Preparation and Characterization of Polyureas from Divalent Metal (Ba, Sr, Pb, Zn) Salts of Sulfanilic Acid

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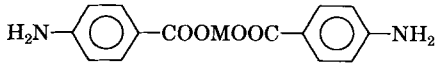
SYNOPSIS

Metal-containing polyureas containing ionic linkages in the main chain can be obtained by the polyaddition reactions of 2,4-tolylene diisocyanate with mixtures of divalent metal salts of sulfanilic acid (*p*-aniline sulfonic acid [ASA]) and 4,4′-diaminodiphenylmethane. Ba, Zn, Pb, and Sr were used as divalent metals, and their structures were characterized by ^{1}H-NMR, ^{13}C-NMR, and IR. The polyureas were obtained with ASA(M) up to 100% in feed diamines and they were all soluble in DMF and DMSO. The inherent viscosity of the polyureas decreased markedly with an increase in metal content. The thermal properties of these polyureas were also investigated by DSC and TG. It was found that introducing the metal into the polyurea increased the thermal stability. © 1993 John Wiley & Sons, Inc.

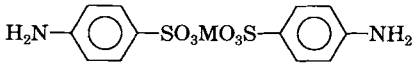
INTRODUCTION

Metal-containing diamines have many uses.[1] For example, divalent metal salts of *p*-aminobenzonic acid (ABA):

(M = Ca, Mg). The ABA(M) salts have been used as additives[2,3] for rubbers and sunscreen materials.[4] Polymers from ABA(M) were also prepared.[1,5] Large increases have been produced in the T_g of polymers by introducing metal in them.[6,7] Relatively,



has a lower decomposition temperature than does



and it is hoped that introducing the latter (ASA) may increase the thermal stability of the resulting polymers. In this paper, the metal-containing polyureas were synthesized by the polyaddition reactions of a diisocyanate with mixtures of ASA(M) and a diamine, 2,4-Tolylene diisocyanate (TDI) was used as the diisocyanate and 4,4′-diaminodiphenylmethane was used as the diamine. Attention is also paid to the preparation of polyureas from metal-containing diamine and TDI.

EXPERIMENTAL

Materials and Instrumentation

4,4′-Diaminodiphenylmethane (MDA) was of chemical pure grade. ASA, pyridine, DMF, and other solvents were of analysis pure grade and TDI was of laboratory pure grade.

Infrared spectra were recorded with a 7400 instrument; ^{13}C-NMR spectra were obtained with an XL-200. ^{1}H-NMR spectra were measured using an FT-80A spectrometer. DSC and TG were carried out with a Perkin-Elmer 7 series thermal analysis system at a heating rate of 20°C min^{-1} in N_2. Viscosities were determined at 25°C with a SanSe viscometer. For elemental analyses, C, H, and N contents were determined using a 204C elemental anal-

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ysis instrument. Metal contents were determined with the method of coordination titration with EDTA.

Preparation of ASA(M)

A mixture containing 300 mL water and 34.6 g (0.20 mol) ASA was placed into a flask fitted with a mechanical stirrer, and then 31.5 g (0.10 mol) $Ba(OH)_2 \cdot 8H_2O$ was added in one portion with stirring. The mixture was stirred at ambient temperature for 30 min and then was warmed to 60°C and kept at this temperature for 1 h with constant stirring. The white solution was filtered. To the filtrate was added a large quantity of *t*-butanol and the mixture was allowed to stand for some time. The precipitate was filtered, washed several times with *t*-butanol, and dried *in vacuo* at 80°C for 5 h and then to 150°C for an additional 2 h. A white powder was obtained.

ANAL: Calcd for $C_{12}H_{12}N_2O_6S_2Ba$: C, 29.92%; H, 2.50%; N, 5.81%; Ba, 28.51%.
Found: C, 29.61%; H, 2.44%; N, 5.79%; Ba, 27.03%.

For ASA(Sr), ASA(Zn), and ASA(Pb), the same procedure was used except that Sr(II), Zn(II), and Pb(II) oxides were used. Because a large quantity of *t*-butanol or acetone was needed to precipitate the ASA(M), we synthesized ASA(M) in the solid state. Solid ASA and divalent metal oxides (or hydroxides) were ground effectively and were mixed in a 2 : 1 molar ratio. The mixture reacted *in vacuo* for 15 h and was cooled to ambient temperature.

Synthese of Metal-containing Polyureas

Into a flask equipped with a mechanical stirrer, thermometer, and addition funnel were placed 8.08 mmol diamines [ASA(M) + MDA], 60 mL DMF, and 1.4 mL pyridine, and the diamines were dissolved. The flask was cooled to 0°C, and 8.08 mmol TDI dissolved in 10 mL DMF was added dropwise with the solution stirred over 15 min. The addition funnel was washed with 10 mL DMF. The mixture was stirred at 0°C for 1 h and then at ambient temperature for an additional 1 h. The reaction mixture was filtered and the filtrate was transferred into a large quantity of vigorously stirred acetone and the precipitate was isolated. The solid product was washed with methanol and dried *in vacuo* at 70°C.

RESULTS AND DISCUSSION

Preparation of ASA(M)

We prepared the ASA(M) diamines by two methods: One was adopted from the similar procedure of Matsuda and Takechi,[1] which involved the neutralization of ASA with MO [or $M(OH)_2$] in water. At the beginning of the reaction, ASA and MO [or $M(OH)_2$] were suspended in water with stirring. The mixture gradually became clear and homogeneous with the reaction. The products were precipitated by addition of *t*-butanol or acetone. When heated *in vacuo,* white products were obtained. The yields and elemental analyses are shown in Table I. The found values of the elemental analyses agreed well with the calculated values. The other method involved the solid reactions, and the products have been checked by IR and NMR.

As can be seen in Figure 1, the IR spectra of the ASA and ASA(Ba) diamines give different features. We can conclude that ASA existed as $^+NH_3-$ $-SO_3^-$, for it has the absorption bands at 2890–2080 cm^{-1} and 1575 and 1545 cm^{-1} (all are characteristic absorption of $-^+NH_3$). As compared with Figure 1(a), all absorption bands described above disappeared in Figure 1(b). It means that there is no $^+NH_3$ in ASA(Ba). From Figure 1(b), we can also see that the ASA(Ba) diamine has absorption bands at 3440–3370 and 1630 cm^{-1} ($-NH_2$); 1600, 1500, and 830 cm^{-1} (phenyl ring); 1165, 1035, and 695 cm^{-1} ($-SO_3$); and 1300 cm^{-1} (C—N).

Figure 2 shows the ^{1}H-NMR spectra of the ASA and ASA(Ba) diamine, as contrasted with Figure 2(a). The spectra of Figure 2(b) exhibits the absence of a chemical shift at 7.92 ppm ($^+NH_3$, can

Table I Elemental Analyses of ASA (M) (Calcd)

Products	C (%)	H (%)	N (%)	M (%)
ASA (Ba)	29.61 (29.92)	2.44 (2.50)	5.79 (5.81)	27.03 (28.51)
ASA (Sr)	32.41 (33.36)	2.81 (2.80)	6.53 (6.48)	20.20 (20.28)
ASA (Zn)	34.85 (35.17)	3.00 (2.96)	6.87 (6.84)	16.09 (15.96)
ASA (Pb)	26.21 (26.13)	2.16 (2.19)	5.09 (5.08)	37.12 (37.56)

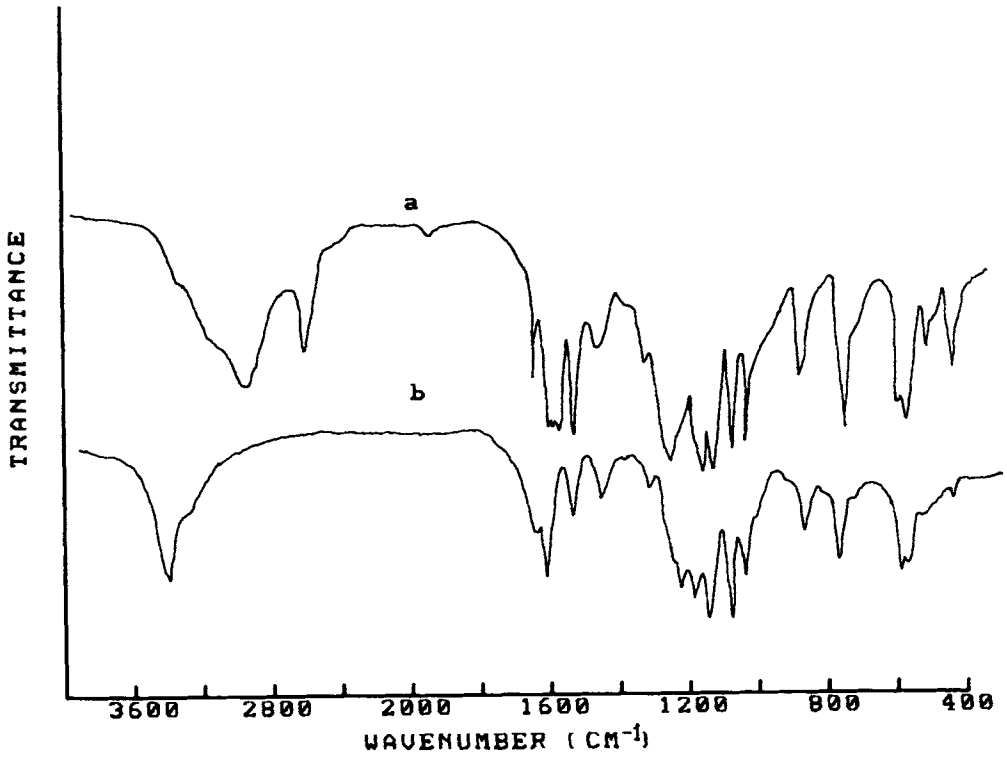
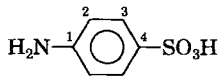


Figure 1 IR spectra of (a) ASA and (b) ASA(Ba).

be exchanged by D_2O). The chemical shifts of the phenyl ring at 7.73–7.20 ppm shifted to upfield and the chemical shift of $-NH_2$ is at 5.16 ppm (can be exchanged by D_2O).

The ^{13}C-NMR spectra of ASA and ASA(Ba) diamine was also obtained in DMSO-d_6. The chemical shifts (ppm) may be assigned to the following structures:



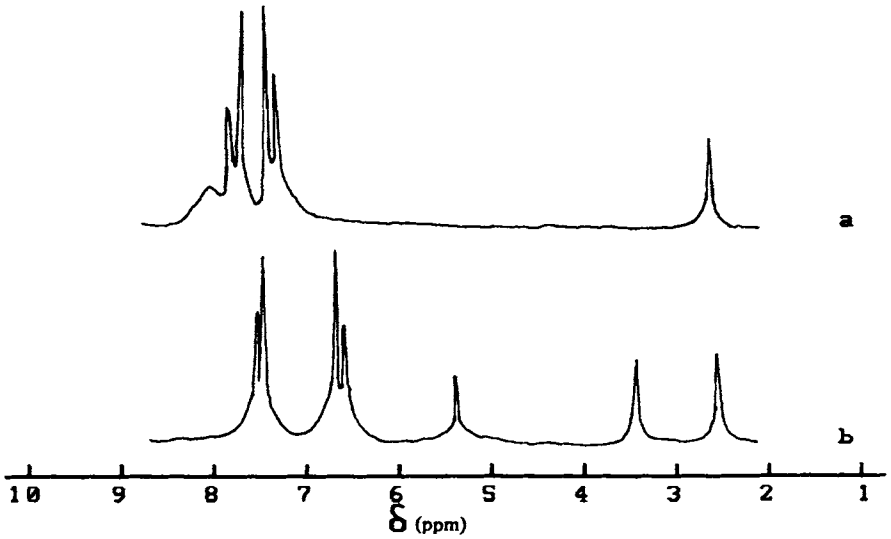


Figure 2 ^1H-NMR spectra of (a) ASA and (b) ASA(Ba) in DMSO-d_6.

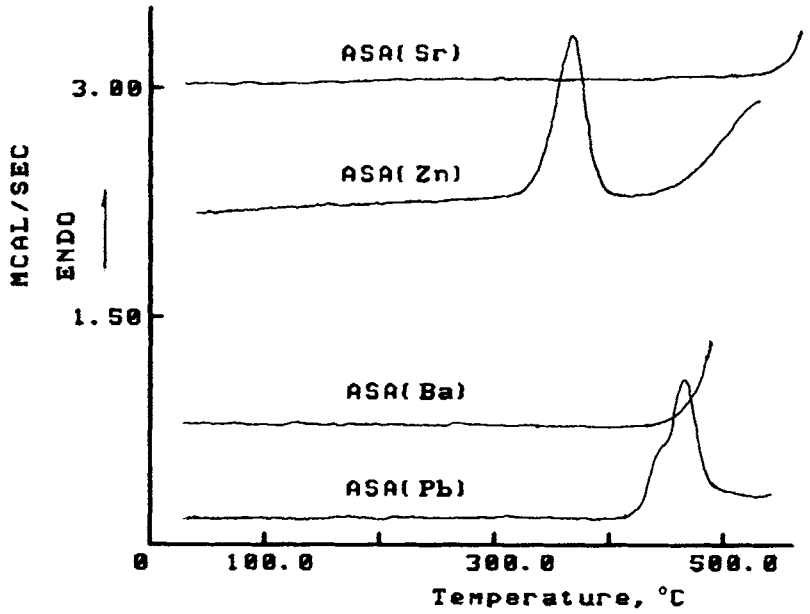
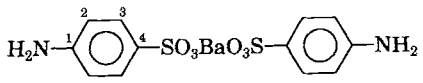


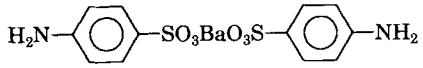
Figure 3 DSC curves of ASA(M).

(1) 150.6; (2) 116.1; (3) 128.0; and (4) 133.2 ppm, respectively;



(1) 149.2; (2) 112.2; (3) 126.8; and (4) 135.2 ppm, respectively.

Based on the elemental analysis and structure characterization described above, we conclude that ASA(Ba) diamine has the structure of



DSC curves of the ASA(M) are shown in Figure 3. From Figure 3, we find that the metal-containing ASA(M) is thermally stable in N_2 up to ca. 400°C. For other ASA(M) diamines, the same methods of characterization were used and the results are listed in Tables II and III.

Preparation of Metal-containing Polyureas

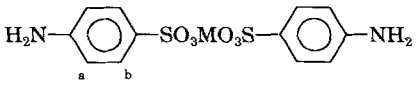
DMF was used as the solvent for the synthesis of the metal-containing polyureas in this study. In the polyaddition reaction of diisocyanate with diamines, isocyanate groups are well known to prefer to react with —NH in the polyureas produced, leading to the formation of the linkages similar to biuret and resulting in cross-linking.[8] It is also reported that cross-linked insoluble and infusible polymers were formed in the reaction of diisocyanate with diamine.[1] An earlier study showed that linear soluble polyurea also could be prepared in a polyaddition reaction of the same kind.[9]

Table IV summarizes the results of the preparation of the metal-containing polyureas by the polyaddition reactions of ASA(M)—MDA with TDI. Parent polyurea was also prepared from MDA and TDI for comparison. Matsuda and Takechi reported that the presence of pyridine allowed the

Table II Wavenumbers of IR (cm^{-1})

Products	Phenyl Ring	$—SO_2—O—$	C—N	$—NH_2$	$—^+NH_3$
ASA	1600 1500 830	1160 1035 680	1320	3440–3310 1630	1575 1545 2890–2080
ASA (Ba)	1600 1500 830	1165 1035 695	1300	3440–3300 1630	
ASA (Sr)	1600 1500 830	1165 1040 695	1300	3400–3240 1630	
ASA (Zn)	1600 1500 830	1180 1040 700	1300	3440–3300 1620	
ASA (Pb)	1600 1500 830	1180 1035 700	1300	3480–3300 1625	

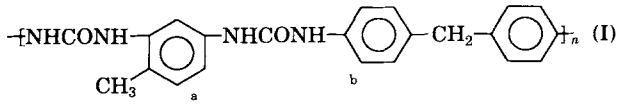
Table III Chemical Shifts of ^1H—NMR (ppm)



Products	a	b	—NH_2	—$^+NH_3$	Peak That Can Be Exchanged by D_2O
ASA	7.30 7.20	7.73 7.63		7.92	7.92
ASA(Ba)	6.50 6.40	7.36 7.26	5.16		5.16
ASA(Sr)	6.50 6.40	7.35 7.25	5.18		5.18
ASA(Zn)	6.49 6.39	7.31 7.21	5.15		5.15
ASA(Pb)	6.56 6.46	7.41 7.31	5.23		5.23

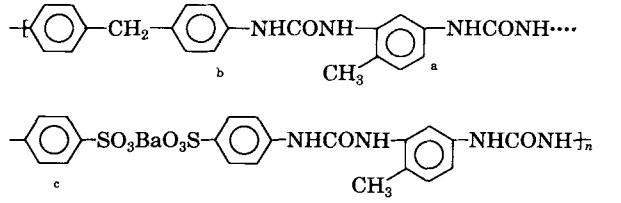
product to be obtained in high yield.[1] The addition of a small amount of pyridine resulted in giving a high yield of polyureas in our experiments.

Shown in Figure 4 are the IR spectra of the parent polyurea and the representative metal-containing polyurea. In Figure 4(a), the bands at 3360 cm^{-1} (ν_{NH}) and 1650 cm^{-1} (C=O of the urea), 1550 cm^{-1} (ν_{C-N} and δ_{NH}), 1310 cm^{-1} (ν_{C-N}), and 1595 and 1510 cm^{-1} (phenyl ring) are consistent with the expected structure as follows:



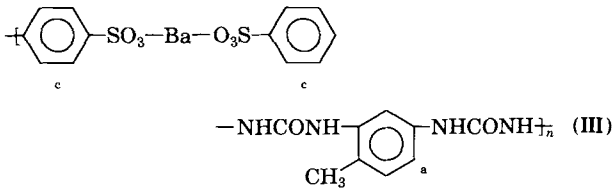
(I)

In Figure 4(b), besides the bands at 3300 (ν_{NH}), 1655 cm^{-1} (C=O of the urea), 1545 cm^{-1} (ν_{CN} and δ_{NH}), 1310 (ν_{C-N}) and 1595 and 1510 cm^{-1} (phenyl ring), there are the absorption bands at 1180, 1035, and 700 cm^{-1} (—SO_2—O—). This suggests that the metal-containing polyurea has the —SO_3—Ba—O_3S— links in the polymer backbone, and, therefore, the structure of product may be represented as follows:



(II)

Figure 4(c) shows the absorption bands of Pu·Ba(100) (no MDA in the feed diamine). The bands at 3360 cm^{-1} (ν_{NH}), 1660 cm^{-1} (C=O of the urea), 1550 cm^{-1} (ν_{NH} and δ_{NH}), and 1315 cm^{-1} (ν_{C-N}) are the characteristic absorption bands of —NHCONH—, whereas the bands at 1175, 1040, and 705 cm^{-1} may be assigned to the structure of —SO_2—O— and the bands at 1595 and 1500 cm^{-1} are contributed by the phenyl rings. On the basis of the results, it is concluded that the product has the following structure:



(III)

Figure 5 shows the ^1H-NMR spectra of the parent polyurea and the representative metal-containing polyureas. DMSO-d_6 was used as the solvent.

From Figure 5(a), the parent polyurea (structure I) exhibits chemical shifts at 8.93 and 8.53 ppm (amide linkage, can be exchanged by D_2O), 7.93 ppm (phenyl ring of a), 7.36 and 7.04 ppm (phenyl ring of b), 3.79 ppm (methylene group), and 2.16 ppm (methyl group).

Figure 5(b) shows the chemical shifts of Pu·Ba(50) [structure (II)] at 9.07 and 8.75 ppm (amide linkage, can be exchanged by D_2O), 7.95–7.63 ppm (phenyl ring of a), 7.49–7.08 ppm (phenyl ring of b), 7.55 ppm (phenyl ring of a), 3.75 ppm (methylene group), and 2.20 ppm (methyl group).

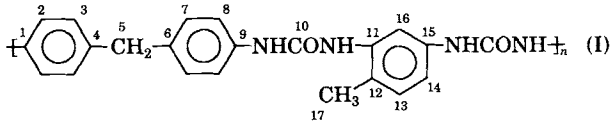
Figure 5(c) shows the chemical shifts of Pu·Ba(100) [structure (III)] at 9.13 and 8.74 ppm (amide linkage, can be exchanged by D_2O), 7.94–7.49 ppm (phenyl ring of a), 7.49 ppm (phenyl ring of c), and 2.18 ppm (methyl group).

The ^{13}C-NMR spectra of the parent polyurea and

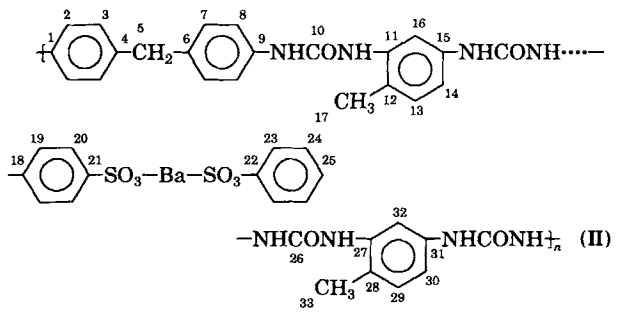
Table IV Properties of Polyureas from ASA(M)—MDA with TDI

Polyurea Code	ASA(M) in Feed Diamine (mol %)	Color	Inherent Viscosity (dL/g)
Pu (0)	0	White	0.60
Pu·Ba (5)	5	White	0.40
Pu·Ba (10)	10	White	0.31
Pu·Ba (15)	15	White	0.24
Pu·Ba (25)	25	White	0.18
Pu·Ba (85)	85	Slightly yellow	0.05
Pu·Ba (100)	100	White	0.09
Pu·Sr (5)	5	Slightly red	0.41
Pu·Sr (15)	15	Slightly red	0.21
Pu·Sr (37)	37	White	0.11
Pu·Sr (77)	77	Slightly yellow	0.04
Pu·Sr (100)	100	White	0.20
Pu·Zn (5)	5	White	0.40
Pu·Zn (10)	10	White	0.51
Pu·Zn (15)	15	White	0.19
Pu·Zn (50)	50	White	0.12
Pu·Zn (85)	85	Slightly yellow	0.09
Pu·Zn (100)	100	Slightly yellow	0.19
Pu·Pb (25)	25	White	0.30

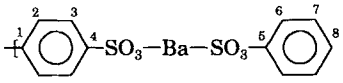
the representative metal-containing polyureas were also obtained in DMSO-d_6. The chemical shift at 152 ppm of the polyurea corresponds to the urea linkage.[1] The chemical shifts (ppm) can be assigned as follows:

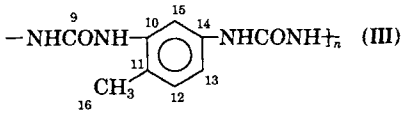


(1) 137.9; (2) 118.7; (3) 129.1; (4) 137.7; (5) 40.0; (6) 137.7; (7) 129.1; (8) 118.7; (9) 137.9; (10) 152.3; (11) 135.8; (12) 120.2; (13) 130.7; (14) 112.4; (15) 135.0; (16) 110.5; (17) 17.1;



(1) 137.6; (2) 118.7; (3) 128.9; (4) 137.6; (5) 40.0; (6) 137.6; (7) 128.9; (8) 118.7; (9) 137.6; (10) 152.4; (11) 134.8; (12) 120.7; (13) 130.2; (14) 112.5; (15) 134.8; (16) 110.9; (17) 17.4; (18) 140.9, 140.3 (resulting from *cis–trans*-isomer); (19) 116.8; (20) 126.4; (21) 137.6; (22) 137.6; (23) 126.4; (24) 116.8; (25) 140.8, 140.3; (26) 152.4; (27) 134.8; (28) 120.7; (29) 130.2; (30) 112.5; (31) 134.8; (32) 110.9; (33) 17.4;





(1) 140.6, 140.8 (resulting from *cis*–trans-isomer); (2) 116.9; (3) 126.4; (4) 137.8, 137.4 (resulted from partial dissociation); (5) 137.8, 137.4; (6) 126.4; (7) 116.9; (8) 140.6, 140.8; (9) 152.4; (10) 136.5; (11) 121.1; (12) 130.2; (13) 112.3; (14) 136.5; (15) 110.5; (16) 17.5.

We can see that the chemical shifts of the urea linkages are 152.3 ppm in Pu(0) [structure (**I**)], 152.4 ppm in Pu·Ba(50%) [structure (**II**)], and 152.4 ppm in Pu·Ba (100%) [structure (**III**)]. We conclude that the conclusions obtained above are correct.

The characterization results of other metal-containing polyureas are listed in Tables V and VI.

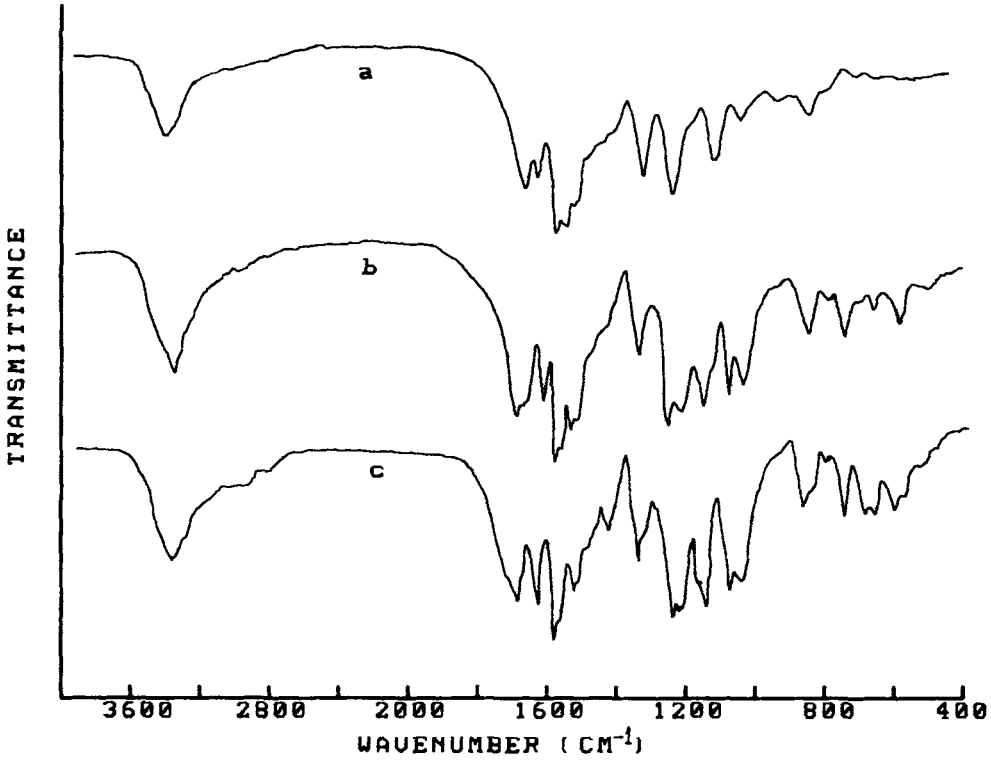


Figure 4 IR spectra of (a) Pu(I), (b) Pu(II), and (c) Pu(III).

Determination of Solution Viscosities

The polyureas prepared with ASA(M) content in feed diamines up to 100% were soluble in DMF and DMSO, and the viscosity behavior of metal-containing polyureas in DMF was investigated.

Figure 6 shows the plot of inherent viscosity in DMF vs. metal content of the polyureas. The inherent viscosity of the parent polyurea is much higher than those of the metal-containing polyureas. The inherent viscosity decreased markedly as the ASA(M) content increased. This indicates that in

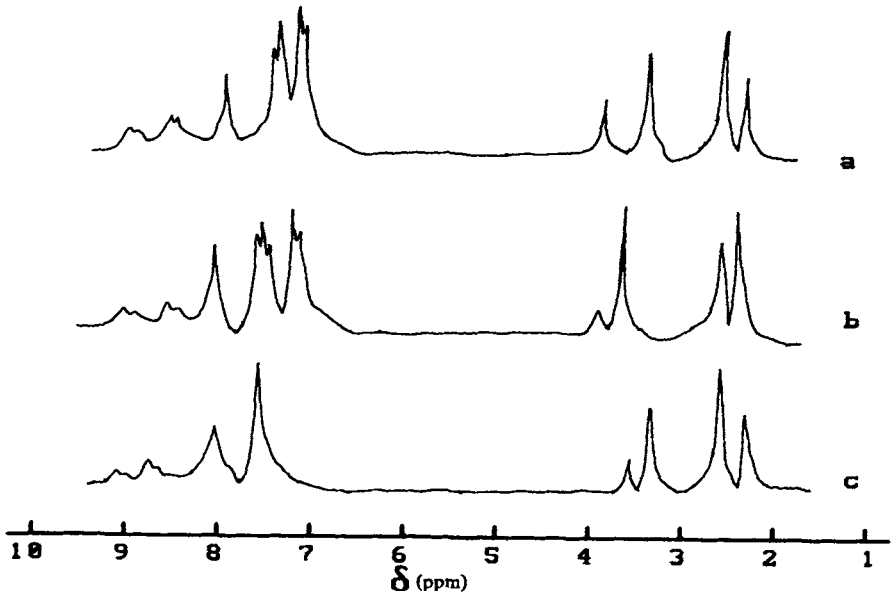
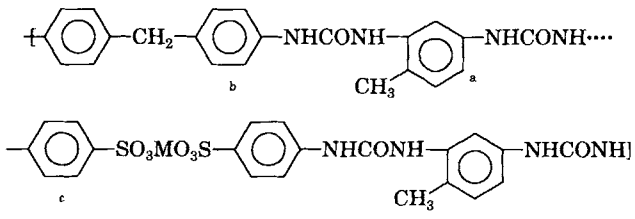


Figure 5 ^{1}H-NMR spectra of (a) Pu(I), (b) Pu(II), and (c) Pu(III) in DMSO-d_6.

Table V Wavenumbers of IR of Metal-containing Polyureas (cm^{-1})

Products	ASA (M) in Feed Diamine (mol %)	—NHCONH—	—SO_2—O—	Phenyl Ring
Pu (0)	0	1650 1550 1310 3360		1595 1510
Pu·Ba (5)	5	1650 1545 1305 3280	1175 1030 690	1595 1500
Pu·Ba (10)	10	1650 1545 1310 3320	1180 1030 695	1595 1510
Pu·Ba (15)	15	1650 1545 1305 3280	1180 1030 690	1595 1500
Pu·Ba (25)	25	1650 1545 1310 3320	1180 1030 700	1595 1510
Pu·Ba (50)	50	1655 1545 1310 3300	1180 1035 700	1585 1510
Pu·Ba (85)	85	1660 1545 1315 3360	1175 1030 700	1595 1500
Pu·Ba (100)	100	1660 1550 1315 3360	1175 1040 705	1595 1500
Pu·Sr (5)	5	1655 1545 1310 3380	1175 1030 700	1600 1510
Pu·Sr (37)	37	1655 1545 1310 3320	1180 1030 700	1595 1510
Pu·Sr (100)	100	1660 1545 1310 3360	1180 1030 700	1595 1500
Pu·Zn (5)	5	1650 1545 1310 3280	1180 1030 695	1595 1510
Pu·Zn (25)	25	1650 1545 1310 3280	1180 1030 700	1595 1510
Pu·Zn (100)	100	1655 1545 1315 3280	1180 1035 695	1585 1500
Pu·Pb (5)	5	1650 1545 1305 3280	1180 1030 690	1595 1510
Pu·Pb (25)	25	1650 1545 1305 3260	1180 1030 700	1595 1510
Pu·Pb (50)	50	1650 1545 1310 3280	1180 1030 690	1595 1510
Pu·Pb (100)	100	1650 1545 1315 3360	1180 1040 680	1595 1505

Table VI H—NMR Chemical Shifts of Metal-Containing Polyureas (ppm)



Products	ASA(M) in Feed Diamine (mol %)	—NHCONH—[a]		Phenyl Ring a	Phenyl Ring b	Phenyl Ring c	—CH_3	—CH_2—	Peak That Can Be Exchanged by D_2O
Pu(0)	0	8.93	8.53	7.93–7.36	7.36–7.04	—	2.16	3.79	8.93–8.52
Pu·Ba(5)	5	9.02	8.66	7.97–7.46	7.46–7.10	[b]	2.19	3.85	9.02–8.6
Pu·Ba(10)	10	8.96	98.58	7.84–7.40	7.40–7.03	[b]	2.15	3.80	8.96–98.58
Pu·Ba(50)	50	9.00	8.75	7.95–7.55	7.49–7.08	7.55	2.20	3.75	9.00–8.75
Pu·Ba(100)	100	9.18	8.78	7.96–7.52	—	7.52	2.18	—	9.18–8.78
Pu·Sr(5)	5	8.96	8.59	7.95–7.42	7.42–7.06	[b]	2.18	3.86	8.96–8.59
Pu·Sr(20)	20	8.98	8.62	7.91–7.44	7.44–7.06	[b]	2.18	3.83	8.98–8.62
Pu·Sr(100)	100	8.98	8.37	7.94–7.44	—	7.44	2.20	—	8.98–8.37
Pu·Zn(5)	5	8.96	8.74	7.93–7.84	7.40–7.07	[b]	2.17	3.82	8.96–8.74
Pu·Zn(50)	50	9.18	8.74	7.96–7.50	7.50–7.09	7.50	2.20	3.84	9.18–8.74
Pu·Zn(100)	100	9.02	8.64	7.84–7.38	—	7.38	2.18	—	9.02–8.64
Pu·Pb(25)	25	8.92	8.53	7.90–7.38	7.38–7.03	[b]	2.17	3.85	8.92–8.53
Pu·Pb(100)	100	9.04	8.63	7.91–7.41	—	7.41	2.18	—	9.04–8.63

[a] The main peaks.
[b] Peak of phenyl ring c was covered by that of phenyl ring a.

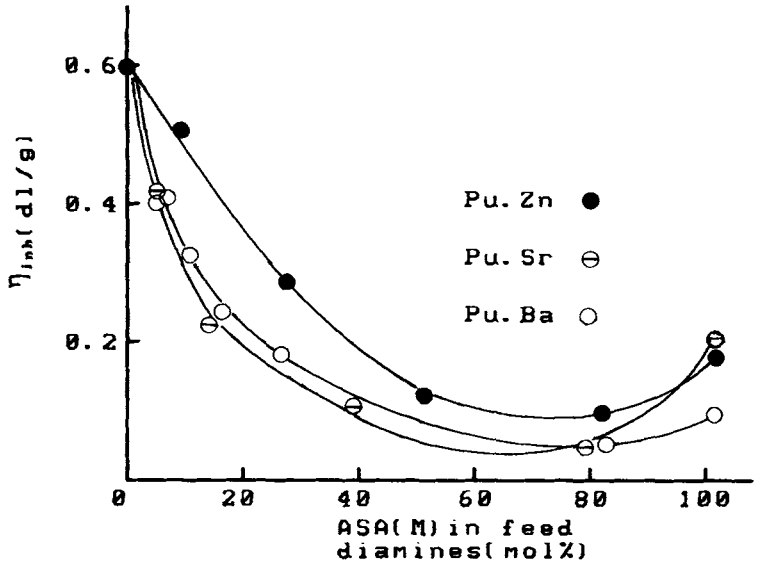


Figure 6 Plot of η_{inh} vs. content of ASA(M).

a typical polar solvent such as DMF the $-SO_3MO_3S-$ partially ionic links in the polymer main chain dissociate into low molecular weight polymers that were terminated by sulfo. In addition, the higher content of ASA in feed diamines, the lower the polymer fragment molecular weight became.

Figure 7 shows the relationship between reduced viscosity and concentration of the polyureas in DMF. The intrinsic viscosity of the parent polyurea, which is metal free, is much greater than those of the metal-containing polyureas. Very few metal-containing diamines were added in the feed diamine, but the intrinsic viscosity of polymer decreased significantly.

Thermal Properties

From Figure 3 we know that the initial decomposition temperature of ASA(Ba) is about 400°C. By

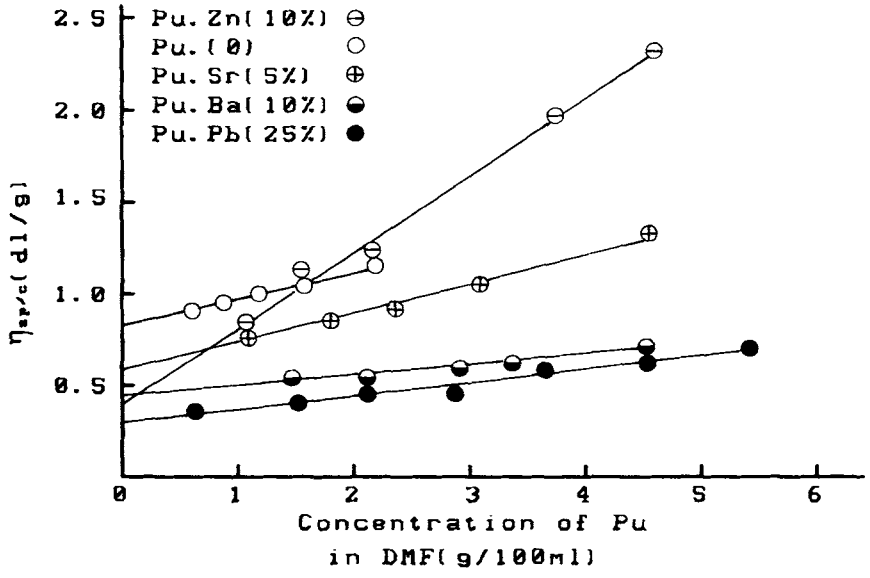


Figure 7 Plot of $\eta_{sp/c}$ vs. concentration of Pu.

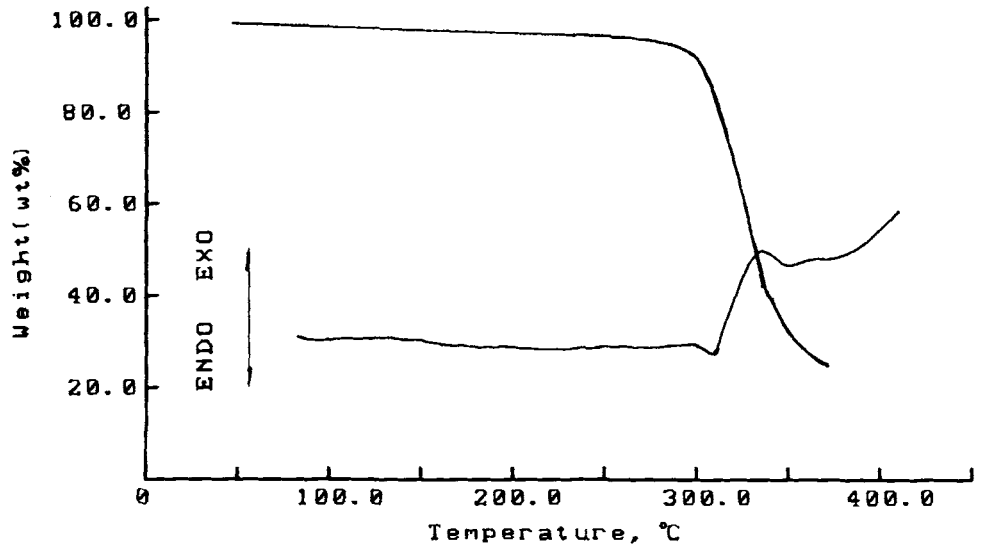


Figure 8 TG and DSC curves of Pu·Ba(10).

comparing Figure 8 with Figure 3, it is clear that the first stage of the thermal decomposition of metal-containing polyureas, at about 300°C, may be assumed to be due to the urea scission. The peak at 300°C [for Pu·Ba (10)] shown in the DSC curves is concordant with the marked weight loss in the TG curves. The slight weight loss up to ca. 150°C is produced by the volatilization of remaining DMF; meanwhile, the marked weight loss is apparently caused by the volatilization of TDI[1] and its derivatives produced by scission. From Figure 9, by comparing decomposition temperatures, it is found that the thermal stability of polyureas increases when the metal is introduced. The result is different from that reported by Matsuda and Takechi.[1] ASA(M) are used as diamines, which have a higher decomposition temperature than does ABA(M). From Figure 10, we also find that with an increase of content of ASA(Ba) in the feed diamine the thermal stability of metal-containing polyureas increases.

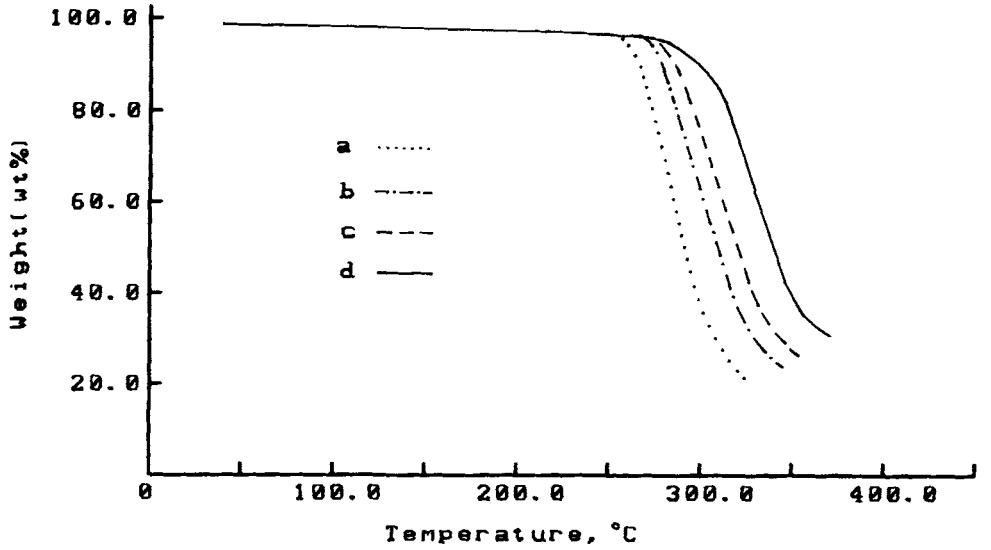


Figure 9 TG curves of (a) Pu(0), (b) Pu·Zn(10), (c) Pu·Ba(10), and (d) Pu·Pb(10).

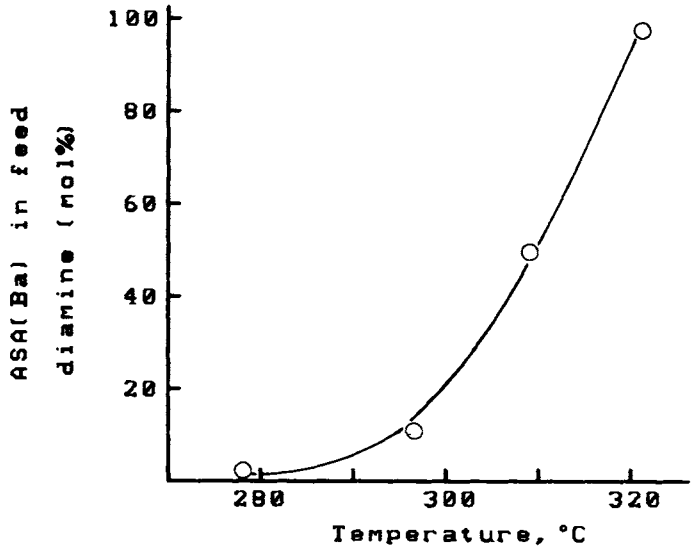


Figure 10 Content of ASA(Ba) vs. decomposition temperature of Pu·Ba.

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