

Studies on Zinc-Containing Poly(urethane-ether)s

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ABSTRACT: Zinc-containing poly(urethane-ether)s (PUEs) were synthesized by the reaction of hexamethylene diisocyanate (HMDI) or toluylene 2,4-diisocyanate (TDI) with a mixture of zinc salt of mono-(hydroxyethoxyethyl)phthalate [Zn(HEEP)₂] and poly(ethylene glycol) (PEG₃₀₀ or PEG₄₀₀) by using di-*n*-butyltin dilaurate as a catalyst. Blank PUEs without [Zn(HEEP)₂] were also prepared by reaction of PEG₃₀₀ or PEG₄₀₀ with HMDI or TDI. Thus prepared PUEs were characterized by FT-IR, ¹H and ¹³C NMR, solid-state ¹³C-CP-MAS NMR, viscosity, solubility, and X-ray diffraction studies. Thermal properties of the polymers were studied by using thermogravimetric analysis and differential scanning calorimetry.

KEY WORDS Zinc-Containing Poly(urethane-ether)s / Spectral Studies / Thermal Properties / Viscosity / X-ray Diffraction Studies /

Polyurethanes (PUs) are a very extensive class of polymers. PUs have wide range of industrial applications such as coating, adhesives, and biomedical materials etc., and they are well known for their mechanical properties. PUs are becoming increasingly important as engineering materials, because it has excellent abrasion resistance and properties of both elastomer and plastics.^{1–4} Some PUs are used as rocket motor liners for securing the composite propellant grain within the rocket motor. PUs possesses excellent mechanical and physical properties, high combustion resistance, and wear resistance with a broad temperature range for use, good blood and tissue compatibility.⁵ PUs are usually composed of multi-phase segments. These alternating hard and soft segment structures are suitable for many applications by imparting various properties.

PUs with flexible polyol backbone have generally good retention properties at low temperatures which make them suitable candidates for use in adhesives, coatings etc., under cryogenic conditions.⁶ 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. The polyurethane adhesives are used in substrates such as glass, wood, leather, plastics, rubber, metal, concrete, and ceramic.^{7–11} Incorporation of metal and functional groups into the polymers has led to wide applications such as aqueous thickeners, impregnates, textile sizings,^{12,13} resins^{14–16} and catalysts.¹⁷ 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.^{18–28}

The present paper deals with the synthesis and characterization of hexamethylene diisocyanate (HMDI) and toluylene 2,4-diisocyanate (TDI) based poly(urethane-ether)s (PUEs) from zinc salt of mono(hydroxyethoxyethyl)phthalate [Zn(HEEP)₂] and poly(ethylene glycol) (PEG₃₀₀ or PEG₄₀₀).

EXPERIMENTAL

Materials

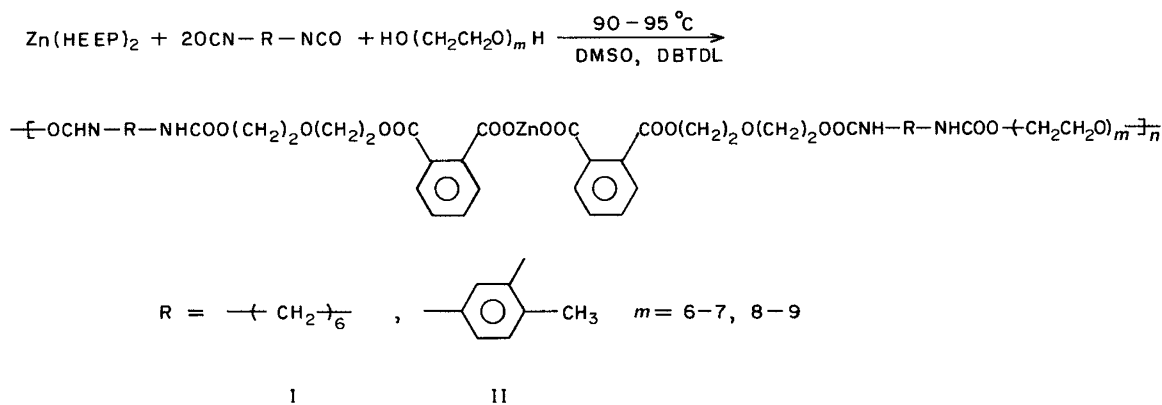
Phthalic anhydride (Merck), diethylene glycol (Merck), PEG₃₀₀ and PEG₄₀₀ (Merck), di-*n*-butyltin dilaurate (DBTDL) (Fluka), HMDI and TDI (Fluka) and zinc acetate (Merck) were used as received. The solvents such as acetone, methyl ethyl ketone, water, methanol, dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), dimethyl acetamide (DMAc), tetrahydrofuran, benzene, toluene, *m*-cresol, and chloroform were purified by standard procedures. Zn(HEEP)₂ was synthesized as reported in our previous paper.¹⁹

Synthesis of PUEs

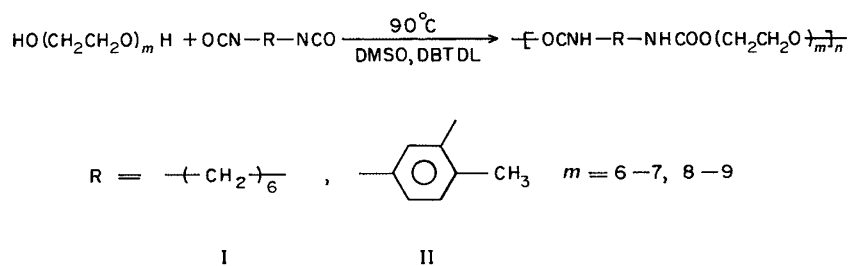
Zn(HEEP)₂ (0.008 mol) and PEG₃₀₀ or PEG₄₀₀ (0.008 mol) were dissolved in 100 mL of DMSO in a 500 mL three necked round bottom flask equipped with a nitrogen inlet, a condenser and a dropping funnel. Then HMDI or TDI (0.016 mol) dissolved in 20 mL of DMSO was added to the mixture maintained at 95 °C

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Polymer	I	II	III	IV
R	I	II	I	II
m	6-7	6-7	8-9	8-9

Scheme 1. Synthesis of zinc-containing PUEs.


Polymer	V	VI	VII	VIII
R	I	II	I	II
m	6-7	6-7	8-9	8-9

Scheme 2. Synthesis of blank PUEs.

over a period of 30 min in the presence of 2–3 drops of DBTDL as a catalyst. The synthesis was completely carried out under a nitrogen atmosphere. Then the reaction mixture was diluted with DMSO and filtered. The filtrate was poured into an excess quantity of methanol under vigorous stirring. The separated product was washed several times with methanol followed by acetone. The precipitate was dried *in vacuo* at 75°C for 24 h. Scheme 1 shows the reactions involved in the synthesis of PUEs based on Zn(HEEP)₂. The blank PUEs were also prepared by the same method without zinc-containing monomer. Scheme 2 shows the reactions involved in the synthesis of blank PUEs.

Measurements

The infrared (IR) spectra of the polymers were recorded on a Testscan Shimadzu FT-IR 8000 series

spectrophotometer at room temperature with the KBr pellet method. The ¹H & ¹³C NMR & DEPT spectra of the polymers were recorded on a JEOL GSX-400 MHz spectrometer in DMSO-*d*₆ using tetramethylsilane (TMS) as an internal standard. The solid-state ¹³C-CP-MAS NMR spectra were obtained using a Bruker MSL 75 MHz spectrometer with adamantane as a chemical shift reference. The 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⁻¹ in air. The differential scanning calorimetric analysis was carried out using a DSC V4.OB Dupont 2100 model differential scanning calorimeter at a heating rate of 10°C min⁻¹ under a nitrogen atmosphere. The X-ray diffractograms were recorded according to a powder method with a Philips PW 1710 diffractometer using CuKα radiation. The in-

Table I. Synthesis and viscosity data of zinc-containing PUEs

Polymer No.	Polymer code (dL g ⁻¹)	Yield (%)	η_{inh} (dL g ⁻¹)	External appearance
I	Zn(HEEP) ₂ -PEG ₃₀₀ -HMDI	78	0.093	White
II	Zn(HEEP) ₂ -PEG ₃₀₀ -TDI	72	0.089	Yellowish White
III	Zn(HEEP) ₂ -PEG ₄₀₀ -HMDI	81	0.103	White
IV	Zn(HEEP) ₂ -PEG ₄₀₀ -TDI	73	0.101	Yellowish White
V	PEG ₃₀₀ -HMDI	78	0.192	White
VI	PEG ₃₀₀ -TDI	72	0.176	Slightly Yellow
VII	PEG ₄₀₀ -HMDI	84	0.202	White
VIII	PEG ₄₀₀ -TDI	82	0.190	Slightly Yellow

herent 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 (1.0 g dL⁻¹) was determined. The 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

The synthesis of zinc-containing PUEs was carried out in DMSO solvent. Zn(HEEP)₂ was not soluble in other solvents like dioxane, toluene, xylene and acetone, and hence the polyaddition reaction did not proceed smoothly in these solvents. During the synthesis of the polymers, the mole ratio of diisocyanate:diol (Zn(HEEP)₂ and PEG₃₀₀ or PEG₄₀₀) was kept to be 1:1 to avoid the formation of crosslinkages. The crosslinked product formed if any was filtered off after stirring the product with excess of DMSO to dissolve the linear polymer. The precipitated polymer was washed with acetone to remove unreacted Zn(HEEP)₂ and then with methanol followed by acetone. With the help of Zn(HEEP)₂, PEG₃₀₀ or PEG₄₀₀ and HMDI or TDI, four PUEs were prepared by the same method. The PUEs are encoded as Zn(HEEP)₂-PEG₃₀₀-HMDI **I**, Zn(HEEP)₂-PEG₃₀₀-TDI **II**, Zn(HEEP)₂-PEG₄₀₀-HMDI **III**, and Zn(HEEP)₂-PEG₄₀₀-TDI **IV**. The blank PUEs are encoded as PEG₃₀₀-HMDI **V**, PEG₃₀₀-TDI **VI**, PEG₄₀₀-HMDI **VII**, and PEG₄₀₀-TDI **VIII**. The yields of the PUEs were good in all the cases. The synthesis data of PUEs and blank PUEs are given in Table I. The PUEs were insoluble in methanol, ethanol, acetone, ethyl methyl ketone, carbon tetrachloride, ethyl acetate, *n*-hexane, benzene, toluene, tetrahydrofuran, and xylene. However, they were soluble in highly polar solvents such as DMF, DMSO, and DMAc.

Characterization of PUEs

FT-IR Spectra. The PUEs show a broad absorp-

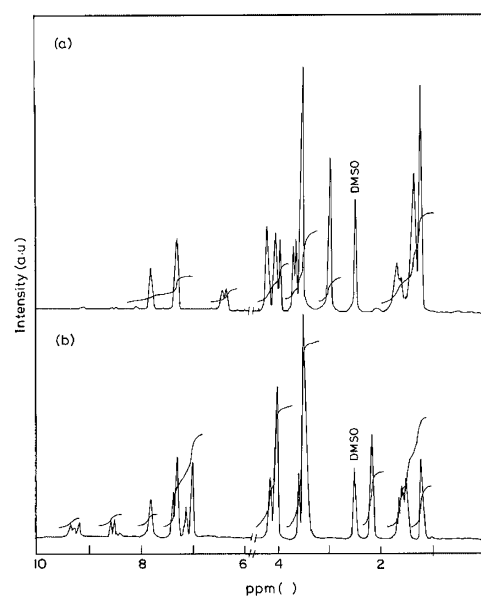


Figure 1. ¹H NMR spectra of PUEs: (a) **I** and (b) **II**.

tion band between 3338 and 3292 cm⁻¹ is due to N–H stretching. The absorption band at 3055–3031 cm⁻¹ is due to the aromatic C–H stretching. The absorption bands at 2939–2925 and 2857–2850 cm⁻¹ are due to the asymmetrical and symmetrical C–H stretching of methylene and methyl groups. The peaks around 1707–1685 cm⁻¹ are due to the carbonyl stretching of urethane and ester groups. The carboxylate ion of the zinc salt gives two broad peaks between 1604–1557 and 1410–1397 cm⁻¹. This confirms the presence of ionic linkages in the PUEs. These bands were not observed in metal-free analogues of these polymers (blank polymers). The peak at 1107–1080 cm⁻¹ are attributed to the C–O stretching of the ester group. The C–H out of plane bending vibrations of aromatic rings is observed between 752 and 743 cm⁻¹.

¹H NMR Spectra. The ¹H NMR spectra of PUEs **I** and **II** are shown in Figure 1. The TDI-based PUEs show peaks at 9.29–9.24 and 8.43–8.39 ppm are due to the urethane N–H protons whereas the HMDI-based PUEs show the corresponding peak at 6.64–6.56 ppm. The aromatic protons of HMDI-based PUEs show res-

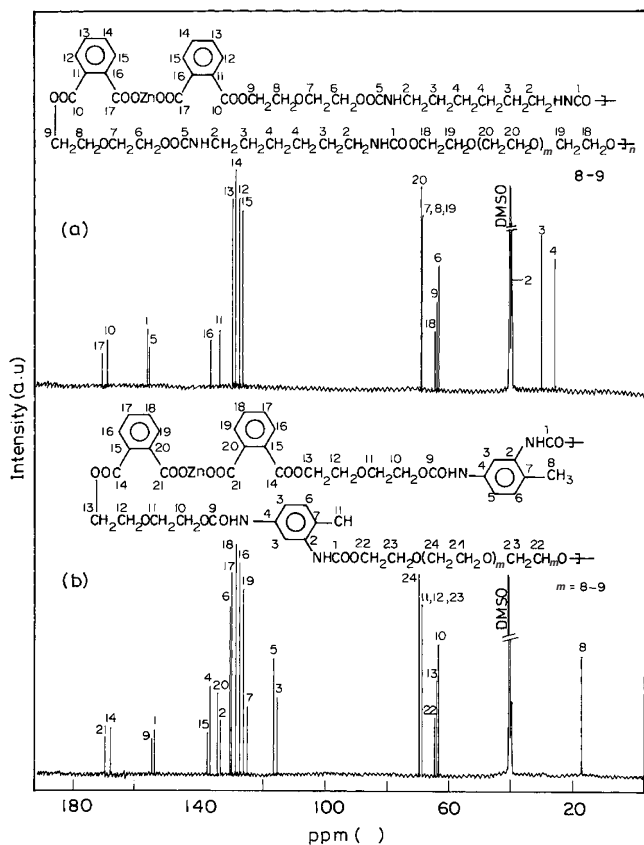


Figure 2. ^{13}C NMR spectra of PUEs: (a) **III** and (b) **IV**.

onance signals at 7.83–7.25 ppm whereas those of TDI-based PUEs show resonance signals at 7.88–7.08 ppm. The peak at 4.25–4.06 ppm is due to the methyleneoxy group attached to the –COPh and –CONH groups. The resonance signal at 3.54–3.52 ppm is due to the –CH₂OCH₂– group. The methylene group attached to the –NH group shows signal between 2.98 and 2.95 ppm. The methyl group attached to the aromatic ring shows resonance signal at 2.14 ppm. The peak at 1.78–1.56 ppm is due to methylene group attached to methyleneoxy group. The other methylene groups show resonance signal between 1.46 and 1.21 ppm.

^{13}C NMR Spectra. The ^{13}C NMR spectra of the PUEs **III** and **IV** are shown in Figure 2. The peaks at 170.83–168.67 ppm are due to the carboxylate and ester carbonyl carbon of the PUEs. The PUEs show signals at 156.29–153.54 ppm are due to the urethane carbonyl carbon. The aromatic carbon signals due to HMDI-based PUEs are observed between 136.72 and 125.52 ppm and those of TDI-based PUEs shows between 137.25 and 115.12 ppm. The methyleneoxy carbon of PEG₃₀₀ or PEG₄₀₀ unit in the PUEs shows resonance signal at 69.48–69.39 ppm. The signal is observed between 68.70–68.15 ppm is due to the –CH₂OCH₂– group. The methylene group attached to the –OCOPh and the –OCONH groups shows peak between 64.32–64.22 and 63.53–63.28 ppm, respectively.

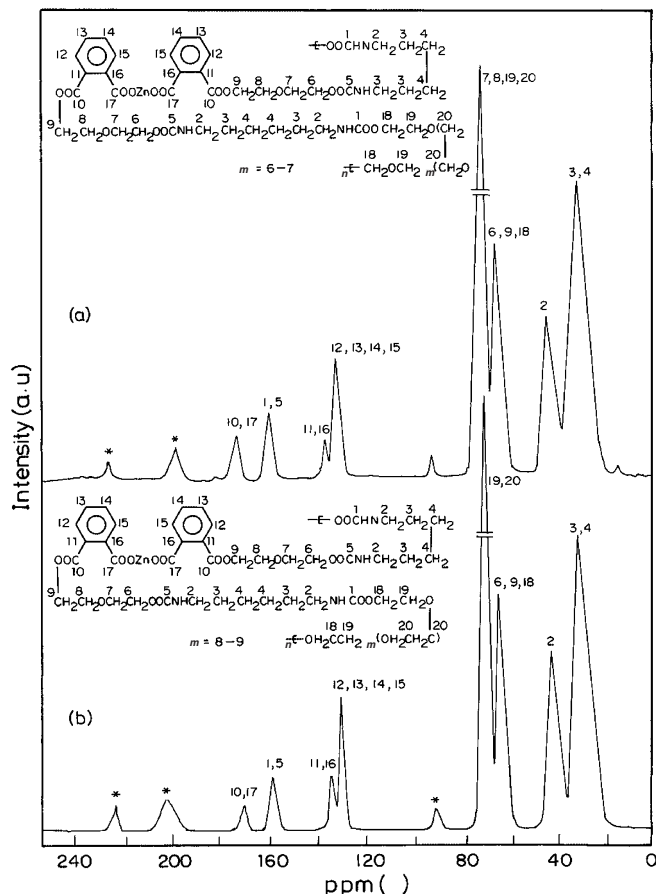


Figure 3. Solid state ^{13}C -CP-MAS NMR spectra of PUEs: (a) **I** and (b) **III**.

The signal due to the methylene group attached to the –NH group is overlapped with the DMSO peak. The other methylene carbon signals are observed between 32.51–26.68 ppm. The methyl group attached to the aromatic ring of the TDI-based PUEs shows peak at 17.33–17.28 ppm.

Solid-State ^{13}C -CP-MAS NMR Spectra

Figure 3 shows the solid-state ^{13}C -CP-MAS NMR spectra of the PUEs **I** and **III**. The PUEs show broad peak at 172.93–172.81 ppm is due to the carboxylate and ester carbonyl carbon of PUEs. The urethane carbonyl carbon shows peak at 157.53–154.12 ppm. The HMDI-based PUEs show a broad peak due to the aromatic carbons at 135.16–129.30 ppm. The peak at 70.27–70.06 ppm is due to the methyleneoxy carbon of PEG₃₀₀ or PEG₄₀₀ unit in the PUEs. The methyleneoxy carbon attached to the –OCOPh and the –OCONH groups show a peak at 65.55–65.12 ppm. The methylene group attached to –NH group shows peak around at 42.56–42.53 ppm in the case of HMDI-based PUEs. The peak is missing in the ^{13}C NMR spectra of the polymers in DMSO. The peak at 30.17–30.06 ppm is due to the other methylene groups.

Table II. TGA and DSC data of zinc-containing PUEs

Polymer No.	T_g (°C)	IDT (°C)	Temperature at weight loss (°C)					Weight loss at 800 °C (%)
			20%	40%	60%	80%	90%	
I	4.1	197	265	310	355	643	721	91.8
II	6.9	215	265	295	326	529	705	92.2
III	3.5	202	279	305	345	621	722	92.3
IV	5.8	230	235	318	345	523	718	92.8
V	-30.2	234	313	339	365	427	531	100
VI	-19.4	229	301	321	340	371	503	100
VII	-37.1	246	322	346	361	407	504	100
VIII	-26.7	241	320	343	357	401	483	100

Inherent Viscosity

The inherent viscosity data of PUEs in DMSO at 40 °C are given in Table I. The viscosities of PUEs are found to be low when compared with that of blank PUEs. This is due to the presence of the ionic linkages in the polymer chains. The inherent viscosities of the PUEs are considerably lower than their non-metal analogues,^{21–28} as is generally known for all metal-containing polyurethanes and poly(urethane-urea)s. The reason for the low viscosity may be that in these polymers the molecular weight builds up may not be very high and there may also be partial reversible dissociation of the metal oxygen bonds leading to lower molecular weight fragments in solutions.^{22–25} With increase in the soft segment content and its length and decrease the metal content in the PUEs, the viscosity increases due to the presence of lower number of ionic linkages. So, the PUEs based on PEG₄₀₀ show higher viscosities than the PUEs based on PEG₃₀₀. The HMDI-based PUEs show higher inherent viscosities than the TDI-based PUEs. This is due to the higher hydrodynamic volume of HMDI-based polymers will be more than TDI-based polymers.

Thermogravimetric Analysis

The TGA data of PUEs are given in Table II. The initial decomposition temperature (IDT) of PUEs shows the range between 197 and 230 °C. The IDT of the PUEs are slightly lower than that of blank PUEs. However, their decomposition temperatures are lesser than those of blank PUEs. This result indicates that the metal acts as a catalyst and facilitates the first stage decomposition but retards the rate of decomposition on further stages. All the PUEs showed multiple stage decomposition. The first stage may be considered to be urethane-ether scission followed by the formation of isocyanate and hydroxyl components.²³ The second stage perhaps involves cyclization and secondary degradation. The third stage corresponds to the formation of ZnCO₃. The PUEs based on PEG₄₀₀ showed

higher IDT than PEG₃₀₀. The initial decomposition takes place at the urethane linkages, and the numbers of urethane linkages are more in a unit length of PEG₃₀₀ based PUEs than that in PEG₄₀₀ based PUEs. The blank PUEs showed 100% weight loss at 650 °C, indicating that PUEs exhibit good thermal stability than the blank PUEs. In all the cases of the polymers the residual weight at 800 °C roughly corresponds to the amount of ZnO formed at this temperature. The TDI-based polymers show higher IDT than the HMDI-based PUEs. This may be due to the presence of stiff phenylene ring present in the polymer chain.

Glass Transition Temperature (T_g)

The T_g data are given in Table II. The T_g values of the zinc-containing PUEs ranges from 4.1 to 6.9 °C. All the PUEs showed single T_g value. This may be due to the absence of formation of mixture of homopolymer or block copolymer.²⁸ This also indicates that the absence of heterogeneous mixing of hard (urethane unit) and soft segment (polyol) in the polymer matrix. The difference in the T_g values between TDI and HMDI-based PUEs is not that much high. This is reason for those HMDI-based polymers have flexible chain, due to the increase in the crystallinity of HMDI-based polymers (revealed by X-ray studies), the T_g value increase and they become close to that of TDI-based PUEs. The T_g value of PUEs decreases with increase in the soft segment.

X-ray Diffraction

Figure 4 shows the XRD pattern of the PUEs. The X-ray diffraction studies show that the HMDI-based PUEs are partially crystalline in nature, whereas the TDI-based PUEs are amorphous in nature. This may be due to the folding of the hexamethylene unit present in the backbone of the PUEs. The HMDI-based polymers show some crystalline nature. This was also confirmed by the solubility studies of the PUEs in DMSO. The TDI-based PUEs were more easily soluble in DMSO

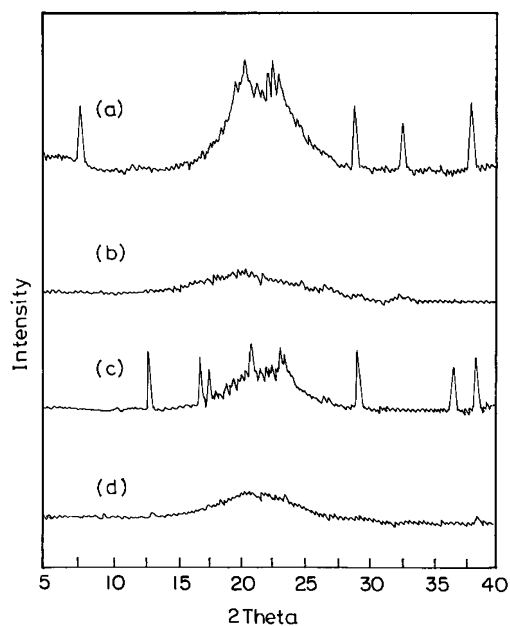


Figure 4. XRD patterns of PUEs: (a) I, (b) II, (c) III, and (d) IV.

than the HMDI-based PUEs. The HMDI-based polymers showed few sharp peaks around at $2\theta = 20\text{--}25^\circ$.

CONCLUSIONS

Zinc containing poly(urethane-ether)s were prepared by the reaction of HMDI or TDI with $\text{Zn}[\text{HEEP}]_2$ and PEG₃₀₀ or PEG₄₀₀. The polymers are soluble in DMF, DMSO, and DMAc and insoluble in most of the other organic solvents. Thermal properties of the polymers showed that the TDI-based PUEs are higher stability than the respective HMDI-based PUEs. The inherent viscosities of the polymers were found to be very low due to chain dissociation in DMSO. X-ray diffraction pattern of the polymers reveals that the TDI-based PUEs are amorphous and HMDI-based PUEs are partially crystalline.

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