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Low Glass Transition Temperature Aliphatic Polyurethanes

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SUMMARY

The present paper deals with the single step syntheses of a few aliphatic polyurethanes using some simple glycols like ethylene, propylene, 1,3- and 1,4-butylene glycols and two different bis(chloromethyl) compounds viz., 1,4-bis(chloromethyl)-2,5-dimethyl benzene (I), and 1,5-bis(chloromethyl)-2,4-dimethyl benzene (II). The glass transition temperatures, T_g, of these polymers were determined using dilatometric techniques and they ranged from -12 to -48°C. The polyurethanes derived from 1,4-butylene and ethylene glycols were amorphous gums with T_g well below -30°C.

INTRODUCTION

Polyurethanes derived from aromatic diisocyanates (MOORE, 1977) generally exhibit considerable crystallinity and are viscoelastic only at temperatures well above room temperature, presumably because of lack of sufficient flexibility in the polymer backbone. To impart additional flexibility in the polymer backbone, and thus to lower its glass transition temperature, T_g, the single step synthesis involving the *in situ* generation of aliphatic diisocyanate and its conversion to polyurethanes was undertaken. These aliphatic polyurethanes, in which the NH groups of the urethane linkages are separated from phenyl rings by methylene linkages, would be expected to lower the polymer T_g. The present paper deals with the synthesis of such aliphatic polyurethanes and the determination of their glass transition temperatures using dilatometric techniques.

The reaction of a bis(chloromethyl) compound and potassium cyanate in DMF in the presence of glycols yields aliphatic polyurethanes (HIMMEL and RICHARDS, 1959; ARGABRIGHT et al., 1965; OZAKI,

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1967; GERHARDT, 1968). In this reaction the bis-(isocyanatomethyl) compound is generated _in situ_ and immediately reacts with the glycol to produce polyurethane. Based on this reaction, a few polyurethanes were synthesized using some simple glycols and two different bis(chloromethyl) compounds viz., 1,4-bis(chloromethyl)-2,5-dimethyl benzene (I), and 1,5-bis(chloromethyl)-2,4-dimethyl benzene (II).

EXPERIMENTAL

Infrared Spectra were recorded using a Perkin-Elmer model 257 spectrophotometer. The glass transition temperatures of the polymers were determined using dilatometric techniques. I and II were prepared in good yields according to the procedure reported by N.A.Peppas et al. (PEPPAS et al., 1976). A typical procedure for the synthesis of poly [ethylene(2,5-dimethyl-1,4-xylylene) carbamate] is described below:

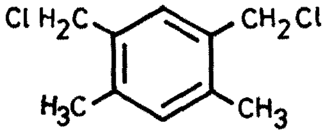
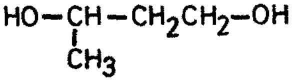
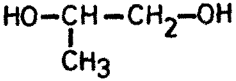
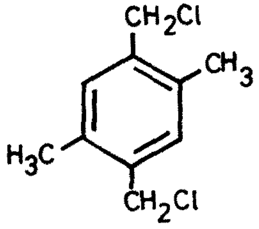
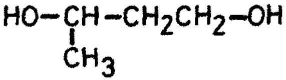
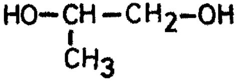
To a mixture of 2.03g (0.01 mole) of I and 1.8g of (0.022 mole), potassium cyanate in 40 ml of DMF was added 0.78g (0.0125 mole) of ethylene glycol. The reaction mixture was vigorously stirred and heated at 90-95°C for 3 hrs under nitrogen atmosphere. The polymer was isolated from ice cold water, filtered through sintered crucible, and washed with benzene (to remove the unreacted I) water, and then with small quantity of acetone and dried in a vacuum desicator for 6 hrs. The yield of the polymer was 68 % with an intrinsic viscosity of 0.15 dl/g (DMF). IR($CHCl_3$): 3280 (NH) and 1690 cm^{-1} (C=O).

RESULTS AND DISCUSSION

The results of the polymerization are summarized in TABLE-1. The polymers were obtained in high yields (above 65 %). The IR spectra of all these polyurethanes showed strong absorption bands around 3300-3280, (NH), 1695-1690 (C=O), 1540 (C-N-H) and 1250 cm^{-1} (C-O) confirming the urethane linkage. The rather low value for carbonyl absorption may be attributed to the presence of hydrogen bonded (ISHIHARA et al., 1974) aliphatic urethane linkages.

The glass transition temperatures of the polymers are also given in TABLE-1. In general no systematic dependence of T_g on the structure of these polyurethanes has been observed. This may be due to the difference in the intrinsic viscosities (FOX and FLORY, 1950) of the polymers prepared. However, polymers derived from 1,4-butylene and

TABLE-1

Bis(chloromethyl) compound	Diol	Polymer Code No.	Nature of polymer	Yield (%)	η_{int}^{a} (dl/g)	T_g (^{o}C)
	$HO(CH_2)_4OH$	PU-1	Gum	78	0.17	-48
	$HO(CH_2)_2OH$	PU-3	Gum	79	0.16	-30
	 $HO-\underset{\underset{CH_3}{\vert}}{CH}-CH_2CH_2-OH$	PU-5	Semi-solid	76	0.12	-21
	 $HO-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-OH$	PU-7	Semi-solid	72	0.14	-18
	$HO(CH_2)_4OH$	PU-2	Gum	81	0.21	-43
	$HO(CH_2)_2OH$	PU-4	Gum	68	0.15	-35
	 $HO-\underset{\underset{CH_3}{\vert}}{CH}-CH_2CH_2-OH$	PU-6	Semi-solid	76	0.18	-25
	 $HO-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-OH$	PU-8	Semi-solid	67	0.07	-12

a: Measured at a concentration of 0.1 % in DMF at 30°C.

ethylene glycols were amorphous gums with T_g well below -30°C. The two polymers PU-1 and PU-2 showed comparatively lower T_g values than PU-3 and PU-4, due to the flexibilizing effect of the two additional methylene linkages (FARROW et al., 1960; PRICE et al., 1961) in the polymer backbone. Introduction of methyl groups in the backbone of the polymers PU-5, PU-6, PU-7 and PU-8 might have introduced considerable steric hindrance by restricting the internal rotation along the polymer chain thus resulting in the increase in their T_g values significantly (DANNIS,1959; MURPHY,1960; LEE,1978). The somewhat higher values of T_g for PU-5 and PU-6 as compared to PU-3 and PU-4 may probably be due to an increase in per cent crystallinity (CHRICHELY and WHITE, 1972) of the former, which may not be present in the latter polymers. Though these polyurethanes separately prepared from p-bis(chloromethyl) compound (I) and m-bis(chloromethyl) compound (II) showed appreciable difference in their T_g, the difference is not uniform and is apparently not structure-dependent.

The thermal stabilities of the polymers PU-5, PU-6, PU-7 and PU-8 were determined by thermogravimetry. Their TG curves in air follow more or less the same pattern. They were stable upto around 260°C with about 8 % decomposition. In all these cases, decomposition occurred catastrophically around 340°C and at 400°C, the weight loss was over 80 % .

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