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R. Jayakumar[a]; R. Arun Prasath[a]; S. Radhakrishnan[b]; S. Nanjundan[a]
[a] Department of Chemistry, Anna University, Chennai, India [b] Department of Chemistry, Merit International Institute of Technology, The Nilgiris, Ootacamund, India

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STUDIES ON ZINC-CONTAINING POLYURETHANES AND POLYURETHANE-UREAS

R. Jayakumar,[1] R. Arun Prasath,[1] S. Radhakrishnan,[2] and S. Nanjundan[1,*]

[1]Department of Chemistry, Anna University, Chennai 600 025, India
[2]Department of Chemistry, Merit International Institute of Technology, Ootacamund, The Nilgiris 643 002, India

ABSTRACT

Zinc salt of mono(hydroxypentyl)phthalate [$Zn[HPP]_2$] was synthesized by reacting 1,5-pentane diol, phthalic anhydride and zinc acetate. Zinc containing polyurethanes having ionic linkages in the main chain were synthesized by the polyaddition reaction of hexamethylene diisocyanate (HMDI) or toluylene 2,4-diisocyanate (TDI) with $Zn[HPP]_2$, using di-n-butyltin dilaurate (DBTDL) as catalyst. Four different bisureas were prepared by reacting ethanolamine or propanolamine with HMDI or TDI. Zinc containing polyurethane-ureas were synthesized by reacting HMDI or TDI with 1:1 mixtures of $Zn[HPP]_2$ and each of the bisureas. $Zn[HPP]_2$ and the polymers were characterized by solubility, viscosity study, elemental analysis, FT-IR, ^{1}H-NMR, ^{13}C-NMR spectroscopy and thermogravimetric analysis (TGA).

Key Words: Zinc salt of mono(hydroxypentyl)phthalate; Ionic monomer; Bisureas; Polyurethanes; Polyurethane-ureas; Thermogravimetric analysis and spectral studies

*Corresponding author. Fax: +91-044-2200660; E-mail: snanjundan@hotmail.com

INTRODUCTION

Polyurethanes with flexible polyol backbone have generally good retention properties at low temperatures which makes them suitable candidates for use in adhesives, coatings etc., for cryogenic conditions.[1] The low temperature properties are dependent on the nature of polyol used. Urethane-based materials are of commercial interest in many applications because of their excellent properties such as abrasion resistance, low temperature flexibility, high strength and aging and chemical resistance. There are various ways of combining polyols and diisocyanates in order to produce tailor made polyurethanes.[2,3] The proper combination of these and other reagents results in very versatile polymers which can be fitted in a wide range of applications as foams, elastomers, coatings and elastomeric fibers.[4–7]

Poly(urethane-urea)s are the most important class of copolymers. Poly(urethane-urea)s are composed of a class of elastomers exhibiting superior extensibility, toughness and durability over segmented polyurethanes and are used extensively, ranging from textile fibers to medical prosthesis.[8] Introduction of urea group into the polymer backbone is expected to improve the solubility of the polymer without decreasing the thermal stability significantly. High modulus polyurethane-urea elastomer has many practical applications, the most important are in the automotive industry.[9]

Incorporation of metal and functional groups into the polymers have emerged that possess wide applications such as aqueous thickeners, impregnants, textile sizers,[10] additives,[11] resins,[12,13] catalysts[14] and in the biomedical field.[15,16] Ionic diols containing ionic linkages between COO^- and M^{++} 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 chain.[17–19]

The present paper deals with the synthesis and characterization of HMDI and TDI based polyurethanes and polyurethane-ureas from zinc salt of mono(hydroxypentyl)phthalate [$Zn[HPP]_2$], hexamethylene bis(ω,N-hydroxyethylurea) [HBHEU], toluylene 2,4-bis(ω,N-hydroxyethylurea] [TBHEU], hexamethylene bis(ω,N-hydroxypropylurea) [HBHPU] and toluylene 2,4-bis (ω,N-hydroxypropylurea] [TBHPU].

EXPERIMENTAL

Materials

Phthalic anhydride (BDH), 1,5-pentane diol (Fluka), DBTDL and zinc acetate of extra pure grades were used without any purification. Hexamethylene diisocyanate (Fluka) and toluylene 2,4-diisocyanate (Fluka) were used without further purification after estimating the isocyanate content. The

solvents such as acetone, methanol, dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), dimethyl acetamide (DMAc), benzene, toluene, m-cresol and chloroform were purified by standard procedures.

Synthesis of $Zn[HPP]_2$

1,5-Pentane diol (0.4 mol) was placed in a three-necked flask equipped with a thermometer, condenser, and guard tube. To this phthalic anhydride (0.1 mol) was added slowly over a period of half an hour and the contents were stirred constantly using a magnetic stirrer in an oil bath at 60–70°C for a further period of half an hour. Then, 0.05 mole of zinc acetate was added to the reaction mixture. The temperature was raised to 80°C and the solution was stirred continuously for about three hours. The product, separated as white powder, was contaminated with impurities. The contaminations were removed from the product by washing successively with methanol and acetone. The product was dried in vacuum at 50°C.

Synthesis of Bisureas

Bisureas, such as HBHEU and TBHEU, were synthesized according to the reported method.[20] For the synthesis of HBHPU and TBHPU, 0.5 mole of propanolamine and 100 mL of toluene were placed in a three necked round bottom flask equipped with a thermometer, mechanical stirrer and a dropping funnel. The flask was maintained at 0°C using a thermostat. Then, 0.25 mole of diisocyanate (HMDI or TDI) dissolved in 50 mL of toluene was added to the flask dropwise through the dropping funnel over a period of one hour with constant stirring. The reaction mixture was stirred for a further period of one hour at room temperature. The product separated as white powder was washed successively with acetone. The powder was dried in vacuum at 50°C.

Synthesis of Polyurethanes

In a three-necked round bottom flask equipped with a condenser, a nitrogen inlet tube, stirrer and an additional funnel 0.01 mole of $Zn[HPP]_2$ and 100 mL of purified DMSO were placed and the mixture was stirred well. The flask was placed in an oil-bath and the reaction mixture was maintained approximately at 95°C with constant stirring. To this, 2–3 drops of di-n-butyltin dilaurate (DBTDL) catalyst was added, followed by 0.01 mole of HMDI or TDI dissolved in DMSO over a period ranging from 20–45 min, depending on the diisocyanates used. After the addition of 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 N_2. The mixture was then allowed to stand overnight and the solution was mixed with DMSO to make the viscosity suitable for filtration. The filtrate was poured into large excess of chloroform to precipitate the product. The polymer was filtered, washed with acetone and dried at 60°C in vacuum for 10 h. The HMDI and TDI based polyurethanes are coded as $Zn[HPP]_2$-HMDI (I) and $Zn[HPP]_2$-TDI (II,) respectively.

Synthesis of Polyurethane-Ureas

Zinc containing polyurethane-ureas were synthesized by reacting $Zn[HPP]_2$, (0.005 mol) and HBHEU, HBHPU, TBHEU or TBHPU (0.005 mol) dissolved in 200 mL of DMSO with HMDI or TDI (0.01 mol) dissolved in 25 mL of the same solvent using DBTDL as catalyst. The temperature was maintained at 95°C. After the addition, the mixture was stirred at the same temperature for 4 h. Then, 50 mL of DMSO was added to the mixture and the solution was filtered. The filtrate was poured into a large excess of vigorously stirred chloroform to precipitate the product. The product was further washed with acetone several times and dried at 60°C in vacuum. The synthesis data of polyurethane-ureas are given in Table 1. With the help of $Zn[HPP]_2$ and four bisureas, eight zinc containing polyurethane-ureas were synthesized based on HMDI or TDI. The polymers are coded as $Zn[HPP]_2$-HMDI-HBHEU(III), $Zn[HPP]_2$-HMDI-HBHPU(IV), $Zn[HPP]_2$-HMDI-TBHEU(V), $Zn[HPP]_2$-HMDI-TBHPU(VI), $Zn[HPP]_2$-TDI-HBHEU(VII), $Zn[HPP]_2$-TDI-HBHPU(VIII), $Zn[HPP]_2$-TDI-TBHEU(IX) and $Zn[HPP]_2$-TDI-TBHPU[X].

Table 1. Synthesis, Viscosity, and Analytical Data of Zinc Containing Polymers

Polymer	Yield (%)	Intrinsic Viscosity (η)	Analytical Data Found (Calculated)		
			C (%)	H (%)	Zn (%)
I	77	0.0592	54.80 (55.49)	5.68 (5.75)	9.01 (8.88)
II	82	0.0775	56.21 (56.66)	4.80 (4.89)	8.95 (8.81)
III	75	0.0917	55.43 (54.39)	6.53 (6.59)	5.10 (5.48)
IV	73	0.0923	54.31 (55.11)	6.83 (6.77)	4.82 (5.36)
V	79	0.0985	54.82 (55.03)	6.33 (6.21)	4.84 (5.45)
VI	74	0.0997	54.12 (55.73)	6.55 (6.40)	4.76 (5.32)
VII	81	0.1009	53.95 (55.75)	5.81 (5.68)	4.89 (5.42)
VIII	83	0.1017	55.11 (56.43)	5.99 (5.88)	4.76 (5.30)
IX	86	0.1093	55.20 (56.47)	5.23 (5.16)	4.91 (5.39)
X	84	0.1108	56.03 (57.13)	5.60 (5.36)	4.51 (5.27)

Instrumentation

The Infrared spectra of the samples as KBr pellets were recorded with the Testscan Shimadzu FT-IR 8000 series spectrophotometer. The ^{1}H-NMR and ^{13}C-NMR spectra of the products were recorded with a JEOL-GSX-400 MHz spectrometer in DMSO-d_6 solvent. Thermogravimetric analysis (TGA) was performed using a Mettler-3000 analyzer at a heating rate of 20°C/min in an air atmosphere. Perkin-Elmer 2400 carbon-hydrogen analyzer was used for elemental analysis. Solubility of the polymers was tested in various polar and non-polar solvents. An Ubbelhode viscometer was used for the determination of the intrinsic viscosity of the polymers in DMSO at 40°C. To estimate the zinc content, $Zn[HPP]_2$ and its polymers were digested with conc. HCl, the filtrate and the washings were neutralized, treated with aqueous NH_3/NH_4Cl buffer and the solution at pH 10 was titrated against standardized EDTA solution using solochrome black as the indicator.

RESULTS AND DISCUSSION

Synthesis and Characterization of $Zn[HPP]_2$

Mono(hydroxypentyl)phthalate was prepared by reacting phthalic anhydride and an excess of 1,5-pentane diol with constant stirring at 70°C for one hour. An excess of 1,5-pentane diol was used to avoid the formation of polyester. Preparation of zinc salt of mono(hydroxypentyl)phthalate ($Zn[HPP]_2$) was carried out by the reaction between mono(hydroxypentyl)-phthalate and the zinc acetate. The reaction were completed in 4 h with constant stirring at 80°C. The product was separated as a white powder. For the synthesis of metal containing monomer the optimum mole ratio of ethylene glycol to phthalic anhydride used was investigated,[18] and it was found that the yield was higher when the glycol to phthalic anhydride ratio was higher than 3. When the amount of diol was small, it was difficult to stirring. So the reactions were carried out with the pentane diol to phthalic anhydride ratio of 4, with this ratio, the yield was higher. The product may be contaminated with the unreacted mono(hydroxypentyl)phthalate, zinc acetate, pentane diol and the polyester. These contaminations were removed from the product by washing with methanol and then with acetone.

The FT-IR spectrum of $Zn[HPP]_2$ is shown in Fig. 1. The spectrum shows a broad band at 3425 cm^{-1} due to -OH stretching of the hydrogen-bonded diol. The C-H asymmetrical and symmetrical stretching due to the methylene group is observed at 2932 and 2860 cm^{-1}, respectively. The peak at 1714 cm^{-1} is due to carbonyl stretching of the ester group. The carboxylate ions of the salts show two characteristic peaks at 1570 and 1393 cm^{-1}. This confirms the presence of ionic link in the diol. A strong band at 1151 cm^{-1} is due to the asymmetrical -C-O-C stretching. The -C-O stretching

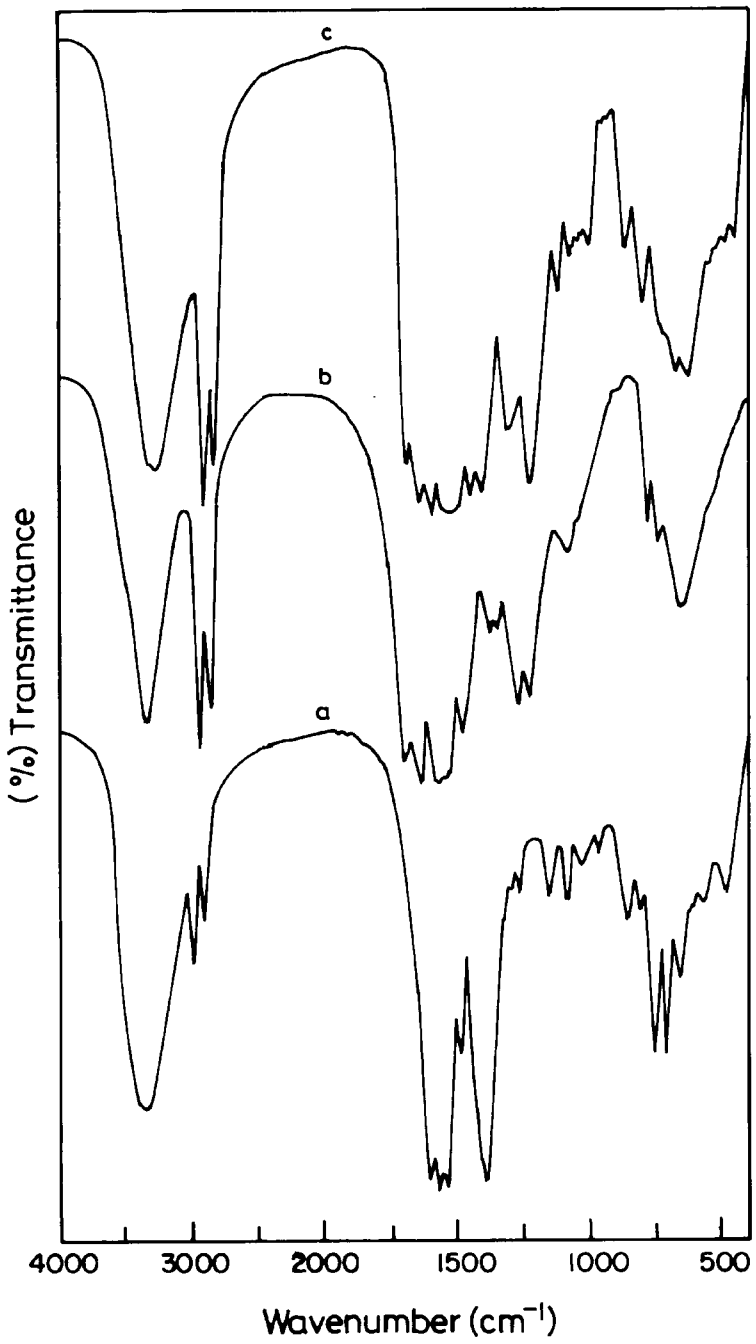


Figure 1. IR Spectrum of: (a) $Zn[HPP]_2$; (b) $Zn[HPP]_2$-HMDI; (c) $Zn[HPP]_2$-TDI.

due to the primary alcohol is observed at 1034 cm^{-1}. The peak at 756 cm^{-1} is due to the C-H out of plane bending vibrations of the aromatic system.

The FT-NMR spectrum of the ionic diol shows resonance signals due to the aromatic protons at 7.74–7.38 ppm. The hydroxyl proton shows a signal at 4.48 ppm. Methylene group attached to -OCOPh shows a signal at 4.08 ppm. Methylene group attached to the alcoholic group shows signal at 3.42 ppm. Of the three central methylene groups one which is attached to the $-CH_2OCOPh$ shows a signal at 1.72 ppm. The central and other methylene group attached to $-CH_2OH$ show signal between 1.62–1.20 ppm.

The proton decoupled ^{13}C-NMR spectrum of $Zn[HPP]_2$ is shown in Fig. 2. The chemical shifts assignments were made from the off-resonance decoupled spectra of the monomer. The resonance signals at 169.87 (C_3) and 167.23 (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 136.85 (C_{12}) and 132.72 (C_7) ppm, respectively. The other aromatic carbons gave four signals at 127.89 (C_9), 127.14 (C_{10}), 126.14 (C_8), and 125.17 (C_{12}) ppm. The methylene carbons attached to -OOCAr group and -OH group gave signals at 62.12 (C_5) and 59.15 (C_4) ppm, respectively. The signals at 33.35 (C_2) and 28.14 (C_4) ppm are attributed to the methylene carbons attached to $-CH_2OH$ and $COOCH_2$- groups, respectively. The central methylene carbon of the hydroxy pentyl group shows a signal at 25.89 (C_3) ppm.

Analytical data of $Zn[HPP]_2$ showed that the found and the calculated values were well within the range. Found: Zn = 11.55%. C = 55.00% and

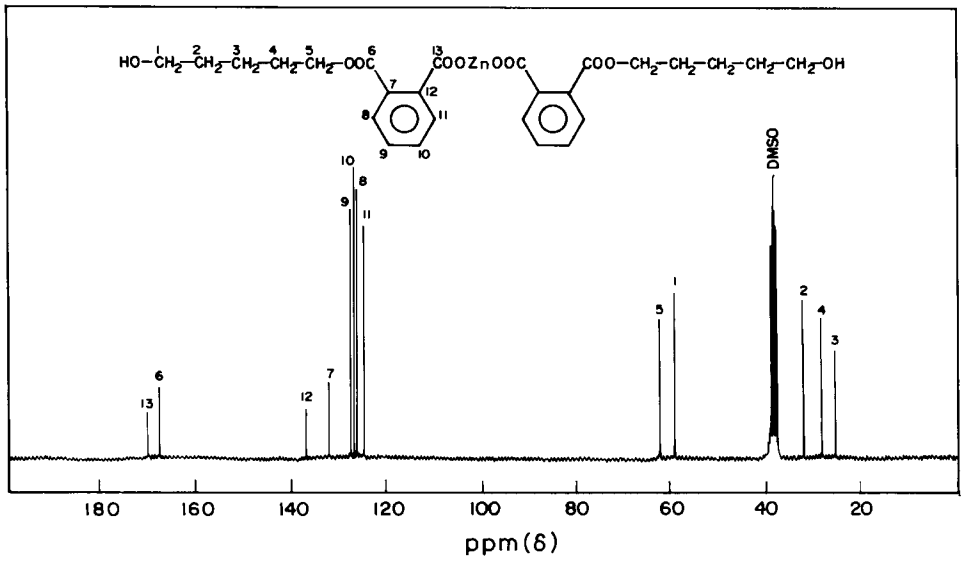


Figure 2. ^{13}C-NMR Spectrum of $Zn[HPP]_2$.

H = 5.33% calculated: Zn = 11.51%, C = 54.94% and H = 5.4%. $Zn[HPP]_2$ is soluble in highly polar solvents like DMF, DMSO, DMAc and is insoluble in n-hexane, chloroform, ethyl methyl ketone, and tetrahydrofuran. The TGA shows that $Zn[HPP]_2$ was stable up to 312°C. The residual weight at 800°C corresponds to 15.02%. The above value roughly corresponds to the amount of ZnO formed at this temperature. The Zn salt shows single stage decomposition. Figure 3 shows TGA curves of $Zn[HPP]_2$.

Synthesis and Characterization of Bisureas

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. Therefore, in a 1:2 system consisting of diisocyanate and aminoalcohol, the diisocyanate will react with amino group only. For the synthesis of bisureas, HMDI or TDI was allowed to react with twice the amount of ethanolamine or propanolamine in an ice bath. Since the reaction is highly exothermic, the use of a

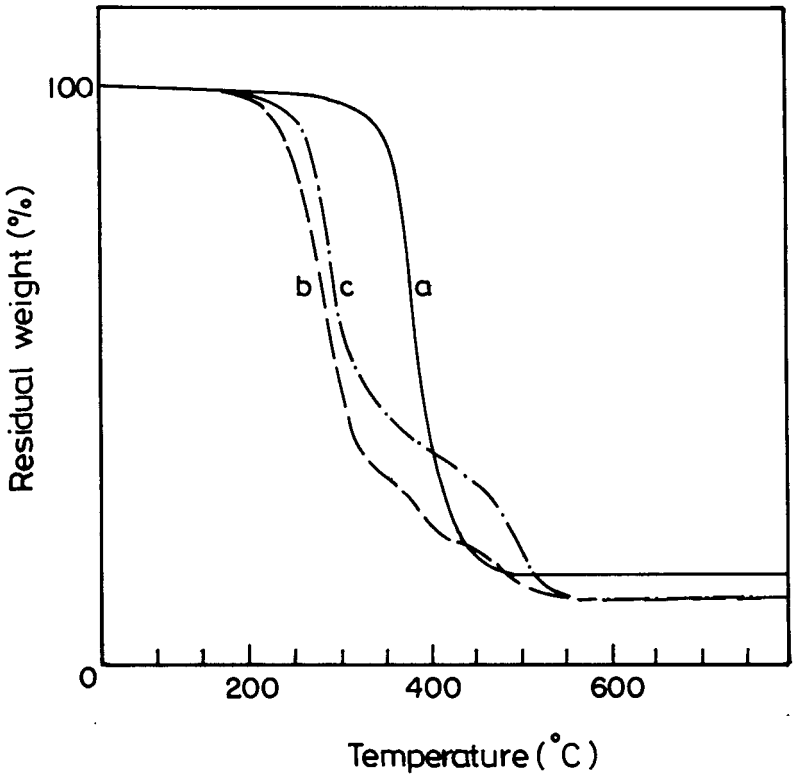
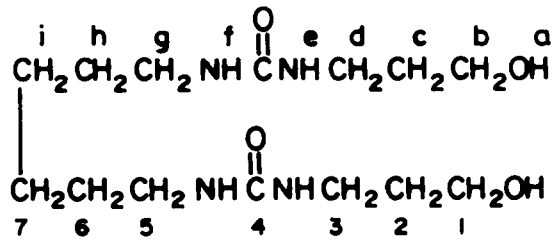
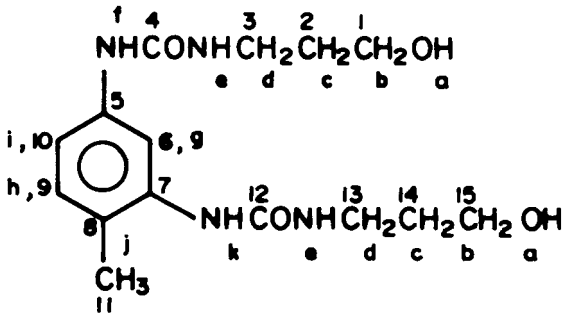


Figure 3. TGA Curves of: (a) $Zn[HPP]_2$; (b) $Zn[HPP]_2$-HMDI; (c) $Zn[HPP]_2$-TDI.

solvent is necessary. The yield was generally high (80–92%). IR, ^{1}H-NMR, ^{13}C-NMR spectra and elemental analysis confirmed the formation of the bisureas. The structures of HBHPU and TBHPU are shown in Schs. 1 and 2, respectively.



Scheme 1.



Scheme 2.

HBHPU

IR (cm^{-1}): 3373 (OH and NH stretching), 2988 and 2867 (asymmetrical symmetrical C-H stretching), 1647 (C=O stretching), 1584 (NH bending) and 1069 (C-O stretch).

^{1}H-NMR (ppm): 5.77 (t, 2H, H_e), 5.75 (t, 2H, H_f), 4.42 (s, 2H, H_a), 3.46 (q, 4H, H_b), 3.07 (q, 4H, H_d), 2.95 (q, 4H, H_g), 1.46 (p, 4H, H_c) and 1.41–1.22 (m, 8H, $H_{h,i}$).

^{13}C-NMR (ppm): 158.26 (C_4), 58.39 (C_1), 40.15 (C_5), 36.35 (C_3), 33.22 (C_2), 29.97 (C_6), and 26.12 (C_7).

Elem. Anal. Found (Calcd.): C = 52.78% (52.83%); H = 9.40% (9.43%); N = 17.57% (17.61%).

TBHPU

IR (cm^{-1}): 3381 (O-H and N-H stretching), 3084 (aromatic C-H stretch), 2963 and 2879 (asymmetrical and symmetrical C-H stretching), 1644 (C=O stretching), 1613 (C=C stretch), 1576 (N-H bending, and 1077 (C-O stretch).

^{1}H-NMR (ppm): 8.29 (NH-hydrogen bonded), 7.64 (s, 1H, H_f), 7.51 (s, 1H, H_k), 7.12 (s, 1H, H_j), 6.89 (d, 1H, H_g), 6.46 (d, 1H, H_h), 5.97 (t, 1H, H_e), 4.42 (s, 2H, H_a), 3.46 (q, 4H, H_b), 3.12 (q, 4H, H_d), 2.04 (s, 3H, H_j) and 1.45–1.56 (m, 4H, H_c).

^{13}C-NMR (ppm): 155.46 (C_{12}), 155.34 (C_4), 138.57 (C_7), 138.15 (C_5), 129.83 (C_9), 119.26 (C_8), 111.61 (C_{10}), 110.24 (C_6), 58.46, 58.38 (C_1, C_{15}), 36.27, 36.18 (C_3, C_{13}), 32.93 (C_2, C_{14}) and 17.17 (C_{11}).

Elem. Anal. Found (Calcd.): C = 62.17% (62.28%); H = 7.22% (7.27%); N = 19.36% (19.41%).

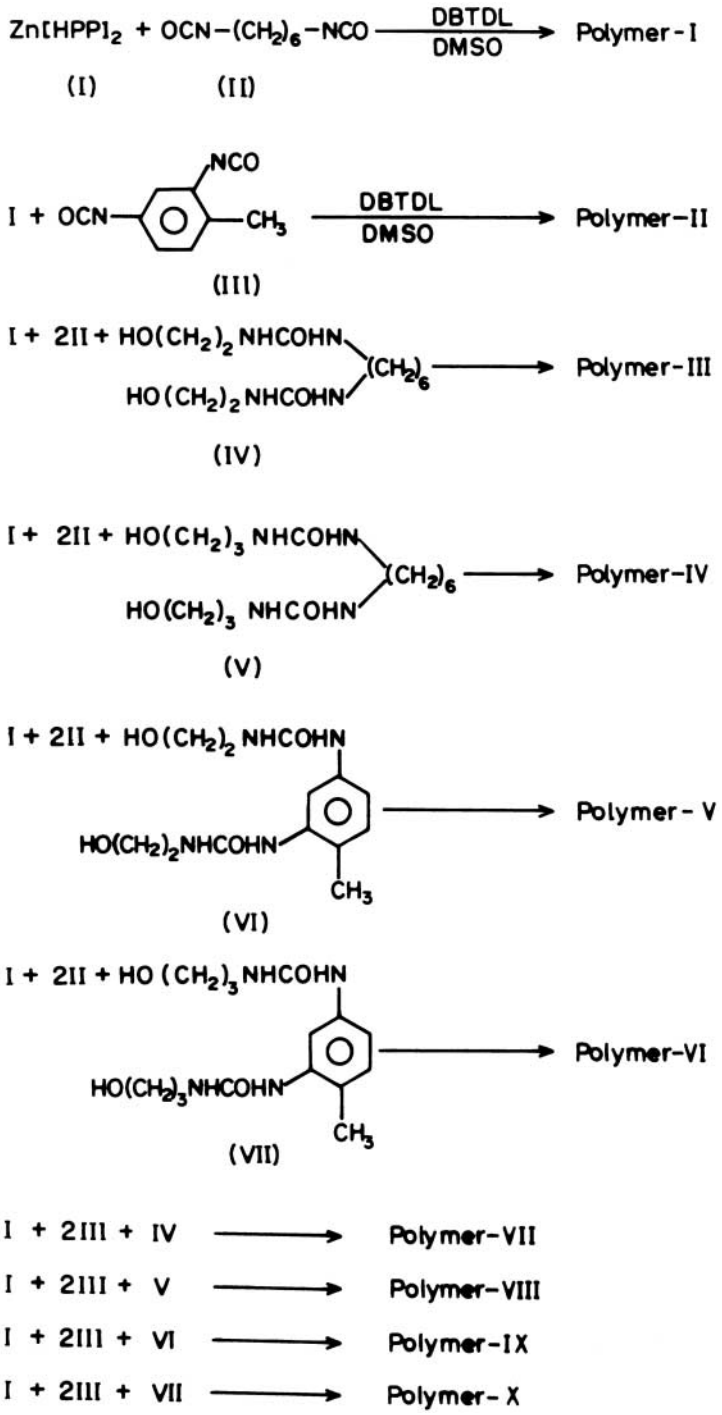
Synthesis and Characterization of Polymers

$Zn[HPP]_2$ is insoluble in most of the organic solvents and the polymerization of the salts with diisocyanates had to be done only in those solvents which dissolve the resulting polymers. Since DMSO was a good solvent for polyurethanes and polyurethane-ureas, it was selected as the solvent for polymerization. The reaction of diisocyanates with diols catalyzed by DBTDL took place via the formation of the ternary complex between the catalyst and the reagent.[21]

In the synthesis of polymer, the mole ratio of diisocyanate: diol ($Zn[HPP]_2$ and bisureas) was taken as 1:1 to avoid the formation of crosslinkages. The crosslinked product formed was filtered off after mixing the product with excess of DMSO to dissolve the linear polymer. The dissolved linear polymer was reprecipitated by the addition of non-solvent. The yield was found between 73 to 86% and the polymers were dried in vacuum at 70°C for 10 h. The synthesis data of the polymers are given in Table 1. The reactions involved in the synthesis of polyurethane and polyurethane-ureas are shown in Sch. 3.

The IR spectrum of HMDI based polyurethane is shown in Fig. 1. The spectrum shows a broad band at 3333 cm^{-1} due to -NH stretching. The C-H asymmetrical and symmetrical stretching due to the methylene group is observed between 2930–2856 cm^{-1}. The carbonyl stretching of the urethane group occurs at 1690 cm^{-1}. The carboxylate ion shows two broad peaks at 1628 and 1377 cm^{-1}. This confirms the presence of ionic linkages in the polymer. These bands were not found in metal-free analogue of these polymers. The N-H bending modes are observed at 1628 cm^{-1}. The peak at 1078 cm^{-1} is due to C-O stretching. The C-H out of plane bending vibrations of aromatic system is shown at 770 cm^{-1}.

Figure 1 shows the IR-spectrum of $Zn[HPP]_2$-TDI. The -NH stretching shows absorption band at 3310 cm^{-1}. The C-H asymmetrical and symmetrical stretching are observed at 2924–2855 cm^{-1}. The peak at 1692 cm^{-1} is due to the carbonyl stretching of the urethane group. The two broad bands shown between 1547 and 1416 cm^{-1} is due to carboxylate ion stretching.



Scheme 3.

The peak at 1626 cm^{-1} is due to N-H bending mode vibrations. The C-O stretching shows peak at 1080 cm^{-1}. The C-H out of plane bending vibrations of aromatic system is seen at 765 cm^{-1}.

The IR spectra of HMDI based polyurethane-ureas are shown in Fig. 4. The broad absorption band at 3360–3321 cm^{-1} is due to the N-H stretching. The C-H asymmetrical and symmetrical stretching due to the methylene group is observed between 2930–2858 cm^{-1}. The peak at 1684–1680 cm^{-1} is due to the carbonyl stretching of the urethane, urea and ester groups. The carboxylate ion of the zinc salt gives two broad bands around 1600 and 1439 cm^{-1}. This confirms the presence of ionic links in the polymers. The peak at 770–765 cm^{-1} is due the C-H out of plane bending vibrations of aromatic system.

The IR spectra of TDI based polyurethane-ureas are shown in Fig. 5. The spectra show similar characteristic peaks at 3304–3288 cm^{-1} due to -NH stretching. The C-H asymmetrical and symmetrical stretching due to the methylene group is observed between 2933–2853 cm^{-1}. The peak at 1697–1683 cm^{-1} is due to the carbonyl stretching of the urethane, urea and ester groups. The carboxylate ion of the zinc salt gives two peaks at 1599–1410 cm^{-1}. The peak at 773–763 cm^{-1} is due to the C-H out of plane bending vibrations of aromatic system.

Figure 6 shows the ^{1}H-NMR spectrum of HMDI-Zn[HPP]$_2$. It shows a signal at 7.90–7.72 ppm for the -NH protons of the urethane groups which are actually shifted to the down field due to the inter- and intramolecular hydrogen bonding between N-H group with C=O group and with the S=O group of the solvent (DMSO-d_6). The aromatic protons show signal at 7.51–7.28 ppm. The peak at 6.54–6.43 ppm is due to non-hydrogen bonded -NH protons. The methylenoxy group attached -COPh group shows signal at 4.17–4.13 ppm. The methylenoxy group attached to -CONH group shows peak at 4.02–3.97 ppm. The polyurethanes show a proton signal at 3.06–2.96 ppm due to the methylene group attached to -NH group. The other methylene groups in the polymer show signals at 1.41–1.13 ppm.

Figure 7 shows the ^{1}H-NMR spectrum of TDI-Zn[HPP]$_2$. The hydrogen bonded -NH protons show a signal at 7.98–7.88 ppm and the non-hydrogen bonded -NH protons show signal at 6.41–6.28 ppm. The aromatic protons show a signal at 7.53–6.97 ppm. The signal at 4.20–4.15 ppm is due to the methylenoxy group attached to -COPh group. The peak at 4.08–4.01 ppm is due to the methylenoxy group attached to -CONH group. The methyl group attached to the aromatic ring shows a signal at 2.14–2.06 ppm. The other methylene groups show signal between 1.81–1.49 ppm.

Figure 8 shows the ^{1}H-NMR spectrum of Zn[HPP]$_2$-HMDI-HBHEU. 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 hydrogen bonding between -NH group with C=O group and with the S=O group of the solvent (DMSO-d_6). The -NH

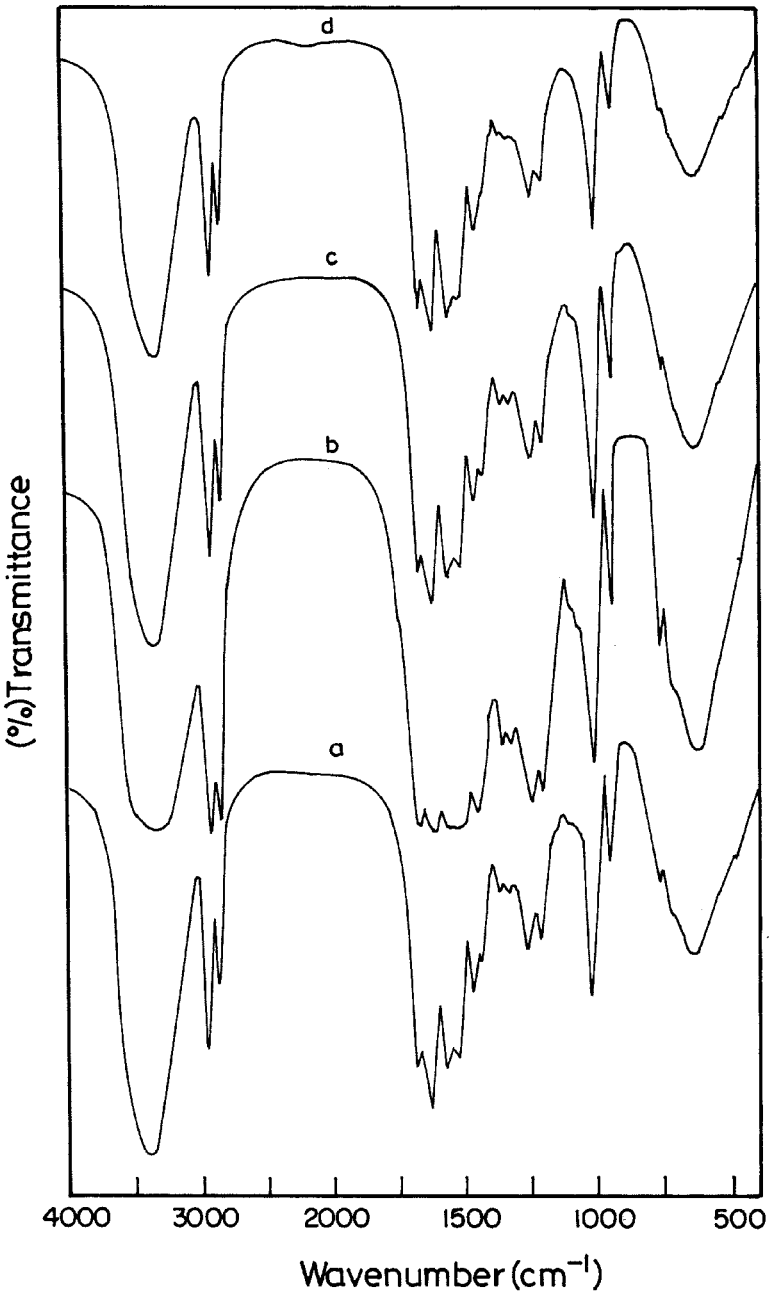


Figure 4. IR Spectrum of: (a) $Zn[HPP]_2$-HMDI-HBHEU; (b) $Zn[HPP]_2$-HMDI-HBHPU; (c) $Zn[HPP]_2$-HMDI-TBHEU; (d) $Zn[HPP]_2$-HMDI-TBHPU.

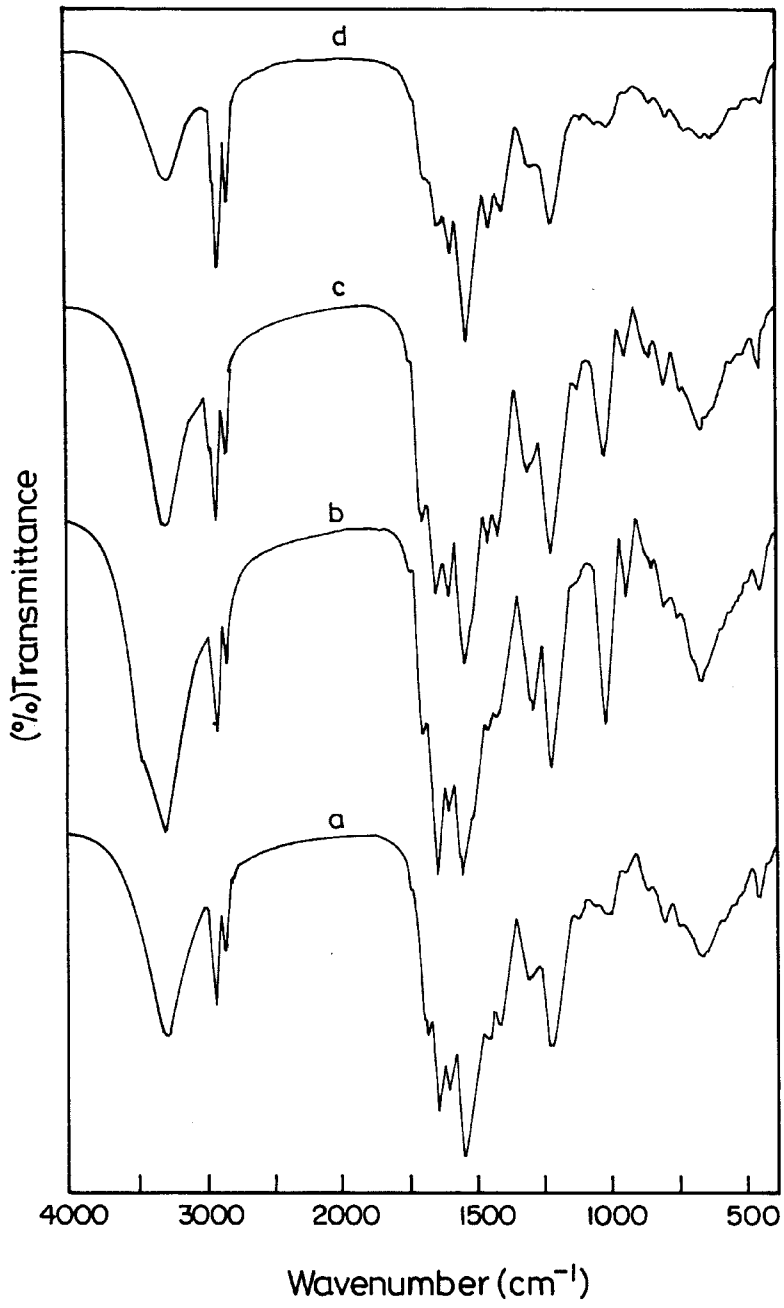


Figure 5. IR Spectrum of: (a) $Zn[HPP]_2$-TDI-HBHEU; (b) $Zn[HPP]_2$-TDI-HBHPU; (c) $Zn[HPP]_2$-TDI-TBHEU; (d) $Zn[HPP]_2$-TDI-TBHPU.

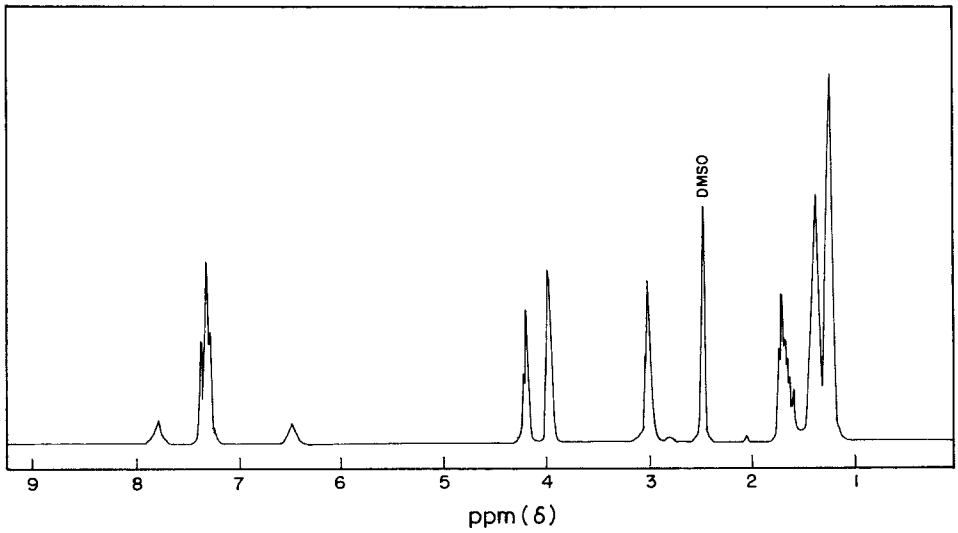


Figure 6. ^{1}H-NMR Spectrum of Zn[HPP]$_2$-HMDI.

protons appear between 8.25–8.137 ppm. The aromatic protons show signals between 7.78–7.28 ppm. The urethane (-NHCOO) peak is observed between 6.65–6.61 ppm. The urea peaks appears between 5.85–5.59 ppm. The methylene group attached to ArCOO- and NHCOO- group shows signals between 4.19–4.09 ppm and 3.90–3.81 ppm, respectively. The signals between 3.19–3.08 ppm are due to the methylene protons adjacent to -NHCOO

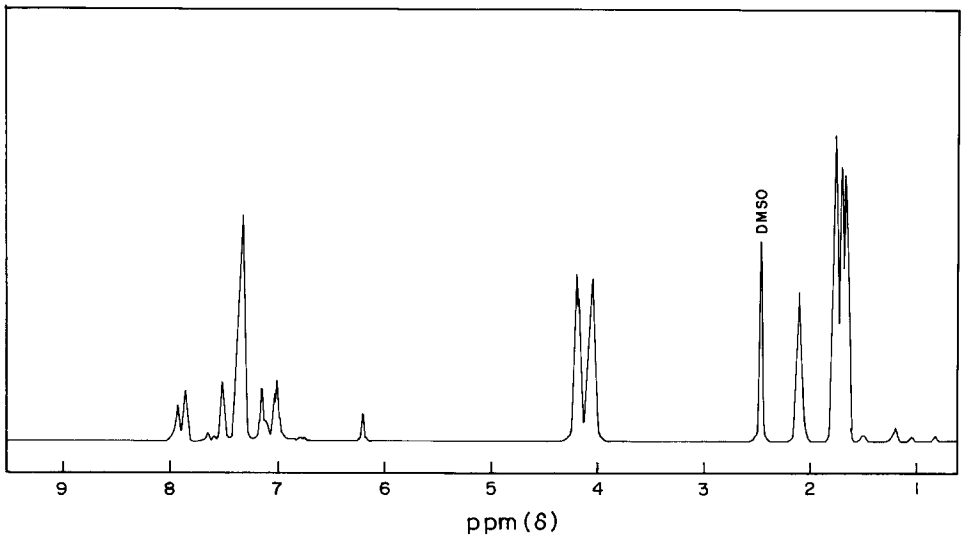


Figure 7. ^{1}H-NMR Spectrum of Zn[HPP]$_2$-TDI.

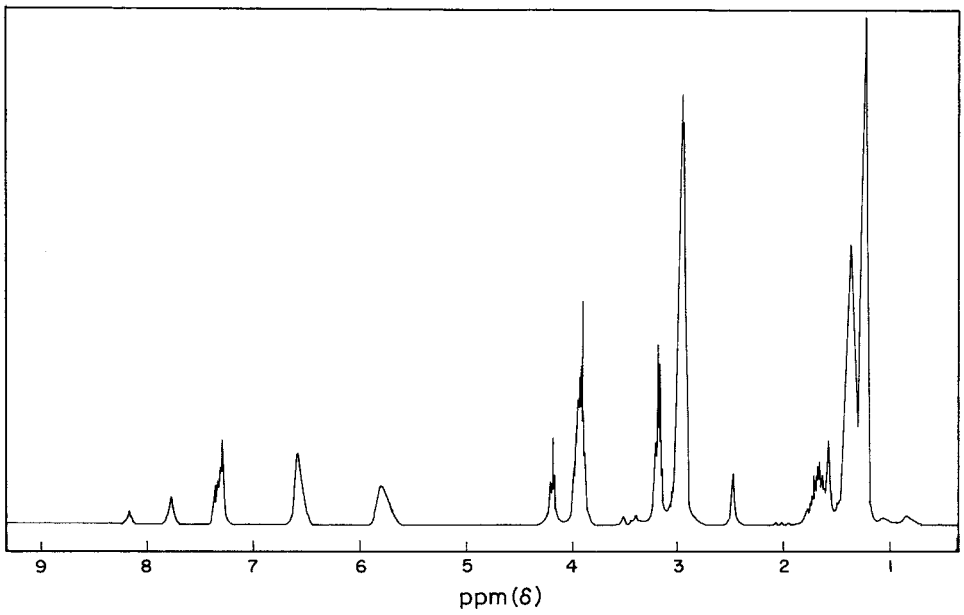


Figure 8. ^{1}H-NMR Spectrum of Zn[HPP]$_2$-HMDI-HBHEU.

and -NHCONH groups. The peak at 1.73–1.51 ppm is attributed to the methylene group adjacent to the methylenoxy groups. Other methylene protons in the polyurethane-ureas show broad peaks between 1.48–1.16 ppm.

Figure 9 shows the ^{1}H-NMR spectrum of Zn[HPP]$_2$-TDI-TBHEU. The peak between 8.52–8.31 ppm is due to the urethane group. The -NHCONH group (urea) shows peaks between 6.58–6.16 ppm. The peak between 7.92–7.03 ppm is due to the aromatic protons. The methylene proton attached to ArCOO- and NHCOO- shows signals between 4.19–4.12 and 3.98–3.89 ppm, respectively. The methyl group attached to the aromatic ring shows a signal between 2.13–2.07 ppm. The peak at 1.84–1.66 ppm is due to the methylene group adjacent to the methylenoxy groups. The other methylene groups in the polymers show a broad peak between 1.35–1.05 ppm.

The ^{13}C-NMR spectrum of Zn[HPP]$_2$-HMDI is shown in Figure 10. The carboxylate ion carbon and the ester carbonyl carbon show peaks at 170.06 (C_{17}) and 167.28 (C_{10}) ppm, respectively. The carbonyl carbon of the urethane group NHCOO- shows a signal at 157.62(4) ppm. The two aromatic carbons to which the ester carbonyl carbon and the carboxylate carbonyl carbon are attached show peaks at 136.10 (C_{11}) and 133.14 (C_{16}) ppm, respectively. The other aromatic carbons gave four signals at 129.95 (C_{13}), 128.91 (C_{14}), 125.97 (C_{12}) and 125.12 (C_{15}) ppm. The methylene carbons attached to ArCOO- and NHCOO- gave signals at 70.03 (C_9) and 62.08 (C_5) ppm, respectively. The other methylene groups show signals at 33.74 (C_6), 29.93 (C_3), 25.82 (C_8), 27.15 (C_7) and 26.14 (C_4) ppm, respectively.

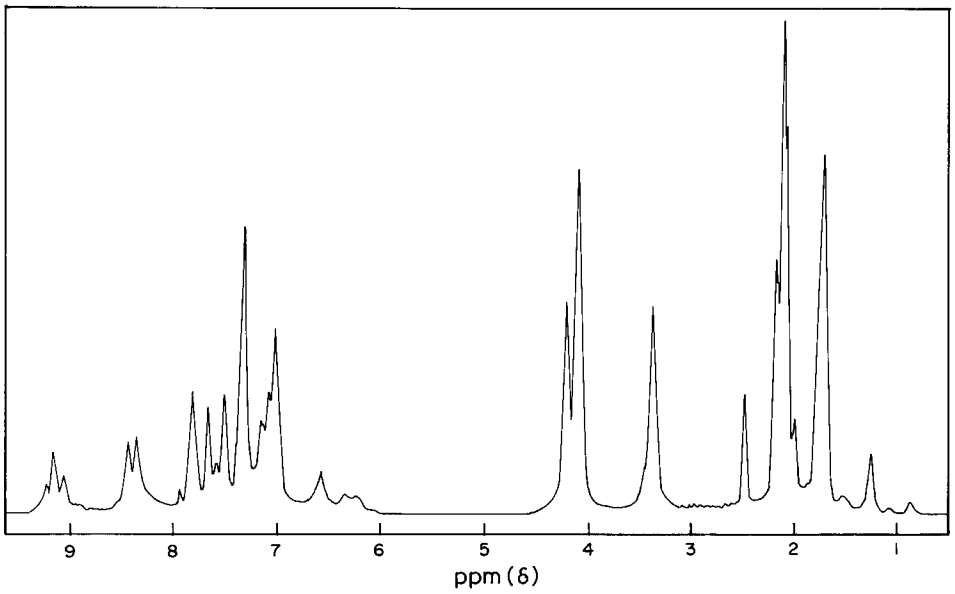


Figure 9. ^{1}H-NMR Spectrum of Zn[HPP]$_2$-TDI-TBHEU.

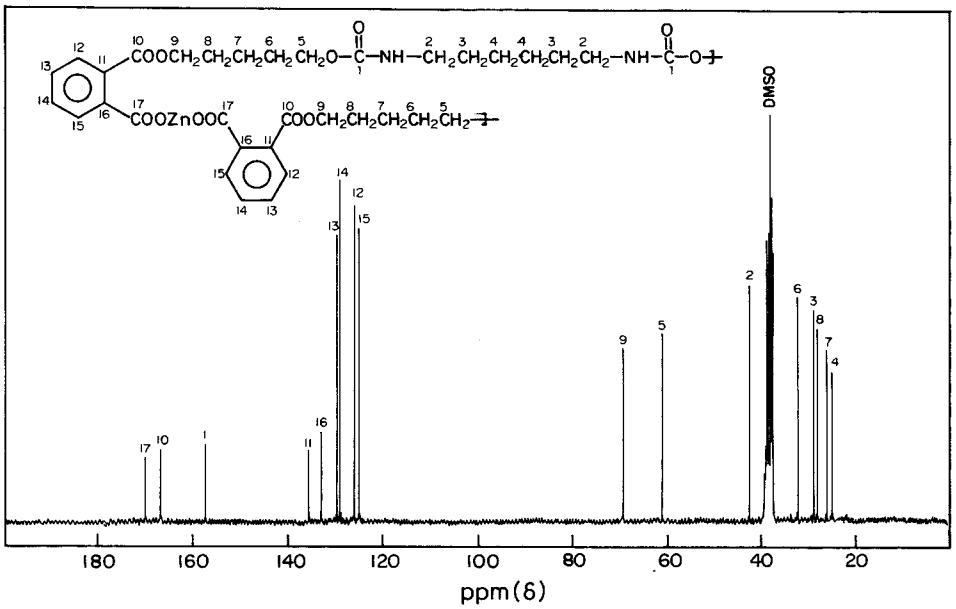


Figure 10. ^{13}C-NMR Spectrum of Zn[HPP]$_2$-HMDI.

The ^{13}C-NMR spectrum of Zn[HPP]$_2$-TDI polyurethane is shown in Fig. 11. The carboxylate carbon and ester carbonyl carbon gave resonance signals at 171.83 (C_{22}) and 168.63 (C_{15}) ppm, respectively. The carbonyl carbon of the urethane group gave signals at 153.80 (C_2) and 153.13 (C_1) ppm. The aromatic carbons gave signal between 137.24 (C_{20}) and 126.13 (C_{18}) ppm. The methylene carbon attached to the ArCOO- and NHCOO- groups show peak at 65.12 (C_{14}) and 63.15 (C_{10}) ppm, respectively. Methylene carbon attached to NHCOOCH$_2$ - and ArCOOCH$_2$ - group shows peak at 32.82 (C_{11}) and 29.97 (C_{13}) ppm, respectively. The other methylene group is observed at 26.84 (C_{12}) ppm and the methyl group attached to the benzene ring shows peak at 17.22 (C_8) ppm.

Figure 12 shows the ^{13}C-NMR spectrum of Zn[HPP]$_2$-HMDI-HBHEU. The chemical shift assignments were made from the off resonance decoupled spectra of the polymer. The carboxylate carbon resonance signal is observed at 171.45 ppm The ester carbonyl carbon and urethane carbonyl carbon signals are observed at 169.21 and 155.68 ppm, respectively. The resonance signal at 157.21 ppm is due to the urea carbonyl carbon. The aromatic carbon to which the carboxylate and ester groups are attached show signals at 133.08 and 136.10 ppm, respectively. The other aromatic carbon signals are observed at 129.96 (C_{13}), 128.08 (C_{14}), 126.57 (C_{12}) and 125.08 (C_{15}). The resonance signals due to the methylene group attached to ArCOO- are seen at 63.34 ppm and that attached to NHCOO- is seen at 62.07 (C_5) and 58.31 (C_{18}) ppm. The methylene carbons attached to -NH group showed signals at 44.09 (C_6) and 42.83 (C_{21}) ppm. The other methylene carbons gave resonance

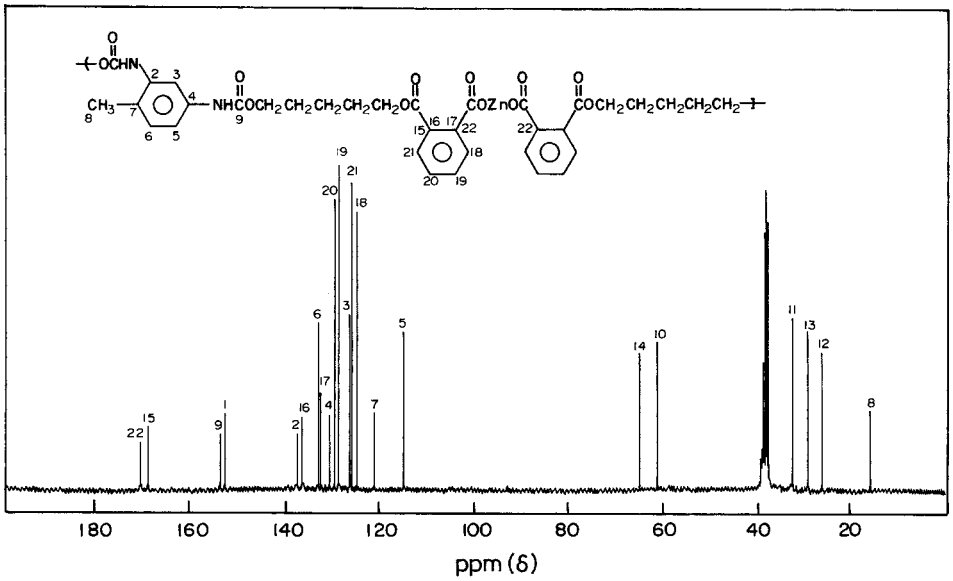


Figure 11. ^{13}C-NMR Spectrum of Zn[HPP]$_2$-TDI.

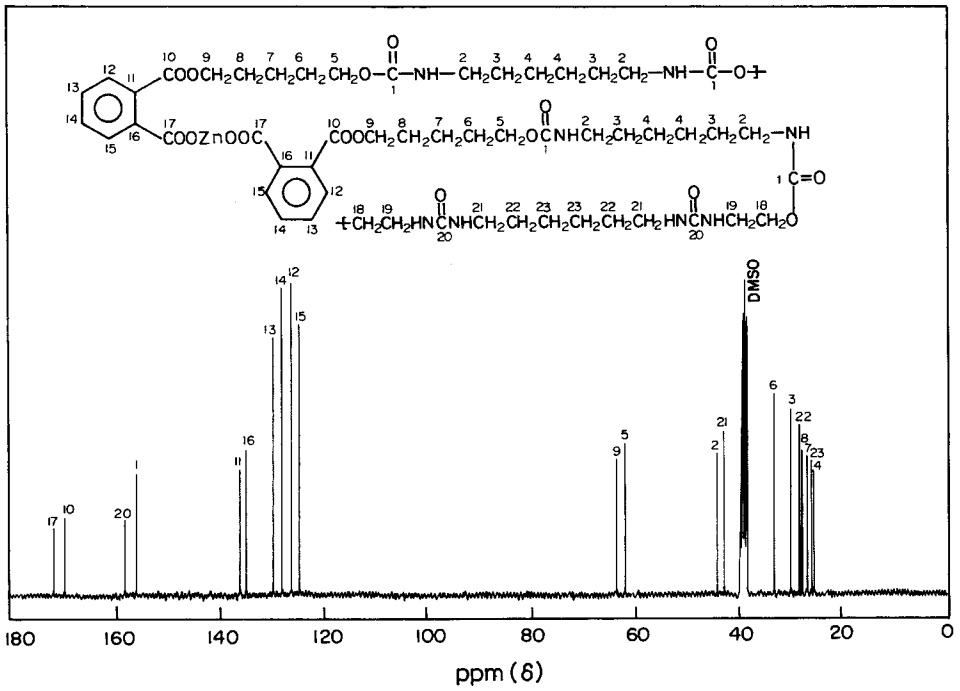


Figure 12. ^{13}C-NMR Spectrum of Zn[HPP]$_2$-HMDI-HBHEU.

signals at 33.69 (C_2), 29.59 (C_3), 28.62 (C_{22}), 28.12 (C_8), 27.11 (C_7), 26.56 (C_{23}) and 26.12 (C_4) ppm.

The ^{13}C-NMR spectrum of Zn[HPP]$_2$-TDI-TBHEU is shown in Fig. 13. The resonance signals at 171.50 and 169.14 ppm are assigned to the carboxylate and ester carbonyl carbons, respectively. The urea carbonyl carbon shows resonance signals at 155.06 ppm. The urethane carbonyl carbon signals are observed at 153.77 (C_9) and 151.27 (C_1). The aromatic carbons to which the carboxylate and ester carbonyl groups are attached show resonance signals at 136.14 (C_{16}) and 133.10 (C_{21}) ppm, respectively. The aromatic carbons to which urethane groups are attached shows signals at 137.28 (C_2) and 131.63 (C_4) ppm. The aromatic carbons to which urea groups are attached show signals at 135.51 (C_{26}) and 129.45 (C_{30}) ppm. The aromatic carbons gave signals between 136.14 and 121.32 ppm. The resonance signal due to methylene group attached to ArCOO- group is seen at 63.56 ppm and that attached to NHCOO- is seen at 62.14 (C_{10}) and 58.33 (C_{23}) ppm. Other methylene carbon signals are seen at 35.25 (C_{24}) 32.82 (C_{11}), 30.01 (C_{13}) and 26.86 (C_{12}) ppm. The methyl group attached to the aromatic ring shows a signal at 17.02 ppm.

For zinc containing polyurethanes, the experimentally determined percentage values of carbon, hydrogen and zinc are well within the calculated

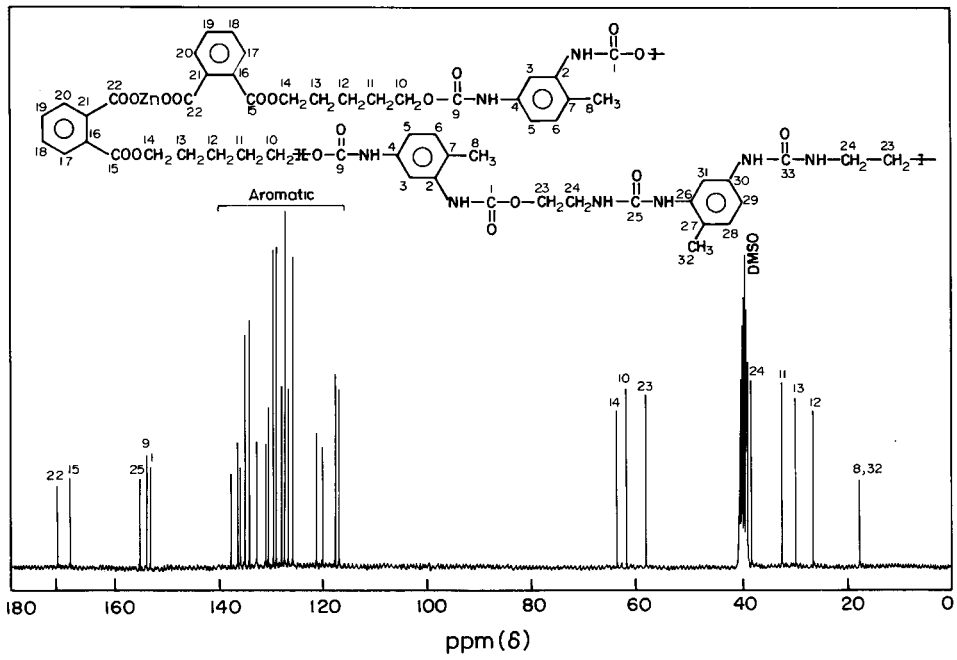


Figure 13. ^{13}C-NMR Spectrum of Zn[HPP]$_2$-TDI-TBHEU.

values. In the case of polyurethane-ureas, the zinc and carbon content are less than the value calculated based on equal reactivity of Zn[HPP]$_2$ and bisureas. This may be due to the lower reactivity of Zn[HPP]$_2$ when compared to the bisureas towards the diisocyanates. The values are incorporated in Table 1.

Solubility tests show that these zinc containing polyurethanes and polyurethane-ureas are insoluble in methanol, ethanol, acetone, ethyl methyl ketone, chloroform, carbon tetrachloride, n-hexane, benzene, toluene, xylene, tetrahydrofuran and dioxane. The polymers are soluble in polar solvents like DMSO, DMF, DMAc and m-cresol. So, the polymers are inferred to be polar in nature.

The intrinsic viscosity of the polymers are not very high, being considerably lower than their non metal analogues[22] as is generally the case for all metal – containing polyurethanes and polyurethane-ureas. The reason for this low viscosity may be that in these polymers the molecular weight built up may not be very high and there may also be partial reversible dissociation of the metal oxygen bonds leading to lower molecular weights in solutions. This was supported by the decrease in viscosity with increasing polarity of the solvents (Table 2) as in the other metal containing polyurethanes. The intrinsic viscosity of polyurethane-ureas are found to be higher than that of polyurethanes due to a lower amount of metal content and hence, less amount of ionic linkages in the polymer or due to their higher molecular weight. The values are incorporated in Table 1.

Table 2. Viscosities of TDI-Zn $[HPP]_2$

Solvent	Dielectric Constant (ϵ)	Intrinsic Viscosity (η)
DMF	36.7	0.0801
DMSO	46.7	0.0785
DMAc	37.8	0.0583
H_2SO_4	100.0	0.0251

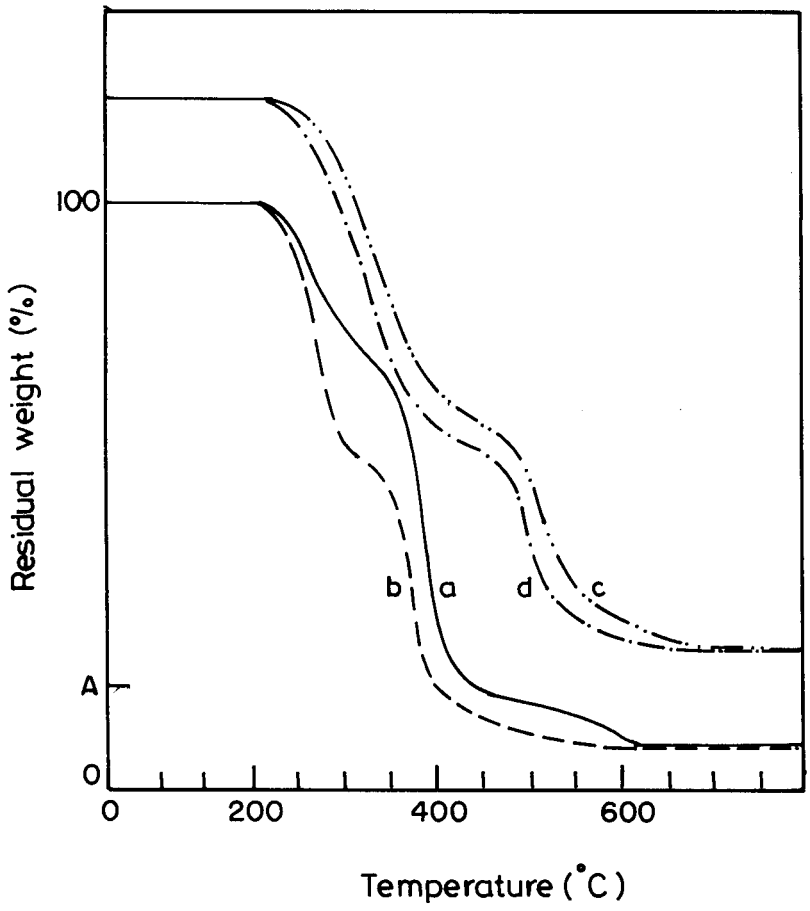


Figure 14. TGA Curves of: (a) $Zn[HPP]_2$-HMDI-HBHEU; (b) $Zn[HPP]_2$-HMDI-HBHPU; (c) $Zn[HPP]_2$-HMDI-TBHEU; (d) $Zn[HPP]_2$-HMDI-TBHPU; (for the polymers c and d the baseline is shifted to A).

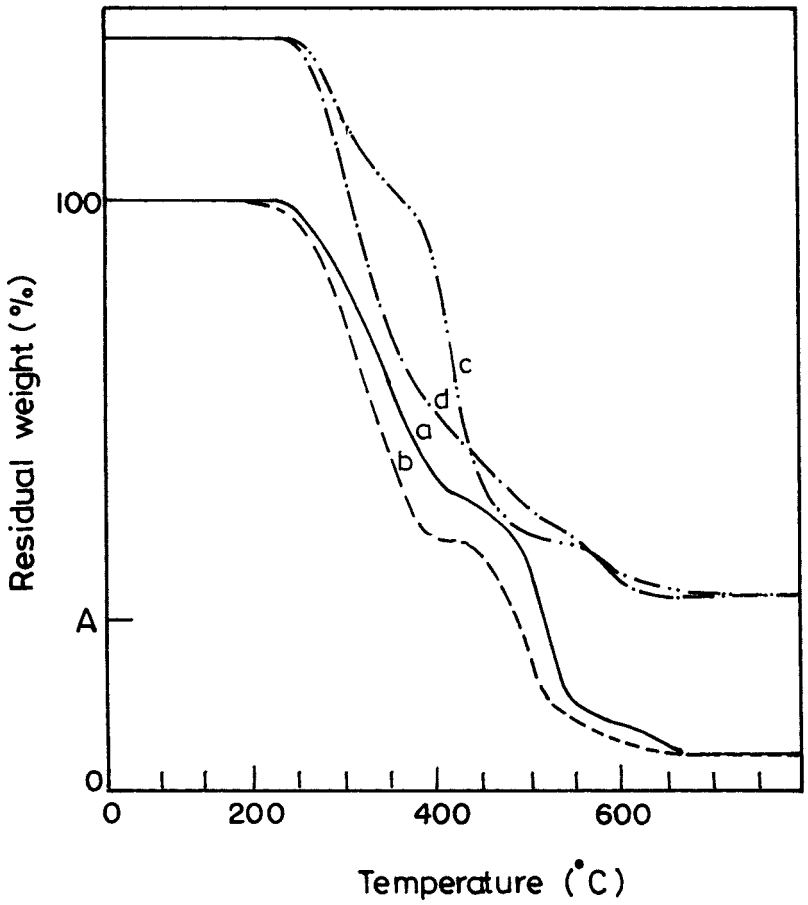


Figure 15. TGA Curves of (a) $Zn[HPP]_2$-TDI-HBHEU; (b) $Zn[HPP]_2$-TDI-HBHPU; (c) $Zn[HPP]_2$-TDI-TBHEU; (d) $Zn[HPP]_2$-TDI-TBHPU (for the polymers c and d the baseline is shifted to A).

Thermal Analysis

The TGA curves of metal containing polyurethanes are shown in Fig. 3 and that of polyurethane-ureas are shown in Figs. 14 and 15. Although all the metal-containing polymers are structurally similar, they exhibit different thermal behavior. Initial decomposition temperatures (IDT) of the polymers are found between 201 and 248°C from the TGA curves. It is found that TDI based polymers are having a slightly higher decomposition temperature than that of HMDI based polymers. In general, all the polyurethane-ureas show slightly higher stability than the polyurethane, this may be due to the presence of more numbers of hydrogen bonding in the polyurethane-ureas. Polyurethane-ureas containing TDI based bisurea (TBHEU or TBHPU) have higher stability than those containing HMDI based bisurea (HBHEU

Table 3. Thermal Data of Zinc Containing Polymers

Polymer	IDT (°C)	Temperature at 50% wt Loss (°C)	Weight Loss at 550°C (%)
I	201	304	87.95
II	214	337	88.10
III	208	393	86.80
IV	203	370	92.47
V	224	405	80.92
VI	221	373	92.46
VII	226	422	84.19
VIII	216	362	87.88
IX	248	413	87.42
X	244	348	87.75

IDT – Initial decomposition temperature.

or HBHPU) due to the presence of stiff phenylene rings in the main chain. In the case of all polymers, the residual weight at 550°C roughly corresponds to the zinc oxide formed. The TGA data of the polymers are shown in Table 3.

CONCLUSION

Zinc salt of mono(hydroxypentyl) phthalate were prepared by the reaction of 1,5-pentane diol, phthalic anhydride, and zinc acetate. $Zn[HPP]_2$ is a very useful starting material for the synthesis of ionic polymer into which the metal is firmly incorporated. As $Zn[HPP]_2$ is insoluble in most of the organic solvents, DMSO was used as the solvent for the synthesis of polymers at higher temperatures. Zinc containing polyurethanes and polyurethane-ureas having ionic links in the main chain were synthesized by the reaction HMDI or TDI with $Zn[HPP]_2$ and 1:1 mixtures of $Zn[HPP]_2$ and HBHEU, HBHPU, TBHEU, TBHPU. The polymers were not soluble in most of the organic solvents, but soluble in DMSO, DMF, and DMAc. The polyurethane-ureas are found to have higher intrinsic viscosity than the polyurethanes. The TDI based polymers show higher intrinsic viscosity than HMDI based polymesr. The IR spectra confirmed the presence of ionic linkage in the polymer. The TDI based polymers are found to have higher thermal stability than the HMDI based polymers.

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