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R. A. Prasath[a]; S. Nanjundan[a]
[a] Department of Chemistry, College of Engineering Anna University, Madras, India

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SYNTHESIS AND CHARACTERIZATION OF METAL CONTAINING POLYURETHANES AND POLYURETHANE-UREAS BASED ON NEW DIVALENT METAL SALTS OF MONO(HYDROXYBUTYL)PHTHALATE

R. Arun Prasath and S. Nanjundan *
Department of Chemistry
College of Engineering
Anna University, Guindy
Madras, 600 025, India

Key Words: Divalent Metal Salts of Mono(hydroxybutyl)phthalate, Ionic Monomers, Polyurethane, Polyurethane-ureas, Spectral Studies, Viscosity, and Thermogravimetric Analysis

ABSTRACT

Divalent metal salts of mono(hydroxybutyl)phthalate were synthesized by the addition of 1,4-butane diol, phthalic anhydride and divalent metal [Ca^{2+}, Mn^{2+} and Pb^{2+}] acetates. A series of metal containing polyurethane and polyurethane-ureas containing ionic links in the main chain were synthesized by the polyaddition reaction of hexamethylene diisocyanate (HMDI) or toluylene 2,4-diisocyanate (TDI) with divalent metal salts of mono(hydroxybutyl)-phthalate [$M(HBP)_2$] and 1:1 mixtures of toluylene 2,4-bis(ω,N-hydroxyethylurea) [TBHEU] and $M(HBP)_2$. $M(HBP)_2$ and the polymers were characterized by elemental analysis, solubility, viscosity, spectral studies (IR and FT NMR) and thermogravimetric analysis (TGA).

INTRODUCTION

Ion containing polymers are perhaps the most important and very useful polymeric materials that are currently being developed. However, among the ionic polymers until relatively recently, mainly the areas of network glasses and polyelectrolytes were receiving extensive scientific interest. When ionic charges are sufficient to completely solublize the polymer in water they are referred to as 'polyelectrolytes'. New families of ionic polymers have emerged that possess a wide variety of properties leading to different application as aqueous thickeners, impregnants, textile sizers, adhesives [1-2], additives [3], resins [4-5], catalysts [6] and in the biomedical field [7-8]. Polymers containing ionic metal linkages in the main chain formed between COO^- and M^{++} have been studied [9-24]. Ionic diols of $M(HBP)_2$ contain ionic linkages formed between COO^- and M^{++} and also contain two hydroxyl groups. These are of interest and are useful as difunctional ionic monomers which are used as starting materials for the synthesis of ionic polymers in which metal is firmly incorporated in the back bone. Metallopolymers containing metal in the backbone of the polymer chain have been prepared [25-28]. The present paper deals with the synthesis and characterization of new metal containing polyurethanes and polyurethane-ureas derived from calcium, manganese and lead salts of mono(hydroxybutyl)phthalate, toluylene 2,4-bis(ω,N-hydroxyethylurea) and hexamethylene diisocyanate or toluylene 2,4-diisocyanate.

EXPERIMENTAL

Materials

Phthalic anhydride, 1,4-butane diol and metal (calcium, manganese and lead) acetates of extra pure grade were used as received. Hexamethylene diisocyanate (Fluka), toluylene 2,4-diisocyanate (Fluka) and di-n-butyltindilaurate catalyst (Fluka) were used as received. The solvents such as acetone, methanol, dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), benzene, toluene and chloroform were purified by standard procedures.

Synthesis of $M(HBP)_2$ and TBHEU

1,4-Butane diol (0.4 mol) was placed in a three-necked flask equipped with a thermometer, a condenser and a guard tube. To this, phthalic anhydride (0.1 mol) was added slowly over a period of 30 minutes and the contents were stirred constantly in an oil bath at 85-90°C for an additional 30 minutes. Then, metal (calcium, manganese or lead) acetate (0.05 mol) was added to the reaction mixture little by little for 30 minutes and the solution was stirred continuously for another $1^{1/2}$ hours. The product was obtained as white precipitate. Toluylene 2,4-bis(ω,N hydroxy-ethylurea) was synthesized according to the method reported by H. Matsuda [10].

Synthesis of Polymers

To synthesize metal containing polyurethane, $M(HBP)_2$ (0.01 mol) [$M=Ca^{2+}$, Mn^{2+} or Pb^{2+}] dissolved in DMF or DMSO (100 mL) was placed in a three-necked flask fitted with a nitrogen inlet, a condenser and a dropping funnel. To this, approximately 2 drops of di-n-butyltindilaurate (DBTDL) was added as a catalyst. Then, 0.011 mol of HMDI or TDI dissolved in 20 mL of DMF or DMSO was put in a dropping funnel and this solution was added slowly to the reaction mixture at 80-90°C for over 1 hour under a stream of nitrogen. After the addition, the reaction temperature was raised to 90-100°C and the mixture was stirred at the same temperature for about 4 hours. After the reaction was completed, DMF or DMSO (50 mL) was added to the mixture and the solution was filtered. The filtrate was poured into a large quantity of vigorously stirred chloroform to precipitate the polymer. The metal containing polymers were washed several times with chloroform and then dried *in vacuo* at 60-70°C.

To synthesize metal containing polyurethane-ureas, $M(HBP)_2$ (0.005 mol) [$M=Ca^{2+}$, Mn^{2+} or Pb^{2+}] and TBHEU (0.005 mol) dissolved in 80 mL of DMF or DMSO was placed in a three-necked flask fitted with a nitrogen inlet, a condenser and a dropping funnel. To this, approximately 2 drops of di-n-butytindilaurate were added as a catalyst. The temperature of the reaction mixture was kept at 80-90°C with the help of an oil bath. Then, 0.011 mol of HMDI or TDI dissolved in 20 mL of DMF or DMSO was placed in a dropping funnel and this solution was added slowly to the reaction mixture for over 1 hour under a stream of nitrogen. After the addition, the reaction temperature was raised to 90-100°C and the mixture was stirred at the same temperature for 4 hours. Then, the flask was taken out of the oil bath, and DMF or DMSO (40 mL) was added to the mixture to make the viscosity suitable for filtration. The filtrate was poured into 100 mL of acetone and the product formed was filtered and further washed with alcohol and acetone and then dried in vacuum at 60-70°C.

Instrumentation

IR spectra of $M(HBP)_2$ and the polymers were recorded using Perkin-Elmer Model 598 Spectrophotometer at room temperature with a KBr disk method.

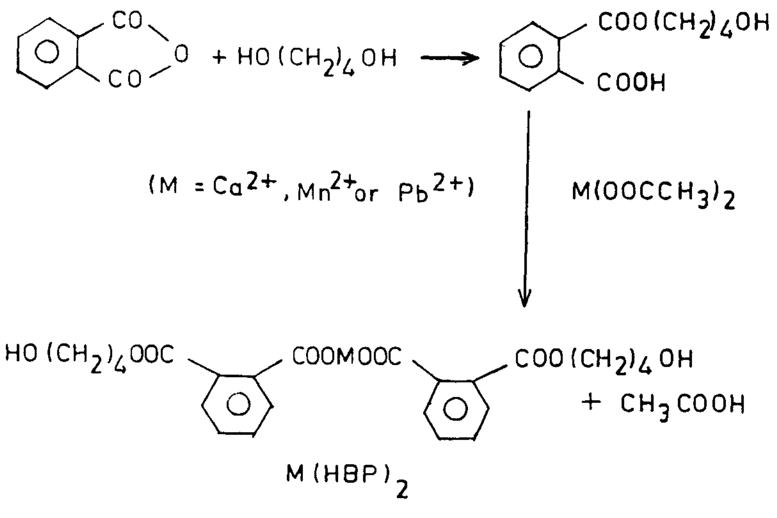
A JEOL-GSX 400MHz Spectrometer was used to record ^{1}H NMR spectra of $M(HBP)_2$ and the polymers in DMSO-d_6 solvent using TMS as internal standard. TGA was carried out in Metler-3000 Thermal Analyzer at a heating rate of 20°C/min in air atmosphere for $M(HBP)_2$ and the polymers. The intrinsic viscosity of polymers were determined in DMSO at 40°C using a Ubbelohde viscometer. Solubility studies for the $M(HBP)_2$ and the polymers were tried in various polar and nonpolar solvents at room temperature. Perkin Elmer 2400 Carbon-Hydrogen Analyzer was used for elemental analysis of $M(HBP)_2$ and the polymers. Standard analytical methods were used to determine the metal content of different $M(HBP)_2$ and the polymers.

RESULTS AND DISCUSSION

Synthesis and Characterization of $M(HBP)_2$

Mono(hydroxybutyl)phthalate was prepared by reacting phthalic anhydride with an excess of 1,4-butane diol. Metal salts of mono(hydroxybutyl)phthalate were prepared by the reaction between mono(hydroxybutyl)phthalate and metal acetates. The reaction were completed in 3 hours with constant stirring at 90°C. The product separated as white precipitate was contaminated with the unreacted mono(hydroxybutyl)phthalate, 1,4-butane diol and metal acetate. These contaminations were removed from the product by washing with appropriate solvents and dried *in vacuo* at 70°C. In the case of calcium and manganese salts, the filtered precipitate was washed several times with acetone, then with methyl alcohol to remove unreacted calcium and manganese acetates and, finally, washed once again with acetone. $Ca(HBP)_2$ and $Mn(HBP)_2$ are white in color and their yield was 81 and 80%, respectively. In the case of lead salt, the filtered precipitate was washed several times with acetone, then with dilute acetic acid to remove unreacted lead acetate and, finally, once again washed with acetone. $Pb(HBP)_2$ is bright white in color and its yield was 85%.

The optimum mole ratio of glycol to phthalic anhydride was investigated by Hideaki Matsuda [9] and it was found that the yield was higher when the glycol to phthalic anhydride ratio was higher than 3. The condition for obtaining optimum yield of calcium salt of mono(hydroxybutyl)phthalate was arrived by varying the mole ratio of 1,4-butane diol to phthalic anhydride, time and the temperature. The optimum yield of calcium salt was obtained by maintaining the temperature at 90°C, time 4 hours and the mole ratio of 1,4-butane diol:phthalic anhydride as 4:1. The synthesis data of $Ca(HBP)_2$ for optimum yield is given in the Table 1.



SCHEME 1

TABLE 1. Yield of $Ca(HBP)_2$ at Different Conditions

Calcium acetate mole	Phthalic anhydride (Pa) mole	1,4-Butane diol (Bd) mole	Mole ratio of Bd/Pa mole	Reaction temperature °C	Time hours	Yield %
0.01	0.02	0.04	2	90	2.5	70
0.01	0.02	0.06	3	90	2.5	73
0.01	0.02	0.08	4	90	3	81
0.01	0.02	0.10	5	90	4	81
0.01	0.02	0.08	4	80	3	75
0.01	0.02	0.08	4	100	3	81

The IR spectra of ionic diols are shown in Figure 1. The spectra show a characteristic broad band at 3346-3404 cm^{-1}, due to O-H stretching of the hydrogen bonded diols. The absorption band between 1723-1724 cm^{-1} is due to carbonyl stretching of the ester group. The carboxylate ions of the salts show two broad peaks between 1450-1580 cm^{-1}. This shows that a static ionic bond between COO^- and M^{++} is formed.

FT-NMR spectra of the ionic diols show resonance signals due to aromatic protons between 7.30-7.38 ppm. The signals between 4.65-4.67 ppm are due to

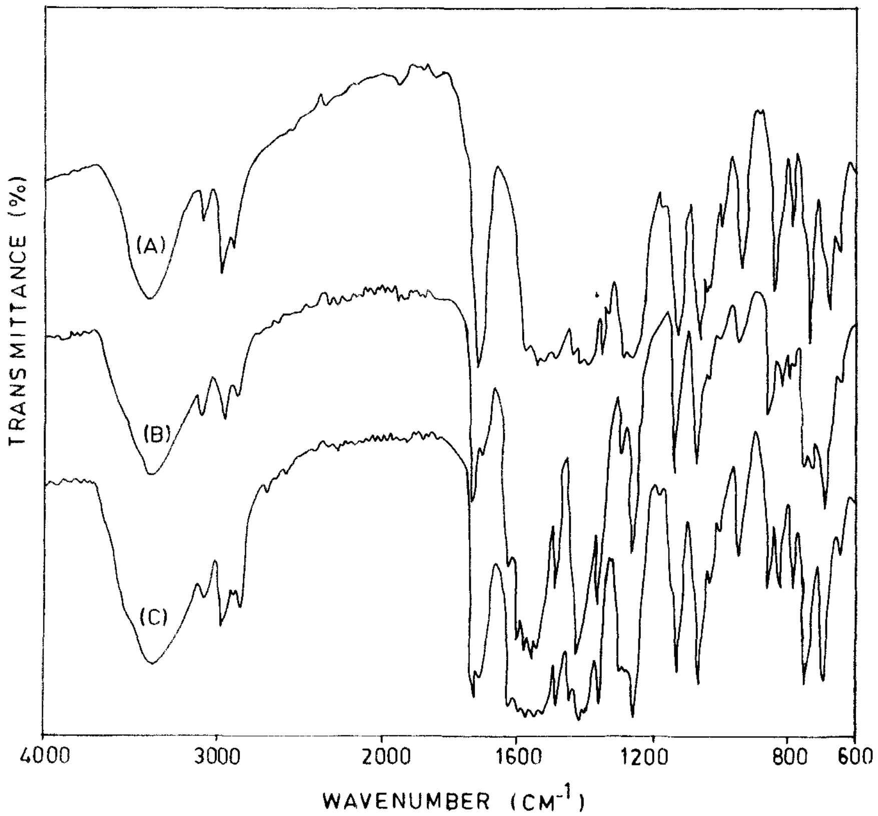


Figure 1. IR spectra of (A) $Pb(HBP)_2$, (B) $Mn(HBP)_2$ and (C) $Ca(HBP)_2$.

hydroxyl protons. Methylene groups attached to -OCOPh- show signals between 4.15-4.17 ppm. Methylene group attached to the alcoholic group show signals between 3.40-3.42 ppm. Of the two central methylene groups, one which is attached to the -CH_2OCOPh-, shows signal between 1.65-1.68 ppm and the other methylene group attached to -CH_2OH shows signal between 1.50-1.51 ppm. Figure 2 shows the NMR spectrum of $Ca(HBP)_2$.

The analytical data for different metal salts of mono(hydroxybutyl)phthalate are given in Table 2. $Ca(HBP)_2$ and $Mn(HBP)_2$ are soluble in water while $Pb(HBP)_2$ is only sparingly soluble. These ionic diols are soluble in highly polar solvents like DMF, DMSO and m-cresol, and insoluble in most of the other organic solvents. Figure 3 shows TGA curves of $M(HBP)_2$ salts. The TGA shows that $Ca(HBP)_2$ salt was stable up to 230°C, $Mn(HBP)_2$ salt was stable upto 270°C whereas $Pb(HBP)_2$ was stable up to 170°C. The weight loss at 550°C corresponds

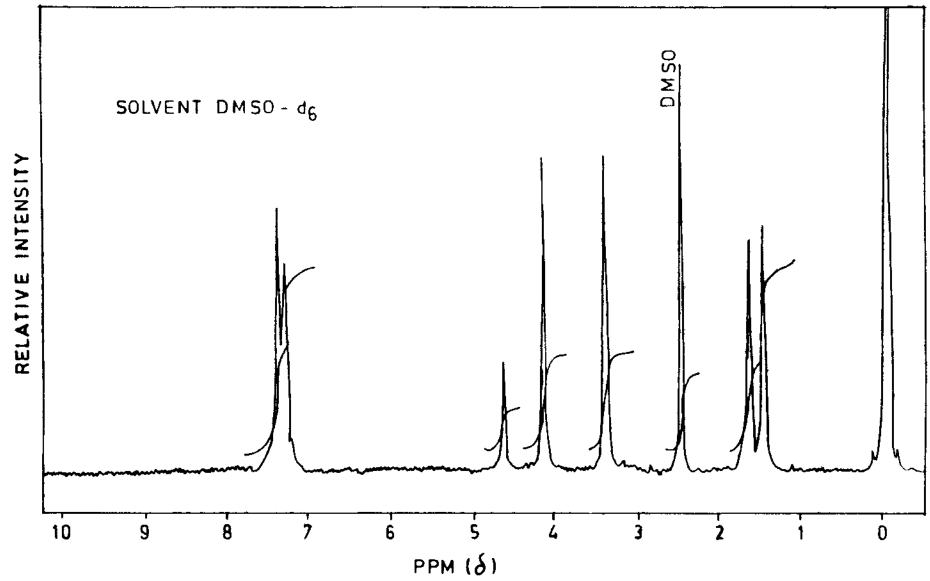


Figure 2. ^1H NMR spectrum of $Ca(HBP)_2$.

TABLE 2. Analytical Data of $M(HBP)_2$

$M(HBP)_2$	Formula	Analytical data found (Calculated) %		
		C	H	M
$Ca(HBP)_2$	$CaC_{24}H_{26}O_{10}$	56.17 (56.03)	5.02 (5.09)	7.84 (7.79)
$Mn(HBP)_2$	$MnC_{24}H_{26}O_{10}$	54.52 (54.45)	5.05 (4.95)	10.65 (10.37)
$Pb(HBP)_2$	$PbC_{24}H_{26}O_{10}$	42.34 (42.29)	3.97 (3.84)	31.07 (30.39)

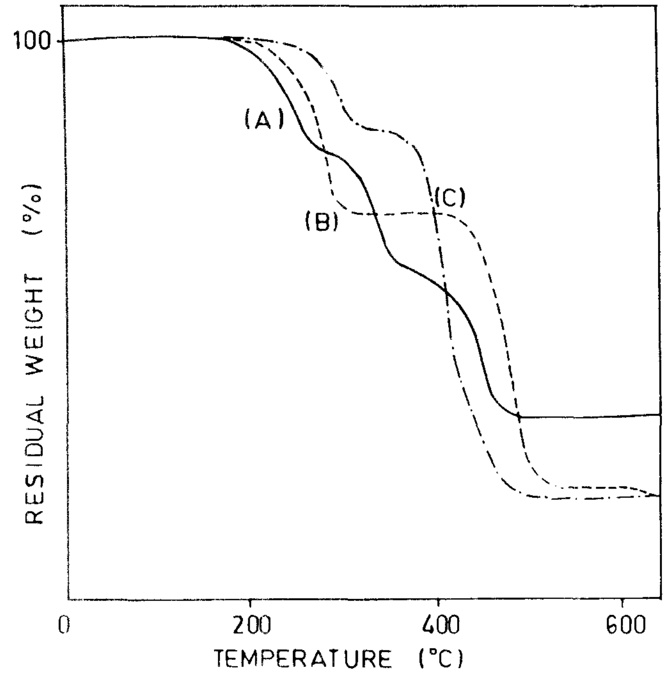


Figure 3. TGA curves of (A) $Pb(HBP)_2$ (B) $Ca(HBP)_2$ and (C) $Mn(HBP)_2$.

to 80%, 85% and 67%, respectively for calcium, manganese and lead salts. The residual values roughly corresponds to the amount of $CaCO_3$, Mn_2O_3 or PbO formed at that temperature.

Synthesis and Characterization of Polymers

As $M(HBP)_2$ is insoluble in most of the organic solvents, the polymerization of these salts with diisocyanates had to be done only in those solvents which dissolve the resulting polymers. Since DMF and DMSO are good solvents for polyurethanes and polyurethane-ureas, they were selected as the solvents for the polymerization. In the case of calcium and manganese salts of mono(hydroxybutyl)phthalate [$Ca(HBP)_2$ and $Mn(HBP)_2$], DMF was found to be a very good solvent, while it was found to be a poor solvent for $Pb(HBP)_2$. So polymerization of $Pb(HBP)_2$ with diisocyanate and polymerization of 1:1 mixture of $Pb(HBP)_2$ and TBHEU with diisocyanates had to be done only with DMSO. The reaction of diisoycanates with diols catalyzed by DBTBL took place via the forma-tion of a ternary complex between the catalyst and the reagents [29].

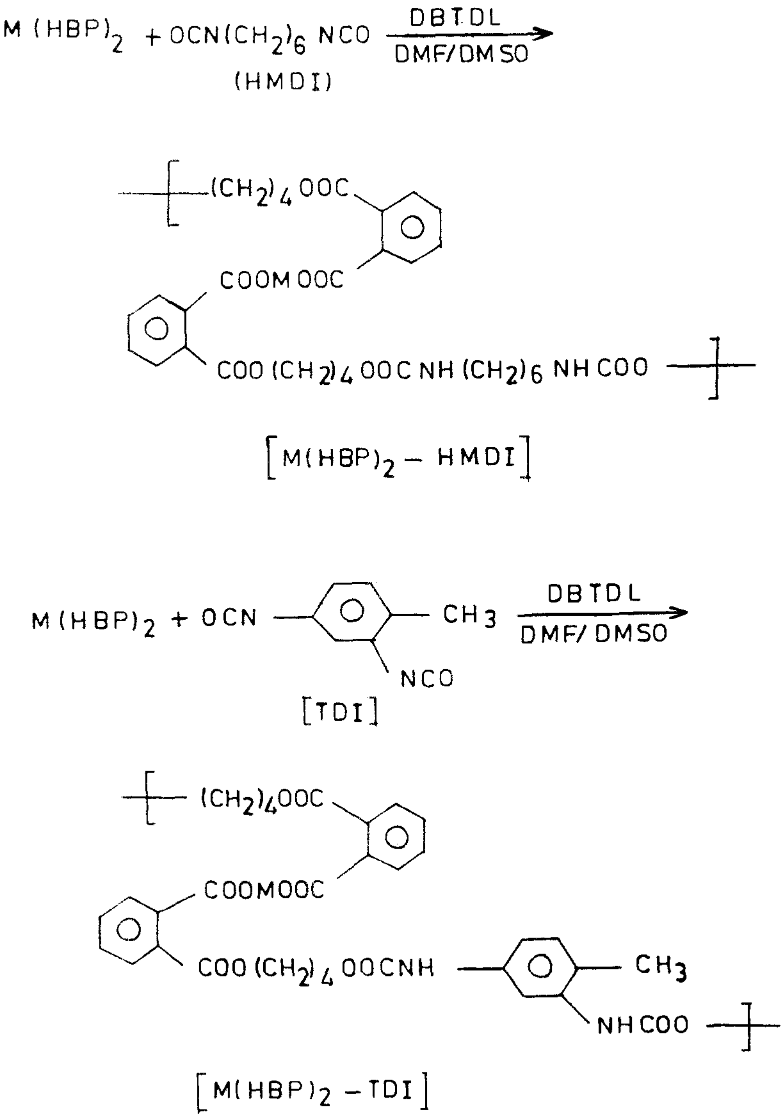
TABLE 3. Synthesis Data and Intrinsic Viscosity of Various Metal Containing Polyurethanes

Polymer	Yield* %	External appearance	Intrinsic viscosity [η]
$Ca(HBP)_2$-HMDI[a]	87	White	0.0668
$Mn(HBP)_2$-HMDI[a]	83	Slightly yellow	0.0961
$Pb(HBP)_2$-HMDI[b]	89	Grey	-
$Ca(HBP)_2$-TDI[a]	87	White	0.0791
$Mn(HBP)_2$-TDI[a]	80	Slightly yellow	0.0834
$Pb(HBP)_2$-TDI[b]	87	Slightly grey	-

a DMF was used as solvent for polymer synthesis
b DMSO was used as solvent for polymer synthesis
* Reaction temperature 90-100°C
* Reaction duration 5 hours

In the synthesis of polyurethanes, the mole ratio of diisocyanate/diol was taken as 1.1, so as to avoid side reactions such as the ring formation of dimeric and trimeric diisocyanates, branching, and crosslinking due to the formation of allophanate linkages. Any crosslinked product formed was filtered off after mixing the product with excess of DMF or DMSO to dissolve the linear polymer. Subsequently, the dissolved linear polymer was reprecipitated by the addition of a non-solvent. The yields of polyurethanes are good in all the cases. Using the monomers $Ca(HBP)_2$, $Mn(HBP)_2$ and $Pb(HBP)_2$, six metal containing polyurethane were prepared based on HMDI and TDI. They are $Ca(HBP)_2$-HMDI, $Mn(HBP)_2$-HMDI, $Pb(HBP)_2$-HMDI, $Ca(HBP)_2$-TDI, $Mn(HBP)_2$-TDI and $Pb(HBP)_2$-TDI. The results of synthesis of metal containing polyurethanes are shown in Table 3.

In the synthesis of polyurethane-ureas, the diisocyanate (HMDI or TDI), TBHEU and $M(HBP)_2$ were taken in the mole ratio of 1.1:0.5:0.5. With the help of the monomers $Ca(HBP)_2$, $Mn(HBP)_2$, $Pb(HBP)_2$ and TBHEU, six metal containing polyurethane-ureas were prepared based on HMDI and TDI. They are $Ca(HBP)_2$-TBHEU-HMDI, $Mn(HBP)_2$-TBHEU-HMDI, $Pb(HBP)_2$-TBHEU-HMDI, $Ca(HBP)_2$-TBHEU-TDI, $Mn(HBP)_2$-TBHEU-TDI and $Pb(HBP)_2$-TBHEU-TDI. The results of synthesis of metal containing polyurethane-ureas are shown in Table 4.



SCHEME 2

The IR spectra of polyurethanes show characteristic broad bands between 3308-3350 cm^{-1} due to N-H stretching. The carbonyl stretching frequency due to urethane groups are seen between 1650-1700 cm^{-1}. The carboxylate ion gives two broad peaks between 1448-1560 cm^{-1}. This confirms the presence of the ionic links in the polyurethane synthesized. Figure 4 shows IR spectra of HMDI and TDI

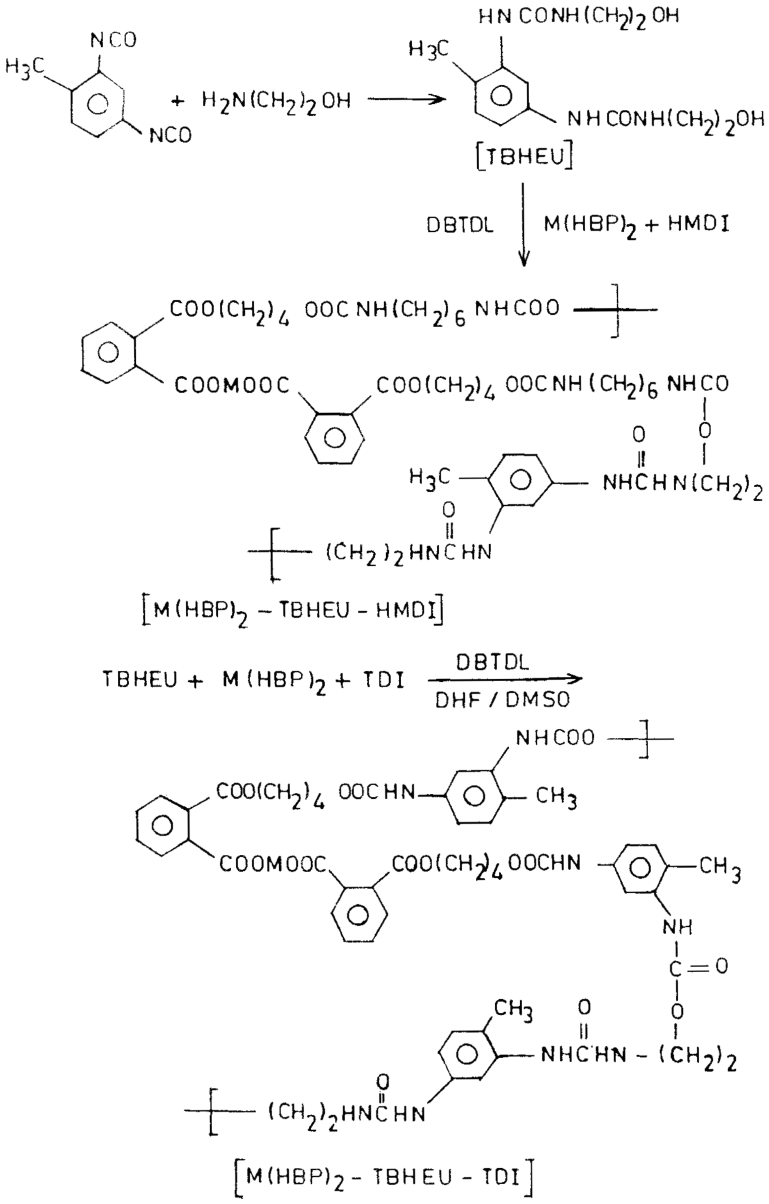
TABLE 4. Synthesis Data and Intrinsic Viscosity of Various Metal Containing Polyurethane-Ureas

Polymer	**Yield*** %	**External appearance**	**Intrinsic viscosity** [η]
Ca(HBP)$_2$-TBHEU-HMDI[a]	92	White	0.0985
Mn(HBP)$_2$-TBHEU-HMDI[a]	88	Slightly yellow	0.1016
Pb(HBP)$_2$-TBHEU-HMDI[b]	92	Grey	-
Ca(HBP)$_2$-TBHEU-TDI[a]	90	Slightly yellow	0.1042
Mn(HBP)$_2$-TBHEU-TDI[a]	85	Slightly yellow	0.1081
Pb(HBP)$_2$-TBHEU-TDI[b]	91	Slightly grey	-

a DMF was used as solvent for polymer synthesis
b DMSO was used as solvent for polymer synthesis
* Reaction temperature 90-100°C

based polyurethanes of M(HBP)$_2$. The broad bands between 3300-3385 cm^{-1} in the polyurethane-ureas are attributed to N-H stretching. The carbonyl stretching frequency due to ester, urea and urethane groups are seen between 1600-1720 cm^{-1}. The carboxylate ion gives two broad peaks between 1400-1560 cm^{-1}. This confirms the presence of ionic links in the polyurethane-ureas. Figure 5 shows the IR spectra of HMDI and TDI based polyurethane-ureas of M(HBP)$_2$ and TBHEU.

The ^{1}H NMR spectra for polyurethanes show signals for the -NH protons of the urethane groups which are shifted to down field due to the inter and intra molecular hydrogen bonding between -NH group with C=O group and with the S=O group of the solvent (DMSO-d$_6$). These signals appear between 7.80-7.95 ppm. The aromatic protons show resonance signals between 7.30-7.40 ppm. The signals between 4.18-4.20 ppm are attributed to the methylene protons attached to -OCOPh- groups. The methylene groups attached to -OCONH- show signals at 3.42 ppm for TDI polymers and at 3.30 ppm for HMDI polymers. Methyl group attached to aromatic group show signal at 2.05 ppm for the TDI polymers. Figure 6 gives the ^{1}H NMR spectra of calcium containing HMDI polyurethane [Ca(HBP)$_2$-HMDI] and calcium containing TDI polyurethene [Ca(HBP)$_2$-TDI]. The ^{1}H NMR spectra for polyurethane-ureas show signals for the -NH protons of the urethane and urea groups which are shifted to down field due to the inter and intra-molecular


NCO
H3C
NCO
+ H2N(CH2)2OH
HNCONH(CH2)2OH
H3C
NHCONH(CH2)2OH
[TBHEU]
DBTDL
M(HBP)2 + HMDI
COO(CH2)4 OOCNH(CH2)6 NHCOO
COOMOOC
COO(CH2)4 OOCNH(CH2)6 NHCO
O
H3C
NHCHN(CH2)2
(CH2)2HNCHN
[M(HBP)2 – TBHEU – HMDI]
TBHEU + M(HBP)2 + TDI
DBTDL
DHF / DMSO
NHCOO
COO(CH2)4 OOCHN
CH3
COOMOOC
COO(CH2)4 OOCHN
CH3
NH
C=O
O
CH3
NHCHN – (CH2)2
(CH2)2HNCHN
[M(HBP)2 – TBHEU – TDI]

SCHEME 3

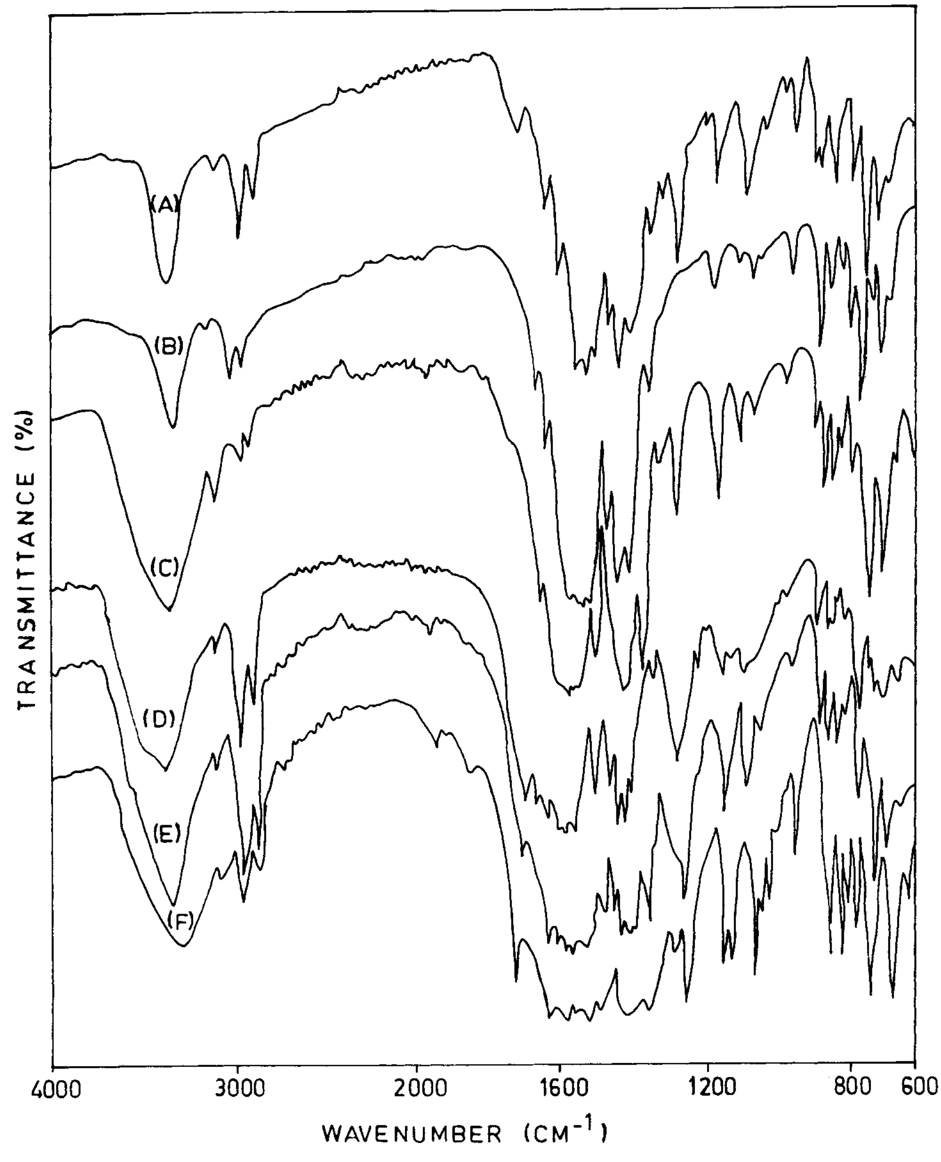


Figure 4. IR spectra of (A) $Pb(HBP)_2$-HMDI, (B) $Pb(HBP)_2$-TDI, (C) $Mn(HBP)_2$-TDI, (D) $Ca(HBP)_2$-HMDI, (E) $Mn(HBP)_2$-HMDI and (F) $Ca(HBP)_2$-TDI.

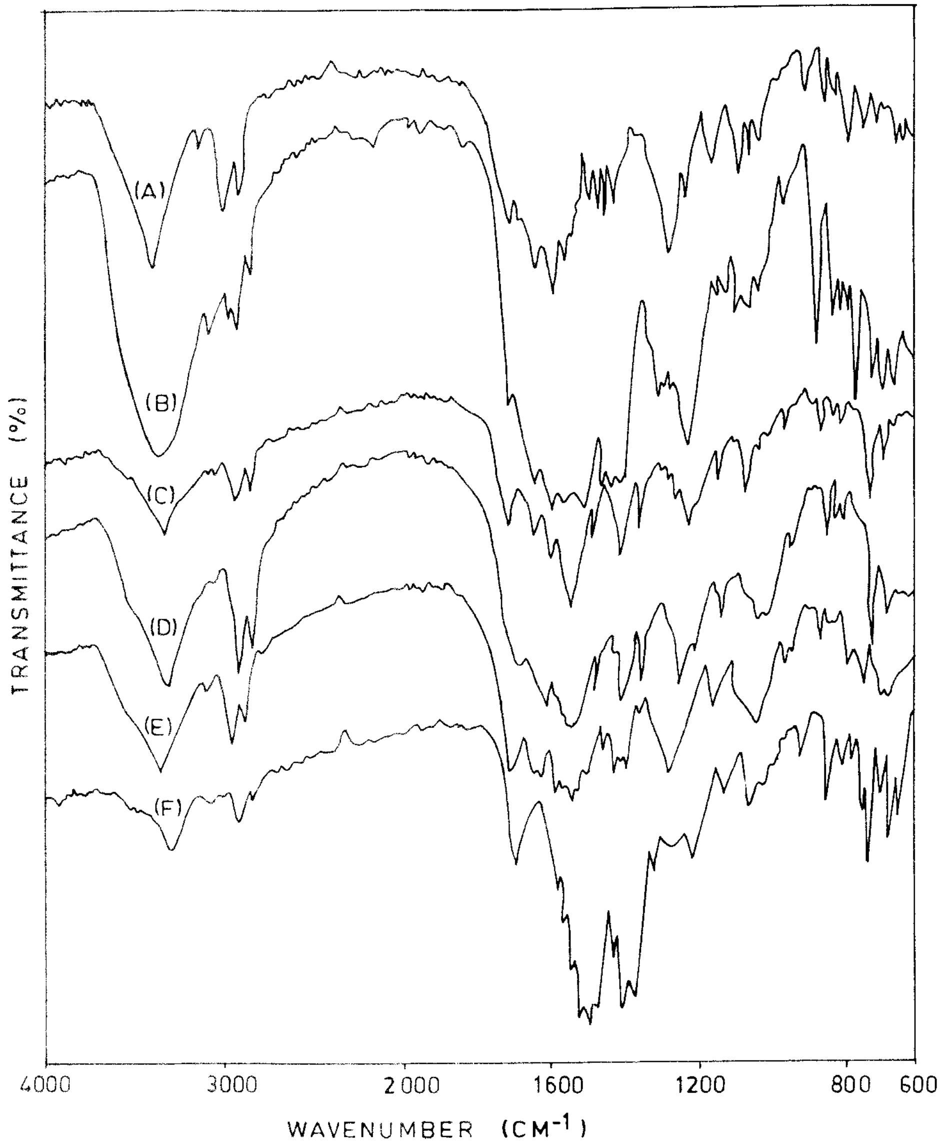


Figure 5. IR spectra of (A) Ca(HBP)$_2$-TBHEU-HMDI, (B) Ca(HBP)$_2$-TBHEU-TDI,(C) Mn(HBP)$_2$-TBHEU-TDI, (D) Mn(HBP)$_2$-TBHEU-HMDI, (E) Pb(HBP)$_2$-TBHEU-HMDI and (F) Pb(HBP)$_2$-TBHEU-TDI.

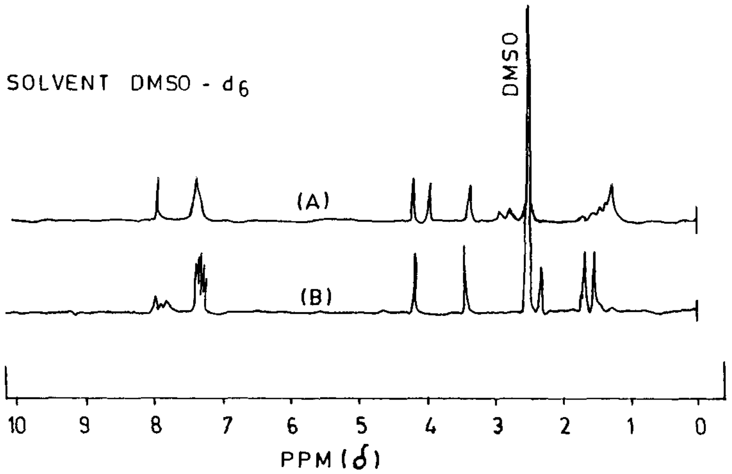


Figure 6. NMR spectra of (A) Ca(HBP)$_2$-HMDI and (B) Ca(HBP)$_2$-TDI.

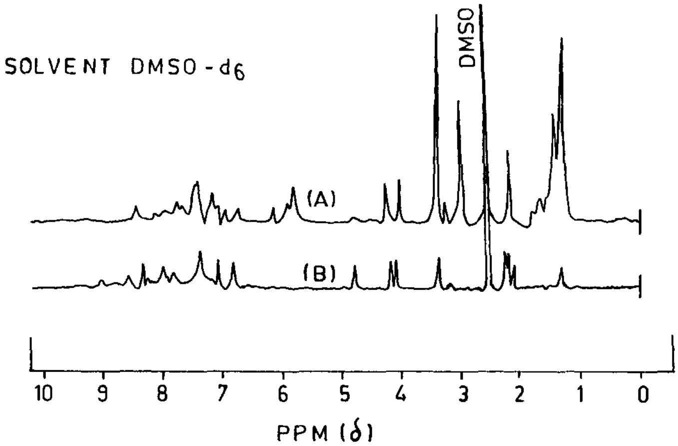


Figure 7. NMR spectra of (A) Ca(HBP)$_2$-TBHEU-HMDI and (B) Ca(HBP)$_2$-TBHEU-TDI.

hydrogen bonding between -NH group with C=O group and with the S=O group of the solvent (DMSO-d$_6$). They appear between 7.73-8.57 ppm. The aromatic protons give signals between 6.74-7.43 ppm. The methyleneoxy protons show peaks between 3.93-4.20 ppm. The signals between 3.15-3.31 ppm in the case HMDI based polyurethane-ureas are due to methylene protons adjacent to

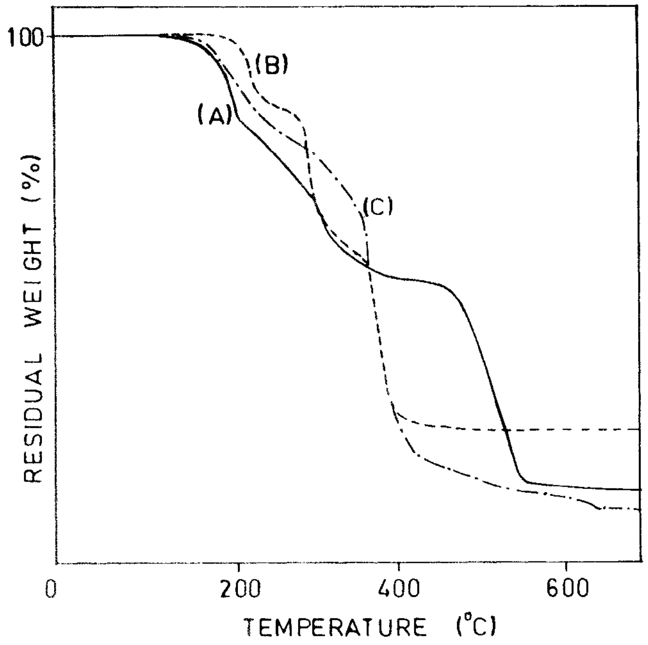


Figure 8. TGA curves of (A) $Ca(HBP)_2$-HMDI (B) $Pb(HBP)_2$-HMDI and (C) $Mn(HBP)_2$-HMDI.

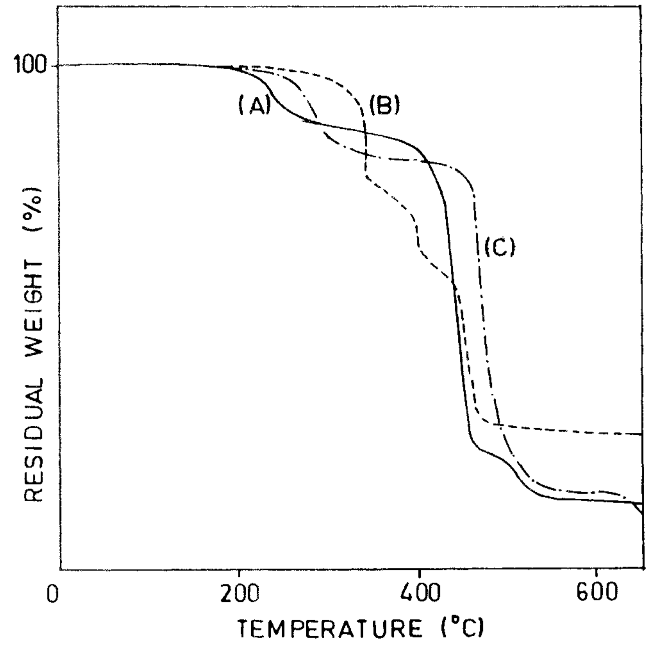


Figure 9. TGA curves of (A) $Mn(HBP)_2$-TDI, (B) $Pb(HBP)_2$-TDI and (C) $Ca(HBP)_2$-TDI.

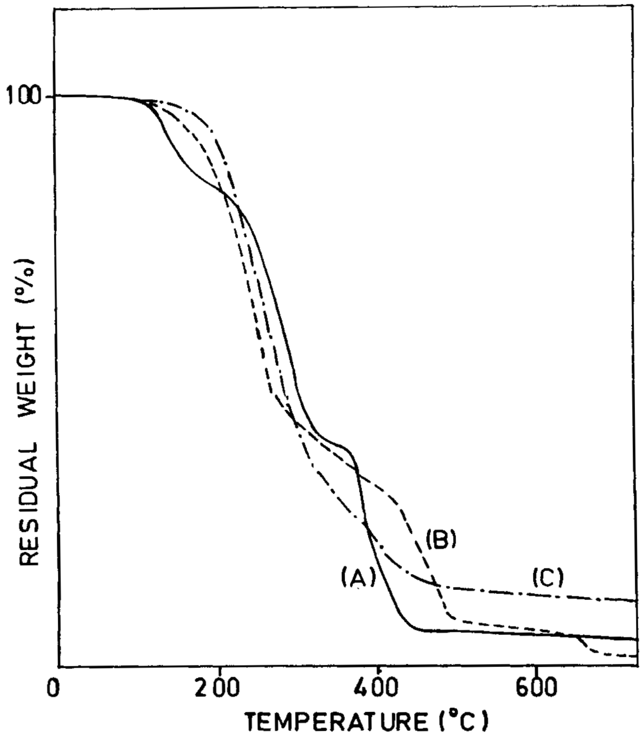


Figure 10. TGA curves of (A) $Mn(HBP)_2$-TBHEU-HMDI, (B) $Ca(HBP)_2$-TBHEU-HMDI and (C) $Pb(HBP)_2$-TBHEU-HMDI.

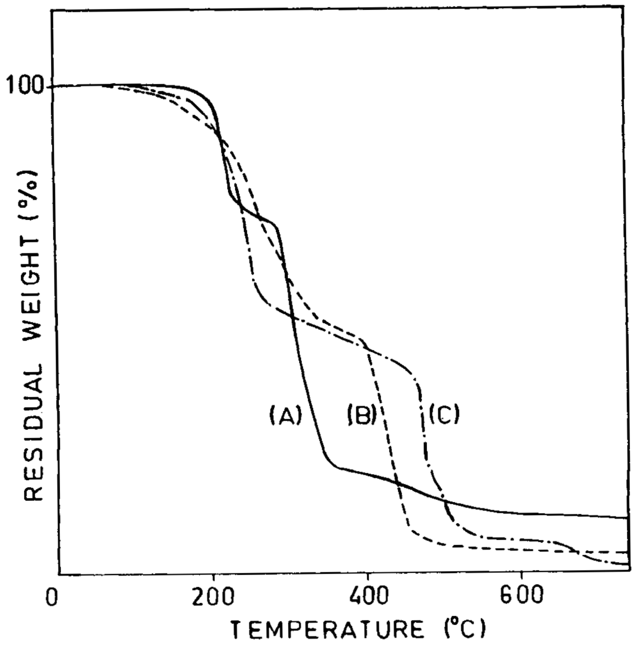


Figure 11. TGA curves of (A) $Pb(HBP)_2$-TBHEU-TDI, (B) $Mn(HBP)_2$-TBHEU-TDI and (C) $Ca(HBP)_2$-TBHEU-TDI.

TABLE 5. Thermal Data of Metal Containing Polyurethanes

Polymer	**Initial decomposition temperature °C**	**Temperature at 50% weight loss °C**	**Weight loss at 550°C %**
$Ca(HBP)_2$-HMDI	152	477	85
$Mn(HBP)_2$-HMDI	177	388	88
$Pb(HBP)_2$-HMDI	202	388	74
$Ca(HBP)_2$-TDI	243	480	86
$Mn(HBP)_2$-TDI	205	448	89
$Pb(HBP)_2$-TDI	295	461	74

-NHCOO- and -NHCONH- groups. The signals due to methyl protons are seen between 2.01-2.21 ppm. Figure 7 gives the ^{1}H NMR spectra of calcium containing HMDI polyurethane-ureas [$Ca(HBP)_2$-TBHEU-HMDI] and calcium containing TDI polyurethane-ureas [$Ca(HBP)_2$ TBHEU-TDI].

Figures 8, 9, 10 and 11 show the TGA curves of metal containing polyurethanes and polyurethane-ureas based on HMDI and TDI. The initial decomposition temperature for these polymers are found to be somewhat low. It was found that the initial decomposition temperature for polyurethanes based on HMDI are lower than that of the TDI based polyurethanes. Also, the initial decomposition temperature for polyurethane-ureas based on HMDI are lower than that of the TDI based polyurethane-ureas. Generally the stability of TDI based polyurethanes and polyurethane-ureas are found to be greater than the respective HMDI based polyurethanes and polyurethane-ureas. Polyurethanes are found to be more stable than the polyurethane-ureas. Thermal data of metal containing polyurethanes and polyurethane-ureas based on HMDI and TDI are given in the Tables 5 and 6 respectively. The residual weight at 550°C for the metal containing polymers corresponds to $CaCO_3$, Mn_2O_3 or PbO.

The metal containing polyurethanes and polyurethane-ureas are insoluble in most of the organic solvents but calcium and manganese containing polymers are soluble in highly polar solvents such as DMF, DMSO and m-cresol, lead containing polymers are sparingly soluble in these solvents. From their solubility in DMF and DMSO, the polymers are inferred to be polar in nature.

TABLE 6. Thermal Data of Metal Containing Polyurethane-Ureas

Polymer	**Initial decomposition temperature °C**	**Temperature at 50% weight loss °C**	**Weight loss at 550°C %**
$Ca(HBP)_2$-TBHEU-HMDI	162	268	94
$Mn(HBP)_2$-TBHEU-HMDI	131	302	95
$Pb(HBP)_2$-TBHEU-HMDI	182	285	87
$Ca(HBP)_2$-TBHEU-TDI	177	360	94
$Mn(HBP)_2$-TBHEU-TDI	135	383	96
$Pb(HBP)_2$-TBHEU-TDI	192	315	87

The intrinsic viscosity of the polymers in DMSO were found to be very low (values are incorporated in Tables 3 & 4) which shows that the ionic links in the polymer chain dissociate into low molecular weight fragments [9, 10, 24 & 26]. The intrinsic viscosity of polyurethane-ureas are found to be higher than that of polyurethanes due to lower amount of metal content hence less amount of ionic linkages in the polymer or due to their higher molecular weight.

For the metal containing polyurethanes, the experimentally determined percentage values of carbon, hydrogen and metal content are well within the range of calculated values. But, in the case of polyurethane-ureas, the percentage of carbon and hydrogen determined were higher than the calculated values assuming that there was 1:1 ratio of $M(HBP)_2$ and TBHEU units in the polyurethane-ureas. The metal content in polyurethane-ureas are found to be less than the calculated values, showing that reactivity of TBHEU is higher than that of metal containing ionic diols towards the diisocyanates. Analytical data of the metal containing polyurethane and polyurethane-ureas are given in Tables 7 and 8, respectively.

CONCLUSION

$M(HBP)_2$ salts are useful starting materials for the synthesis of ionic polymers into which metal is firmly incorporated. Thermal studies of $M(HBP)_2$ shows that $Ca(HBP)_2$ and $Mn(HBP)_2$ show two stage decomposition, while $Pb(HBP)_2$ show three stage decomposition, even though their structure are similar to one

TABLE 7. Analytical Data of Metal Containing Polyurethanes

Polymer	Repeating unit	Analytical data found (Calculated)		
		C	H	M
Ca(HBP)$_2$-HMDI	$CaC_{32}H_{38}N_2O_{12}$	56.64 (56.30)	5.82 (5.61)	5.97 (5.87)
Mn(HBP)$_2$-HMDI	$MnC_{32}H_{38}N_2O_{12}$	55.35 (55.10)	5.58 (5.49)	7.79 (7.87)
Pb(HBP)$_2$-HMDI	$PbC_{32}H_{38}N_2O_{12}$	45.51 (45.22)	4.72 (4.50)	24.28 (24.38)
Ca(HBP)$_2$-TDI	$CaC_{33}H_{32}N_2O_{12}$	57.75 (57.47)	4.81 4.67)	5.92 (5.87)
Mn(HBP)$_2$-TDI	$MnC_{33}H_{32}N_2O_{12}$	56.57 (56.34)	4.63 (4.58)	7.88 (7.80)
Pb(HBP)$_2$-TDI	$PbC_{33}H_{32}N_2O_{12}$	46.64 (46.31)	3.70 (3.76)	24.12 (24.21)

TABLE 8. Analytical Data of Metal Containing Polyurethane-Ureas

Polymer	Repeating unit	Analytical data found (Calculated)		
		C	H	M
Ca(HBP)$_2$-TBHEU-HMDI	$CaC_{53}H_{70}N_8O_{18}$	55.82 (55.48)	6.95 (6.50)	3.25 (3.49)
Mn(HBP)$_2$-TBHEU-HMDI	$MnC_{53}H_{70}N_8O_{18}$	55.03 (54.77)	6.42 (6.07)	4.26 (4.73)
Pb(HBP)$_2$-TBHEU-HMDI	$PbC_{53}H_{70}N_8O_{18}$	48.98 (48.43)	5.93 (5.36)	14.81 (15.76)
Ca(HBP)$_2$-TBHEU-TDI	$CaC_{55}H_{58}N_8O_{18}$	57.29 (56.98)	5.30 (5.04)	3.28 (3.45)
Mn(HBP)$_2$-TBHEU-TDI	$MnC_{55}H_{58}N_8O_{18}$	56.54 (56.26)	5.34 (4.99)	4.34 (4.67)
Pb(HBP)$_2$-TBHEU-TDI	$PbC_{55}H_{58}N_8O_{18}$	50.32 (49.80)	4.82 (4.40)	14.84 (15.62)

another. M(HBP)$_2$ salts are soluble in highly polar solvents like DMF, DMSO and m-Cresol and insoluble in most of the other organic solvents. Thus DMF or DMSO were used as solvent media for the synthesis of polymers based on M(HBP)$_2$. Thermal analysis of polymers show that the stability of metal containing TDI based polyurethanes and polyurethane-ureas are found to be greater than the respective metal containing HMDI based polyurethanes and polyurethane-ureas. Generally, metal containing polyurethanes are found to be more stable than metal containing polyurethane-ureas. The metal containing polymers are insoluble in most of the organic solvents, but soluble in highly polar solvents such as DMF or DMSO and m-cresol. From intrinsic viscosity measurements (in DMSO) of polymers, it was found that the presence of metal in the resulting polyurethanes and polyurethane-ureas decreases the intrinsic viscosity due to chain dissociation in DMSO solvent. Metal containing polyurethane-ureas are found to have higher intrinsic viscosity than that of metal containing polyurethanes. From the analytical method, it was found that the metal content in polyurethane-ureas are found to be lesser than calculated values which shows that reactivity of TBHEU is higher than that of metal containing ionic diols towards diisocyanates.

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