Synthesis and characterization of metal-containing polyurethane-ureas

P. Rajalingam and Ganga Radhakrishnan*
Polymer Division, Central Leather Research Institute, Adyar, Madras-600 020, India

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A new series of metal-containing polyurethane-ureas containing ionic links in the main chain were synthesized by the reaction of toluene diisocyanate with Mn, Cu, Co and Pb salts of mono(hydroxyethyl)-phthalate and a bisurea. The polymers obtained were brown to green in colour. These polymers were well characterized by solubility, viscometry, spectral studies (i.r., u.v. and n.m.r.) and thermogravimetric analysis.

(Keywords: polyurethane-ureas; metal-containing diols; viscosity; thermogravimetric analysis)

INTRODUCTION

Incorporation of metals and functional groups into polymers find applications as aqueous thickners, impregnants, adhesives and textile sizers. Because they are polyelectrolytes, they also have potential application in soil conditioning[1]. Generally polyurethanes contain covalent bonds 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 reported by Rembaum *et al.*[2–4]. Metal-containing polymers with ionic links formed between $-COO^-$ and Mn^{2+} in the main chain have also been studied[5–7]. A fibre-forming condensate probably containing urethane and urea groups is formed in a modification of the reaction of diamine with urea when an alkylene glycol is one of the initial components. When the amount of alkylene glycol is increased at the expense of the diamine true polyurethanes can be made. Metal-containing polyurethanes, polyurethane-ureas and polyesters would possess ionic links and hence would be expected to have applications in adhesives, coatings and biomedical fields[8–10]. Hence the present investigation is aimed at the synthesis and characterization of polyurethane-ureas from metal-containing (Mn^{2+}, Cu^{2+}, Co^{2+} and Pb^{2+}) diols, toluene diisocyanate (TDI) and a bisurea, prepared from 2-aminoethanol and TDI.

EXPERIMENTAL

TDI (80%, 2,4- and 20% 2,6-isomers, AG Fluka) was used without further purification after estimating the isocyanate content. *N,N'*-dimethyl formamide (DMF) and 2-aminoethanol were purified by distillation. 1,4-Dioxane was purified by the standard procedure. Ethylene glycol (Sarabhai M. Chemicals) was purified by drying over anhydrous Na_2SO_4 and distilling. Mono(hydroxyethyl)phthalate $(HEP)_2M$ (where M = Mn, Cu, Co and Pb) and bisurea were prepared by reported procedures.

Preparation of polyurethane-ureas

Into a 100 ml flask equipped with a stirrer, a thermometer, a condenser and a nitrogen inlet, a mixture (0.03 mol) of metal salts of $(HEP)_2M$ (M = Mn, Cu, Co and Pb) and bisurea, DMF (20 g) and two to three drops of di-n-butyltindilaurate (catalyst) were placed. Then TDI (0.03 mol) dissolved in DMF (10 g) was added gradually with stirring at 80°C over 2 h under a nitrogen stream. After the addition the mixture was stirred at the same temperature for a fixed time. After the reaction DMF (30 g) was added to the mixture and the solution was filtered. The filtrate was poured into a large excess of vigorously stirred water to precipitate the product (polyurethane-urea). The product was further washed with acetone several times and dried at 90°C. The preparation conditions for the various polyurethane-ureas are given in *Table 1*.

Characterization of the polymers

I.r. spectra of the polymers were recorded with a Perkin–Elmer model 598 spectrometer using KBr pellets.

The electronic spectra of the polymers in concentrated sulphuric acid were recorded with a Hitachi 320 spectrophotometer using a closed cell in the u.v. region.

N.m.r. spectra of the polymers in DMSO-d_6 were taken in a Varian XL 100 spectrometer.

Inherent viscosities of the polymers were determined at a concentration of $0.5\ g\ dl^{-1}$ in DMSO at 30°C, using an Ubbelohde Viscometer.

Thermogravimetric analysis (t.g.a.) was carried out with a DuPont 951 thermal analyser at a heating rate of $20°C\ min^{-1}$ from ambient to 700°C in air.

RESULTS AND DISCUSSION

The polymers obtained were soluble in DMSO, *m*-cresol and H_2SO_4 in the cold and in DMF on heating. The viscosity measurements were carried out in DMSO at 30°C. The viscosities increase significantly due to the presence of metal in the following order: $Cu < Co < Mn < Pb$. The solubility data of all the polymers are given in *Table 2*.

The ^1H n.m.r. spectra were recorded in DMSO-d_6 and the characteristic signals are presented in *Table 3*.

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* To whom correspondence should be addressed

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Table 1 Synthesis data and inherent viscosity of polyurethane-ureas prepared from TDI and $(HEP)_2M$-Bu(TDI)

Diols[a]						
Bisurea	$(HEP)_2M$	Temperature (°C)	Time (h)	Yield (%)	Colour	η_{inh}[b] (dl g^{-1})
Bu(TDI)	$(HEP)_2$ Cu	80	3	91	Dark green powder	0.11
Bu(TDI)	$(HEP)_2$ Mn	80	4	98	Dark brown powder	0.30
Bu(TDI)	$(HEP)_2$ Pb	80	3	93	Slightly yellow powder	0.34
Bu(TDI)	$(HEP)_2$ Co	80	3	80	Brownish red powder	0.22

[a] Composition of diols: 50 mol% Bu(TDI) and 50 mol% $(HEP)_2M$
[b] Determined at a concentration of 0.05 g per 10 ml in DMSO at 30°C

Table 2 Solubility data for polyurethane-ureas

Solvents	Cu	Mn	Pb	Co
Water	–	–	–	–
Acetone	–	–	–	–
Chloroform	–	–	–	–
Dioxane	–	–	–	–
Toluene	–	–	–	–
Benzene	–	–	–	–
Xylene	–	–	–	–
m-Cresol	+	+	+	+
H_2SO_4	+	+	+	+
DMF	(+)	(+)	(+)	(+)
DMSO	+	+	+	+

–, Insoluble; (+), soluble on heating; +, soluble

Table 3 ^1H n.m.r. data of polyurethane-ureas

Polyurethane-ureas	Characteristic signals
Bu(TDI)-$(HEP)_2$ Cu	8.0 (NHCONH) 8.5 (–NH–CO–) 6.9–7.7 (aromatic) 4.0–4.5 ($-CH_2-CH_2-$) 2.20 ($-CH_3$ in benzene)
Bu(TDI)-$(HEP)_2$ Mn	8.10 (–NH–CONH–) 8.30 (–NH–CO–) 7.0–7.7 (aromatic) 4.0–4.5 ($-CH_2-CH_2-$) 2.1 ($-CH_3$ in benzene)
Bu(TDI)-$(HEP)_2$ Pb	8.0 (NH–CONH) 8.3 (–NHCO–) 7.0–7.8 (aromatic) 4.1–4.4 ($-CH_2-CH_2-$) 2.1 ($-CH_3$ in benzene)
Bu(TDI)-$(HEP)_2$ Co	8.1 (–NH–CO–NH–) 8.4 (–NH–CO–) 6.8–7.3 (aromatic) 4.0–4.6 ($-CH_2-CH_2-$) 2.0 ($-CH_3$ in benzene)

The i.r. spectra showed the following characteristic absorption bands: 3300–3400 cm^{-1} (NH stretching), 1620–1720 cm^{-1} (carbonyl of urethane, urea and ester), 1530–1550 cm^{-1} (NH bending) and 1220–1250 (C–O stretching). The 1390–1410 and 1550–1600 cm^{-1} bands of the carboxylate groups could not be observed in the blank polymer[6].

The electronic spectra of Cu^{2+}, Mn^{2+} and Pb^{2+}-containing polyurethane-urea were recorded in concentrated sulphuric acid. Three peaks were observed in all the cases. The peak corresponding to 220 nm is probably due to charge transfer taking place between the metals and carboxylate ions. The absorption band at ~260 nm may be due to the π–π^* transition of the aromatic ring. This is slightly shifted in the case of Cu^{2+} and vanishes in the case of Mn^{2+}. This may be due to the effect of odd electrons present in the d-orbital. The n–π^* transition of carbonyl groups and –NH– groups probably accounts for the peak around 300–310 nm.

It is clear that introducing metal into the polyurethane-ureas produces some decrease in decomposition temperature. The plateau above 350 K in all four polyurethane-ureas corresponds to the formation of either metal oxides or metal carbonates in air irrespective of the metal[5]. Though all the polyurethane-ureas are structurally similar, these polymers exhibit different behaviour in thermal analysis. This difference is attributed to the presence of different metals in the polyurethane-ureas. The initial 10% weight loss for all the polyurethane-ureas occurred in the temperature range 458–473 K, whereas an appreciable difference was found in the temperature range for 70% weight loss of polyurethane-ureas with respect to their metals. The rate of degradation of polyurethane-ureas in the first and second stages was found to be first order by the Freeman and Caroll[11] method. Knowing the order of the degradation reactions, the activation energies of degradation were calculated for all the polyurethane-ureas by the Murray

Table 4 Degradation and activation energies of polyurethane-ureas

	Stage 1			Stage 2		
Polyurethane-ureas	Temperature (K)	Weight loss (%)	E_a (kJ mol^{-1})	Temperature (K)	Weight loss (%)	E_a (kJ mol^{-1})
Bu(TDI)-$(HEP)_2$ Cu	468–598	60.0	42.83	598–798	19.8	25.37
Bu(TDI)-$(HEP)_2$ Mn	468–548	48.2	71.18	548–713	31.7	39.68
Bu(TDI)-$(HEP)_2$ Pb	448–573	46.0	66.99	573–823	33.2	32.23
Bu(TDI)-$(HEP)_2$ Co	448–573	63.9	34.75	573–783	16.0	25.37

and White method[12]. The activation energies are given in *Table 4*. The temperature change is less in the first stage than in the second stage, whereas the weight loss and the activation energy are higher in the first stage than in the second stage for all the polyurethane-urea systems studied. Therefore the major first stage may be considered to be urethane-urea chain scission followed by the formation of isocyanate and hydroxyl components. The second stage perhaps involves cyclization and secondary degradation. Based on the activation energies of polyurethane-ureas the thermal stability of the four metal-containing polyurethane-ureas is in the order: Mn > Pb > Cu > Co. However, as metals are present in the main chain of polyurethane-urea by ionic linkage, the thermal stability of the transition metals (Mn, Co and Cu) can be explained by the presence of odd electrons, in the outermost orbital, which probably enhances the ionic hold of the metal in the polymer chain. Hence Mn^{2+} exhibits a thermally more stable ionic link in the backbone chain of polyurethane-urea by the support of the d^5 orbital. The same explanation can be given with respect to polyurethane-urea containing Cu^{2+} which is more stable than the Co^{2+} counterpart.

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