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STUDIES ON METAL-CONTAINING POLYURETHANES BASED ON DIVALENT METAL SALTS OF MONO(HYDROXYETHOXYETHYL)PHTHALATE

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ABSTRACT

By reacting phthalic anhydride with excess of diethylene glycol and metal acetate, the metal salts of mono(hydroxyethoxyethyl)phthalate were prepared (metal = Cu^{2+}, Mn^{2+} and Zn^{2+}). Polyurethanes containing metal ions in the main chain were synthesized by reacting hexamethylene diisocyanate (HMDI) or tolulylene 2,4-diisocyanate (TDI) with Cu^{2+}, Mn^{2+} and Zn^{2+} salts of mono(hydroxyethoxyethyl)phthalate using di-n-butyltin dilaurate (DBTDL) as catalyst. The prepared monomers and polyurethanes were characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR, UV spectra, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), elemental analysis, solubility and viscosity studies. The antibacterial activity of these polyurethanes have also been investigated using agar diffusion method.

Key Words: Metal salts of mono(hydroxyethoxyethyl)phthalate; Ionic monomer; Polyurethanes; Thermogravimetric analysis; Differential scanning calorimetry; Spectral studies; Antibacterial activity.

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INTRODUCTION

Divalent metal salts of mono(hydroxyethoxyethyl)phthalate are useful starting materials for synthesis of ionic polymers into which metal is firmly incorporated. Incorporation of metal and functional groups into the polymers have emerged that possess wide application as aqueous thickeners, impregnants, textile sizers, adhesives [1, 2], additives [3], resins [4-6], catalysts [7], and in the biomedical field [8, 9]. Generally, polyurethanes contain covalent bond in the polymer chain, and polyurethanes having ionic bonds in the polymer backbone are rare. Polymers containing ionic linkages in the main chain have been studied [10-15]. Polyurethane polyelectrolytes having potential application in soil conditioning have been studied [16].

When exposed to the atmosphere or used as adhesives, coatings, and in the field of biomedical practice, polymers may get contaminated or infected by microorganisms such as bacteria. Microorganisms have been found to be the cause for disbonding and blistering of protective coatings in various service situations. Some reports indicate the presence of a large number of microorganisms in areas where coatings have been detoriorated. Coating material itself can be infected by microorganisms from outside and bring about the deterioration in such a way that the physical reactions leading to disbonding and blistering can take place [17]. One of the techniques to overcome this problem is to develop polymer materials having biocidal activities [18]. Metal containing monomeric and polymeric materials with antibacterial activity have been patented [19-21].

The present investigation is aimed at the synthesis and characterization of copper, manganese and zinc containing polyurethanes from the ionic diols, metal salts of mono(hydroxyethoxyethyl)phthalate [$M(HEEP)_2$] and HMDI or TDI. The antibacterial activity of metal containing polyurethanes has also been examined against *Escherichia coli (E.coli), Streptococcus* sp., *Pseudomonas fluorescence* and *Salmonella* sp.

EXPERIMENTAL

Materials

Phthalic anhydride, diethylene glycol and metal (copper, manganese, zinc) acetates of extra pure grade were used as received. Hexamethylene diisocyanate (Fluka), toluylene-2,4-diisocyanate (Fluka) and di-n-butyltin dilaurate catalyst (Fluka) were used as received. The solvents such as acetone, methanol, dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), dimethyl acetamide (DMAc), benzene, toluene, and chloroform were purified by standard procedures. The organisms *Escherichia coli, Pseudomonas fluorescence, Streptococcus* sp. and *Salmonella* sp. were isolated from different environmental domains.

Synthesis of M[HEEP]$_2$

Diethylene glycol (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 over an oil bath at 60-70°C for an additional 30 minutes. Then metal (copper, manganese or zinc) acetate (0.05 mol) was added to the reaction mixture little by little over a period of 30 minutes and the temperature was raised to 80°C and the solution was stirred continuously for about three hours. The product, contaminated with impurities, was purified by washing successively with methanol and acetone. Then the product was dried *in vacuo* at 50-60°C.

Synthesis of Polymer

For the synthesis of metal containing polyurethanes M[HEEP]$_2$ (M=Cu^{2+}, Mn^{2+} and Zn^{2+}) (0.02 mol) was dissolved in DMSO solvent (100 ml) at 90°C in a three-necked round bottom flask fitted with a nitrogen inlet, a condenser, and a dropping funnel. After the mixture became homogenous, two drops of DBTDL catalyst were added. Then, 0.02 mol of HMDI or TDI dissolved in 50 ml of DMSO was added to the mixture over a period ranging from 20-30 minutes, depending on the diisocyanates used. The reaction mixture was stirred for about 4 hours under a stream of nitrogen. Then, it was diluted with 50 ml of DMSO and kept overnight. The solution was then filtered and the filtrate was treated with methanol to precipitate the polymer. The product obtained was washed several times successively with acetone and then dried *in vacuo* at 60°C for one hour.

Antibacterial Activity

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

The antibacterial activity was evaluated using nutrient agar medium by agar diffusion method [22]. One loopful of bacteria was innoculated in 10 ml of nutrient broth (peptone 5 g/L, beef extract 3.0 g/L, pH 6.8) and incubated at 37°C for 28 hours in a test tube shaker at 100 rpm. The actively growing bacterial cells were used for inhibition studies. 20 ml of nutrient agar was poured into sterile petriplates and allowed to solidify at room temperature. After solidification, 0.1 ml of the bacterial culture was spread on the nutrient agar. A circular well (9mm diameter) was made at the center for each petriplate with a sterilized steel borer. As DMSO had no effect on the growth of microorganism, the polyurethane test samples were prepared using this as the solvent at a concentration of 20 mg/ml. Then 0.1 ml of each test solution was added to the well and incubated at 37°C ± 0.5°C for 24 hours. After incubation the zone of inhibition were measured and were represented as (-), (+), (++) and (+++) depending upon the diameter and clarity.

Instrumentation

The IR spectra were recorded in a Testscan Shimadzu FT-IR 8000 series spectrophotometer at room temperature with KBr pellet method. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded in JEOL GSX-400 MHz spectrometer in DMSO-d_6 solvent using TMS as the internal standard. The UV spectra of the polymers in DMSO were recorded by using a Shimadzu UV-1601 model spectrophotometer. Thermogravimetric analysis (TGA) was performed using a Mettler-3000 thermal analyzer at a heating rate of 20°C/per minute in an air atmosphere. The differential scanning calorimetric analysis was carried out using a DSC V4.0B Dupont 2100 model. A Perkin-Elmer 2400 Carbon-Hydrogen analyzer was used for elemental analysis. Standard analytical methods were used to determine the metal content.

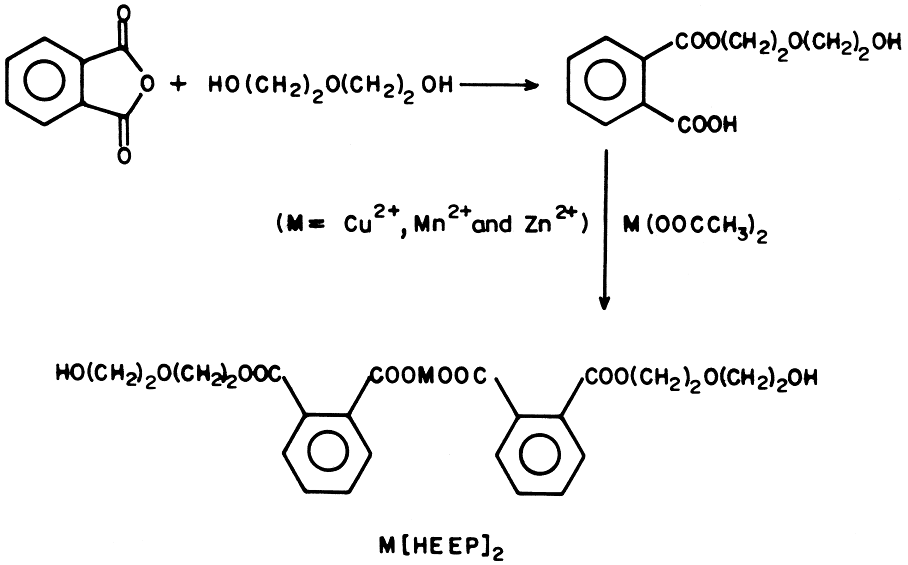
Intrinsic viscosities of the polymers were determined in DMSO at 40°C using an Ubbelohde viscometer. Solubility of the polymers was tested in various polar and non-polar solvents by taking 10 mg of the polymers in 2 ml of different solvents in a closed test tube and set aside for one day.

RESULTS AND DISCUSSION

Synthesis and Characterization of M[HEEP]$_2$

Metal salt of mono(hydroxyethoxyethyl)phthalate was synthesized by reacting phthalic anhydride, excess of diethylene glycol, and metal (Cu^{2+}, Mn^{2+} and Zn^{2+}) acetate for 4 hours with constant stirring at 80°C. The reactions are shown in Scheme 1. For the synthesis of metal containing monomers the mole ratio of ethylene glycol to phthalic anhydride used was investigated [10] and it was found that for obtaining a higher yield, the optimum mole ratio of diethylene glycol to phthalic anhydride was 4. The use of a lower mole ratio of diethylene glycol leads to polyester formation. The product obtained may be contaminated with the unreacted mono(hydroxyethoxyethyl)phthalate, metal acetate, diethylene glycol and the polyester. These contaminations were removed from the product by washing with methanol and then with acetone. The yield obtained was between 75-82%.

The IR spectra of monomers are shown in Figure 1. The spectra of the ionic diols show a broad band between 3418-3440 cm^{-1} due to the stretching of the hydrogen bonded -OH group. The absorption band at 1714-1720 cm^{-1} is attributed to the carbonyl stretching of the ester group. The carboxylate ions of the salts show two characteristic peaks, one at 1480-1495 cm^{-1} and another at 1558-1580 cm^{-1} which indicate that static ionic bonds are formed between COO^- and M^{2+}. A strong band at 1124-1128 cm^{-1} is due to the asymmetrical-C-O-C stretching. The



Scheme 1.

-C-O- stretching due to the primary alcohol was observed between 1042-1050 cm^{-1}. The C-H out of plane bending vibrations due to the benzene nucleus are seen at 712-739 cm^{-1}.

Figure 2 shows the ^1H-NMR spectrum of Zn[HEEP]$_2$. The ionic diols show resonance signals at 7.24-7.58 ppm due to the aromatic protons. The -COOCH$_2$-group shows a signal at 4.21-4.25 ppm. The resonance signals at 3.95-3.98 ppm are due to the hydroxyl proton. The methylene group attached to the alcoholic group shows a signal at 3.71-3.76 ppm. The signals at 3.52-3.56 ppm are attributed to the -CH$_2$-O-CH$_2$- group protons.

Figure 3 shows the proton decoupled ^{13}C-NMR spectrum of Zn[HEEP]$_2$. The chemical shift assignments were made from the off resonance decoupled spectra of the monomer. The resonance signals at 169.28 and 166.12 ppm are due to the -COO groups attached to Zn and CH$_2$ group, respectively. The resonance signals at 136.53 and 132.24 ppm are attributed to the aromatic carbon atoms to which the -COO groups are attached. The other aromatic carbons show signal at 128.51, 128.23, 126.80, and 125.38 ppm. The signals at 73.40 and 72.13 ppm are due to the methylene carbons attached to -OH and -OOCAr groups, respectively. The methylene carbon attached to the -CH$_2$OH group gave a resonance signal at 61.76 ppm. The other methylene carbon appears at 69.6 ppm.

The analytical data of M[HEEP]$_2$ is given in Table 1. For the metal salts of mono(hydroxyethoxyethyl)phthalate, the experimentally determined percentage values of carbon, hydrogen and metal content are well within the range of calculated values. The thermogravimetric analysis of the monomers show that Cu[HEEP]$_2$, Mn[HEEP]$_2$ and Zn[HEEP]$_2$ were stable up to 263, 350, and 346°C,

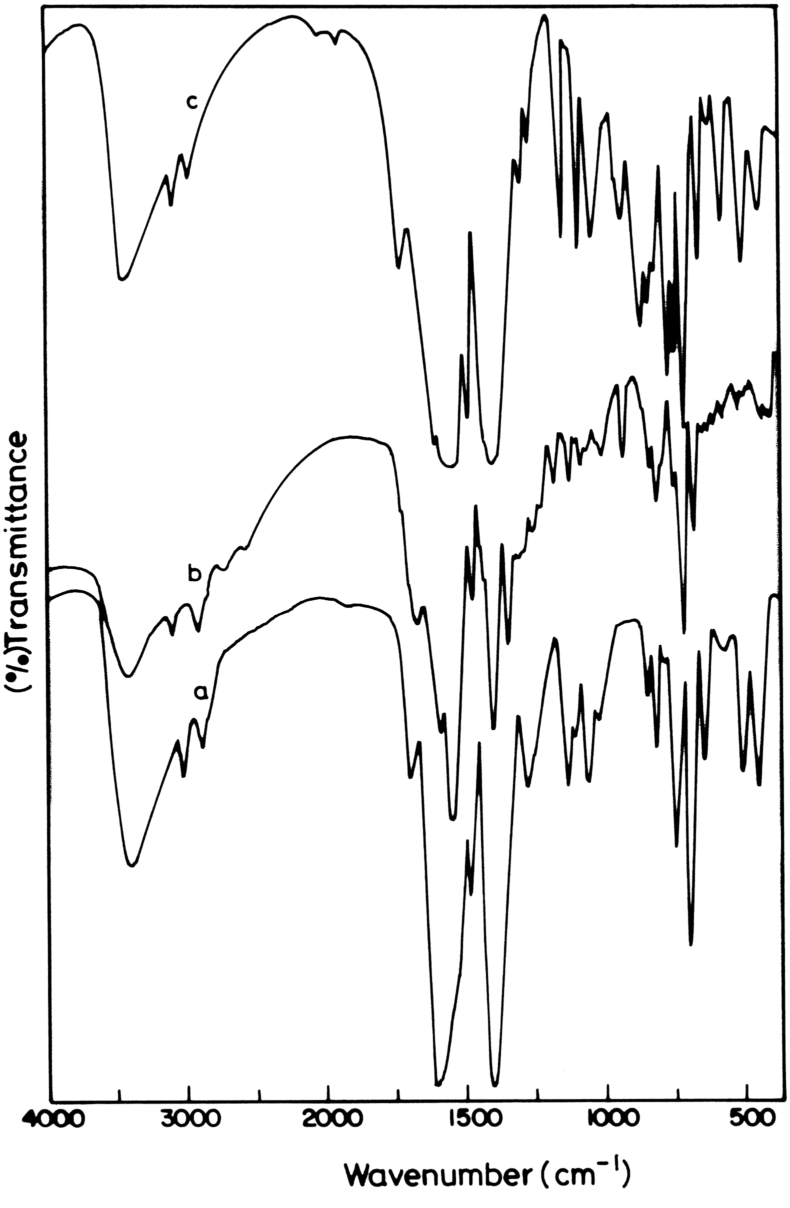


Figure 1. IR spectra of (a) Cu[HEEP]$_2$; (b) Mn[HEEP]$_2$; (c) Zn[HEEP]$_2$.

respectively. A weight loss of 50% occurred for copper, manganese and zinc containing monomers at the temperatures, 286, 380 and 435°C, respectively. The residual weight at 800°C corresponds to 14.2, 14.4, and 14.5%, respectively. These values roughly correspond to the amount of CuO, Mn_2O_3, and ZnO formed at this temperature. These values are close to the theoretically calculated values

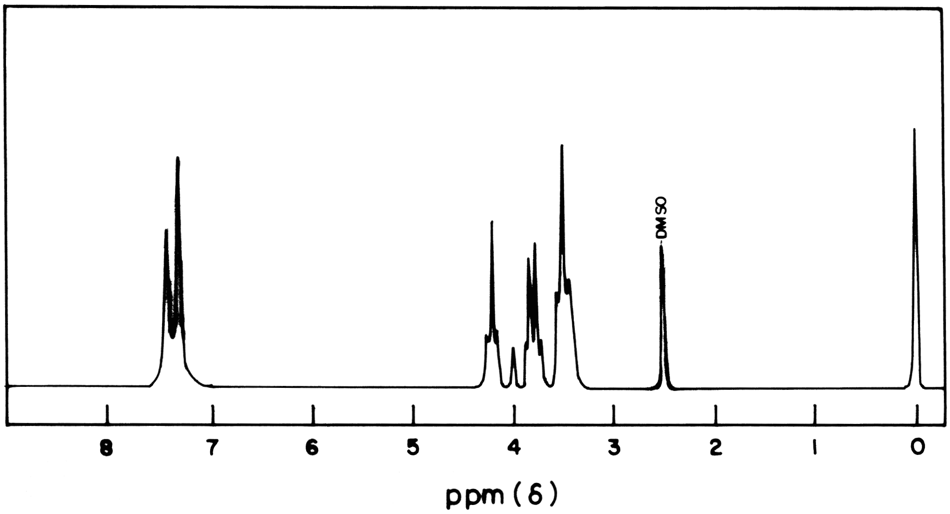


Figure 2. ^{1}H-NMR spectrum of Zn[HEEP]$_2$.

(13.96, 14.06, and 14.24%). The stability of metal containing monomers follows the order Mn>Zn>Cu (Figure 4).

The monomers Cu[HEEP]$_2$, Mn[HEEP]$_2$ and Zn[HEEP]$_2$ are soluble in highly polar solvents like DMF, DMSO, and DMAc and insoluble in benzene,

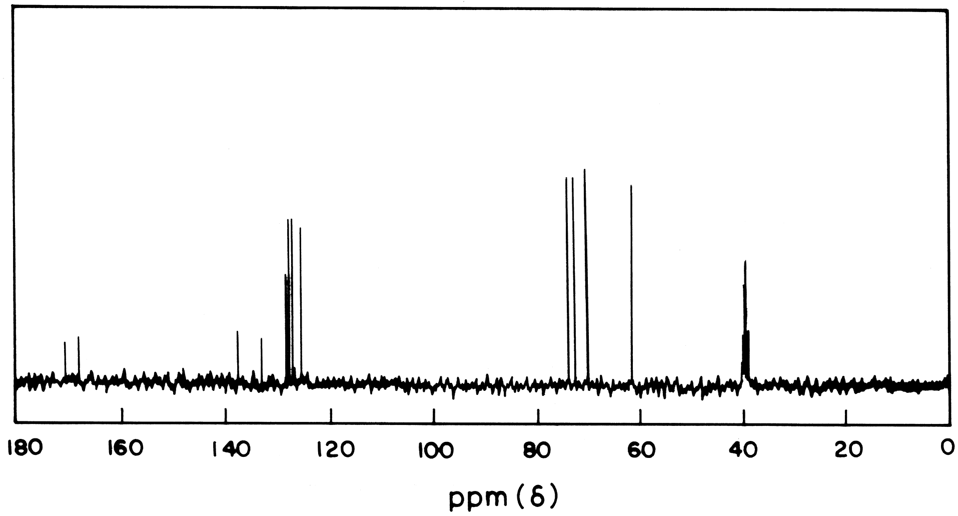


Figure 3. ^{13}C-NMR spectrum of Zn[HEEP]$_2$.

Table 1. Analytical Data on Divalent Metal Salts of Mono(hydroxyethoxyethyl)phthalate

		Analytical Data Found (Calculated)		
Monomer	Formula	C (%)	H (%)	M (%)
Cu[HEEP]2	CuC24$H_{26}O_{12}$	50.60 (50.58)	4.62 (4.60)	11.19 (11.15)
$Mn[HEEP]_2$	$MnC_{24}H_{26}O_{12}$	52.52 (52.48)	4.80 (4.77)	10.04 (10.00)
$Zn[HEEP]_2$	$ZnC_{24}H_{26}O_{12}$	50.55 (50.21)	4.62 (4.59)	10.48 (10.45)

toluene, xylene, tetrahydrofuran, dioxane, n-hexane, chloroform, carbon tetrachloride, carbon disulphide, ethyl methyl ketone, acetone, ethyl acetate, ethanol, and methanol.

Synthesis and Characterization of Polyurethanes

The metal salts of mono(hydroxyethoxyethyl)phthalate were insoluble in most of the organic solvents. Hence, the polymerization of these salts with diisocyanates were done in a polar solvent like DMSO. It was established that the reaction between diols and diisocyanates catalyzed by DBTDL takes place via the formation of a ternary complex between the reagents and the catalyst [23]. To avoid

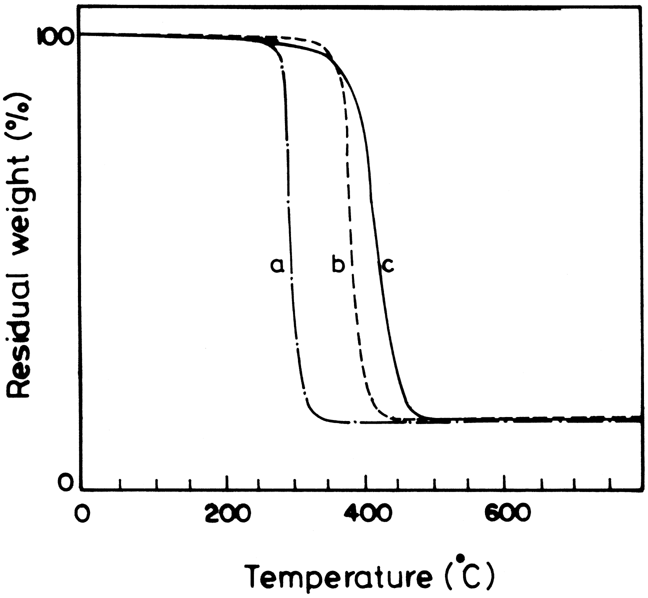


Figure 4. TGA curves of (a) $Cu[HEEP]_2$; (b) $Mn[HEEP]_2$; (c) $Zn[HEEP]_2$.

crosslinking of the polymers, the mole ratio of the diols and the diisocyanates was taken as 1:1. After the completion of the reaction, DMSO was added in large excess to dissolve the linear polymer. Filtration was carried out in order to separate out any crosslinked polymer formed. Subsequently, the dissolved polymer was reprecipitated by the addition of non-solvents like acetone or chloroform. The yields of polyurethanes were considerably good in all the cases. The polyurethanes based on TDI gave slightly higher yields than those based on HMDI. This may be due to the higher reactivity of TDI as compared to HMDI. Using the monomers Cu[HEEP]$_2$, Mn[HEEP]$_2$ and Zn[HEEP]$_2$ six metal containing polyurethanes were prepared based on HMDI and TDI. These polyurethanes are represented as HMDI-Cu[HEEP]$_2$, HMDI-Mn[HEEP]$_2$, HMDI-Zn[HEEP]$_2$, TDI-Cu[HEEP]$_2$, TDI-Mn[HEEP]$_2$ and TDI-Zn[HEEP]$_2$. The synthesis data of the polymers are given in Table 2.

The FT-IR spectra of HMDI based polyurethanes are shown in Figure 5. The band between 3323-3335 cm^{-1} is due to the N-H stretching. The C-H symmetrical and unsymmetrical stretching due to the methylene groups are observed between 2858-2932 cm^{-1}. The carbonyl stretching due to the urethane group is seen between 1680-1688 cm^{-1}. The carboxylate ion gives two broad peaks between 1470-1522 cm^{-1}. The N-H bending modes are observed between 1625-1628 cm^{-1}. The C-H out of plane bending vibrations of aromatic system are seen at 770-772 cm^{-1}.

The characteristic ^{1}H-NMR spectrum for the polyurethane, HMDI-Zn[HEEP]$_2$ is shown in Figure 6. The ^{1}H-NMR signals for the -NH protons are shifted to down field due to inter and intramolecular hydrogen bonding between -NH group and C=0 group and with the S=0 group of the solvent (DMSO). The -NH group shows a peak at 8.30-8.50 ppm. The aromatic protons show resonance signals between 7.24-7.72 ppm. The signal at 4.20 ppm is attributed to the methylene group attached to -COOPh. The methylene group attached to -OCONH shows a signal at 3.93 ppm. The -CH$_2$-O-CH$_2$$^-$ group shows a signal at 3.40 ppm. The methylene group attached to -NH shows a signal at 3.53 ppm. The other methylene groups show a signal between 1.32-1.64 ppm.

Table 2. Synthesis and Viscosity Data of Various Metal Containing Polyurethanes Based on HMDI and TDI

Polymer	Reaction Temp. (°C)	Reaction Duration (hrs)	Yield (%)	Appearance	Intrinsic Viscosity (η)
HMDI - Cu[HEEP]$_2$	90	4	80	Brown	0.0598
HMDI - Mn[HEEP]$_2$	90	4	83	Gr y powder	0.0774
HMDI - Zn[HEEP]$_2$	90	4	82	Light brown	0.0610
TDI - Cu[HEEP]$_2$	90	4	88	Light brown	0.0812
TDI - Mn[HEEP]$_2$	90	4	89	Light grey	0.0986
TDI - Zn[HEEP]$_2$	90	4	84	Light brown	0.0823

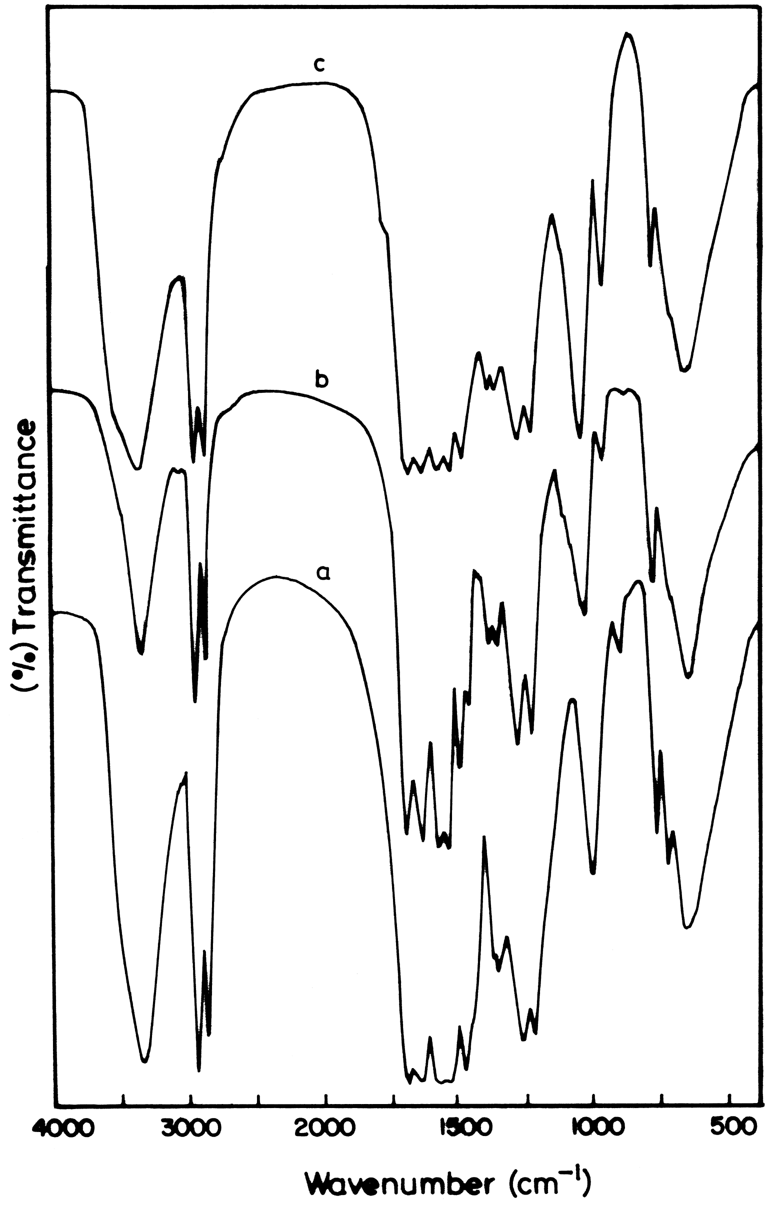


Figure 5. IR spectra of (a) HMDI - Cu[HEEP]$_2$; (b) HMDI - Mn[HEEP]$_2$; (c) HMDI - Zn[HEEP]$_2$.

Figure 7 shows the ^{13}C-NMR spectrum of HMDI based polyurethanes of Zn[HEEP]$_2$. The signals at 169.01 and 166.53 ppm are due to the -COO groups attached to the aromatic nucleus. The signal at 154.11 ppm is due to -NHCOO- group. The aromatic carbon atoms to which -COO groups are attached show signals at 136.65 and 132.22 ppm. The other aromatic carbon atoms show signals at

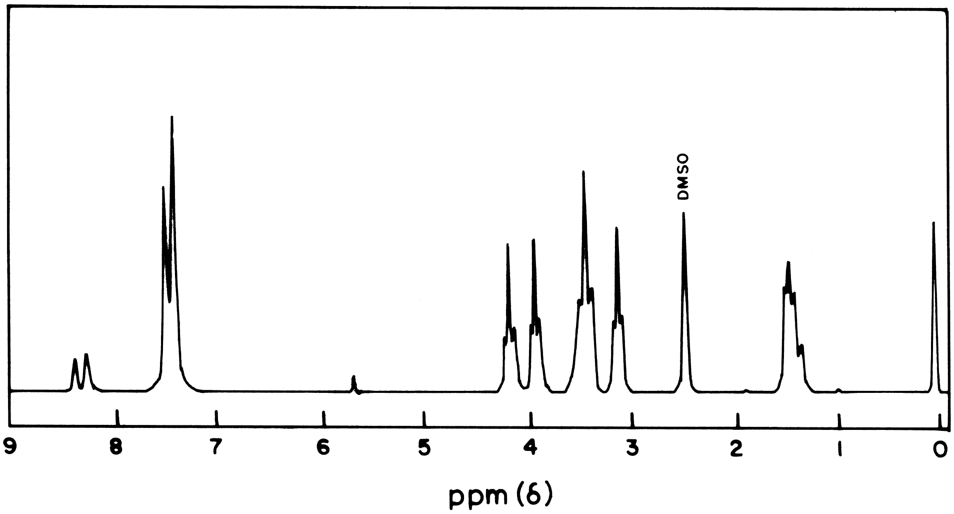


Figure 6. ^{1}H-NMR spectrum of HMDI - Zn[HEEP]$_2$.

128.59, 128.23, 126.75, and 125.73 ppm. The signals at 71.01, 69.83, 68.66, and 63.30 ppm correspond to the methylene carbons in the -$OCH_2CH_2OCH_2CH_2O$- group. The methylene carbons of the HMDI unit gave signals at 43.16, 32.21, and 26.21 ppm.

The UV spectrum of the polyurethane, HMDI-Cu[HEEP]$_2$ shows strong absorption peak at 257 nm and a shoulder at 291 nm. The former peak may be associated with the n-π* transition of the carboxylate group. The shoulder could be an absorption due to the charge transfer involving the metal and ligand (overlap of π-π* and n-π* transitions). The UV spectrum of HMDI-Mn[HEEP]$_2$ polyurethane has a strong absorption peak at 256 nm (n-π* transition of the carboxylate carbonyl) and shoulder at 290 nm, probably due to the charge transfer between Mn and the ligand. Similarly, the UV spectrum of HMDI-Zn[HEEP]$_2$ polymer shows an intense peak at 254 nm and a shoulder at 293 nm.

The broad band appearing between 3290-3344 cm^{-1} is due to N-H stretching. The C-H symmetrical and unsymmetrical stretching due to the methylene and methyl groups are observed between 2858-2924 cm^{-1}. The peak at 1690-1700 cm^{-1} is due to the carbonyl stretching of the urethane group. The peak between 1600-1610 cm^{-1} is attributed to aromatic C=C stretching. Two broad peaks between 1421-1548 cm^{-1} are due to the carboxylate ions. This confirms the presence of ionic linkage in the molecule. The C-H out-of-plane bending vibrations of the aromatic system are seen between 808-812 cm^{-1}. The FT-IR spectra of TDI based polyurethanes derived from M[HEEP]$_2$ (where M=Cu^{2+}, Mn^{2+} and Zn^{2+}) are shown in Figure 8.

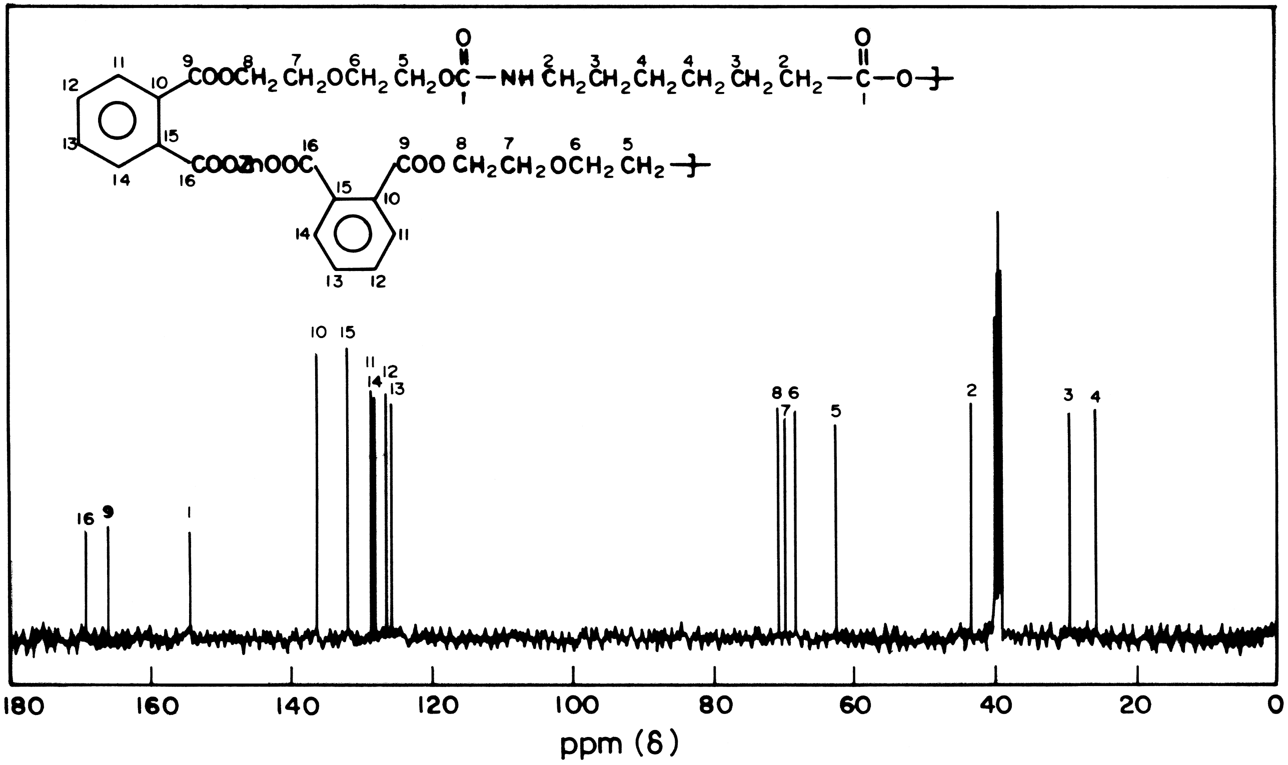


Figure 7. ^{13}C-NMR spectrum of HMDI - Zn[HEEP]$_2$.

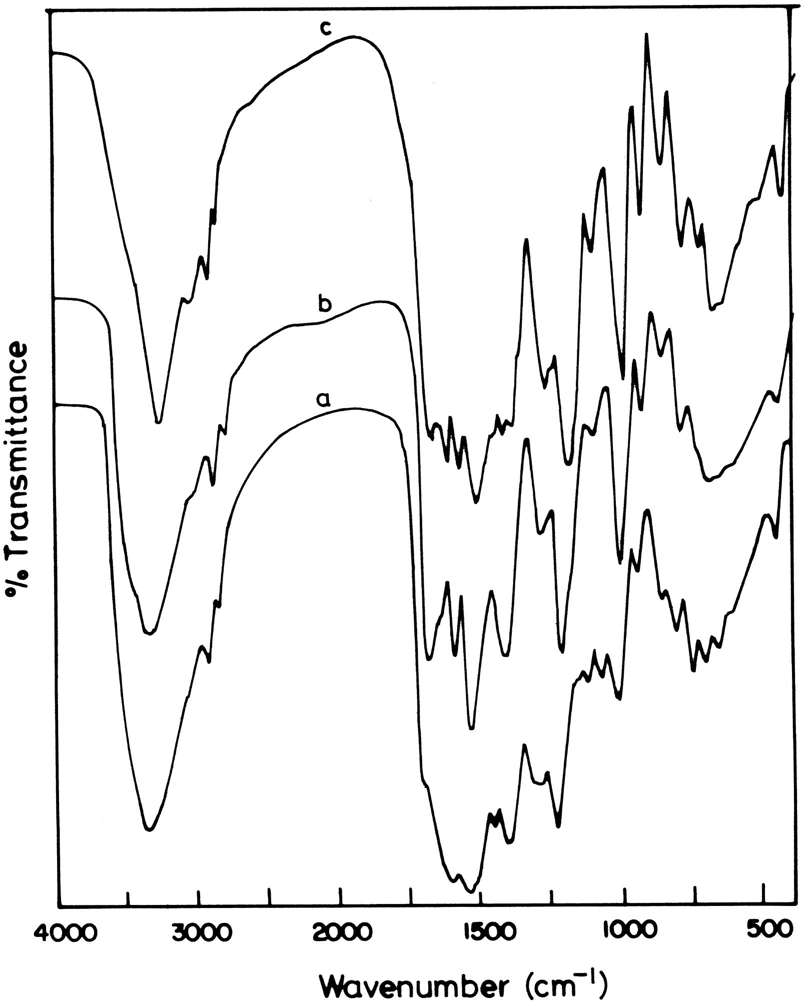


Figure 8. IR spectra of (a) TDI - Cu[HEEP]$_2$; (b) TDI - Mn[HEEP]$_2$; (c) TDI - Zn[HEEP]$_2$.

The ^{1}H-NMR spectra of TDI based polyurethanes show signals between 8.63-8.90 ppm due to the -NH protons. The aromatic protons gave signals between 7.39-7.90 ppm. The methylene group attached to-COOPh shows a resonance signal at 4.20-4.22 ppm. The peak at 4.12-4.14 ppm is due to the proton signals of methylene group attached to -COONH group. The -CH$_2$-O-CH$_2$- group shows signals at 3.51-3.52 ppm. The signal at 2.27-2.28 ppm is due to the methyl group attached to the aromatic ring. The representative ^{1}H-NMR spectrum of TDI based polyurethane derived from Zn[HEEP]$_2$ is shown in Figure 9.

The ^{13}C-NMR spectrum of TDI-Zn[HEEP]$_2$ polyurethane is shown in Figure 10. The -COO groups attached to the aromatic nucleus gave signals at 169.09 and 166.50 ppm. The signals observed at 154.13 and 154.00 ppm are due to -NHCOO

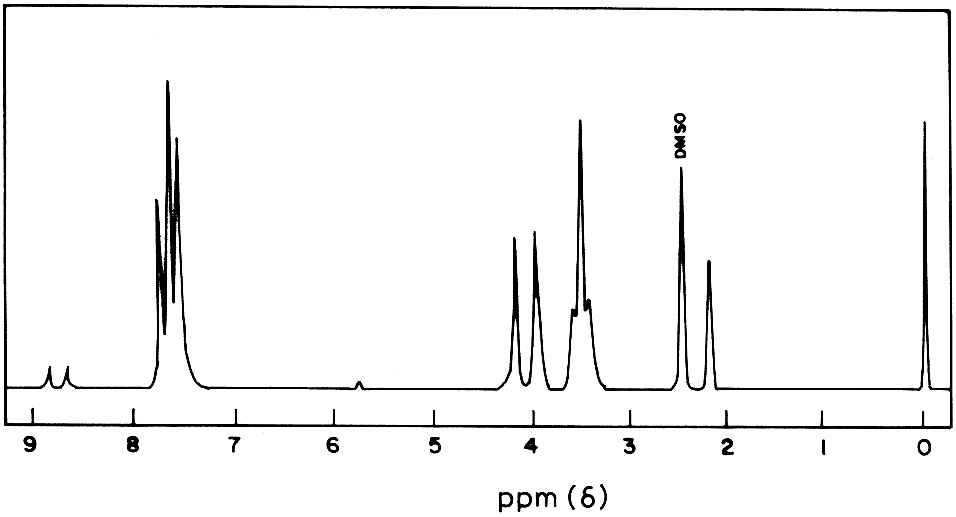


Figure 9. ^{1}H-NMR spectrum of TDI - Zn[HEEP]$_2$.

groups. The signals at 137.23, 136.71, 134.75, 132.23, 130.23, 128.62, 128.22, 127.80, 126.93, 125.75, 121.13, and 116.92 ppm are due to the aromatic carbons. The methylene carbons gave signals at 72.09, 69.82, 69.38, and 68.70 ppm. The peak at 17.31 ppm is due to the methyl carbon attached to the aromatic nucleus.

The UV spectra of TDI based Cu, Mn, and Zn containing polyurethanes show strong prominent peaks at 260, 257, and 258 nm and a shoulder at 294, 292, and 293 nm, respectively. The sharp intense peak is due to the n-π* transition of the carboxylate ions and the shoulder could be an absorption due to the charge transfer involving the metal and the ligand.

The solubility of polyurethanes were tested in various polar and non-polar solvents. The polymers are soluble in polar solvents like DMSO, DMF, and DMAc. The polyurethanes are insoluble in water, acetone, ethyl methyl ketone, ethyl acetate, toluene, benzene, xylene, dioxane, chloroform, carbon tetrachloride, carbon disulphide, n-hexane and tetrahydrofuran.

The elemental analysis data of all the prepared polyurethanes show that the experimentally determined percentage values of carbon, hydrogen and metal are well within the range of calculated values. The values are summarized in Table 3.

Table 2 shows the intrinsic viscosity of metal containing polyurethanes. The intrinsic viscosity of polyurethanes are not very high, being considerably lower than their non-metal analogues [6, 10], as is generally the case for all metal-containing polyurethanes. The reasons for this low viscosity may be that these polymers may undergo reversible dissociation of the metal oxygen bonds leading to lower molecular weights in solutions. The TDI based polyurethanes show slightly higher intrinsic viscosity than HMDI based polyurethanes.

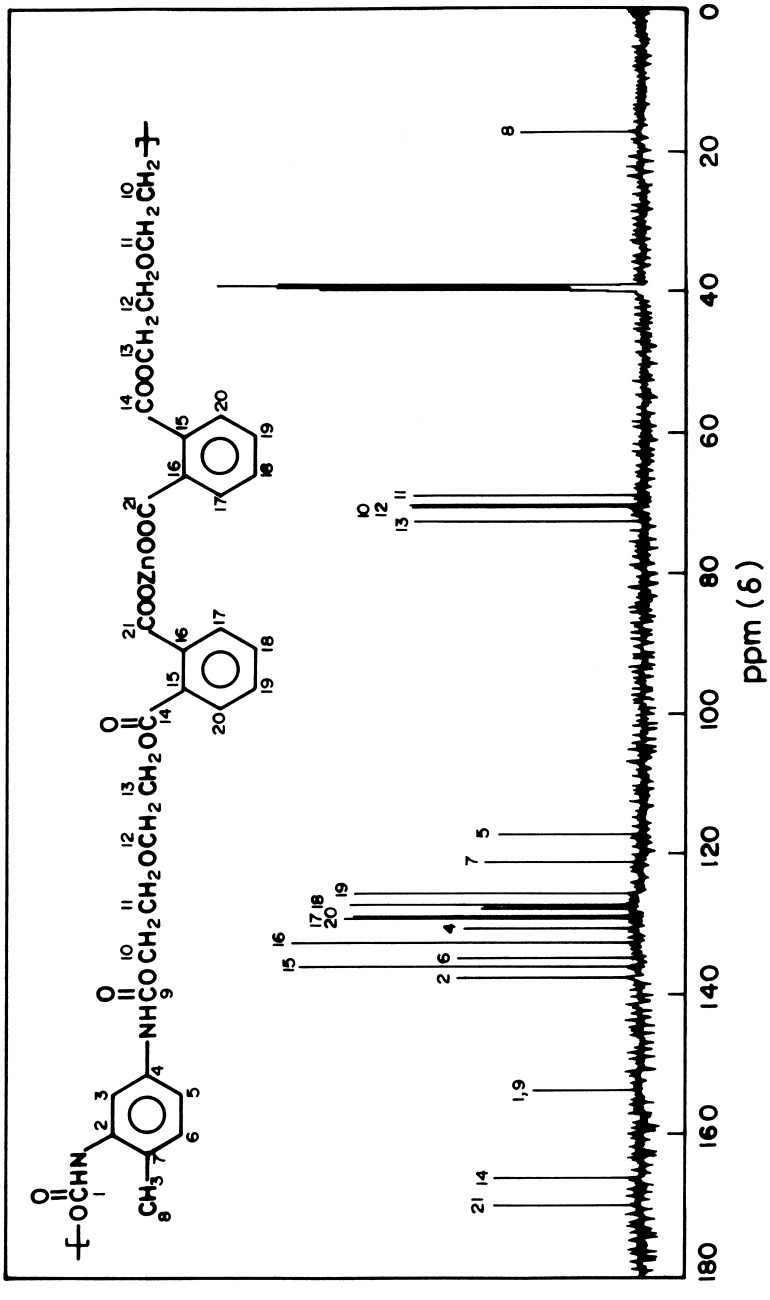


Figure 10. ^{13}C-NMR spectrum of TDI-Zn[HEEP]$_2$.

Table 3. Analytical Data of Metal Containing Polyurethanes

Polymer	Formula (Repeating Unit)	Analytical Data Found (Calculated)		
		C (%)	H (%)	M (%)
HMDI - Cu[HEEP]$_2$	$CuC_{32}H_{36}N_2O_{14}$	52.30 (52.22)	4.95 (4.93)	8.66 (8.63)
HMDI - Mn[HEEP]$_2$	$MnC_{32}H_{36}N_2O_{14}$	52.85 (52.83)	5.02 (4.99)	7.59 (7.56)
HMDI - Zn[HEEP]$_2$	$ZnC_{32}H_{36}N_2O_{14}$	52.10 (52.09)	4.91 (4.92)	8.89 (8.86)
TDI - Cu[HEEP]$_2$	$CuC_{33}H_{32}N_2O_{14}$	53.26 (53.27)	4.36 (4.34)	8.57 (8.54)
TDI - Mn[HEEP]$_2$	$MnC_{33}H_{32}N_2O_{14}$	53.92 (53.89)	4.37 (4.39)	7.49 (7.47)
TDI - Zn[HEEP]$_2$	$ZnC_{33}H_{32}N_2O_{14}$	53.18 (53.14)	4.31 (4.32)	8.78 (8.76)

Thermal Analysis

The TGA curves of HMDI based metal-containing polyurethanes are shown in Figure 11. The initial decomposition temperature for the polymers and TGA data for percentage weight loss from 300°C to 800°C are shown in Table 3. It was shown that 50% weight loss occurred for copper, manganese, and zinc containing

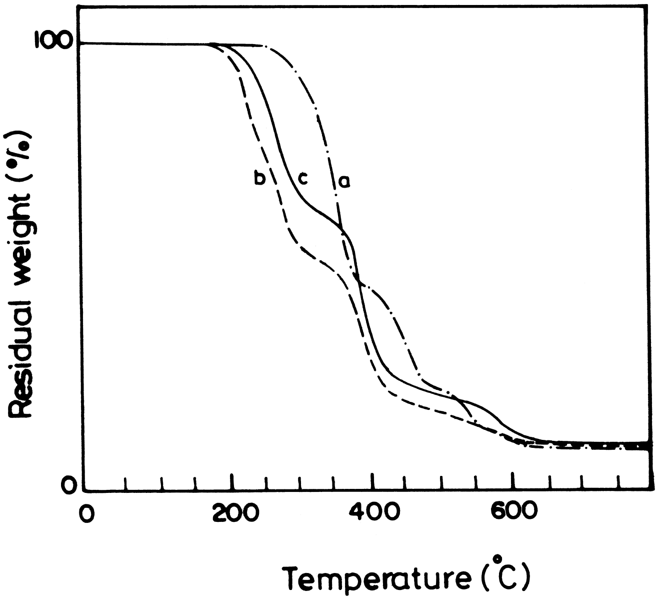


Figure 11. TGA curves of (a) HMDI - Cu[HEEP]$_2$; (b) HMDI - Mn[HEEP]$_2$; (c) HMDI - Zn[HEEP]$_2$.

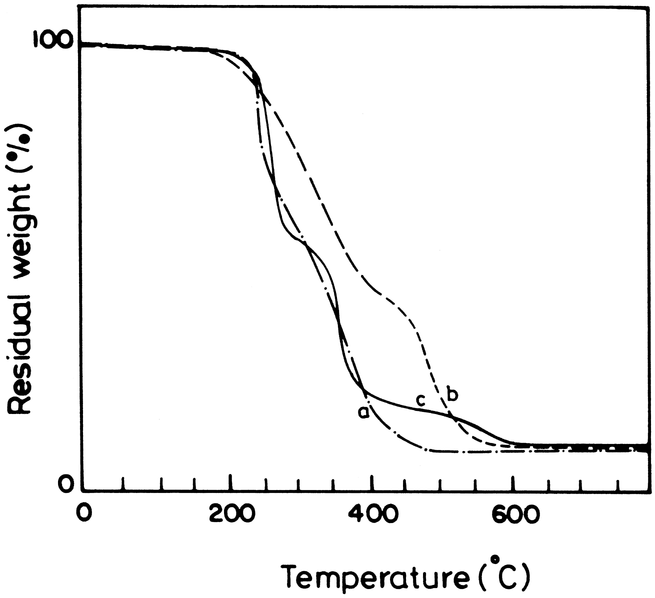


Figure 12. TGA curves of (a) TDI - Cu[HEEP]$_2$; (b) TDI - Mn[HEEP]$_2$; (c) TDI - Zn[HEEP]$_2$.

HMDI based polyurethanes at the temperature 372, 348, and 380°C, respectively. The residual weight at 800°C corresponds to 10.6, 10.8, and 11.4%, respectively. These values roughly correspond to the metal oxide (CuO, Mn_2O_3, and ZnO) formed as residue to this temperature. These values are very close to the theoretically calculated values (10.16,10.82, and 11.00%). The thermal stability of the metal-containing HMDI based polyurethanes follow the order Cu>Zn>Mn.

The TGA curves of TDI based metal containing polyurethanes are shown in Figure 12. The initial decomposition temperature for the polymers and TGA data for percentage weight loss from 300°C to 800°C are shown in Table 4. It was found that 50% weight loss occurred for copper, manganese, and zinc containing TDI based polyurethanes at the temperature, 329, 370, and 349°C, respectively. The residual weight at 800°C corresponds to 10.9, 10.8, and 11.1%, respectively.

Table 4. TGA Data for Metal Containing Polyurethanes

Polymer	IDT (°C)	Weight Loss (%) at Temperature (°C) 300	400	500	600	700	800
HMDI - Cu[HEEP]$_2$	258	06.4	54.3	78.1	88.9	89.4	89.4
HMDI - Mn[HEEP]$_2$	181	45.1	70.2	82.2	88.8	89.2	89.2
HMDI - Zn[HEEP]$_2$	204	33.3	65.2	79.9	88.2	88.6	88.6
TDI - Cu[HEEP]$_2$	209	40.1	82.1	89.1	89.1	89.1	89.1
TDI - Mn[HEEP]$_2$	176	24.2	53.8	76.8	89.2	89.2	89.2
TDI - Zn[HEEP]$_2$	224	49.1	77.2	81.7	88.7	88.9	88.9

Table 5. DSC Data of Metal Containing Polyurethanes

Polymer	Glass Transition Temperature (Tg) (°C)	Melting Point (°C)
HMDI-Cu[HEEP]$_2$	8.3	117.8
HMDI-Mn[HEEP]$_2$	6.1	131.9
HMDI-Zn[HEEP]$_2$	1.8	120.3
TDI-Cu[HEEP]$_2$	10.8	111.4
TDI-Mn[HEEP]$_2$	7.7	111.7
TDI-Zn[HEEP]$_2$	−3.7	114.2

These values roughly corresponds to the amount of metal oxide (CuO, Mn_2O_3 and ZnO) formed as residue at this temperature. These values are very close to the theoretically calculated values (10.69, 10.73 and 10.90%). The stability of the TDI based metal containing polyurethanes follow the order Zn>Cu>Mn.

The glass transition temperature (T_g) and melting point of the polymers are shown in Table 5. The T_g values of the polymers are generally low. The HMDI based metal containing polyurethanes have a slightly lower T_g value than the corresponding TDI based polyurethanes, as they have greater flexibility due to the hexamethylene group.

Antibacterial Activity of Polyurethanes

The antibacterial activity of the metal containing polyurethanes was identified based on the zone of inhibition for bacterial growth around the wells and were expressed as inactive, mild, moderate and high. The results are shown in Table 6. The results indicated that HMDI-Zn[HEEP]$_2$ and TDI-Zn[HEEP]$_2$ exhibited higher antibacterial activity against all bacterial strains. TDI-Zn[HEEP]$_2$ exhibited higher antibacterial activity against *Pseudomonas flourescence* and *Salmonella*

Table 6. Antibacterial Activity of Metal Containing Polyurethanes

Polymer	*Streptococcus* sp.	E. coli	*Pseudomonas fluorescence*	*Salmonella* sp.
HMDI-Cu[HEEP]$_2$	−	+	+	+
HMDI-Mn[HEEP]$_2$	+	+	+	+
HMDI-Zn[HEEP]$_2$	+	+	++	+
TDI-Cu[HEEP]$_2$	+++	+	−	−
TDI-Mn[HEEP]$_2$	−	−	−	+
TDI-Zn[HEEP]$_2$	++	+	++	++

(−) Inactive; (+) Mildly active; (++) Moderately active; (+++) Highly active.

sp. (18 mm and 17mm, respectively) and HMDI-Zn[HEEP]$_2$ exhibited higher activity against *Pseudomonas fluorescence* (15 mm).

TDI-Cu[HEEP]$_2$ exhibited highest activity against *Streptococcus* sp. (22 mm) and was inactive to *Pseudomonas fluorescence* and *Salmonella* sp. The polymer, HMDI-Cu[HEEP]$_2$ was inactive against *Streptococcus* sp. and exhibited mild activity against the other three bacterial strains.

HMDI-Mn[HEEP]$_2$ compound exhibited mild activity against all the bacterial strains and TDI-Mn[HEEP]$_2$ had a mild effect against *Salmonella* sp. and was inactive against the rest of the bacterial strains.

CONCLUSION

Divalent metal salts of mono(hydroxyethoxyethyl)phthalate were synthesized by the reaction of diethylene glycol, phthalic anhydride, and metal acetates. The metal containing polyurethanes having ionic links in the main chain were synthesized by the reaction of HMDI or TDI with M[HEEP]$_2$. The structure of polyurethanes was confirmed by IR and NMR spectra. The polymers were not soluble in most of the organic solvents and soluble in DMF, DMSO and DMAc. For metal-containing polyurethanes, the experimentally determined percentage values of carbon, hydrogen and metal are well within the calculated values. The TDI based polyurethanes are found to have higher intrinsic viscosity than HMDI based metal containing polyurethanes. The viscosity of the polyurethanes were low, indicating chain dissociation in solution. The HMDI based polyurethanes show higher thermal stability than TDI based polyurethanes. The glass transition temperature of the polymers range from -3.7 to 10.8°C. The antibacterial activity of different test compounds indicated that Zn containing polyurethanes had strong inhibitory effects on all the bacteria and the polyurethanes containing other metals had varying antibacterial activity depending on the bacterium. All the metal-containing polyurethanes used for the study exhibited antimicrobial activity and hence may be used as antibacterial coatings.

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