}H-NMR.

Solution Viscosities of Metal-containing Polyamic Acids

Figure 1 shows the plots of inherent viscosity in DMF vs. the metal content of the polyamic acids. The inherent viscosity decreased markedly as the ABA(M) content increased. This indicates that in a typical polar solvent such as DMF the —CO$_2$MO$_2$C— partially ionic links in the polymer main chain dissociated into low molecular weight polymers that were terminated by carboxyl. A sim-

Table II ^{1}H-NMR Results of PAA (M) (ppm)

Sample	a	Phenyl Ring a	Phenyl Ring b	Phenyl Ring c	—COOH	—CONH—	—CH$_2$—
PAA (0)	0	7.93 (s)	7.66–7.14 (dd)	—	10.43 (s)	8.47–8.21 (td)	3.72 (s)
PAA (Ca)	10	7.93 (s)	7.65–7.13 (dd)	b	10.46 (s)	8.47–8.19 (td)	3.72 (s)
PAA (Ca)	20	7.92 (s)	7.63–7.12 (dd)	b	10.50 (s)	8.75–8.27 (td)	3.74 (s)
PAA (Ca)	30	7.93 (s)	7.66–7.12 (dd)	b	10.55 (s)	8.84–8.29 (td)	3.74 (s)
PAA (Mg)	10	7.93 (s)	7.66–7.14 (dd)	b	10.44 (s)	8.54–8.21 (td)	3.72 (s)
PAA (Mg)	50	7.95 (s)	7.68–7.14 (dd)	7.88 (s)	10.20 (s)	8.89–8.30 (td)	3.72 (s)
PAA (Mg)	85	8.03 (s)	7.68–7.12 (dd)	7.89 (s)	10.84 (s)	8.92–8.27 (td)	3.72 (s)
PAA (Sr)	10	7.92 (s)	7.65–7.14 (dd)	b	10.45 (s)	8.58–8.29 (td)	3.72 (s)
PAA (Sr)	50	7.93 (s)	7.66–7.12 (dd)	7.89 (s)	10.85 (s)	8.54–8.27 (td)	3.72 (s)
PAA (Ba)	10	7.94 (s)	7.67–7.15 (dd)	b	10.44 (s)	8.43–8.28 (td)	3.73 (s)
PAA (Ba)	50	7.93 (s)	7.67–7.13 (dd)	7.84 (s)	10.53 (s)	8.54–8.27 (td)	3.72 (s)
PAA (Pb)	10	7.92 (s)	7.65–7.12 (dd)	b	10.53 (s)	8.52–8.26 (td)	3.72 (s)
PAA (Pb)	30	7.92 (s)	7.63–7.10 (dd)	b	10.75 (s)	8.53–8.23 (td)	3.72 (s)
PAA (Co)	10	7.95 (s)	7.63–7.05 (dd)	b	10.85 (s)	8.54–8.27 (td)	3.73 (s)
PAA (Co)	30	7.96 (s)	7.51–6.91 (dd)	b	Δ	Δ	3.72 (s)
PAA (Ni)	10	7.97 (s)	7.65–7.14 (dd)	b	10.50 (s)	8.45–8.29 (td)	3.72 (s)

Δ, covered by the broader peak; s, singlet; dd, double doublet; td, tetrad. PAA–Ni (30%) has two broader peaks at 7.58 ppm and 7.16 ppm.

^{a} ABA (M) in feed diamines (mol %).

^{b} Covered by that of phenyl ring b.

ilar tendency has been observed for metal-containing polyureas.[7-9]

Thermal Properties

All TG curves of polyamic acids have three weight-loss processes. As shown in Table III, the first slight loss that occurs below 100°C is due to the volatization of moisture (not listed in Table III). The second slight weight loss at 120–290°C is considered to be due to the dehydration in the imidization process and the volatilization of the remaining DMF. The imidization temperature range varied with the metals and the content of metal and all are below 300°C. As compared with the parent polyamic acid, alkaline earth metal-containing polyamic acids have little effect on the imidization temperature range, but a marked decrease in imidization temperature was observed in transition metal-containing polyamic acids. The plateau observed above ca. 300°C corresponds to the formation of polyimides, and the third marked weight loss is considered to be due to
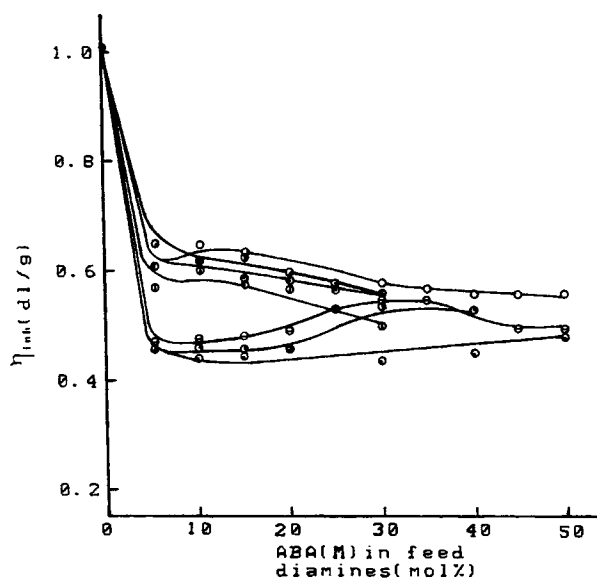

Figure 1 Plot of η_{inh} vs content of ABA (M): (O) PAA–Ca; (◉) PAA–Pb; (◉) PAA–Ni; (⊕) PAA–Co; (⊖) PAA–Mg; (◐) PAA–Sr; (◑) PAA–Ba.

Table III   TG-DTA Data of PAA(_M_) (°C)

Sample	TG		DTA			
	T_1	T_2	T_3	T_4	T_5	
PAA(0)	171.8–246.4	520.0	196.8	402.8	578.8	
PAA–Ca(10%)	178–267.5	443.8	189.0	414.0	508.6	
PAA–Ca(20%)	123.0–185.0	443.8	166.2	402.2	508.6	
PAA–Ca(25%)	184.2–246.2	440.2	188.8	411.2	508.2	
PAA–Ca(30%)	165.4–258.2	439.2	196.8	426.0	508.2	
PAA–Ca(35%)	134.2–288.8	414.0	234.0	390.2	473.0	503.0
PAA–Ca(40%)	209.2–276.8	384.5	238.2	378.5	484.8	496.5
PAA–Ca(45%)	211.2–273.2	385.0	258.5	371.5	466.0	508.2
PAA–Mg(5%)	196.8–246.2	450.2	196.2	399.5	573.0	
PAA–Mg(10%)	190.5–246.2	449.8	196.8	402.2	561.0	
PAA–Mg(20%)	184.2–258.5	447.8	232.0	407.2	543.5	
PAA–Mg(30%)	141.8–258.5	443.8	—	426.0	520.0	
PAA–Mg(40%)	153.0–271.4	447.2	—	414.0	508.2	
PAA–Mg(45%)	137.0–247.0	447.2	—	437.6	519.0	
PAA–Mg(50%)	203.02–294.8	449.8	253.4	437.8	525.8	
PAA–Sr(5%)	171.8–237.2	432.0	178.0	413.2	555.0	
PAA–Sr(10%)	184.8–234.0	432.0	185.8	402.2	528.0	543.5
PAA–Sr(20%)	171.8–246.2	426.0	184.2	395.0	514.0	549.2
PAA–Sr(30%)	109.8–234.6	443.8	—	414.6	496.5	
PAA–Sr(40%)	165.5–252.5	437.8	—	414.0	496.5	
PAA–Sr(50%)	159.2–234.0	437.8	—	—	484.8	416.5
PAA–Ba(5%)	165.5–226.5	426.0	185.0	407.0	549.2	555.0
PAA–Ba(10%)	174.2–234.0	426.0	184.0	410.0	520.0	
PAA–Ba(20%)	159.2–258.5	414.0	190.5	414.0	508.2	525.6
PAA–Ba(30%)	146.8–282.0	408.2	—	408.2	496.5	
PAA–Ba(40%)	159.2–286.8	414.0	—	408.2	496.5	
PAA–Ba(50%)	164.2–270.8	426.0	236.5	—	449.8	461.4
PAA–Pb(5%)	159.2–221.8	420.0	182.4	—	450.2	
PAA–Pb(10%)	159.2–209.2	414.0	184.2	—	426.0	
PAA–Pb(20%)	140.5–234.0	378.5	199.0	378.5	414.0	
PAA–Pb(30%)	159.2–234.0	354.8	203.0	366.8	402.2	458.0
PAA–Co(5%)	159.2–246.2	437.8	187.6	402.2	510.0	
PAA–Co(10%)	159.2–246.2	426.0	191.0	429.2	496.5	
PAA–Co(20%)	146.8–246.2	414.0	184.2	—	484.2	
PAA–Co(30%)	159.2–258.8	414.0	196.8	307.0	461.4	
PAA–Ni(5%)	159.2–234.4	425.8	216.8	402.2	531.8	
PAA–Ni(10%)	153.0–246.2	395.2	234.0	402.2	484.8	
PAA–Ni(20%)	184.0–282.8	392.5	234.0	402.2	449.8	
PAA–Ni(30%)	194.0–276.8	390.2	243.6	—	437.2	

T_1, temperature of second weight loss; T_2 temperature of third weight loss; T_3, temperature of the small endothermic peak in imidization; T_4, temperature of the small exothermic peak; and T_5, temperature of the exothermic peaks.

degradations occurring via oxidation. The DTA curves show two small endothermic peaks below 250°C that are due to the volatilization of moisture and imidization in polyamic acids, and the major exothermic peak above 450°C corresponds to the degradations occurring via oxidation. For polyimides, the TG curves give one weight loss due to degradation; meanwhile, only one exothermic peak appeared in the DTA curves.

Figure 2 gives the relationships between the initial decomposition temperature of the polyimides and the metal content in the polyimides. It can be observed that the thermooxidative stability decreases as the metals are introduced into the polymers. The
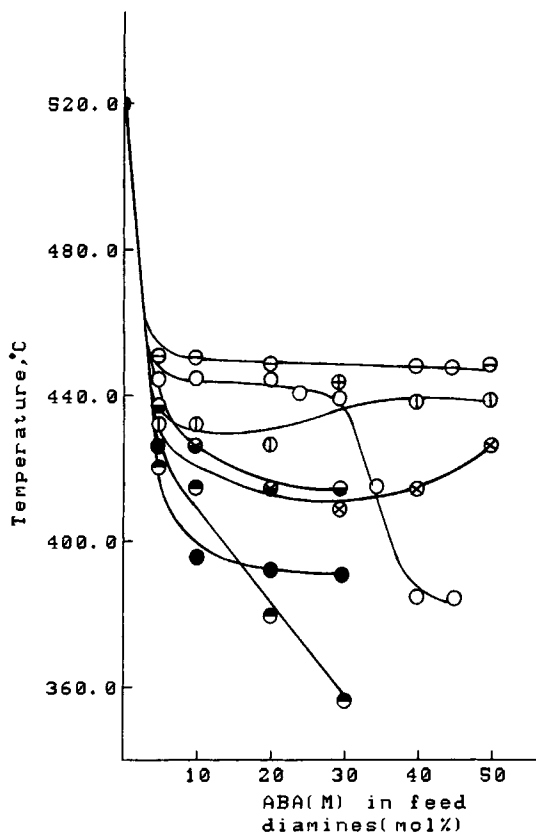
Figure 2   Content of ABA(M) vs. decomposition temperature of PI(M). (O) PI–Ca; (⊖) PI–Mg; (Φ) PI–Sr; (⊗) PI–Ba; (◖) PI–Co; (●) PI–Ni; (◑) PI–Pb.

initial degradation temperature (T_d) decreases markedly as the ABA(M) content increases even when very little metal is introduced. In addition, as the ABA(M) content increases to a certain degree, the T_d of Mg-, Co-, and Ni-containing polyimides tend toward a constant, the T_d of Ba- and Sr-con-

taining polyimides varied slightly, and the tendency of the T_d of Ca-containing polyimides was different from the others. Perhaps this behavior was caused by the decreasing of the molecular weight as the metal content increases.

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