

Synthesis and Characterization of Metal-Containing Polyurethanes with Antibacterial Activity

R. JAYAKUMAR,¹ M. RAJKUMAR,² R. NAGENDRAN,² S. NANJUNDAN¹

¹ Department of Chemistry, Anna University, Chennai-600 025, India

² Centre for Environmental Studies, Anna University, Chennai-600 025, India

Received 29 May 2001; accepted 26 October 2001

ABSTRACT: Metal salts of mono(hydroxypentyl)phthalate [M(HPP)₂, where M is Ca²⁺, Cd²⁺, Pb²⁺, or Zn²⁺] were synthesized by the reaction of 1,5-pentane diol, phthalic anhydride, and metal acetate. A new series of metal-containing polyurethanes containing ionic links in the main chain were synthesized by the reaction of hexamethylene diisocyanate or toluylene 2,4-diisocyanate with the M(HPP)₂ salts. The structures of the monomers and polymers were confirmed with infrared, ¹H-NMR, and ¹³C-NMR spectra and elemental analysis. The polymers were also characterized with thermogravimetric analysis, differential scanning calorimetry, and solubility and viscosity measurements. The antibacterial activity of these polyurethanes was investigated with the agar diffusion method. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1194–1206, 2002

Key words: metal salts of mono(hydroxypentyl)phthalate; ionic monomers; polyurethanes; spectral studies; antibacterial activity; thermal properties

INTRODUCTION

The introduction of metal to a urethane–urea backbone results in a considerable decrease in the decomposition temperature.¹ Polyurethane can be tailor-made with versatile applications. The incorporation of metal and functional groups into polymers gives them applications as aqueous thickeners, impregnants, textile sizers, adhesives,^{2,3} additives,⁴ resins, and catalysts.^{5–8} Polyurethanes have been used extensively in biomedical applications. Poly(ether urethane)s have been proven to have sufficient biocompatibility and biodegradability for short-term use in a variety of blood-contact applications, such as leaf-ventricular-assist devices for experimental artificial hearts⁹ and

blood pumps.¹⁰ Polyurethanes are widely used in the development of medical devices for tissue-contact and blood-contact applications such as mammary-prosthesis vascular catheters, artificial-skin vascular grafts, and artificial-heart diaphragms and valves. Ionic diols containing ionic linkages between COO[−] and M²⁺ are interesting and very important starting materials for the syntheses of ionic polymers in which metal is firmly incorporated. Metal-containing polymers with ionic links formed between COO[−] and M²⁺ have been studied.^{11–17}

When polymers are exposed to the atmosphere or are used as adhesive coatings and in biomedicine, they are contaminated or infected by microorganisms such as bacteria. Microorganisms have been found to be the cause of the unbonding and blistering of protective coatings in various service situations. Literature reports indicate the presence of a large number of microorganisms from outside that bring about deterioration in such a way that the physical reactions leading to un-

Correspondence to: S. Nanjundan (snanjundan@yahoo.com).

Contract grant sponsor: CSIR.

Journal of Applied Polymer Science, Vol. 85, 1194–1206 (2002)
© 2002 Wiley Periodicals, Inc.

bonding and blistering can take place.¹⁸ One of the methods to overcome this problem is to develop polymer materials with biocidal activities.¹⁹ Metal-containing monomers and polymeric materials with antibacterial activity have been patented.^{20–22}

This article describes the synthesis, characterization, and antibacterial activity of polyurethanes derived from metal-containing (Ca^{2+} , Cd^{2+} , Pb^{2+} , and Zn^{2+}) diols with hexamethylene diisocyanate (HMDI) or toluylene 2,4-diisocyanate (TDI).

EXPERIMENTAL

Materials

Phthalic anhydride (BDH, India), 1,5-pentane diol (Fluka, Switzerland), and extra-pure-grade metal (Ca, Cd, Pb, and Zn) acetates were used without any purification. HMDI (Fluka) and toluylene 2,4-diisocyanate (Fluka) were used without further purification after the isocyanate content was estimated. Solvents such as acetone, methanol, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dimethylacetamide (DMAc), benzene, toluene, and chloroform were purified by standard procedures. The organisms *Escherichia coli*, *Pseudomonas fluorescense*, *Salmonella* sp., and *Streptococcus* sp. were isolated from different environmental domains.

Synthesis of Metal Salts of Mono(hydroxypentyl)phthalate [M(HPP)₂, where M is Ca^{2+} , Cd^{2+} , Pb^{2+} , or Zn^{2+}]

1,5-Pentane diol (0.4 mol) was placed in a three-necked, round-bottom flask equipped with a thermometer, a condenser, and a guard tube. Phthalic anhydride (0.1 mol) was added little by little over a period of 30 min, and the contents were stirred with a magnetic stirrer over an oil bath at 70°C for 30 min. Metal acetate (0.05 mol) was then

added to the reaction mixture little by little for 30 min, and the solution was stirred further for 3 h at 80°C. M(HPP)₂, separated as a white powder, was washed successively with acetone and methanol and dried *in vacuo* at 60°C for 10 h.

Synthesis of Polyurethanes

In a three-necked, round-bottom flask fitted with a water-cooled condenser, a nitrogen inlet tube, a mechanical stirrer, and an additional funnel, 0.01 mol of the metal-containing diol, M(HPP)₂, and 100 mL of purified DMF or DMSO were placed, and the mixture was stirred well. The flask was placed in an oil bath, and the reaction mixture was maintained at approximately 95°C with continuous stirring. To this solution, two or three drops of di-*n*-butyltin dilaurate (DBTDL) were added as the catalyst, followed by 0.01 mol of the diisocyanate (HMDI or TDI) dissolved in DMF or DMSO over a period of 20–45 min, depending on the diisocyanate used. After the addition of the diisocyanate was completed, the reaction mixture was stirred continuously at the same temperature for 4 h. The reaction was carried out completely in an atmosphere of N₂. The mixture was then allowed to stand overnight, and the solution was mixed with DMF or DMSO to make the viscosity suitable for filtration. The filtrate was then run into excess chloroform to precipitate the product. This polymer was filtered, washed with acetone, and dried at 60°C *in vacuo* for 10 h.

Antibacterial Activity

The metal-containing polyurethanes were screened for their antibacterial activity against *E. coli*, *P. fluorescense*, *Salmonella* sp., and *Streptococcus* sp. isolated from water samples collected in different regions.

The antibacterial activity was evaluated with

Table I Synthesis Data for Various M(HPP)₂ Salts

Monomer	Molar Ratio of PD ^a /PA ^b	Reaction Temperature (°C)	Reaction Duration (h)	Yield (%)
Ca(HPP) ₂	4/1	80	4	83
Cd(HPP) ₂	4/1	80	4	84
Pb(HPP) ₂	4/1	80	4	79
Zn(HPP) ₂	4/1	80	4	81

^a 1,5-Pentane diol.

^b Phthalic anhydride.

Table II Yields of Ca(HPP)_2 Under Different Conditions

Calcium Acetate (mol)	PA ^a (mol)	PD ^b (mol)	Molar Ratio of PD/PA (mol)	Reaction Temperature (°C)	Yield (%)
0.01	0.02	0.04	2	80	68
0.01	0.02	0.06	3	80	74
0.01	0.02	0.08	4	80	83
0.01	0.02	0.10	5	80	81
0.01	0.02	0.08	4	70	76
0.01	0.02	0.08	4	90	79

^a Phthalic anhydride.

^b 1,5-Pentane diol.

the agar diffusion method.²³ One loopful of bacteria was inoculated in 10 mL of a nutrient broth (peptone, 5 g/L; beef extract, 3.0 g/L; pH 6.8) and

incubated at 37°C for 28 h in a test-tube shaker at 100 rpm. The actively growing bacterial cells were used for inhibition studies. The nutrient agar (20 mL) was poured into sterile petri plates and allowed to solidify at room temperature. After the solidification, 0.1 mL of the bacterial culture was spread on the agar. A circular well (9 mm in diameter) was made at the center for each petri plate with a sterilized borer. Because DMSO had no effect on the growth of the microorganisms, the polyurethane test samples were prepared with this as the solvent at a concentration of 50 $\mu\text{g/mL}$. Then, 0.1 mL of each test solution was added to the well and incubated at $37 \pm 5^\circ\text{C}$ for 24 h. After incubation, the zones of inhibition were measured; they are represented as -, +, ++, and +++, depending on the diameter and clarity.

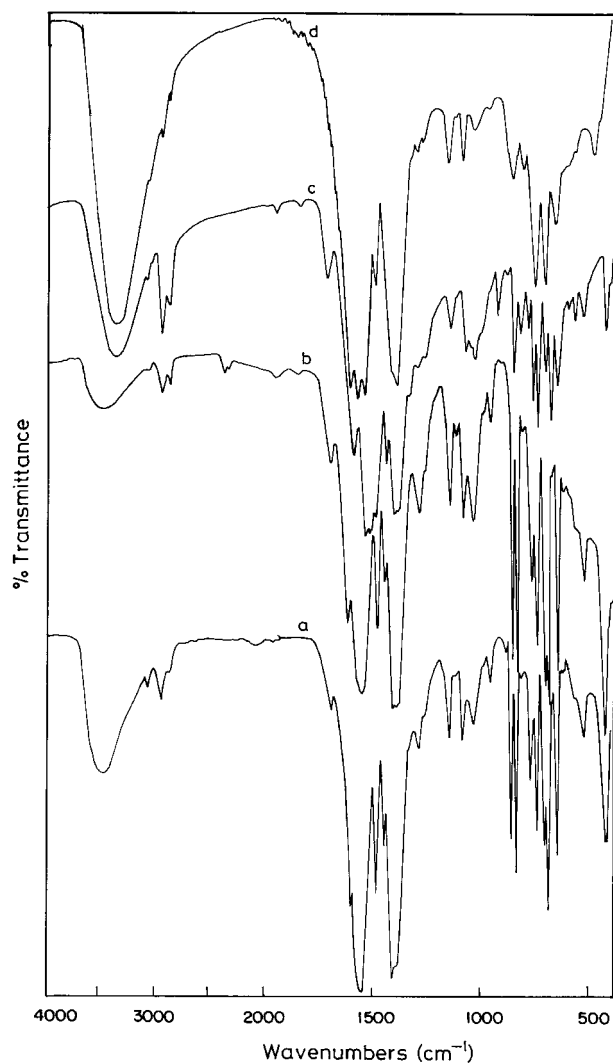


Figure 1 IR spectra of (a) Ca(HPP)_2 , (b) Cd(HPP)_2 , (c) Pb(HPP)_2 , and (d) Zn(HPP)_2 .

Measurements

The infrared (IR) spectra of the samples (KBr pellets) were recorded with the a Shimadzu Testscan FTIR 8000 series spectrophotometer (Japan). The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of the products were recorded with a JEOL GSX 400-MHz spectrometer (Switzerland) in $\text{DMSO-}d_6$ as the solvent. Thermogravimetric analysis (TGA) was performed with a Mettler-3000 (U.K.) analyzer at a heating rate of $10^\circ\text{C}/\text{min}$ in an air atmosphere. A PerkinElmer 2400 carbon-hydrogen analyzer (Italy) was used for elemental analyses. Standard analytical methods were used to determine the metal contents. The intrinsic viscosity ($[\eta]$) of the polymers was determined in DMSO at 40°C with an Ubbelohde viscometer. The solubility of the polymers was tested in various polar and nonpolar solvents by 10-mg samples being added to 2 mL of a solvent and kept overnight.

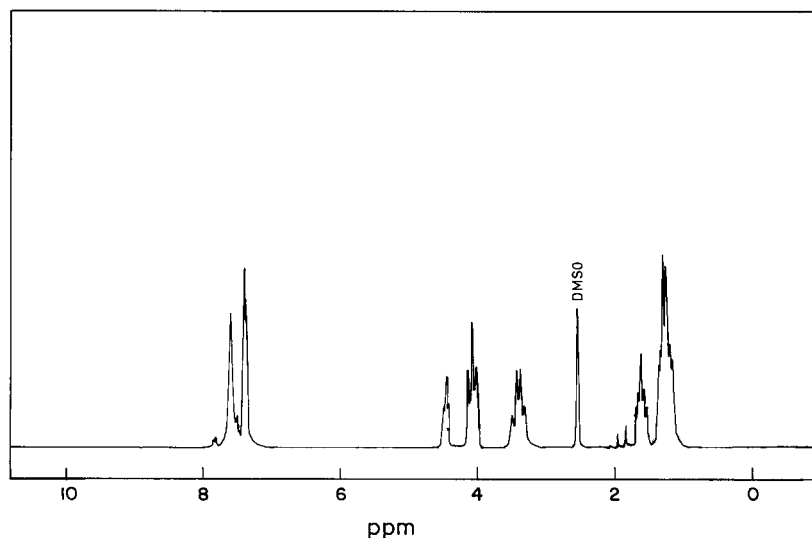


Figure 2 $^1\text{H-NMR}$ spectrum of Ca(HPP)_2 .

RESULTS AND DISCUSSION

Synthesis and Characterization of M(HPP)_2

The formation of M(HPP)_2 was very slow with the metals used in this investigation. The slow formation of these diols might have been due to the similar orders of stability of the metal acetates and the M(HPP)_2 salts. When the reactions were carried out with a 1/4 ratio of phthalic anhydride and 1,5-pentane diol, the yields were high. When the ratio of the pentane diol taken was small, not only was the yield less but the stirring of the mixture also became difficult. The ionic diols might have been contaminated with the unreacted M(HPP)_2 , metal acetate, pentane diol, and polyester. The contaminants were removed from the diols through washing first with methanol and then with acetone. All these metal-containing diols were white. The synthesis data are given in Table I.

The conditions for obtaining an optimum yield of the calcium salt Ca(HPP)_2 were determined with variations in the molar ratio of 1,5-pentane diol to phthalic anhydride and with variations in the temperature. At 80°C , a higher yield of the calcium salt was obtained when the molar ratio was maintained at 4/1. Below and above 80°C , the yield was very low. This might have been due to the lower rate of salt formation below 80°C and an increase in the rate of polyester formation above 80°C . The synthesis data for Ca(HPP)_2 are given in Table II.

The FTIR spectra of the diols are shown in Figure 1. The spectra show a broad band at 3470--

3370 cm^{-1} due to —OH stretching of the hydrogen-bonded diols. The carbonyl stretching of the ester group shows an absorption band between 1714 and 1697 cm^{-1} . The carboxylate ions of the salt show two broad peaks between 1610 and 1393 cm^{-1} . This confirms the presence of the ionic link. The peak at $1042\text{--}1034\text{ cm}^{-1}$ is due to the —C—O— stretching due to primary alcohol. The =C—H peak between 751 and 747 cm^{-1} is due to the out-of-plane bending vibrations.

The $^1\text{H-NMR}$ spectrum of Ca(HPP)_2 is shown in Figure 2. The Fourier transform NMR spectra of the ionic diols show resonance signals due to the aromatic protons between 7.72 and 7.42 ppm . The signals between 4.61 and 4.47 ppm are due to hydroxyl protons. The methylene groups attached to —OCOPh show a signal at $4.13\text{--}4.01\text{ ppm}$. The methylene groups attached to the alcoholic group show a signal between 3.55 and 3.38 ppm . Of the three central methylene groups, the one that is attached to the $\text{—CH}_2\text{OCOPh}$ shows a signal between 1.72 and 1.61 ppm , and the other methylene groups attached to $\text{—CH}_2\text{OH}$ show a signal at $1.41\text{--}1.24\text{ ppm}$.

The proton-decoupled $^{13}\text{C-NMR}$ spectrum of Ca(HPP)_2 is shown in Figure 3. The chemical-shift assignments were made from the off-resonance decoupled spectra of the monomers. The resonance signals at 169.89 (C_{13}) and 167.21 (C_6) ppm are due to the carboxylate ion carbon and the ester carbonyl carbon, respectively. The aromatic carbons to which the carboxylate and ester carbonyl carbons are attached show signals at 136.83 (C_{12}) and 132.70 (C_7) ppm, respectively. The other

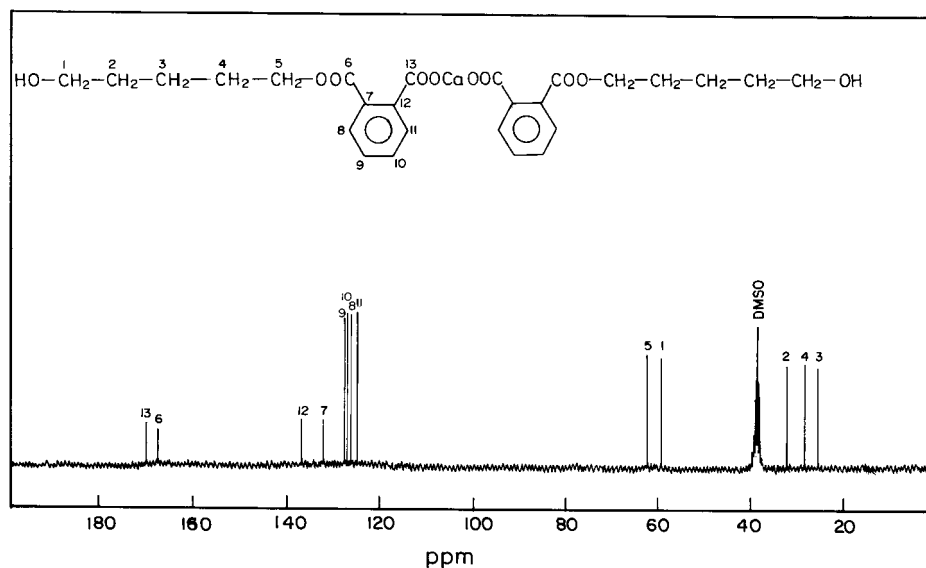


Figure 3 ^{13}C -NMR spectrum of $\text{Ca}(\text{HPP})_2$.

aromatic carbons give four signals at 127.92 (C_9), 127.12 (C_{10}), 126.18 (C_8), and 125.12 (C_{11}) ppm. The methylene carbons attached to the $-\text{OOCAR}$ group and $-\text{OH}$ group gave signals at 62.10 (C_5) and 59.42 (C_1) ppm. The signals at 32.31 (C_2) and 28.12 (C_4) ppm are attributable to the methylene carbons attached to OHCH_2- and COOCH_2- groups, respectively. The central methylene carbon of the hydroxy pentyl group shows a signal at 25.80 (C_3) ppm.

The analytical data for different $\text{M}(\text{HPP})_2$'s are given in Table III. The experimentally determined values are within the calculated values. These ionic diols are soluble in highly polar solvents such as DMF, DMSO, and DMAc and insoluble in most of the organic solvents. Figure 4 shows the TGA curves of $\text{M}(\text{HPP})_2$. TGA shows that $\text{Ca}(\text{HPP})_2$, $\text{Cd}(\text{HPP})_2$, $\text{Pb}(\text{HPP})_2$, and $\text{Zn}(\text{HPP})_2$ salts were stable up to 334, 280, 320, and 312°C, respectively. The residual weight loss at 800°C corresponds to 10.1, 20.06, 30.08, and 15.02% Ca, Cd, Pb, and Zn salts, respectively. The

residual values roughly correspond to the amount of CaO, CdO, PbO, and ZnO formed at this temperature. The Ca, Cd, and Zn salts show single-stage decomposition, whereas the Pb salt shows two-stage decomposition.

Synthesis and Characterization of Polyurethanes

For salts of Ca- and Pb-containing ionic diols, DMF was a very good solvent, but it was a poor solvent even at high temperatures for the Cd and Zn salts. Therefore, for the preparation of polyurethanes based on $\text{Cd}(\text{HPP})_2$ and $\text{Zn}(\text{HPP})_2$, DMSO was used as the solvent at 95°C. The reaction of diisocyanates with diols catalyzed by DBTDL took place via the formation of a ternary complex between the catalyst and the reagents.²⁴ In the preparation of polyurethanes, side reactions such as the ring formation of dimeric and trimeric diisocyanates, branching, and crosslinking due to the formation of allophanate linkages are known to occur. However, the polyurethanes

Table III Analytical Data of $\text{M}(\text{HPP})_2$

Monomer	Formula	Analytical Data Found (Calcd)		
		C (%)	H (%)	M (%)
$\text{Ca}(\text{HPP})_2$	$\text{CaC}_{26}\text{H}_{30}\text{O}_{10}$	57.60 (57.56)	5.61 (5.57)	7.46 (7.39)
$\text{Cd}(\text{HPP})_2$	$\text{CdC}_{26}\text{H}_{30}\text{O}_{10}$	50.86 (50.79)	4.97 (4.92)	18.23 (18.28)
$\text{Pb}(\text{HPP})_2$	$\text{PbC}_{26}\text{H}_{30}\text{O}_{10}$	44.05 (44.00)	4.30 (4.26)	29.28 (29.20)
$\text{Zn}(\text{HPP})_2$	$\text{ZnC}_{26}\text{H}_{30}\text{O}_{10}$	55.00 (54.97)	5.33 (5.31)	11.55 (11.51)

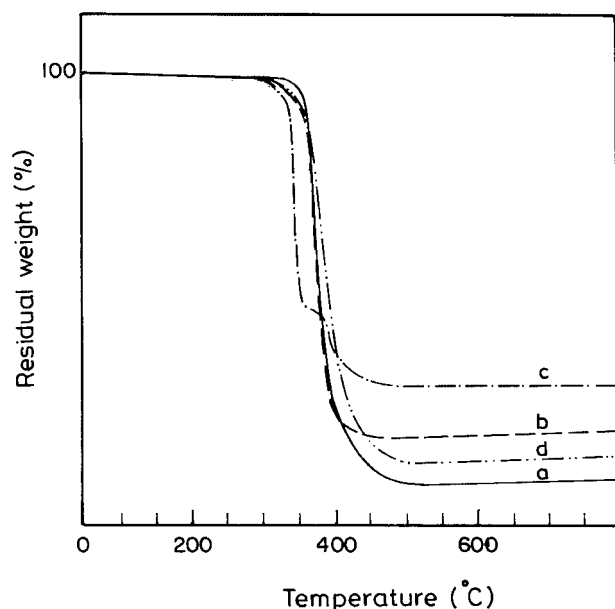


Figure 4 TGA curves of (a) Ca(HPP)_2 , (b) Cd(HPP)_2 , (c) Pb(HPP)_2 , and (d) Zn(HPP)_2 .

prepared at a diisocyanate/diol molar ratio of 1 were highly viscous and easily soluble in DMF or DMSO. Therefore, it is thought that no crosslinking occurred in this case. The polyurethanes prepared with TDI were precipitated with methanol, whereas those from HMDI were precipitated with chloroform. The polyurethanes based on TDI gave higher yields than those based on HMDI. This might have been due to the higher reactivity of TDI. With the monomers Ca(HPP)_2 , Cd(HPP)_2 , Pb(HPP)_2 , and Zn(HPP)_2 , eight metal-containing polyurethanes were prepared based on HMDI and TDI. These polyurethanes are denoted as HMDI- Ca(HPP)_2 , HMDI- Cd(HPP)_2 , HMDI- Pb(HPP)_2 ,

HMDI- Zn(HPP)_2 , TDI- Ca(HPP)_2 , TDI- Cd(HPP)_2 , TDI- Pb(HPP)_2 , and TDI- Zn(HPP)_2 . The synthesis data for these polymers are given in Table IV.

IR Spectra

The IR spectra of HMDI-based polyurethanes are shown in Figure 5. The spectra show similar characteristic peaks at $3336\text{--}3333\text{ cm}^{-1}$ due to N—H stretching. The C—H symmetrical and asymmetrical stretching due to the methylene groups can be observed between 2932 and 2855 cm^{-1} . The carbonyl stretching of the urethanes show a peak at $1690\text{--}1685\text{ cm}^{-1}$. The two broad peaks shown between 1580 and 1400 cm^{-1} are due to carboxylate ion group. This confirms the presence of ionic linkages in the polymer. These bands were not found in the metal-free analogue of these polymers. The N—H bending modes can be observed between 1628 and 1622 cm^{-1} . The C—H out-of-plane bending vibrations of the aromatic system can be seen at $773\text{--}768\text{ cm}^{-1}$.

The TDI-based polyurethanes are shown in Figure 6. The peak at $3310\text{--}3297\text{ cm}^{-1}$ is due to N—H stretching. The C—H symmetrical and asymmetrical stretching is observed between 2924 and 2852 cm^{-1} . The carbonyl stretching of the urethane groups shows a peak at $1700\text{--}1680\text{ cm}^{-1}$. The two broad bands between 1557 and 1440 cm^{-1} are due to the carboxylate ion group. The N—H bending modes can be observed between 1610 and 1598 cm^{-1} . The C—H out-of-plane bending vibrations of the aromatic system can be seen at $753\text{--}747\text{ cm}^{-1}$.

$^1\text{H-NMR}$ Spectra

The $^1\text{H-NMR}$ spectra of polyurethanes show a signal at $7.92\text{--}7.75\text{ ppm}$ for the —NH protons of

Table IV Synthesis and Viscosity Data of Various Metal-Containing Polyurethanes Based on HMDI and TDI

Polymer	Reaction Temperature ($^{\circ}\text{C}$)	Reaction Duration (h)	Yield (%)	Appearance	$[\eta]$
HMDI- $\text{Ca(HPP)}_2^{\text{a}}$	95	4	83	White	0.0627
HMDI- $\text{Cd(HPP)}_2^{\text{b}}$	95	4	79	White	0.0615
HMDI- $\text{Pb(HPP)}_2^{\text{a}}$	95	4	80	Grey	0.0583
HMDI- $\text{Zn(HPP)}_2^{\text{b}}$	95	4	77	White	0.0592
TDI- $\text{Ca(HPP)}_2^{\text{a}}$	95	4	88	Light white	0.0733
TDI- $\text{Cd(HPP)}_2^{\text{b}}$	95	4	83	Light white	0.0722
TDI- $\text{Pb(HPP)}_2^{\text{a}}$	95	4	85	Grey	0.0701
TDI- $\text{Zn(HPP)}_2^{\text{b}}$	95	4	82	Dirty white	0.0775

^a DMF was used as solvent for synthesis.

^b DMSO was used as solvent for synthesis.

the urethane groups, which are actually shifted to the downfield because of the intermolecular and intramolecular hydrogen bonding between the N—H group and the C=O group and S=O group of the solvent (DMSO- d_6). The aromatic protons show a signal between 7.52 and 7.30 ppm. The peak at 6.56–6.42 ppm is due to non-hydrogen-bonded —NH protons. The methylenoxy group attached to the —COPh group shows a signal at 4.17–4.14 ppm. The methylenoxy group attached to the —CONH group shows a peak at 4.01–3.95 ppm. The polyurethanes show a proton signal at 3.08–2.98 ppm due to the methylene group attached to the —NH group. The other methylene groups in the polymers are shown at 1.40–1.15 ppm. Figure 7 shows the $^1\text{H-NMR}$ spectrum of HMDI-Ca(HPP) $_2$.

The $^1\text{H-NMR}$ spectrum of TDI-Ca(HPP) $_2$ is shown in Figure 8. The hydrogen-bonded —NH

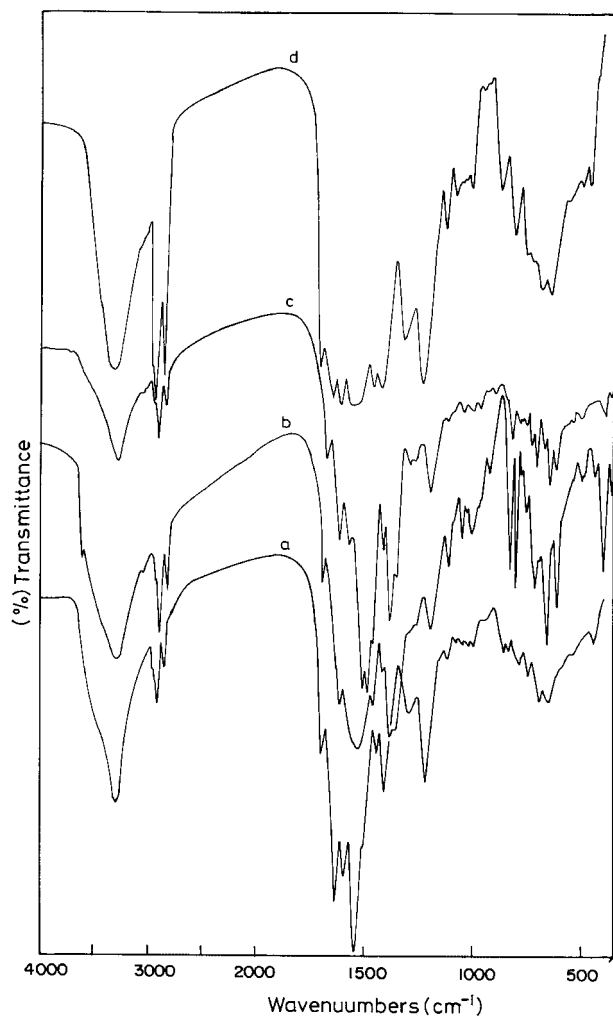


Figure 5 IR spectra of (a) HMDI-Ca(HPP) $_2$, (b) HMDI-Cd(HPP) $_2$, (c) HMDI-Pb(HPP) $_2$, and (d) HMDI-Zn(HPP) $_2$.

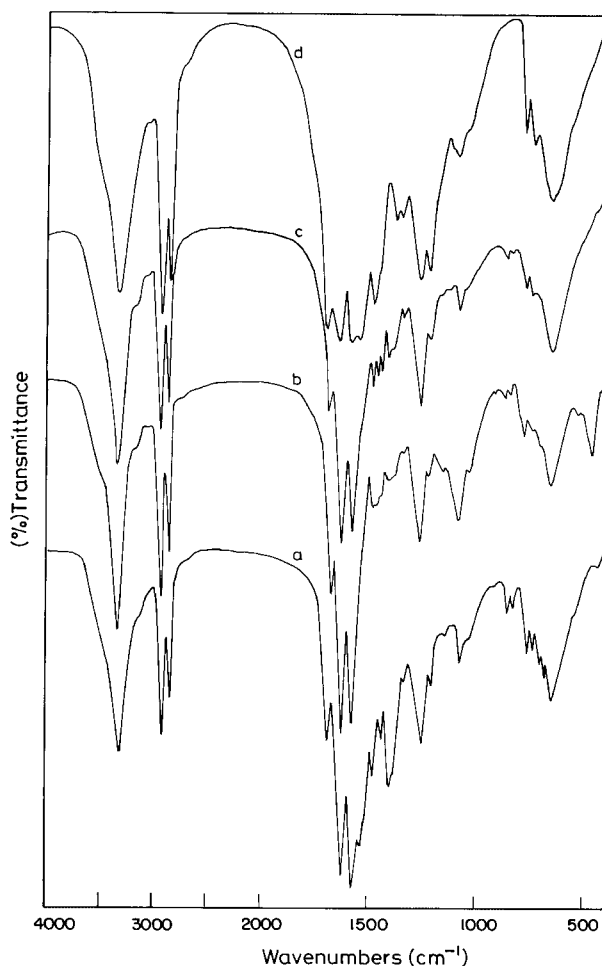


Figure 6 IR spectra of (a) TDI-Ca(HPP) $_2$, (b) TDI-Cd(HPP) $_2$, (c) TDI-Pb(HPP) $_2$, and (d) TDI-Zn(HPP) $_2$.

protons show signal sat 7.99–7.89 ppm, and the non-hydrogen-bonded —NH protons show a signal at 6.42–6.30 ppm. The aromatic protons show a signal at 7.51–6.98 ppm. The methylenoxy group attached to the —COPh group shows a signal at 4.19–4.16 ppm. The methylenoxy group attached to the —CONH group shows a peak at 4.09–4.01 ppm. The methyl group attached to the aromatic ring shows a signal at 2.05–2.12 ppm. The other methylene groups show a signal between 1.5 and 1.82 ppm.

$^{13}\text{C-NMR}$ Spectra

The $^{13}\text{C-NMR}$ spectrum of Ca(HPP) $_2$ -HMDI is shown in Figure 9. The carboxylate ion carbon and the ester carbonyl carbons show resonance signals at 170.08 (C_{17}) and 167.31 (C_{10}) ppm, respectively. The carbonyl carbon of the urethane group NHCOO— shows a peak at 157.60 (C_1)

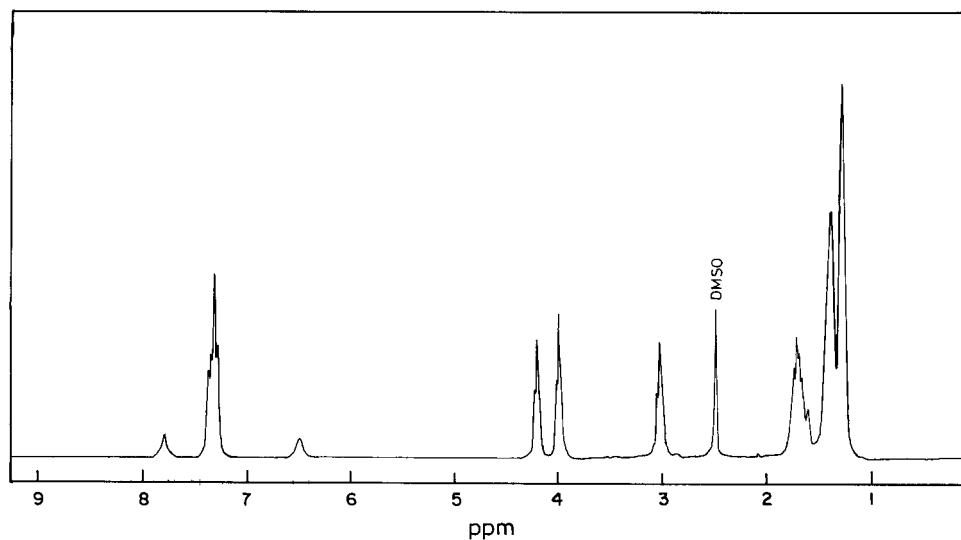


Figure 7 $^1\text{H-NMR}$ spectrum of HMDI-Ca(HPP)_2 .

ppm. The two aromatic carbons to which the ester carbonyl carbon and the carboxylate carbonyl carbon are attached show a signal at 136.12 (C_{11}) and 133.10 (C_{16}) ppm, respectively. The other aromatic carbons gave four signals at 129.98 (C_{13}), 128.93 (C_{14}), 125.94 (C_{12}), and 125.10 (C_{15}) ppm. The methylene carbons attached to ArCOO- and NHCOO- gave signals at 70.01 (C_9) and 62.10 (C_5) ppm, respectively. The methylene carbon attached to the nitrogen atom shows a peak at 44.12 (C_2) ppm. The other methylene groups are observed at 33.71 (C_6), 29.92 (C_3), 25.80 (C_8), 27.13 (C_7), and 26.10 (C_4) ppm, respectively.

The $^{13}\text{C-NMR}$ spectrum of $\text{Ca(HPP)}_2\text{-TDI}$ polyurethane is shown in Figure 10. The carboxylate

ion carbon and ester carboxyl carbon gave resonance signals at 171.80 (C_{22}) and 168.61 (C_{15}) ppm, respectively. The carbonyl carbon of the urethane groups gave signals at 153.82 (C_2) and 153.10 (C_1) ppm, respectively. The aromatic carbons gave signal between 137.26 (C_{20}) and 126.11 (C_{18}) ppm. The methylene carbon attached to the ArCOO- and NHCOO- groups shows signals at 65.10 (C_{14}) and 63.12 (C_{10}) ppm, respectively. The methylene carbon attached to the $\text{NHCOOCH}_2\text{-}$ and $\text{ArCOOCH}_2\text{-}$ groups shows signals at 32.80 (C_{11}) and 29.98 (C_{13}) ppm, respectively. The other methylene group is observed at 26.82 (C_{12}) ppm. The methyl group attached to the benzene ring shows a signal at 17.20 (C_8) ppm.

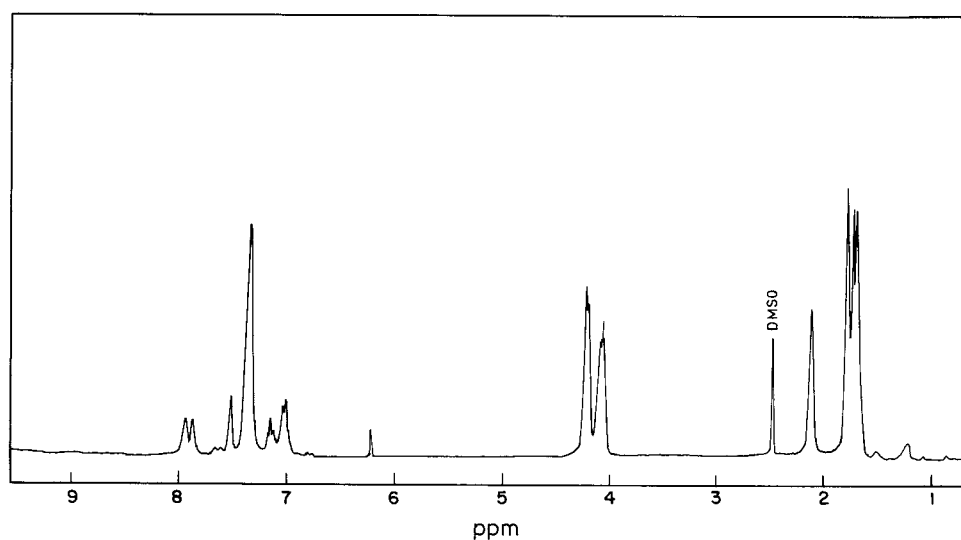


Figure 8 $^1\text{H-NMR}$ spectrum of TDI-Ca(HPP)_2 .

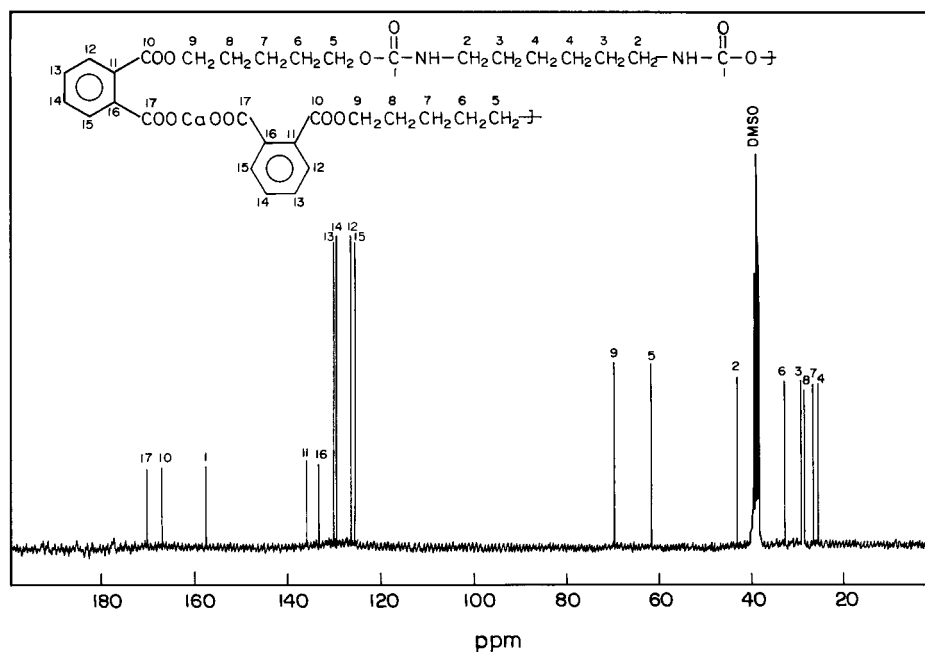


Figure 9 ^{13}C -NMR spectrum of HMDI-Ca(HPP) $_2$.

Elemental Analysis

The elemental analysis data of all the polymers show that the experimentally determined percentage values of carbon, hydrogen, and metal are within the calculated values. The values are shown in Table V.

Solubility

The solubility of the polyurethanes was tested in various polar and nonpolar solvents. The polyure-

thanes were soluble in polar solvents such as DMSO, DMF, and DMAc. The polyurethanes were insoluble in water, acetone, ethyl methyl ketone, ethyl acetate, toluene, benzene, xylene, dioxane, chloroform, carbon tetrachloride, carbon disulfide, *n*-hexane, and tetrahydrofuran.

Viscosity

The $[\eta]$ values of the polymers are shown in Table IV. The viscosities of the polyurethanes were very

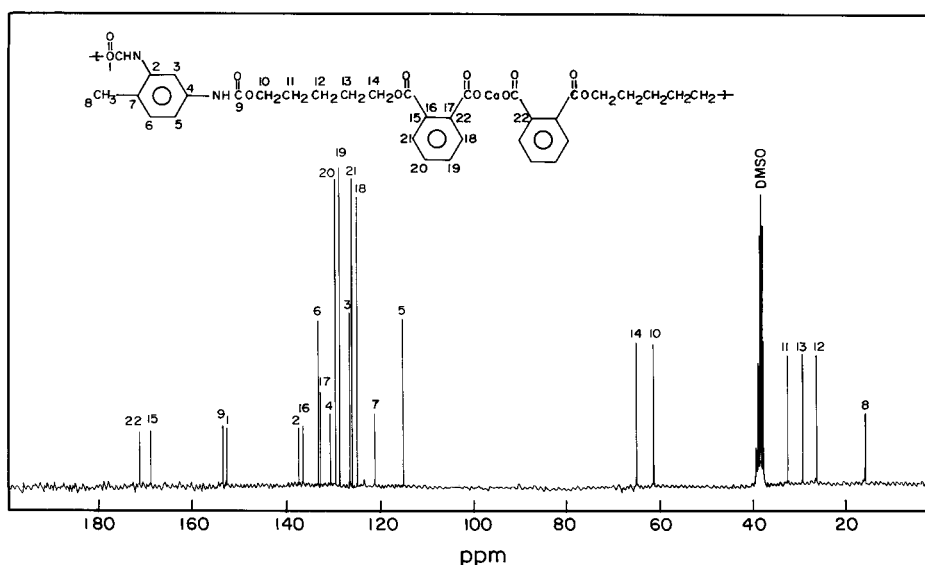


Figure 10 ^{13}C -NMR spectrum of TDI-Ca(HPP) $_2$.

Table V Analytical Data of Metal-Containing Polyurethanes

Polymer	Formula (Repeating Unit)	Analytical Data Found (Calcd)		
		C (%)	H (%)	M (%)
HMDI-Ca(HPP) ₂	CaC ₃₄ H ₄₂ N ₂ O ₁₂	57.31 (57.46)	5.99 (5.96)	5.67 (5.64)
HMDI-Cd(HPP) ₂	CdC ₃₄ H ₄₂ N ₂ O ₁₂	52.18 (52.15)	5.46 (5.41)	14.32 (14.36)
HMDI-Pb(HPP) ₂	PbC ₃₄ H ₄₂ N ₂ O ₁₂	46.56 (46.52)	4.78 (4.82)	23.53 (23.60)
HMDI-Zn(HPP) ₂	ZnC ₃₄ H ₄₂ N ₂ O ₁₂	56.72 (56.66)	4.81 (4.89)	8.78 (8.81)
TDI-Ca(HPP) ₂	CaC ₃₄ H ₃₆ N ₂ O ₁₂	57.87 (57.95)	5.19 (5.15)	5.63 (5.69)
TDI-Cd(HPP) ₂	CdC ₃₄ H ₃₆ N ₂ O ₁₂	52.60 (52.56)	4.71 (4.66)	14.51 (14.47)
TDI-Pb(HPP) ₂	PbC ₃₄ H ₃₆ N ₂ O ₁₂	46.71 (46.84)	4.19 (4.16)	23.71 (23.77)
TDI-Zn(HPP) ₂	ZnC ₃₄ H ₃₆ N ₂ O ₁₂	54.46 (54.39)	6.65 (6.59)	5.53 (5.48)

low.¹⁴ This is generally the case for all metal-containing polyurethanes. The lowering of the viscosity may be attributed to the reduction in the molecular weights of these polyurethanes on dissolution due to the dissociation of the metal-oxygen bonds. The TDI-based polyurethanes showed higher $[\eta]$ values than the HMDI-based polyurethanes.

Thermal Analysis

The TGA curves of HMDI-based polyurethanes are shown in Figure 11. The initial decomposition temperatures (IDTs) for the polymers and weight-loss percentages at 300 and 800°C are described in Table VI. A 50% weight loss occurred for Ca-

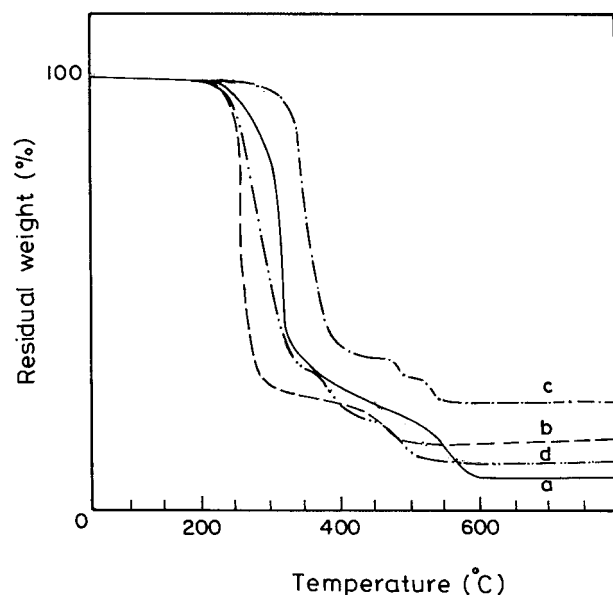


Figure 11 TGA curves of (a) HMDI-Ca(HPP)₂, (b) HMDI-Cd(HPP)₂, (c) HMDI-Pb(HPP)₂, and (d) HMDI-Zn(HPP)₂.

Cd-, Pb-, and Zn-containing HMDI-based polyurethanes at 322, 265, 374, and 304°C, respectively. The residual weight loss at 800°C corresponds to 7.91, 16.52, 25.43, and 11.03%, respectively. These values roughly correspond to the metal oxide (CaO, CdO, PbO, or ZnO) formed at this temperature. These values are very close to the theoretically calculated values (7.89, 16.4, 25.43, and 11.06%). The Ca- and Cd-containing polymers showed two-stage decomposition, whereas the Pb- and Zn-containing polymers showed three-stage decomposition.

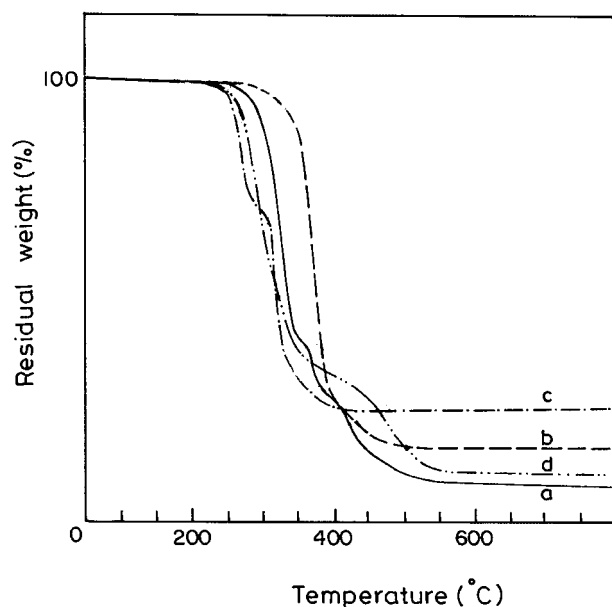
The TGA curves of TDI-based polyurethanes are shown in Figure 12. The IDTs for the polymers and the weight-loss percentages at 300 and 800°C are given in Table VI. A 50% weight loss occurred for Ca-, Cd-, Pb-, and Zn-containing TDI-based polyurethanes at 351, 386, 326, and 337°C, respectively. The residual weight loss at 800°C corresponds to 7.94, 16.52, 25.62, and 10.97%, respectively. These values roughly correspond to the metal oxide (CaO, CdO, PbO, or ZnO) formed at this temperature. These values are very close to the theoretically calculated values (7.96, 16.53, 25.60, and 11.0%). The Cd-containing polymer showed single-stage decomposition, the Pb- and Zn-containing polymers showed two-stage decomposition, and the Ca-containing polymer showed three stages of decomposition. The TDI-based polymers showed higher thermal stability than the HMDI-based polymers because of the additional aromatic rings present in the polymer backbone.

The glass-transition temperatures (T_g 's) of the HMDI- and TDI-based metal-containing polymers are given in Table VI. The T_g values of the TDI-based polymers range from -11.3 to 2.0°C, and those of the HMDI-based polymers range from -19.2 to -2.4°C. In both series, the T_g val-

Table VI DSC and TGA Data of Metal-Containing Polyurethanes

Polymer	T_g (°C)	IDT (°C)	Weight Loss (%) at Temperature (°C)					
			300	400	500	600	700	800
HMDI-Ca(HPP) ₂	-2.4	224	14.55	74.12	79.99	92.09	92.09	92.09
HMDI-Cd(HPP) ₂	-6.8	210	71.95	79.50	82.61	83.6	83.6	83.6
HMDI-Pb(HPP) ₂	-19.2	276	1.67	63.22	69.91	74.54	74.54	74.54
HMDI-Zn(HPP) ₂	-4.3	226	47.46	79.91	87.90	88.97	88.97	88.97
TDI-Ca(HPP) ₂	5.1	254	3.34	74.30	90.02	92.06	92.06	92.06
TDI-Cd(HPP) ₂	2.3	272	1.67	71.30	83.42	83.48	83.48	83.48
TDI-Pb(HPP) ₂	-11.3	224	25.84	73.11	73.48	73.48	73.48	73.48
TDI-Zn(HPP) ₂	4.2	230	16.67	66.71	81.51	89.53	89.53	89.53

ues of the metal-containing polyurethanes follow the order $\text{Ca} > \text{Zn} > \text{Cd} > \text{Pb}$. This order may be attributed to the fact that with an increase in the size of the metal atom, the free volume of the polymer increased and the T_g value decreased. The HMDI-based polyurethanes were expected to have much lower T_g values than the TDI-based polyurethanes on the basis of their main-chain structure. However, the difference in the T_g values of the HMDI-based polymers and the respective TDI-based polyurethanes was somewhat less. This may be due to the fact that HMDI-based polyurethanes generally have higher crystallinity than TDI-based polyurethanes.²⁵

**Figure 12** TGA curves of (a) TDI-Ca(HPP)₂, (b) TDI-Cd(HPP)₂, (c) TDI-Pb(HPP)₂, and (d) TDI-Zn(HPP)₂.

Antibacterial Activity of Polyurethanes

The antibacterial activities of polymers were identified on the basis of the zone of inhibition for bacterial growth around the wells and were shown to be inactive, mild, moderate, and highly inactive. The results are given in Table VII. The results showed that the polymers HMDI-Pb(HPP)₂ and TDI-Cd(HPP)₂ had higher antibacterial activity against all the bacterial strains.

The polyurethanes HMDI-Pb(HPP)₂, TDI-Cd(HPP)₂, TDI-Pb(HPP)₂, and TDI-Zn(HPP)₂ were highly active against *P. fluorescens*. HMDI-Cd(HPP)₂ and TDI-Ca(HPP)₂ were moderately active against *P. fluorescens*, but HMDI-Ca(HPP)₂ and HMDI-Zn(HPP)₂ were inactive against *P. fluorescens*.

The polymers HMDI-Pb(HPP)₂, TDI-Ca(HPP)₂, and TDI-Cd(HPP)₂ exhibited high activity against *E. coli*. The other polymers showed moderate activity against *E. coli*. The polymers TDI-Ca(HPP)₂ and TDI-Cd(HPP)₂ showed high activity against the *Salmonella* sp. The polymers, HMDI-Pb(HPP)₂, HMDI-Cd(HPP)₂, HMDI-Zn(HPP)₂, TDI-Pb(HPP)₂, and TDI-Zn(HPP)₂ exhibited moderate activity against the *Salmonella* sp. The polymer HMDI-Ca(HPP)₂ was mildly active against the *Salmonella* sp.

The polymers HMDI-Pb(HPP)₂ and TDI-Cd(HPP)₂ showed high activity against the *Streptococcus* sp. TDI-Ca(HPP)₂ exhibited moderate activity against the *Streptococcus* sp. HMDI-Ca(HPP)₂, TDI-Pb(HPP)₂, and TDI-Zn(HPP)₂ were mildly active against the *Streptococcus* sp. The polymers HMDI-Ca(HPP)₂ and HMDI-Zn(HPP)₂ were inactive against the *Streptococcus* sp.

Table VII Antibacterial Activity Data of Metal-Containing Polyurethanes

Polymer	<i>P. fluorescense</i>	<i>E. coli</i>	<i>Salmonella</i> sp.	<i>Streptococcus</i> sp.
HMDI-Ca(HPP) ₂	-	++	+	-
HMDI-Cd(HPP) ₂	++	++	++	+
HMDI-Pb(HPP) ₂	+++	+++	++	+++
HMDI-Zn(HPP) ₂	-	++	++	-
TDI-Ca(HPP) ₂	++	+++	+++	++
TDI-Cd(HPP) ₂	+++	+++	+++	+++
TDI-Pb(HPP) ₂	+++	++	++	+
TDI-Zn(HPP) ₂	+++	++	++	+

- = Inactive (0–10 mm); + = mildly active (10–15 mm); ++ = moderately active (16–20 mm); +++ = highly active (21–30 mm).

The antibacterial activity of all the polymers may not be entirely due to the metal alone. It may also be due to the residual isocyanate groups in the polymers. That is why Ca-containing polymers also were found to have some antibacterial activity.

CONCLUSIONS

M(HPP)₂ was prepared by the reaction of 1,5-pentane diol, phthalic anhydride, and a metal acetate. M(HPP)₂ salts were used for the preparation of ionic polymers in which the metal was firmly incorporated into the backbone. The monomers were characterized with IR, ¹H-NMR, and ¹³C-NMR spectroscopy. The metal-containing polyurethanes, with ionic links in the main chain, were synthesized by the reaction of M(HPP)₂ with HMDI or TDI. The presence of ionic linkage was established with IR spectra. The polymers were soluble in DMF, DMSO, and DMAc and insoluble in most other organic solvents. For the metal-containing polyurethanes, the experimentally determined percentage values of carbon, hydrogen, and metal were well within the calculated values. The [η] values of the polyurethanes were very low because of chain dissociation in solution, resulting in a lower molecular weight. The TDI-based polymers showed higher values of [η] than the HMDI-based polymers. The TDI-based polymers showed higher thermal stability than the HMDI-based polymers. The antibacterial activities of different test compounds indicated that Pb- and Cd-containing polyurethanes had strong inhibitory effects on all the bacteria and that the polyurethanes containing other metals had various antibacterial activities depending on the bacterium. All the metal-containing polyurethanes used for

this study exhibited antibacterial activity and so may be used as antifungal coatings for various applications.

R. Jayakumar gratefully acknowledges the award of a senior research fellowship from Council of Scientific and Industrial Research (India) for his research work.

REFERENCES

- Matsuda, H.; Takechi, S. *J Polym Sci Part A: Polym Chem* 1991, 29, 83.
- Matsuda, H.; Kanaoka, K. *J Appl Polym Sci* 1985, 30, 1229.
- Matsuda, H. *J Appl Polym Sci* 1970, 23, 2603.
- Matsuda, H.; Takechi, S. *J Polym Sci Part A: Polym Chem* 1990, 28, 1895.
- Matsuda, H. *J Appl Polym Sci* 1978, 22, 2093.
- Matsuda, H. *J Polym Sci Polym Chem Ed* 1977, 15, 2239.
- Matsuda, H. *J Polym Sci Polym Chem Ed* 1974, 12, 455.
- Matsuda, H. *J Appl Polym Sci* 1978, 22, 3371.
- Poirier, P. *Trans ASIO Proceedings* 1990, 36, 787.
- Hayashi, K.; Takano, H.; Matsuda, T.; Umezu, M. *J Biomed Mater Res* 1985, 19, 179.
- Arun Prasath, R.; Nanjundan, S. *J Macromol Sci Pure Appl Chem* 1998, 35, 821.
- Arun Prasath, R.; Jayakumar, R.; Nanjundan, S. *J Macromol Sci Pure Appl Chem* 2000, 37, 469.
- Arun Prasath, R.; Vijayanand, P. S.; Nanjundan, S. *Polym Int* 2000, 49, 1464.
- Arun Prasath, R.; Nanjundan, S. *Eur Polym J* 1999, 35, 1939.
- Rajalingam, P.; Radhakrishnan, G.; Savitha, G.; Selvi, D.; Rao, K. V. *Acta Polym* 1990, 41, 169.
- Jayakumar, R.; Rajkumar, M.; Nagendran, R.;

- Nanjundan, S. *J Macromol Sci Pure Appl Chem* 2001, A38(9), 869.
17. Paul, S.; Ranby, B. *Macromolecules* 1976, 9, 337.
 18. Nho, Y. C.; Park, J. S.; Jin, J. H. *J Macromol Sci Pure Appl Chem* 1999, 36, 731.
 19. Staranger, S.; Johennssen, M. In *Biodegradation*; Oxley, T. A.; Becker, G.; Allsopp, D., Eds.; Pitman: London, 1986; p 143.
 20. Yoichi, S.; Kazuo, T.; Kazuo, H.; Toshio, Y.; Michiro, Y.; Yochio, A. *Jpn. Kokai Tokkyo Koho JP01*, 1989, 958.
 21. Toshikai, S.; Inoue, S. S.; Yoshihia, Y.; Takagi, S.; Umiharuru, T. *Jpn. Kokai Tokkyo Koho JP09*, 1997, 952.
 22. Nishida, R. *Jpn. Kokai Tokkyo Koho JP09*, 1997, 911.
 23. Pelczar, M. J., Jr.; Chen, E. C. S.; Reid, R. D. *Microbiology*, 5th Edns.; Tata; McGraw-Hill: New York, 1990; Vol. 5, p 488.
 24. Salakhova, M. S.; Guseinov, M. H.; Treivus, E. M.; Salakhova, R. S.; Umaeva, V. S. *Azerb Khim Zh* 1977, 6, 27.
 25. Rajalingam, P.; Radhakrishnan, G. *Polym Commun* 1990, 31, 243.