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Studies on Metal-Containing Co-polyurethanes Based on Mono(hydroxyethoxyethyl)phthalate

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Metal salts of mono(hydroxyethoxyethyl)phthalate [M(HEEP)$_2$](M = ca^{2+} and Zn^{2+}) were synthesized by the reaction of diethylene glycol, phthalic anhydride and metal acetates. Metal-containing co-polyurethanes (MCPUs) having ionic linkages in the main chain were synthesized by the polyaddition reaction of hexamethylene diisocyanate or tolylene 2,4-diisocyanate with 1 : 1 mixtures of [M(HEEP)$_2$] and 1,5-pentane diol (PD) by using di-n-butyltin dilaurate as a catalyst. The MCPUs were characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR elemental analysis, solubility, viscosity and X-ray diffraction. Thermal properties of the polymers were also studied using thermogravimetric analysis and differential scanning calorimetry. The MCPUs were soluble only in highly polar solvents. The thermogravimetric analysis of MCPUs showed that the metal ions influence the initial decomposition temperature and overall thermal stability.

Keywords metal salt of mono(hydroxyethoxyethyl)phthalate, co-polyurethanes, thermal analysis, X-ray diffraction

Introduction

Polyurethanes are probably the most versatile class of polymers due to the great variety of raw materials that can be used in their formation (1). Polyurethanes are usually used as adhesives, coatings, foams, and different kinds of plastics and elastomers, as well as rocket motor liners for securing the composite propellant grain within the rocket motor. Polyurethanes possess excellent mechanical and physical properties, high combustion resistance, and wear resistance with a broad range good blood and tissue compatibility (2). These polymers are usually composed of multi-phase segments, and these alternating hard and soft structures are suitable for many applications by imparting various properties.

Metal-containing polymers represent a broad classification of polymers with inorganic salt groups attached to the polymer chain. They are generally referred to as 'polyelectrolytes' when they have sufficient ionic charge to be soluble in water, and as 'ionomers' if the concentration of ion-containing groups is too low for water solubility. Unlike homogeneous polymer systems, polymers containing ionic groups interact to form ion rich aggregates contained in the non-polar polymer matrix. The resulting interactions strongly influence polymer properties and applications, which have made this a fertile area of research and development. Metal-containing polymers are the most

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versatile and useful of the new polymeric materials currently being developed. These polymers have been investigated for several decades, attracting scientific and commercial attention. Incorporation of metal and functional groups into the polymers has led to a wide range of applications such as aqueous thickeners, impregnates textile sizers (3, 4), resins (5–7) and catalysts (8). Ionic diols containing ionic linkages between COO^- and M^{++} are of interest and very important starting materials for the synthesis of ionic polymers in which the metal is firmly incorporated into the backbone of the polymer (9–29). Here, we report the synthesis, characterization, and thermal studies of MCPUs derived from metal-containing (Ca^{++} and Zn^{++})diols, 1,5-pentane diol, (PD) with hexmethylene diisocyanate (HMDI) or tolylene diisocyanate (TDI).

Experimental

Materials

Phthalic anhydride (BDH), diethylene glycol (Merck), 1,5-pentane diol (PD) (Merck), di-n-butyltin dilaurate (DBTDL) (Fluka), HMDI and TDI (Fluka), calcium acetate (BDH) and Zinc acetate (BDH) were used as received without any purification. Acetone, methanol, dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), dimethyl acetamide (DMAc), benzene, toluene, m-cresol and chloroform were purified by standard procedures. M(HEEP)2 was synthesized as reported in our previous paper (14). The chemical structure of M(HEEP)2 is shown in Figure 1.

Synthesis of MCPUs

The MCPUs were synthesized as follows. A mixture of $M(HEEP)_2$ (0.05 mol) and PD (0.05 mol) in DMF (80 mL) was taken in a three-neck round bottom flask fitted with a nitrogen inlet, a condenser and dropping funnel. To this, 2–3 drops of DBTDL were added as a catalyst. Then, 0.01 mol of HMDI or TDI dissolved in 25 mL of DMF, was added slowly with constant stirring under a nitrogen atmosphere for about 1 h at 80–90°C. The reaction temperature was raised to 95°C, and the mixture was stirred for about 4 h. Finally, the reaction mixture was allowed to cool and treated with an excess amount of DMF. The solution was filtered and poured into a large quantity of methanol to precipitate the polymer. The resulting polymer was washed several times with methanol and acetone, and then dried in vacuum at 65°C for 1 h. The reactions involved in the polymer synthesis are presented in Scheme 1. The synthesis data are given in Table 1.

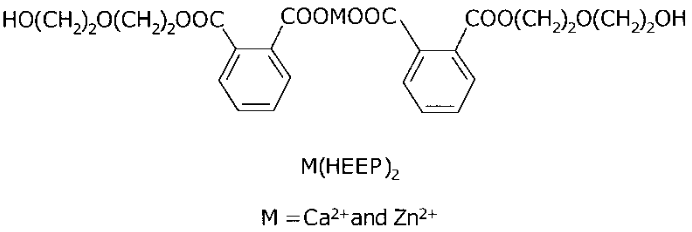
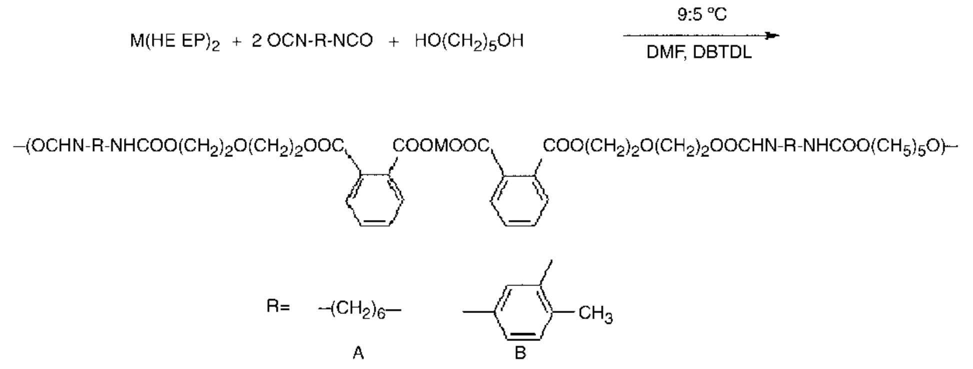


Figure 1. Chemical structure of $M(HEEP)_2$.



Polymer	I	II	III	IV
R	A	A	B	B

M= Ca^{2+} and Zn^{2+}

Scheme 1. Synthesis of MCPUs.

Measurements

The IR spectra of the polymers were recorded in a Testscan Shimadzu FT-IR 8000 series spectrophotometer at room temperature with the KBr pellet method. The ^{1}H-NMR and ^{13}C-NMR spectra of the polymers were recorded with a JEOL GSK-400 MHz spectrometer in $_{\mathrm{DMSO}}$-d^{6} using tetramethylsilane (TMS) as an internal standard. Thermogravimetric analysis (TGA) was performed with a Mettler-3000 thermal analyzer using 2 mg of the sample at a heating rate of 20°C/min in air. Differential scanning calorimetric analysis (DSC) was carried out using a DSC V4.OB Dupont 2100 model differential scanning

Table 1

Synthesis, viscosity and analytical data of MCPUs

Polymer no.	Polymer code	Yield (%)	$\eta_{\mathrm{inh}}{}^{a}$ (dL/g)	Repeating unit (formula)	Analytical data found (calculated) (%)		
					C	H	M
I	Ca(HEEP)$_2$ – PD-HMDI	86	0.081	$CaC_{45}H_{60}O_{19}N_4$	54.41 (54.00)	6.21 (6.04)	3.18 (4.00)
II	Zn(HEEP)$_2$ – PD-HMDI	83	0.089	$ZnC_{45}H_{60}O_{19}N_4$	53.12 (52.68)	6.02 (5.85)	5.78 (6.37)
III	Ca(HEEP)$_2$ – PD-TDI	80	0.079	$CaC_{47}H_{48}O_{19}N_4$	56.12 (55.73)	4.98 (4.78)	3.05 (3.96)
IV	Zn(HEEP)$_2$ – PD-TDI	76	0.084	$ZnC_{47}H_{48}O_{19}N_4$	54.98 (54.38)	4.80 (4.63)	5.62 (6.30)

[a]dL/g in DMSO.

calorimeter at a heating rate of 10°C/min under a nitrogen atmosphere. X-ray diffractograms were recorded according to a powder method with a Philips PW 1710 diffractometer using CuKα radiation. A Perkin-Elmer 2400 carbon-hydrogen analyzer was used for elemental analysis. The inherent viscosity η_{inh} of the polymers in DMSO was determined using an Ubbelohde-Viscometer at 40°C. The flow time for the solvent as well as the polymer solution was determined.

Solubility Studies

The solubility of the polymers was tested in various polar and non-polar solvents by taking 10 mg of polymers in 2 mL of different solvents in a closed test tube and set aside for one day. The solubility of the polymers was noted after 24 h.

Results and Discussion

Synthesis

M(HEEP)$_2$ is insoluble in many organic solvents. Hence, the copolymerization of M(HEEP)$_2$ and PD with diisocyanates was performed in highly polar solvents such as DMF. It has been known that the reaction between diols and diisocyanates catalyzed by DBTDL takes place via the formation of ternary complex between the reagents and catalysts (30). To avoid crosslinking of the polymers, the mole ratio of diol and diisocyanate was taken as 1 : 1. After completion of the reaction, DMF was added 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 methanol. Using M(HEEP)$_2$ and PD, four metal-containing co-polyurethanes were synthesized based on HMDI and TDI. They are coded as Ca(HEEP)$_2$-PD-HMDI (**I**), Zn(HEEP)$_2$-PD-HMDI (**II**), Ca(HEEP)$_2$-PD-TDI (**III**) and Zn(HEEP)$_2$-PD-TDI (**IV**). Blank polyurethanes were also prepared without the metal-containing monomers, and are designated as PD-HMDI (**V**) and PD-TDI (**VI**). The yield of TDI-based MCPU was lower than that of HMDI-based MCPU. This may he due to the decreased reactivity of TDI because of the presence of steric interaction between TDI and the catalyst as well as the diols (28, 29).

Solubility

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

Elemental Analysis

The elemental analysis data for the MCPUs are given in Table 1. The data reveals that the experimentally determined percentage values of carbon, hydrogen are slightly higher and that of metal is lower than that of calculated values. From this, it may be inferred that the reactivity of M(HEEP)$_2$ is less than that of PD.

Characterization of the Polymers

FT-IR Spectra. The FT-IR spectra of MCPUs show a peak at 3331–3329 cm^{-1} owing to –NH stretching. The peak at 3038–3027 cm^{-1} is due to the aromatic C-H stretching. The carboxylate ion of the salts shows two peaks at 1577–1560 and 1414–1402 cm^{-1}, respectively. The peaks at 1699-1683 cm^{-1} are due to the carbonyl stretching of urethane and ester groups.

FT-NMR Spectra. Figure 2 shows the ^{1}H-NMR spectra of MCPUs (I & III). The TDI-based co-polyurethane shows resonance peaks around 9.43–9.24 and 8.63–8.45 ppm due to the urethane N-H proton. The peak at 6.45 ppm is due to the urethane N-H proton of HMDI-based co-polyurethane. The aromatic protons of the HMDI-based co-polyurethane show peaks at 7.75–7.29 ppm, while those of TDI-based co-polyurethane show peaks at 7.96–7.05 ppm. The methylenoxy group attached to –COPh and –CONH group shows signal at 4.26–4.02 ppm. The resonance signal at 3.56–3.54 ppm is due to $-CH_2OCH_2$-group. The methyl group attached to the aromatic group of TDI-based polymer shows signal at 2.13 ppm. The methylene group attached to $-CH_2O$ groups shows signals between 1.75 and 1.54 ppm. The other methylene groups are observed between 1.46 and 1.19 ppm.

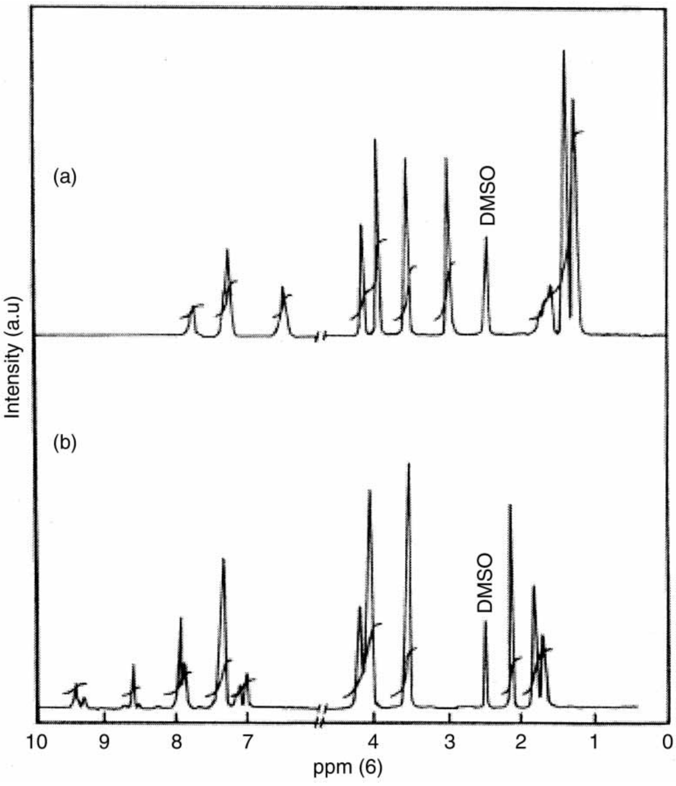


Figure 2. ^{1}H-NMR spectra of MCPUs: a) I and b) III.

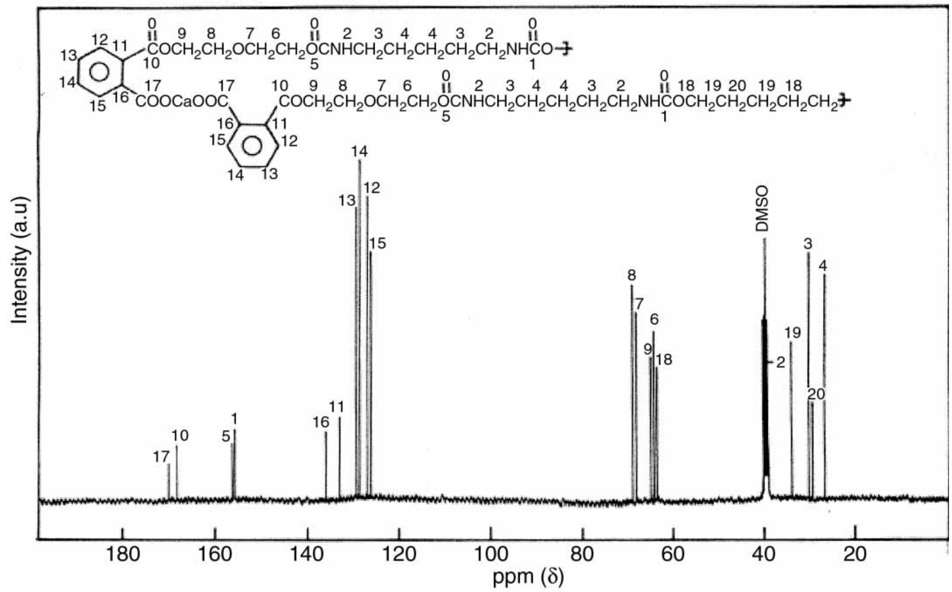


Figure 3. ^{13}C-NMR spectrum of Ca(HEEP)$_2$-PD-HMDI (I).

Figures 3 and 4 show the proton-decoupled ^{13}C-NMR spectra of co-polyurethanes (I and III). The peaks at 170.29–170.24 and 168.47–168.46 ppm are due to the carbonyl carbon of the corboxylate salt and the ester group, respectively. The HMDI-based co-polyurethane shows peaks at 156.56 and 155.98 ppm due to the

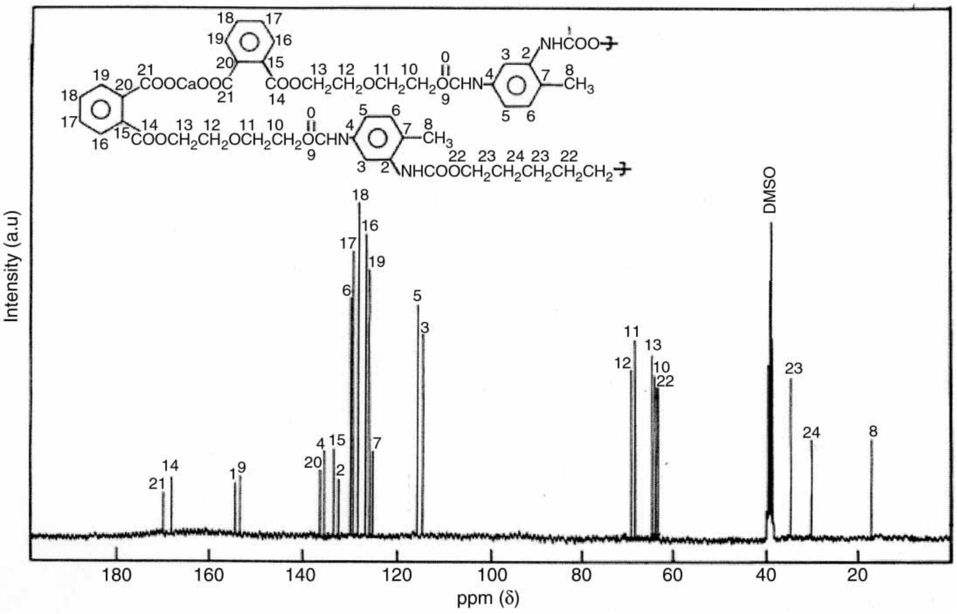


Figure 4. ^{13}C-NMR spectrum of Ca(HEEP)$_2$-PD-TDI (III).

carbonyl carbons of the urethane groups. The TDI-based co-polyurethane shows the corresponding peaks at 153.93–153.17 ppm. The aromatic carbons of HMDI-based co-polyurethane show peaks at 136.25–125.08 ppm while those of TDI-based co-polyurethane show peaks at 136.43–115.42 ppm. The resonance signals at 68.91–68.24 ppm are due to $-CH_2OCH_2$-group.

The peaks around 64.71-64.68 and 63.81-63.21 ppm are due to methylene carbons attached to –OCOPh and –OCONH groups, respectively. The signal due to the methylene group attached to –NH group is overlapped with the DMSO peak. The other methylene groups are observed at 34.42 and 26.64 ppm. The methyl carbon attached to the aromatic ring of TDI-based co-polyurethane shows a signal at 17.22 ppm.

Inherent Viscosity

The inherent viscosity data for the MCPUs are given in Table 1. The viscosities of the copolymers were found to be very low. This may be due to fact that in more polar solvents like DMSO the ionic links present in the polymer chains dissociate, resulting in reduction of the molecular weight of the polymers when the concentration is low (3, 10–12, 28, 29). The HMDI-based polymers showed slightly higher inherent viscosities than TDI-based polymers. Since the chain lengths of HMDI-based polymers were higher than those of TDI-based polymers, the hydrodynamic volumes of HMDI-based polymers may be larger than those of TDl-based polymers, as would be expected.

Thermal Studies

TGA data for the MCPUs and blank polyurethanes are given in Table 2. The initial decomposition temperatures (IDTs) of MCPUs were found to be between 188 and 207°C. The TDI-based polymers showed higher IDTs than the HMDI-based polymers. This may be due to the presence of stiff phenylene rings in the main chain of TDI-based polymer. All the polymers showed multiple stage decompositions. In all cases of MCPUs, the residual weights at 800°C correspond to the amount of metal oxides (CaO and ZnO) formed. The control polymers showed 100% weight loss at 650°C and showed higher IDTs than MCPUs, but showed greater rates of decomposition. In all probability, the metal acts as a catalyst and facilitates the first stage decomposition but retards the rate of decomposition of further stages (28, 29).

Table 2
TGA and DSC data of MCPUs and control polyurethanes

Polymer	T_g (°C)	IDT (°C)	Temperature at weight loss (°C) 20%	40%	60%	80%	90%	Weight loss at 800°C (%)
I	67.5	188	257	261	423	466	688	94.4
II	70.1	192	262	275	438	476	673	91.9
III	71.8	205	264	271	431	477	692	94.6
IV	75.8	207	270	285	425	480	697	92.1
V	5.8	201	256	287	323	402	479	100
VI	8.1	209	286	315	343	408	479	100

The DSC data of MCPUs show single T_g value (Table 2). This may be due to the absence of the formation of mixtures of homo-polymers or block copolymer. The T_g values were observed to be between 67.5 and 75.8°C. The HMDI-based polymers were expected to have much lower T_g values than the TDI-based polymers. However, the T_g values of the TDI-based MCPUs were slightly higher than those of the HMDI-based MCPUs. This result is due to the partial crystallinity of the HMDI-based polymers even though HMDI units are flexible, as revealed by X-ray studies (28, 29).

X-Ray Studies

Figure 5 shows the XRD pattern of the MCPUs. The XRD data reveals that the HMDI-based MCPUs (I and II) are partially crystalline in nature as they show some sharp peaks and a broad peak around $2\theta = 20–25°$. However, the TDI-based MCPUs do not show any sharp peak and hence they are considered to be amorphous in nature. The HMDI-based MCPUs owe their tendency to crystallize to the presence of $-(CH_2)_6-$ units in the backbone of the polymers (28, 29).

Conclusions

MCPUs were synthesized by reacting 1 : 1 mixtures of $M(HEEP)_2$ and PD with HMDI or TDI. The chemical structures of MCPUs were confirmed by FT-IR, ^{1}H-NMR and

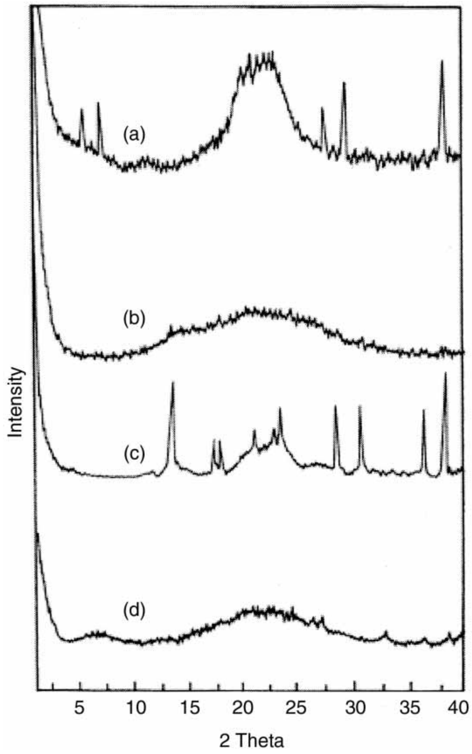


Figure 5. XRD patterns of MCPUs: a) I, b) III, c) II and d) IV.

^{13}C-NMR. The metal content in MCPUs were less than the calculated values based on equal reactivity of the comonomers, indicating that the reactivity of PD is higher than that of the M(HEEP)$_2$ towards the isocyanates. HMDI-based MCPUs showed slightly higher inherent viscosities than the TDI-based MCPUs due to their longer chain lengths. TDI-based MCPUs showed higher thermal stability than the HMDI-based MCPUs. X-ray diffraction data showed that the HMDI-based MCPUs are partially crystalline while TDI-based MCPUs are amorphous in nature.

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