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Mechanisms

Metal-Containing Polyurethanes

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SUMMARY

Metal-containing polyurethanes were prepared from cobalt and copper mono(hydroxyethyl)phthalate with hexamethylene diisocyanate and tolylenediisocyanate and characterized. The presence of ionic links in the polymers was shown by IR spectra, solution viscosity and conductance measurements.

INTRODUCTION

Metal-containing diols, which are useful for the preparation of condensation polymers, with ionic links formed between $-COO^-$ and M^{2+} in the main chain have not been studied to a great extent (1-9). The synthesis and characterization of Co^{2+} and Cu^{2+} salts of mono (hydroxyethyl)phthalate (HEP) and their polymers with hexamethylenediisocyanate and tolylenediisocyanate are reported in this communication for the first time.

EXPERIMENTAL

Preparation of diols

In a three-necked flask fitted with a stirrer, condenser and a thermometer, 2 moles of ethyleneglycol was placed and 0.5 moles of phthalic anhydride was added slowly with stirring at 90-100°C over 30 minutes. The reaction mixture was stirred for 1 hr at the same temperature. To this solution, 0.25 moles of $Co(CH_3COO)_2 \cdot 4H_2O$ (experiment 1) or $Cu(CH_3COO)_2 \cdot H_2O$ (experiment 2) was added. The solution was stirred continuously for an additional 30 minutes at the same temperature.

In the case of experiment 1, the precipitate obtained after cooling was filtered, washed several times first with acetone, then with alcohol (to remove unreacted cobalt acetate) and finally with acetone. The product was dried in vacuum at 60°C.

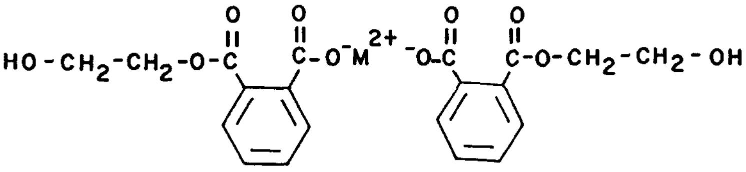
In the case of experiment 2, the viscous solution obtained after cooling was poured into water and the product obtained was filtered, washed several times with ether (to remove the unreacted copper acetate) and dried in vacuum at 60°C.

Preparation of polyurethanes

To a four-necked 100 ml flask fitted with a stirrer, nitrogen inlet, condenser and a dropping funnel, 0.015 moles of $M(HEP)_2$, 10 g of DMF and 0.25 g of dibutyltindilaurate were placed. Then 0.0165 moles of diisocyanate (hexamethylenediisocyanate or tolylenediisocyanate) dissolved in 10 g of DMF was added slowly with stirring under a stream of nitrogen for 30 minutes at room temperature. Then the temperature of the reaction mixture was raised first to 80°C, stirred for 30 minutes and then raised further to 100°C and stirred further for 60 minutes. After allowing it to stand overnight, the solution was poured into cold water with stirring to precipitate the polymer. The separated product was filtered, washed several times with water and dried in vacuum at 70°C.

RESULTS AND DISCUSSION

The diols,



where M = Co or Cu, prepared for the first time, were characterized by IR(Perkin-Elmer Model 598, using KBr pellets), elemental analysis and hydroxyl group estimation (table 1).

Table 1

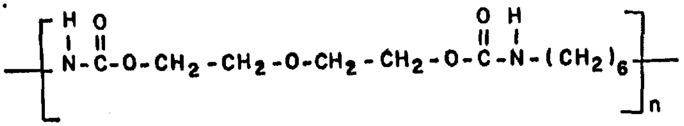
Expt. No.	Metal Salts	Elemental Analysis C%	H%	M%	Hydroxyl Group%
1	Co^{2+}Salt				
	Found	50.22	3.68	12.32	3.51
	Calculated	50.30	3.80	12.35	3.56
2	Cu^{2+}Salt				
	Found	49.75	3.72	12.93	3.49
	Calculated	49.82	3.77	13.19	3.53

The characteristic IR frequencies of the cobalt-diol and copper-diol were 3225 and 3490 cm^{-1} (OH stretch), 1735 and 1730 cm^{-1}(C=O stretch), and 1405, 1550 and 1410, 1620 cm^{-1} (carboxylate group) respectively.

The rose-red cobalt-containing diol was soluble in water and DMSO and insoluble in benzene, toluene and DMF whereas the bluish green copper-containing diol was soluble in DMF and DMSO and insoluble in water, toluene and benzene.

The IR spectra of the metal-containing polyurethanes exhibit absorption bands at 3325-3360 cm^{-1}(NH stretch), 1700-1730 cm^{-1} (C=O stretch), 1540-1560 cm^{-1}(NH bend) and 1400-1410 cm^{-1} and 1560-1610 cm^{-1} (carboxylate group).

In order to confirm the ionic structure of the polymers, the following metal-free analogue of these polymers was prepared.



$$\left[\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6 \right]_n$$

In accordance with our expectations, the characteristic frequencies of the carboxylate group (1400-1410 and 1560-1610 cm^{-1}) were absent on the IR spectrum of this polymer.

All the polymers were soluble in polar solvents like DMF and DMSO and insoluble in all other solvents.

Inherent viscosities of the polymers were determined in DMF (0.05 g/dl) at 25°C using an Ubbelohde Viscometer (table 2).

Table 2

Diol	Diisocyanate	Colour	Inherent viscosity dl/g
CoHEP	HMDI	Chocolate	0.08
CoHEP	TDI	Brown	0.19
CuHEP	HMDI	Green	0.12
CuHEP	TDI	Pale green	0.11

The viscosities of the polyurethanes were low, indicating chain dissociation. This was supported by the decrease in viscosity with increasing temperature as well as with the increasing polarity of the solvent (table 3).

Table 3 Viscosities of CuHEP-TDI Polymer

Temperature °C	Inherent Viscosity dl/g in DMF	Solvent	Inherent Viscosity dl/g at 25°C
15	0.13	DMF	0.11
25	0.11	DMAc	0.09
40	0.08	Conc. H_2SO_4	0.03
60	0.05		

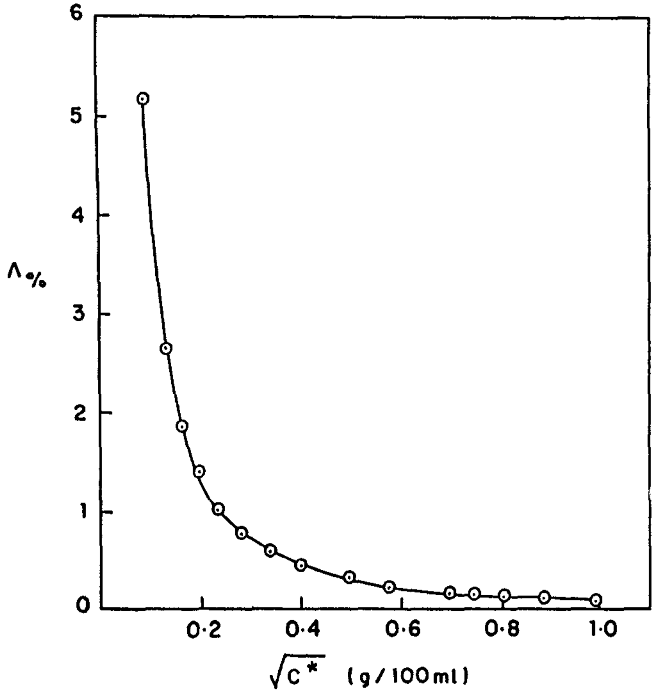


Figure 1: Conductance of CuHEP-TDI in DMF

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