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7SYNTHESIS AND CHARACTERIZATION OF POLYURETHANES AND POLYURETHANE-UREAS BASED ON ZINC SALT OF MONO(HYDROXYBUTYL)PHTHALATE

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

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SYNTHESIS AND CHARACTERIZATION OF POLYURETHANES AND POLYURETHANE-UREAS BASED ON ZINC SALT OF MONO(HYDROXYBUTYL)PHTHALATE

R. Arun Prasath, R. Jayakumar, and S. Nanjundan*

Department of Chemistry
College of Engineering
Anna University, Guindy
Madras-600 025, India

Key Words: Zinc Salt of Mono(hydroxybutyl)phthalate, Ionic Monomer, Bisureas, Polyurethanes, Polyurethane-Ureas, Thermogravimetric Analysis, and Spectral Studies

ABSTRACT

Zinc salt of mono(hydroxybutyl)phthalate [Zn(HBP)$_2$] was synthesized by the reaction of 1,4-butanediol, phthalic anhydride and zinc acetate. Polyurethanes containing zinc ions in the main chain were synthesized by reacting hexamethylene diisocynate (HMDI) or toluylene 2,4-diisocyanate (TDI) with Zn(HBP)$_2$ using di-n-butyltindilaurate (DBTDL) as catalyst. Four different bisureas were prepared by reacting ethanolamine or 2-amino-2-methylpropanol with HMDI or TDI. Zinc containing polyurethane-ureas were synthesized by reacting HMDI or TDI with 1:1 mixture of Zn(HBP)$_2$ and each of the bisureas. Zn(HBP)$_2$ and the polymers were characterized by solubility study, elemental analysis, IR and ^{1}H-NMR spectroscopy, and thermogravimetric analysis.

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*Author to whom correspondence should be addressed. E-mail: snanjundan@hotmail.com

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INTRODUCTION

Incorporation of metal and functional groups into the polymers have emerged that possess wide applications as aqueous thickeners, impregnants, textile sizers, adhesives [1, 2], additives [3], resins [4, 5], catalysts [6] and in the biomedical field [7, 8]. Ionic diols containing ionic linkages between COO^- and M^{tt} are of interest, and are very important starting materials for the synthesis of ionic polymers in which the metal is firmly incorporated into the backbone of the polymer. Metal containing polymers with ionic links formed between COO^- and M^{2+}, in the backbone have been studied [9-11]. Synthesis and characterization of metal containing polyurethanes and polyurethane-ureas based on divalent metal [Ca^2, M^{2+}, and Pb^{2+}] salts of mono(hydroxybutyl)phthalate have been reported in this laboratory [12]. The present investigation is aimed at the synthesis and characterization of HMDI and TDI based polyurethanes and polyurethane-ureas from zinc salt of mono(hydroxybutyl)phthalate [$Zn(HBP)_2$], hexamethylene bis(ω,N-hydroxyethylurea) [HBHEU], toluylene 2,4-bis(ω,N-hydroxy-ethylurea) [TBHEU], hexamethylene bis(ω,N-1-hydroxy-2-methylprop-2-ylurea) [HBHMPU and toluylene 2,4-bis(ω,N-1-hydrox-y-2methylprop-2-ylurea) (TBHMPU).

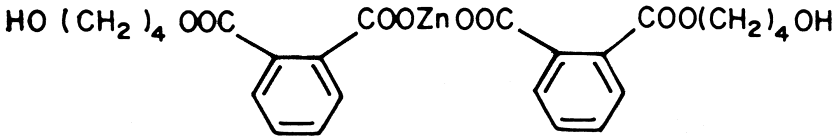
EXPERIMENT

Materials

Extra pure grade plithalic anhydride, 1,4-butanediol and zinc acetate dihydrate were used for the synthesis of the monomers. Fluka grade hexamethylene diisocynate (HMDI), toluylene 2,4,-diisocyanate (TDI) and di-n-butyltindilaurate (DBTDL) catalyst were used as received. The solvents such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc) and dimethylsulphoxide (DMSO) were purified by reduced pressure distillation. The solvents such as methanol, ethanol, ethyl methyl ketone, acetone, toluene, benzene, n-hexane, xylene, tetrahydrofuran, dioxane, chloroform and carbon tetrachloride were purified by standard methods.

Synthesis of $Zn(HBP)_2$

1,4-Butanediol was placed in a three-necked RB flask equipped with a thermometer, condenser, and a guard tube. Phthalic anhydride (0.1 mol) was



Zn (HBP)$_2$

Scheme 1.

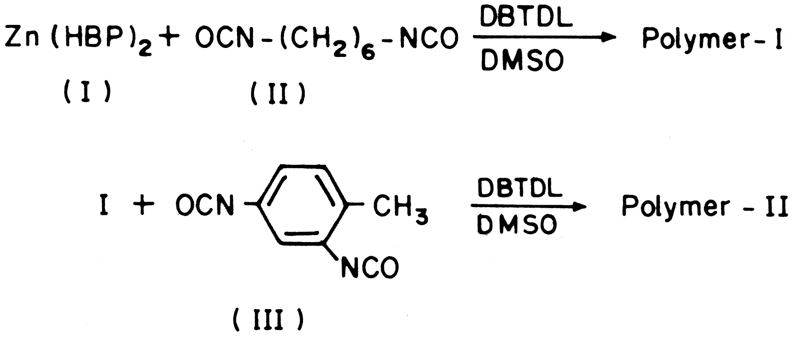
added little by little over a period of 30 minutes and the contents were stirred using a magnetic stirrer over an oil bath at 90°C for 30 minutes. Zinc acetate was then added to the reaction mixture little by little for 30 minutes, and the solution was stirred further for 3 hours at 120°C. Zn(HBP)$_2$ (Scheme 1) separated as white powder, washed first with acetone, then with methanol, and dried in *vacuo* at 60°C.

Synthesis of Bisureas

Bisureas such as HBHEU and TBHEU were synthesized according to the method reported by H. Matusuda [9]. Adopting the same procedure, we have synthesized HBHMPU and TBHMPU. 2-Amino-2-methyl-propan-l-ol (0.2 mol) and 150 mL of toluene were placed in a three-necked RB flask equipped with a mechanical stirrer, a dropping funnel, and a guard tube. The flask was cooled in an ice bath and a solution of HMDI or TDI (0.1 mol) in 50 mL of toluene was added dropwise, with constant stirring over a period of 30 minutes. After the addition, the mixture was stirred further for 30 minutes. The product formed was filtered, washed several times with acetone, then dried *in vacuo* at 60°C.

Synthesis of Polymer

For the synthesis of zinc containing polyurethanes, Zn(HBP)$_2$ (0-01 mol) was dissolved in DMSO solvent (350 mL) at 110°C in a three-necked RB flask fitted with a nitrogen inlet, a condenser, and a dropping funnel. After the mixture became homogenous, the temperature was reduced to 90°C and two drops of DBTDL catalyst was added. Then, 0.0 1 mol of HMDI or TDI dissolved in 20 mL of DMSO was added dropwise over a period of 20 minutes. The mixture was stirred at the same temperature for about 4 hours under a stream of nitrogen, then it was filtered at the hot condition itself. The product obtained was washed sev-



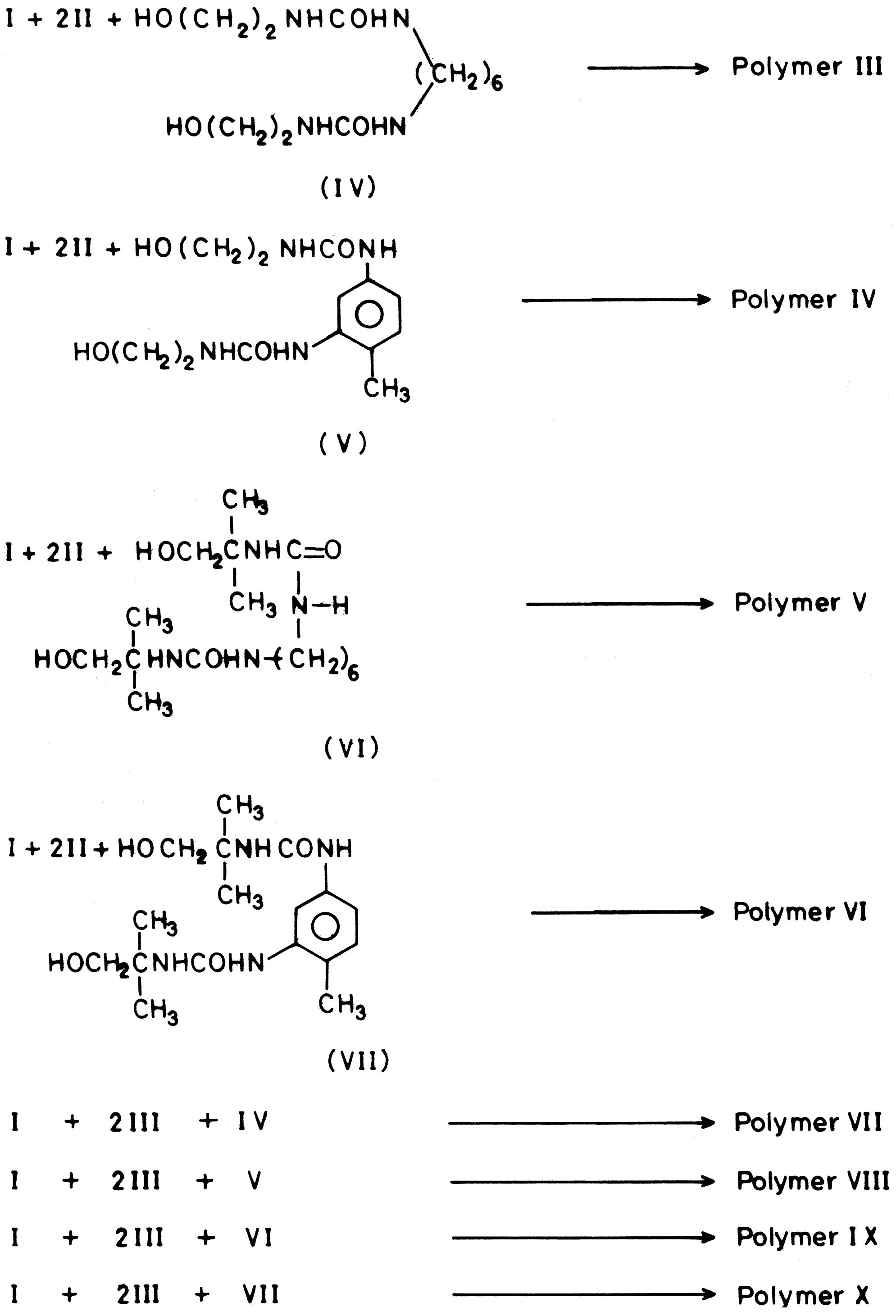
Scheme 2.

eral times successively with alcohol and acetone and then dried *in vacuo* at 60°C for 1 hour. With the help of $Zn(HBP)_2$ we have synthesized two zinc containing polyurethanes based on HMDI and TDI. The polymers are coded as $Zn(HBP)_2$-HMDI (I) and $Zn(HBP)_2$-TDI (II) (Scheme 2).

Similarly, zinc containing polyurethane-ureas were synthesized by reacting $Zn(HBP)_2$ (0.005 mol) and HBHEU, TBHEU, HBHMPU or TBHMPU (0.005 mol) dissolved in 200 mL of DMSO with HMDI or TDI (0.01 mol) in 20 mL of the same solvent using DBTDL as catalyst. The polymers were washed several times sucessively with alcohol and acetone and then dried *in vacuo* at 60°C for 1 hour. With the help of $Zn(HBP)_2$ and four bisureas we have synthesized eight zinc containing polyurethane-ureas based on HMDI or TDI. The polymers are coded as $Zn(HBP)_2$-HMDI-HBHEU(III), $Zn(HBP)_2$-HMDI-TBHEU (IV), $Zn(HBP)_2$-HMDI-HBHMPU (V), $Zn(HBP)_2$-HMDI-TBHMPU (VI), $Zn(HBP)_2$-TDI-HBHEU (VII), $Zn(HBP)_2$-TDITBHEU (VIII), $Zn(HBP)_2$-TDI-HBHMPU (IX), and $Zn(HBP)_2$-TDI-TBHMPU (X) (Scheme 3).

Instrumentation

The IR spectra were recorded in a Perkin-Elmer Model 598 Spectrophotometer at room temperature with KBr pellet method. The ^{1}H-NMR spectra were recorded in JEUOL-GSX-400 MHz Spectrometer in DMSO-d_6, solvent at 100°C using tetramethyl silane (TMS) as the internal standard. Thermogravimetric analysis (TGA) was performed using Metler-3000 Thermal Analyzer at a heating rate of 20°C/min in air atmosphere. Solubility of the polymers was tested in various polar and non-polar solvents. Perkin-Elmer 2400 Carbon Hydrogen Analyzer was used for elemental analysis. To estimate the zinc content, $Zn(HBP)_2$ and its polymers were


I + 2II + HO(CH2)2NHCOHN
(CH2)6
HO(CH2)2NHCOHN
(IV)
Polymer III
I + 2II + HO(CH2)2 NHCONH
HO(CH2)2NHCOHN
CH3
(V)
Polymer IV
I + 2II + HOCH2CNHC=O
CH3
CH3 N—H
HOCH2CHNCOHN-(CH2)6
(VI)
Polymer V
I + 2II + HOCH2 CNH CONH
HOCH2CNHCOHN
CH3
(VII)
Polymer VI
I + 2III + IV
Polymer VII
I + 2III + V
Polymer VIII
I + 2III + VI
Polymer IX
I + 2III + VII
Polymer X

Scheme 3.

digested with 50% aqueous H_2SO_4, the filtrate and the washings were neutralized, treated with aqueous NH_3/NH_4C, buffer and the solution at pH 10 was titrated against standardized EDTA solution using solochrome black as the indicator.

RESULTS AND DISCUSSION

Synthesis of $Zn(HBP)_2$

Zinc salt of mono(hydroxybutyl)phthalate was synthesized by reacting phthalic anhydride, excess of 1,4-butanediol and zinc acetate for 4 hours with constant stirring at 120°C. The product obtained was contaminated with the unreacted mono(hydroxybutyl)phthalate, 1,4-butanediol and zinc acetate. These contaminations were removed from the product by washing first with acetone and then with methanol and then dried *in vacuo* at 60°C. For obtaining higher yield, the optimum mole ratio of 1,4-butanediol to phthalic anhydride was found to be 4. The formation of $Zn(HBP)_2$ was confirmed by IR and ^{1}H-NMR spectrum shown in Figure 1 and 2, respectively. TGA curve of the salt is shown in Figure 3.

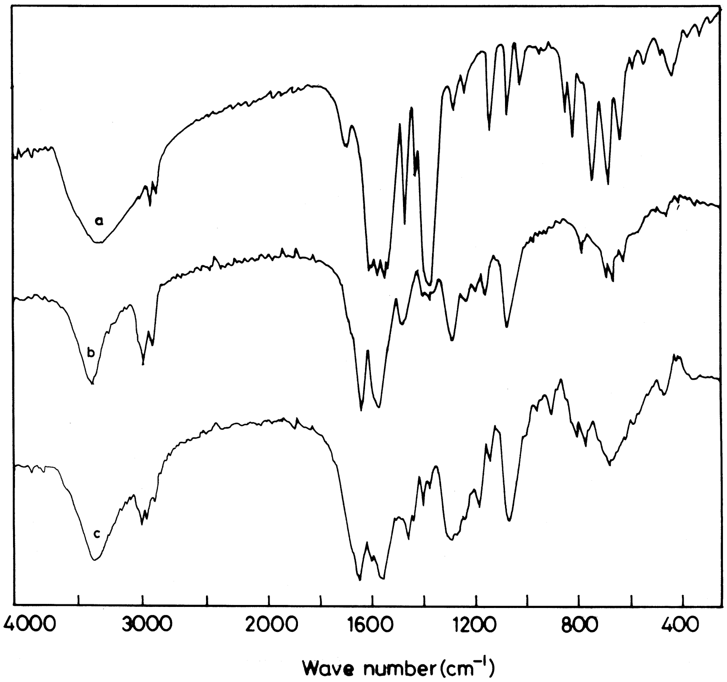


Figure 1. IR spectra of (a) $Zn(HBP)_2$, (b) HBHMPU, and (c) TBHMPU.

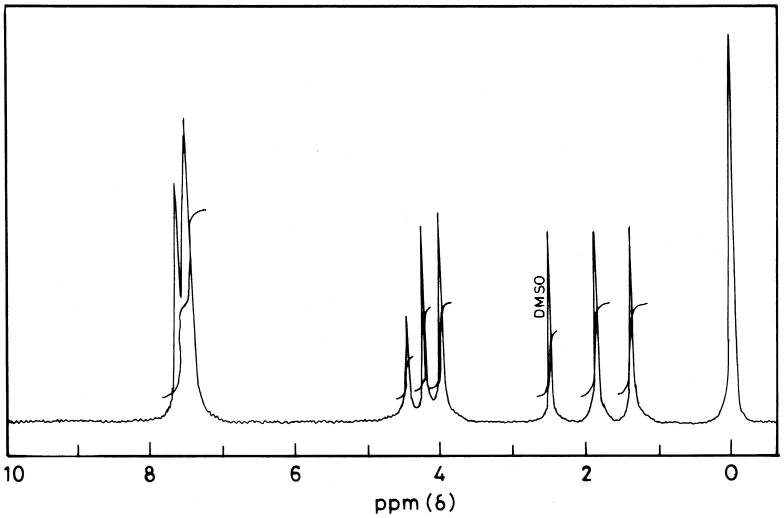


Figure 2. ^{1}H-NMR spectrum of Zn(HBP)$_2$.

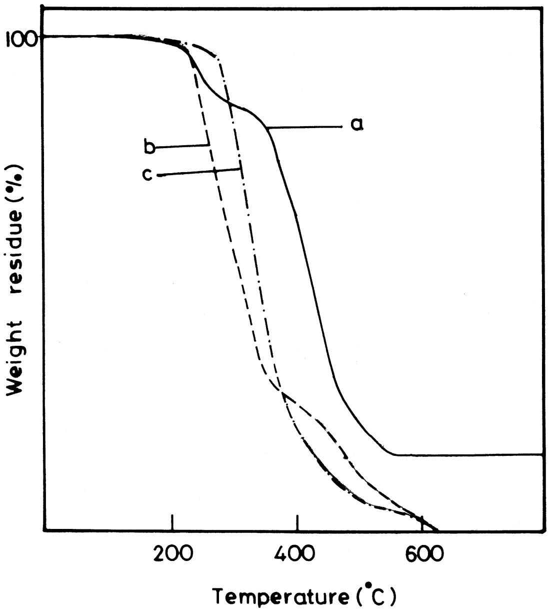


Figure 3. TGA curves of (a) Zn(HBP)$_2$, (b) HBHMPU, and (c) TBHMPU.

IR (cm^{-1}) : 3312(0-H stretching), 2932-2859 (asymmetrical and symmetrical C-H stretching), 1720 (C=O stretching), 1600 and 1385 (carboxylate ion stretching)
^{1}H-NMR (d ppm) : 7.5 (8H) (phenyl), 4.44 (2H) (0-H), 4.18 (4H) (-PhCOO**CH**$_2$-) 3.95 (4H) (-CH$_2$0H), 1.89 (4H) (-PhCOOCH$_2$**CH**$_2$-), 1.42 (4H) (**-CH**$_2$CH$_2$0H)

Analytical data of Zn(HBP)$_2$ showed that the found and the calculated values were well with in the range. Found: Zn = 12.17%, C = 53.52% and H = 4.93%, Calculated: Zn = 12.03%, C = 53.33%, and H = 4.81%. Zn(HBP)$_2$ was found to be insoluble in most of the organic solvents and slightly soluble in DMSO at room temperature and fully soluble at higher temperatures.

Synthesis of HBHMPU and TBHMPU

The reaction between isocyanate and amino group is much more faster than that between isocyanate and hydroxyl group and the reaction rate in the former is about 100 times more than that in the latter. Thus, in a 1:2 system of diisocynate and 2-amino-2-methylpropan-1-ol, the diisocynate will react with amino group only. As the reaction between the diisocyanates and amine is exothermic, the use of a solvent is very important. HBHMPU or TBHMPU is synthesized by the reaction of HMDI or TDI with twice its amount of 2-amino-2-methylpropan-l-ol under an ice bath. The products were obtained as white powder. The yield were generally high (90-95%). The formation of bisureas (HBHMPU and TBHMPU) were confirmed by IR and ‘H-NMR spectra. The IR spectra of the bisureas are shown in Figure 1. Figure 4 shows the ^{1}H-NMR spectra of the bisureas.

HBHMPU IR (cm^{-1}): 3370 (0-H and N-H stretching), 2985 and 2870 (asymmetrical and symmetrical C-H stretching), 1640 (C=O stretching), 1580 (N-H bending), 1395 and 1370 (C-H bending due to gem dimethyl groups), 1075 (C-0 stretching due to primary alcohol).

^{1}H-NMR (d ppm): 5.84 (2H) (-CH$_2$**NH-), 5.56 (2H) (-NH**CMe$_2$-), 5.16 (2H) (-OH), 3.31 (4H) (-CH$_2$0-), 2.94 (4H) (-NH**CH**$_{2\text{-}),\ \mathbf{1.34}}$-1.25 (8H) (-CH2(**CH**$_2$) 4(**CH**$_{2\text{-}}$), 1.13 (12H) (-CH$_3$).

TBHMPU IR (cm^{-1}): 3380 (0-H and N-H stretching), 3050 (Aromatic C-H stretching), 2960 & 2880 (asymmetrical and symmetrical C-H stretching), 1645 (C=O stretching), 1600 (aromatic C=C stretching), 1565 (N-H bending and

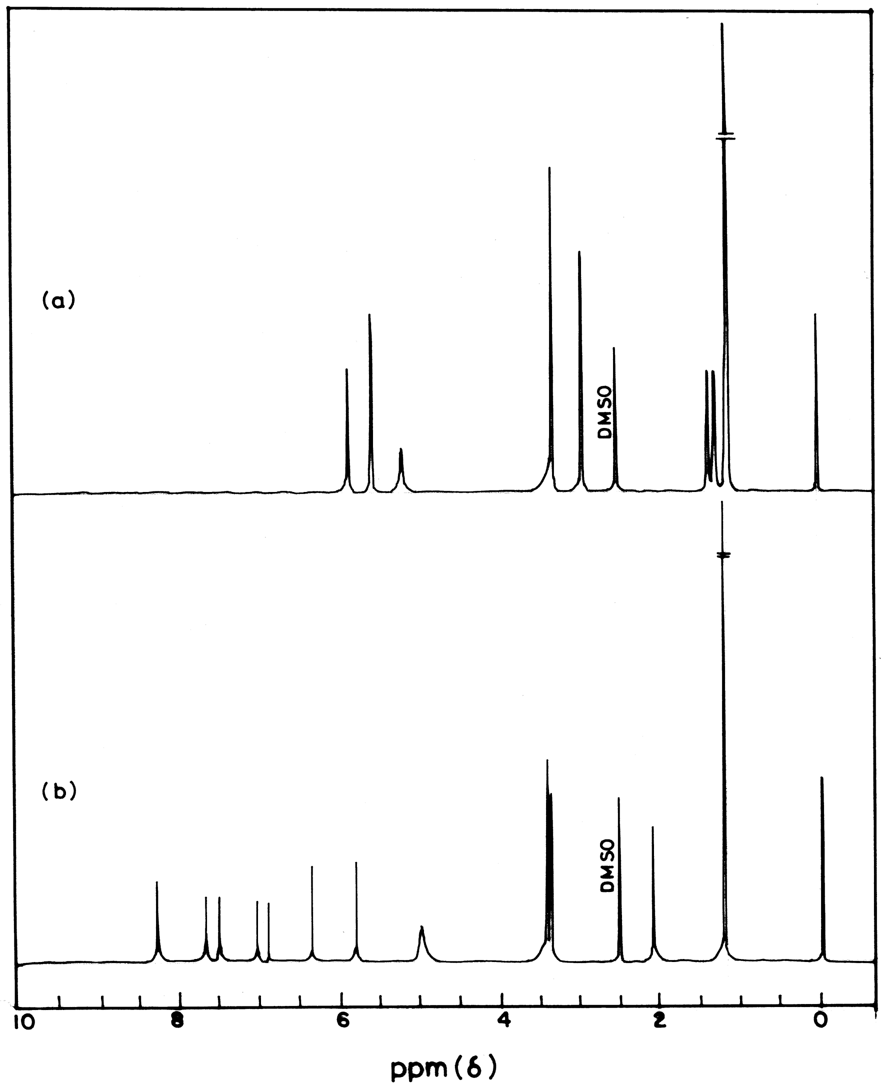


Figure 4. ^{1}H-NMR spectra of (a) HBHMPU and (b) TBHMPU.

C=C stretching), 1390 and 1370 (C-H bending due to gem dimethyl groups), 1070 (C-0 stretching due to primary alcohol).

^{1}H-NMR (d ppm): 8.34-6.88 (3H) (aromatic), 6.31 (2H) (**-NH**Ar), 5.80 (2H) (**-NH**CMe$_2$-), 5.00 (2H) (OH), 3.41 (4H) (-CH$_2$0-), 2.09 (3H) (Ar-CH$_2$), 1.22 (12H) (-CH$_3$).

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The bisureas are insoluble in organic solvents such as acetone, chloroform, toluene, dioxane, n-hexane, and ethylacetate. They are soluble in water on heating but reprecipitate on cooling. They are soluble in DMF and DMSO. TGA curves of bisureas are shown in Figure 3. The initial decomposition temperature of HBHMPU is 220°C, while that of TBHMPU is 252°C.

Synthesis of Polymers

$Zn(HBP)_2$ is insoluble in most of the other organic solvents. Synthesis of zinc containing polymers were carried out in DMSO solvent. As $Zn(HBP)_2$ is fully soluble only at a higher temperature in a large quantity of DMSO, the salt was first dissolved in the solvent at 110°C, and then the temperature was reduced to 90°C for carrying out the polymerization. To avoid the formation of crosslinkages, the ratio between the diols [$Zn(HBP)_2$ and bisureas] and HMDI or TDI was maintained at 1:1. The product, separated as slightly yellowish powder, was filtered at the hot condition itself to avoid any reprecipitation of the unreacted $Zn(HBP)_2$ and the polymer was washed thoroughly with non-solvents such as acetone and methanol. The yield was between 73 to 82% and the polymers were dried *in vacuo* at 60°C. Table 1 shows the synthetic data of the polymers.

Characterization of the Polymers

The solubility test shows that the polymers are insoluble in methanol, ethanol, acetone, ethyl methyl ketone, chloroform, carbon tetrachloride, n-hexane, benzene, toluene, xylene, tetrahydrofuran, dioxane, N,N-dimethylacetamide, N,Ndimethylformamide and sparingly soluble in dimethylsulfoxide. As the polymers were not soluble, the viscosity study was not carried out. The polyurethanes show that the experimentally determined percentage values of carbon, hydrogen, and zinc are well within the range of calculated values. In the case of polyurethane-ureas, the experimentally determined percentage values of carbon and zinc are slightly lower than that of the calculated values, while there does not seem to be much of a difference in the percentage value of hydrogen. This may be due to the fact that the reactivity of the $Zn(HBP)_2$ is lower than that of bisureas towards the diisocynates. The analytical data of the zinc containing polyurethanes and polyurethane-ureas are shown in Table 1.

The IR spectra of polyurethanes and polyurethane-ureas show a broad absorption band at 3350-3300 cm^{-1} due to the N-H stretching. The peaks around 17 101660 cm^{-1} are attributed to the carboxyl stretching of urethane, urea, and ester groups. The carboxylate ion of the zinc salt gives two broad bands around

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TABLE 1. Synthesis Data and Analytical Data of Zinc Containing Polymers

Polymer*	Yield %	Analytical Data Found (Calculated) %		
		C	H	Zn
I	78	53.87 (54.32)	5.45 (5.37)	9.87 (9.19)
II	80	54.72 (55.54)	4.34 (4.48)	9.85 (9.13)
III	82	54.33 (53.52)	6.50 (6.52)	4.92 (5.57)
IV	82	52.73 (54.31)	5.88 (5.97)	4.77 (5.55)
V	79	54.17 (55.03)	6.95 (6.87)	4.74 (5.32)
VI	75	54.85 (55.74)	6.38 (6.35)	4.62 (5.29)
VII	78	53.05 (55.01)	5.43 (5.43)	4.63 (5.52)
VIII	80	53.84 (55.74)	4.81 (4.89)	4.55 (5.48)
IX	73	56.08 (57.09)	5.34 (5.32)	4.45 (5.24)
X	75	55.23 (56.40)	5.93 (5.84)	4.47 (5.26)

* External Appearance : Slightly Yellowish White.

1600 and 1400 cm^{-1}. This confirms the presence of ionic links in the polymers. Figures 5 and 6 show the IR spectra of the polymers based on HMDI and TDI, respectively.

The polymers were not soluble in DMSO at room temperature. Hence, the ^{1}H-NMR spectra of the polymers were recorded at 100°C. The ^{1}H-NMR

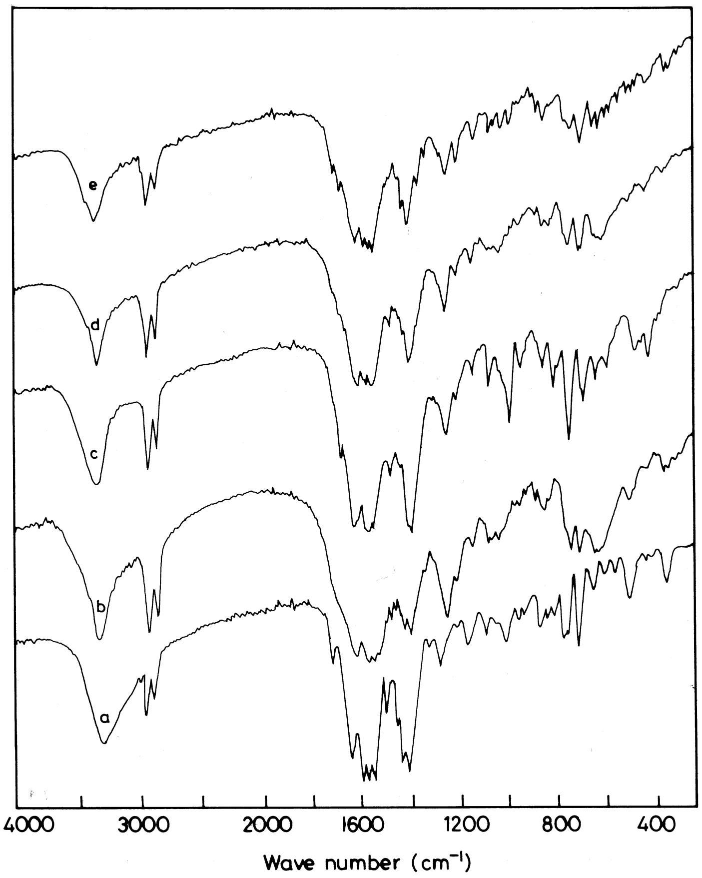

Figure 5. IR spectra of (a) Zn(HBP)$_2$-HMDI, (b) Zn(HBP)$_2$-HMDI-HBHEU, (c) Zn(HBP)$_2$-HMDI-TBHEU, (d) Zn(HBP)$_2$-HMDI-HBHMPU, and (e) Zn(HBP)$_2$-HMDI-TBHMPU.

spectra of polyurethanes show signals at 8.12-8.06 ppm for the N-H proton of the urethane groups which are actually shifted to down field due to the inter and intra-molecular hydrogen bonding between N-H group with C=O group and with S=O group of the solvent (DMSO-d$_6$). The aromatic protons show signal between 7.63-7.32 ppm. The peak at 5.36-5.34 ppm is due to non-hydrogen bonded NH protons. The methyleneoxy group attached to -COPh-group shows signal at 4.17-4.15 ppm. The signal at 3.99-3.97 ppm is attributed to the methyleneoxy group attached to the -CONH- group. The HMDI based polyurethane shows a proton signal at 3.06 ppm due to the methylene group attached to N-H group. The methyl group attached to aromatic zing shows a signal at 2.06 ppm for TDI based polyurethane. The other methylene groups in the polymers show

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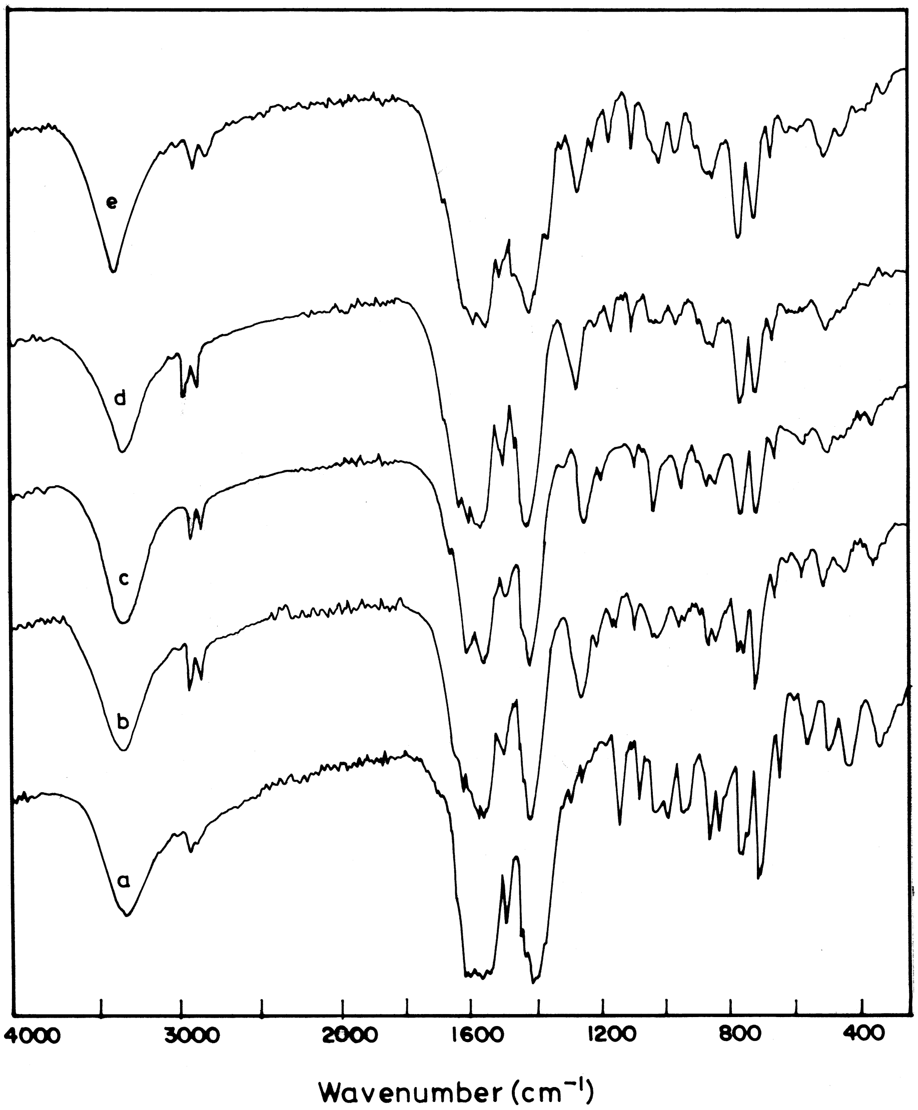

Figure 6. IR spectra of (a) Zn(HBP)$_2$-TDI, (b) Zn(HBP)$_2$-TDI-HBHEU, (c) Zn(HBP)$_2$-TDI-TBHEU, (d) Zn(HBP)$_2$-TDI-HBHMPU, and (e) Zn(HBP)$_2$-TDI-TBHMPU.

resonance signals between 1.44-1.31 ppm. Figure 7 shows the '^{1}H-NMR spectra of Zn(HBP)$_2$-HMDI and Zn(HBP)$_2$-TDI polyurethanes.

The ^{1}H-NMR spectra of polyurethane-ureas show signals for the inter and intramolecular hydrogen bonded N-H protons at 8.37-8.25 ppm and other

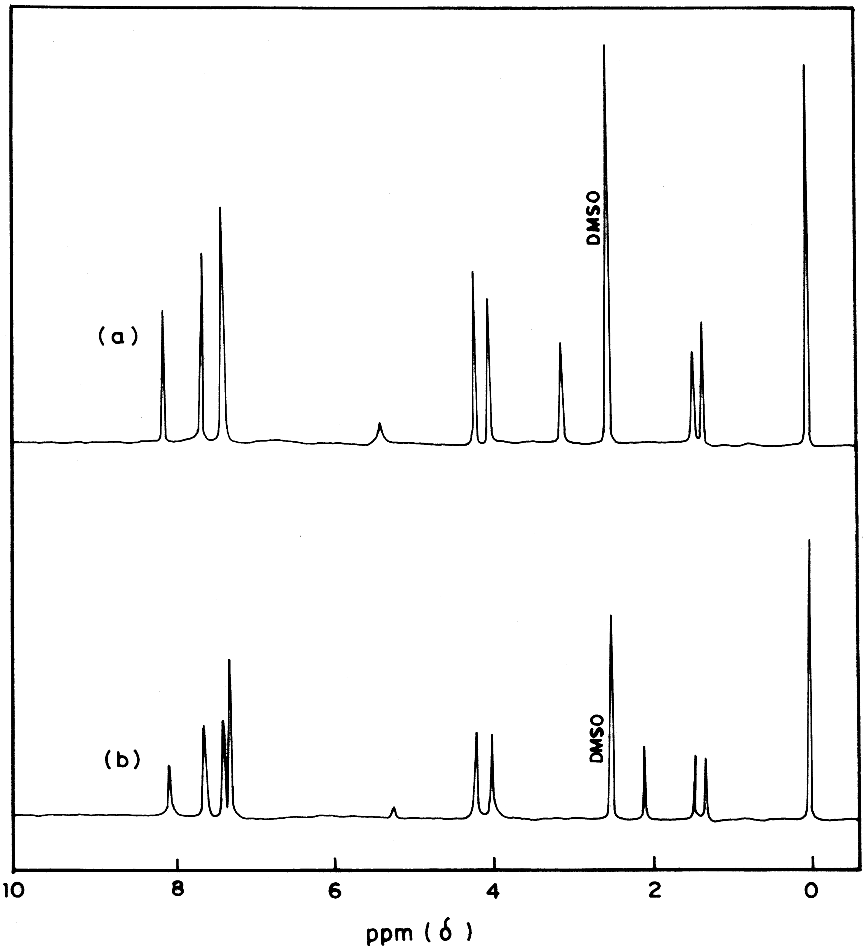

Figure 7. ^{1}H-NMR spectra of (a) Zn(HBP)$_2$-HMDI and (b) Zn(HBP)$_2$-TDI.

non-hydrogen bonded N-H protons at 5.54-5.52 ppm. The aromatic protons show signals between 7.87-7.34 ppm. The methyleneoxy protons show signal between 4.00-3.68 ppm. The methylene group attached to -NH group shows signal at 3.07-3.05 ppm in the case of HMDI based polyurethane-ureas. Methyl group attached to aromatic ring shows signal between 2.14-2.10 ppm for TDI based polyurethane-ureas. The methylene and gem dimethyl groups show resonance signal between 1.47-1.18 ppm.

Figure 8 shows the ^{1}H-NMR spectra of Zn(HBP)$_2$-HMDI-HBHMPU and Zn(HBP)$_2$-TDI-TBHMPU.

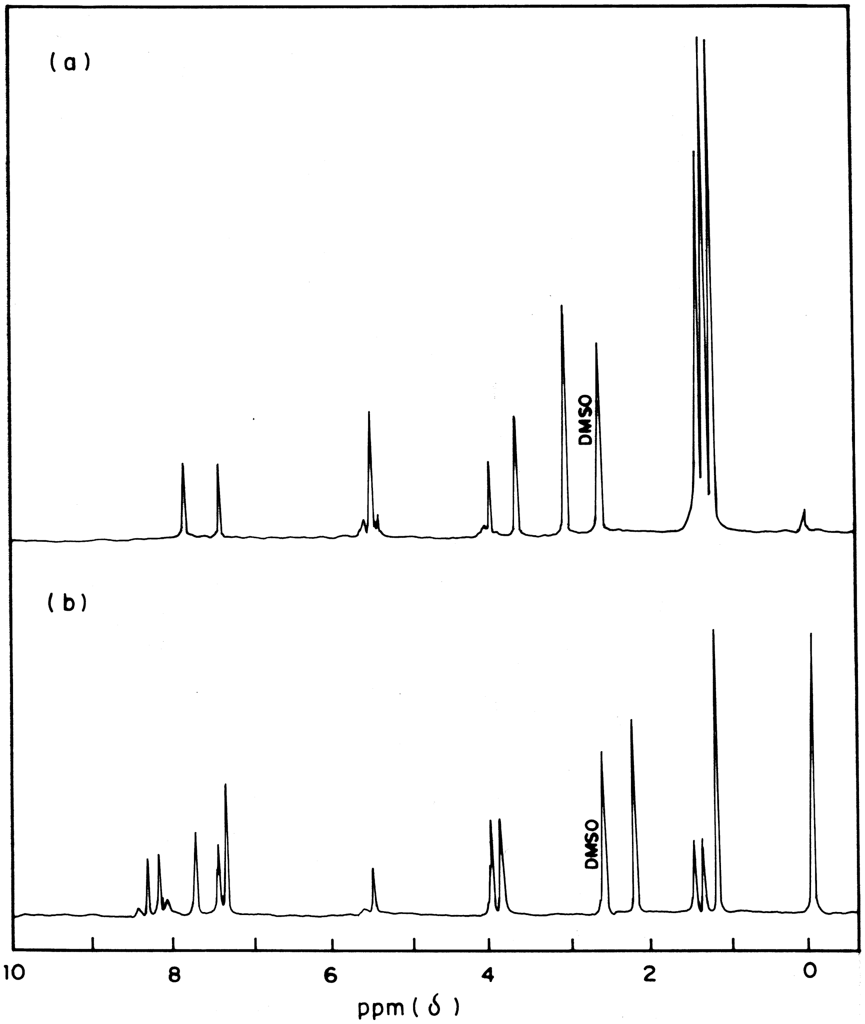

Figure 8. ^{1}H-NMR spectra of (a) Zn(HBP)$_2$-HMDI-HBHMPU and (b) Zn(HBP)$_2$-TDI-TBHMPU.

TGA traces of the polyurethanes and the polyurethane-ureas are shown in Figures 9-13. The initial decomposition temperature (IDT) values of the polymers are found to be between 208 and 232°C. From the TGA curves, it is observed that TDI based polymers are having slightly higher decomposition temperature than that of HMDI based polymers. In general, all the polyurethane-ureas show slightly higher stability than the polyurethanes, this may be

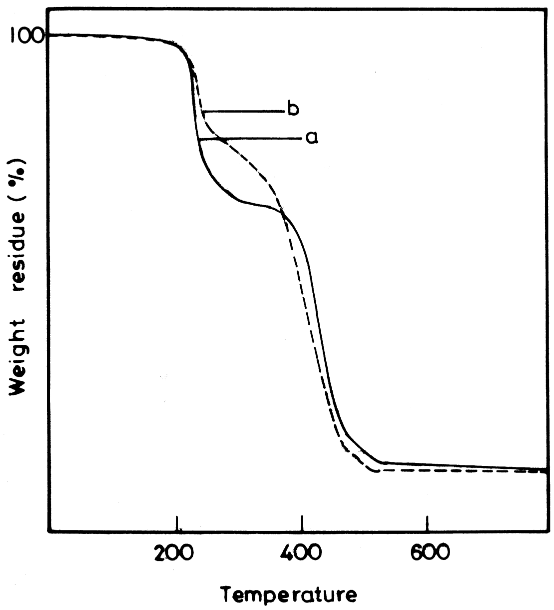

Figure 9. TGA curves of (a) $Zn(HBP)_2$-HMDI and (b) $Zn(HBP)_2$-TDI.

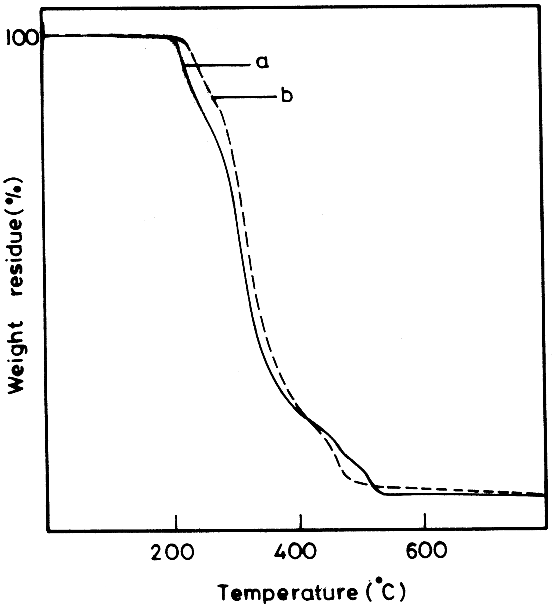

Figure 10. TGA curves of (a) $Zn(HBP)_2$-HMDI-HBHEU and (b) $Zn(HBP)_2$-HMDI-TBHEU.

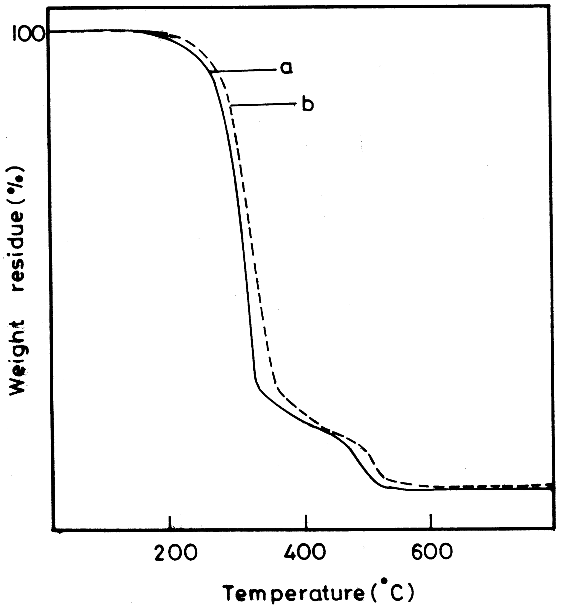

Figure 11. TGA curves of (a) Zn(HBP)$_2$-HMDI-HBHMPU and (b) Zn(HBP)$_2$-HMDI-TBHMPU.

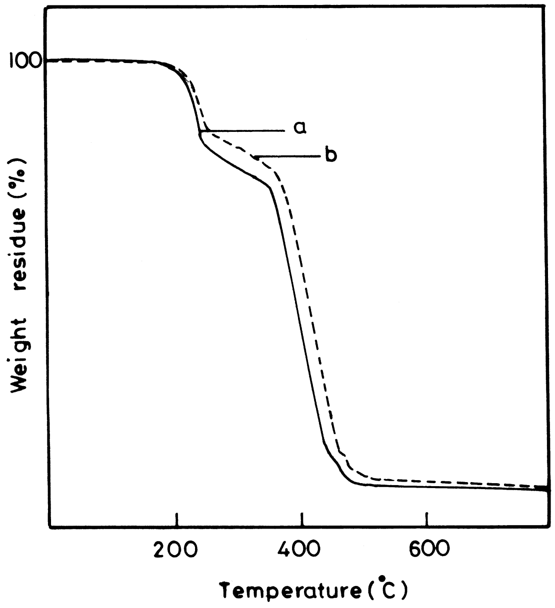

Figure 12. TGA curves of (a) Zn(HBP)$_2$-TDI-HBHEU and (b) Zn(HBP)$_2$-TDI-TBHEU.

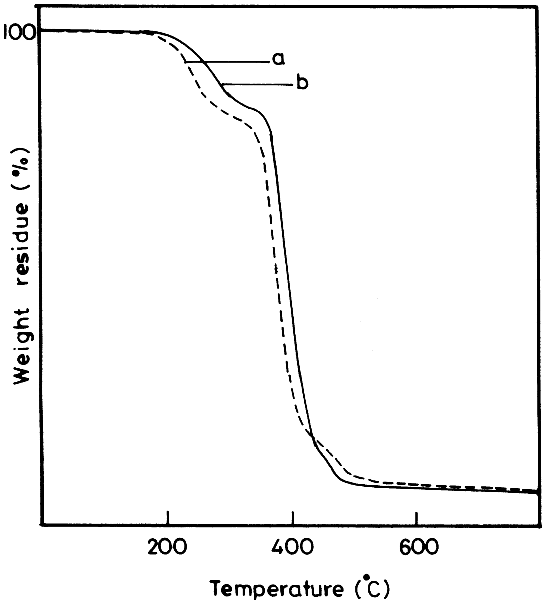

Figure 13. TGA curves of (a) $Zn(HBP)_2$-TDI-HBHMPU and (b) $Zn(HBP)_2$-TDI-TBHMPU.

attributed to the presence of more number of hydrogen bonding in the polyurethane-ureas. Polyurethane-ureas containing TDI based bisurea, (TBHEU or TBHMPU)have higher stability than TGA traces of the polyurethanes and the polyurethane-ureas, are shown in Figures 9-13. The initial decomposition temperature (IDT) values of the polymers are found to be between 208 and 232°C. From the TGA curves it is observed that TDI based polymers are having slightly higher decomposition temperature than that of HMDI based polymers. In general, all the polyurethane-ureas show slightly higher stability than the the polyurethanes, this may be attributed to the presence of a greater number of hydrogen bonding in the polyurethane-ureas. Polyurethane-ureas containing TDI based bisurea, (TBHEU or TBHMPU) have higher stability than those containing HMDI based bisurea, (HBHEU or HBHMPU). In all polymer cases, the residual weight at 550°C roughly corresponds to the zinc oxide formed.

TGA data of the polymers are shown in Table 2.

TABLE 2. Thermal Data of Zinc Containing Polymers

Polymer	IDT (°C)	Temperature at 50% wt. loss (°C)	Weight loss at 550°C (%)
I	208	416	87.0
II	208	432	88.0
III	216	320	93.4
IV	228	336	93.0
V	210	311	92.4
VI	220	326	91.5
VII	216	392	93.6
VIII	232	416	92.6
IX	209	391	93.0
X	228	406	92.8

IDT - Initial Decomposition Temperature.

CONCLUSION

Zinc salts of mono(hydroxybutyl)phthalate was synthesized by the reaction of 1,4-butanediol, phthalic anhydride and zinc acetate. Zn(HBP)$_2$ is insoluble in most of the organic solvents and soluble in DMSO at higher temperatures. Zinc containing polyurethanes and polyurethane-ureas having ionic links in the main chain were synthesized by the reaction of HMDI or TDI with Zn(HBP)$_2$ and 1:1 mixtures of Zn(HBP)$_2$ and HBHEU, TBHEU, HBHMPU, or TBHMPU. The polymers were not soluble in most of the organic solvents and sparingly soluble in DMSO at higher temperatures. For zinc containing polyurethanes, the experimentally determined percentage values of carbon, hydrogen, and zinc are well within the calculated values. But, in the case of polyurethane-ureas, it was found that the zinc and carbon content are less than the value calculated based on an equal reactivity of Zn(HBP)$_2$ bisureas. This may be due to the lower reactivity of Zn(HBP)$_2$ when compared to the bisureas towards the diisocyanates. The presence of ionic linkage in the polymers were confirmed by IR spectra. The polymers were also characterized by ^{1}H-NMR spectra at 100°C in DMSO-d_6 solvent. Thermal studies of the polymers show that the TDI based polymers are having slightly higher IDT than that of HMDI based polymers.

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