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THE INFLUENCE OF THE STRUCTURE OF AROMATIC DIISOCYANATES ON THE PREPARATION AND THE PROPERTIES OF POLYURETHANES

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Abstract—The comparative reactivities of the following aromatic diisocyanates were studied: 4,4'-stilbene diisocyanate-*trans*, 4,4'-diisocyanatodiphenyl ether, methylene-bis-(4-phenylisocyanate), 4,4'-bibenzyl diisocyanate and 1,5-naphthalene diisocyanate. Polyurethanes were prepared from ethylene glycol and these diisocyanates. The more reactive was the diisocyanate, the less stable was the polyurethane to thermal degradation and ultraviolet radiation.

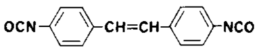
INTRODUCTION

In recent years there has been tremendous growth in the interest in polyurethanes because of their excellent properties and numerous applications. However, for some of them, there are problems due to poor thermostability and photostability, yellow colours developing on exposure to sunlight or mild heating.

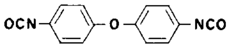
There is some previous work on the degradation of urethanes and polyurethanes under heat or various radiations [1–4]. The first step of degradation appears to be dissociation of the urethane group into the corresponding alcohol and isocyanate, followed by further reactions which lead to the formation of amine, carbodiimide and pseudourea ether groups, responsible for colour and polymer degradation.

The present work was undertaken to prove that thermal dissociation and discolouration in polyurethanes depend on the reactivity of the diisocyanates. The investigated diisocyanates have the two isocyanate groups on different aromatic rings separated by an ethylene group (**I**), by atoms with unshared electron pairs (**II**), or by progressively longer aliphatic chains (**II** and **IV**), or the two isocyanate groups are on adjacent aromatic rings (**V**):

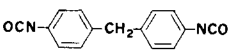
I. 4,4'-stilbene diisocyanate - trans,



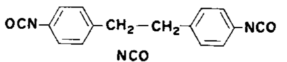
II. 4,4'-diisocyanatodiphenyl ether,



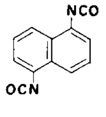
III. methylene-bis-(4-phenylisocyanate),



IV. 4,4'-bibenzyl diisocyanate,



V. 1,5-naphthalene diisocyanate,



EXPERIMENTAL

Materials

The following diisocyanates were prepared by known methods: 4,4'-stilbene diisocyanate [5], m.p. 149–150°; 4,4'-diisocyanatodiphenyl ether [6], m.p. 65.5–66.5°; 4,4'-bibenzyl diisocyanate [7], m.p. 89–90°. Commercial methylene-bis-(4-phenyl-isocyanate) and phenylisocyanate were vacuum distilled, b.p. 170°/1 mm and 57°/17 mm, respectively. 1,5-Naphthalene diisocyanate was purified by sublimation, m.p. 129.5–131°. *n*-Butanol was treated with sodium and distilled, b.p. 118.5–119°, $n_D^{20} = 1.3990$, water content less than 0.1%. Benzene was refluxed over sodium and distilled, b.p. 80°. *N,N*-Dimethylformamide was distilled from methylene-bis-(4-phenylisocyanate), b.p. 153–154°. *N*-Methylpyrrolidone-2 and ethylene glycol were purified by vacuum distillation, b.p. 94–96°/20 mm and 80°/5 mm respectively, water content less than 0.1%.

Diisocyanates reactivity

The rate constants of the reactions of diisocyanates with *n*-butanol were determined in benzene at 30 ± 0.1° using the spectrophotometric method of Bailey [8]. The absorption band of the isocyanate group at $2269 \pm 6\ \text{cm}^{-1}$ allowed following the reaction with *n*-butanol. The conditions were identical for all the diisocyanates: two 0.07 eq/l. solutions of a diisocyanate were prepared in 25 ml volumetric flasks; one of them was the standard, *s*; to the other 0.7 eq/l. of *n*-butanol was added and the volume was made up to the calibration mark with benzene; this was the reaction mixture, *r*. The solutions were placed in 0.1 mm cells with KBr windows and the infrared spectrum was scanned using an Unicam SP-200 spectrophotometer. The concentration of unreacted diisocyanate *D* at intervals *t*, was determined from the absorbance of the standard solution A_s and the absorbance of the reaction mixture A_r:

$$D = \frac{A_r}{A_s} D_0 = \frac{\lg (T_0/T_1)_r}{\lg (T_0/T_1)_s} D_0$$

where $D_0 = 0.07$ eq/l = concentration of isocyanate solution at the beginning of the reaction = concentration of the standard solution.

The reaction of diisocyanates with *n*-butanol proceeds by two consecutive second-order reactions through an intermediate urethano-isocyanate:

$$A + D \xrightarrow{k_1} I$$

$$I + A \xrightarrow{k_2} U$$

where A, D, I and U are the *n*-butanol, the diisocyanate, the intermediate urethano-isocyanate and the diurethane, respectively. In our case, we have a large excess of *n*-butanol and the kinetics were pseudo-first-order. The time ratio method, developed by Frost and Pearson [9] for the determination of the rate constants of consecutive first-order reactions, has been applied.

To analyze our experimental data, we have used the table of values of t_2/t_1 to evaluate K, then the table of K versus τ, leading to k_1. Values of τ and time ratio values are given for 15, 35 and 70% reaction, i.e. $\delta = 0.30$, 0.70 and 1.70. The constants k_1 and k_2 were thus determined.

Synthesis of polyurethanes ($P_I - P_V$). 40 ml N,N-Dimethylformamide and 0.1 mole diisocyanate were placed in a fournecked, round-bottomed flask, equipped with mechanical stirrer, condenser, dropping funnel and thermometer and protected against moisture. As 4,4′-stilbene diisocyanate has poor solubility, a concentration of 0.005 mole/100 ml DMF was used. To the rapidly stirred solution, the equivalent quantity of ethylene glycol in 40 ml of N,N-dimethylformamide was added. The temperature was maintained at 90–95° for 2½ hr with stirring. For 4,4′-stilbene diisocyanate and 1,5-naphthalene diisocyanate, previous heating at 70° was necessary to dissolve the diisocyanates. The reaction mixture was then poured into water with vigorous stirring. The polymer powders were washed with water, and then dried in a vacuum oven at 90° to constant weight.

The TG and DTA curves were found in air with a Metrinpex thermobalance, with a rate of temperature increase of 9°/min.

RESULTS AND DISCUSSION

(a) *Reactivities of diisocyanates*

These are expressed as the rate constants of the reaction with n-butanol in benzene at 30 ± 0.1°. The experimental time ratios used for the determination of K, were obtained from a large scale plot of percentage reaction versus time. Results are given in Table 1.

All investigated diisocyanates have symmetrical structure and both isocyanate groups are equivalent in their reactivities.

The kinetic data indicate that the overal reactivity of a diisocyanate, and its decrease as the reaction progresses, are determined by two factors: (a) the electron attracting power (electrophilicity) of the radical attached to the isocyanate groups and (b) the interaction between the two functional groups.

The initial reactivity of a diisocyanate is similar to that of a monoisocyanate substituted by an activating group. As soon as one isocyanate group has reacted, the remaining isocyanate group has a reactivity similar to that of a monoisocyanate substituted by a urethane group. The urethane group has only a very mild activating effect, much less than that of the isocyanate group [10].

For 4,4′-stilbene diisocyanate (**I**) and for 4,4′-diisocyanatodiphenyl ether (**II**), the extended conjugated systems through the stilbenic C=C double bond and respectively through the unshared electron pairs of the oxygen atom, have an activating effect on the reaction centre. The rate constants are subsequently greater than that of phenylisocyanate. On the other hand, the opposite influence of the substituent groups is possible, so that the rate constants decrease as the reaction passes approximately 50% completion.

In the case of methylene-bis-(4-phenylisocyanate) (**III**) and of 4,4′-bibenzyl diisocyanate (**IV**), the activating influence of the isocyanate and respectively urethane groups is transmitted by an inductive mechanism through the methylene and ethylene groups, respectively. Simultaneously, the methylene and ethylene groups have themselves a deactivating influence. The balance between these opposing effects during the process is illustrated by the rate constants decrease.

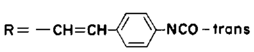
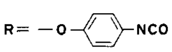
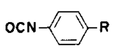
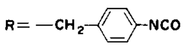
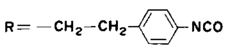
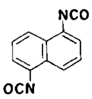
The smaller electron attracting power of the naphthalene ring, as compared with the benzene ring, is indicated by the smaller reactivity for 1,5-naphthalene diisocyanate (**V**). The influence of the isocyanate and urethane groups on the second isocyanate group is very pronounced and the rate constant decreases significantly as the reaction proceeds.

(b) *Synthesis and characterisation of polyurethanes*

Polyurethanes were prepared using Lyman's method [11] from ethylene glycol and the above diisocyanates in equal molar quantities, in dimethylformamide solutions. To minimize side reactions, the temperature was kept under 100°. In the prepared linear polyurethanes P_I–P_V, with the general formula:

$$-[-CO-NH-R-NH-COO-CH_2-CH_2-O-]-R-$$

Table 1. Effects of substituents on the reactivities of diisocyanates with n-butanol

Nr.	Isocyanate	Substituent	$k_1 \cdot 10^2$, (min^{-1})	$k_2 \cdot 10^2$, (min^{-1})	k_1/k_2	Relative k_1*	Relative k_2*
I			7.34	3.64	2.01	3.65	1.81
II			5.47	2.43	2.24	2.72	1.20
III			4.56	1.51	3.02	2.22	0.75
IV			3.72	1.39	2.67	1.85	0.69
V		R= —H	2.01	—	—	1	
VI		—	3.54	1.15	3.06	1.76	0.57

* Relative to phenylisocyanate.

Table 2. Polyurethanes from ethylene glycol and diisocyanates

Nr.	Inherent viscosity, (dl/g)*	Elemental analysis						Remarks on the preparation
		C		H		N		
		calc	found	calc	found	calc	found	
P_{I}	0.16	66.66	68.54 68.48	4.93	4.83 5.18	8.64	9.71 9.78	Precipitated from solution as yellow powder
P_{II}	0.50	61.14	61.20 61.05	4.45	4.40 4.55	8.91	8.98 9.02	Clear, viscous solution
P_{III}	0.44	65.38	65.20 65.35	5.12	5.07 5.12	8.97	8.75 8.95	Clear, viscous solution
P_{IV}	0.54	66.25	66.40 65.93	5.52	5.45 5.64	8.58	8.75 8.51	Precipitated from solution after 10 min. as fine powder
P_{V}	0.21	61.76	62.70 63.00	4.41	4.64 4.86	10.29	10.60 11.00	There was a gelation in solution after 20 min.

* 0.5% solution in N-methylpyrrolidone-2 with 2% LiCl at 20 ± 0.1°.

corresponds to the previous diisocyanates I–V. All polyurethanes are white powders, excepting P_{I} which is light brown. The data on the polymer syntheses and properties are given in Tables 2 and 3.

Solutions of polyurethanes obtained from 4,4′-diisocyanatodiphenyl ether (P_{II}), methylene-bis-(4-phenylisocyanate) (P_{III}) and 4,4′-bibenzyl diisocyanate (P_{IV}) have almost the same viscosities. The polymers P_{II} and P_{III} remain soluble, making possible the growth of macromolecules; polyurethane P_{IV} precipitates at a certain molecular weight. The solution of the polyurethane from 1,5-naphthalene diisocyanate (P_{V}) becomes a gel; the polyurethane from 4,4′-stilbene diisocyanate (P_{I}) precipitates as a powder at a much smaller molecular weight.

No side reactions occur in the syntheses of polymers P_{II}, P_{III} and P_{IV}, as confirmed by elemental analysis and infrared spectra. Infrared spectra of these polymers have only an absorption band at 1700 cm^{-1} assigned to the urethane group [12].

Elemental analysis of polyurethanes P_{I} and P_{V} does not correspond to the urethane unit; in their infrared spectra, besides the 1700 cm^{-1} absorption band, there is a weaker band at 1648 cm^{-1} suggesting another structure derived from a side reaction. This absorption band is assigned to an azomethine group formed in the reaction of the diisocyanate with the solvent (dimethylformamide). It is known that *N*,*N*-dialkylamides react with isocyanates to give amidines [13,14]:

$$\mathrm{RNCO + O{=}CH{-}N(CH_3)_2 \rightarrow R{-}N{=}CH{-}N(CH_3)_2 + CO_2}$$

This reaction occurred only with 4,4′-stilbene diisocyanate and with 1,5-naphthalene diisocyanate, because of the previous heating at 70° which was necessary to dissolve these diisocyanates before addition of ethylene glycol. This side reaction leads to unequal molar quantities of diisocyanates and diol and gives solutions with low viscosities.

The obtained polyurethanes are soluble only in dimethylsulphoxide, sulphuric acid and *N*-methylpyrrolidone-2 with 2% LiCl (Table 3).

Table 3. Solubilities and thermal properties of polyurethanes from ethylene glycol and diisocyanates

	Properties	P_{I}	P_{II}	P_{III}	P_{IV}	P_{V}
Solubilities in*	Dioxan	1	1	1	1	1
	1,2-Dichloroethane	1	1	1	1	1
	Cyclohexanone	1	1	1	1	1
	Butylacetate	1	1	1	1	1
	m-Cresol	2	3	3	2	2
	Pyridine	2	4	3	2	2
	N,*N*-Dimethylformamide	2	4	4	2	2
	Dimethylsulfoxide	2	4	4	4	4
	N-Methylpyrrolidone-2 with 2% LiCl	3	3	4	3	3
	Sulphuric acid	2	4	4	4	4
Polymer melt temperature	With melting point apparatus	Did not melt	260–263	240–245	290–294	260–265
	From DTA curve	—	253	234	288	263
Thermogravimetric analysis	Beginning of decomposition, °C	165	178	192	218	150
	Highest rate of decompos., °C	235	257	252	288	263

* 1 = Insoluble in boiling solvent. 2 = Partially soluble at boiling. 3 = Soluble on heating. 4 = Soluble in cold.

The differences in thermostabilities of the polyurethanes associated with the isocyanate component, are indicated by thermogravimetric analysis. In all cases, the temperatures for start of decomposition are lower than the melting temperatures. Polyurethane P_I does not melt. Polyurethanes P_I and P_V have the lowest thermostabilities, decomposition starting at 165° and 150°, respectively, attributed to the structural inhomogeneity of these polymers. The molecular chains of polyurethanes P_{II}, P_{III} and P_{IV} are composed only of urethane units and their solution viscosities are almost the same. Nevertheless, the thermostabilities of these polymers are different, the most stable being the polyurethane from 4-4'-bibenzyl diisocyanate. Its decomposition begins at 218°, i.e. 26° higher than for the polyurethane from methylene-bis-(4-phenylisocyanate) and 40° higher than for that from 4,4'-diisocyanatodiphenyl ether.

We could not use Beachell's method to determine colour formation in polyurethanes because not all the polymers gave films. The photostabilities were observed only qualitatively; the polymer powders were exposed to u.v. radiation for 30 hr at room temperature. The discoloration tendencies of the investigated polyurethanes are in the same sequences as their thermal decompositions.

CONCLUSIONS

The present study makes it possible to correlate the photo- and thermolstabilities of investigated polyurethanes with the reactivity of the diisocyanate component of the polymers. The same structural factors govern both the mobility of the hydrogen atom in the urethane group and the reactivities of diisocyanates. The stronger the electron-withdrawing capacity of the substituents on the isocyanate molecule, the more reactive is the diisocyanate and the more labile is the hydrogen atom of the resulting urethane group; consequently, polymers are less colour- and thermostable. Polymers P_I and P_V are exceptional due to their heterogeneous structure and low molecular weight.

Based on these general considerations and on experimental observations, an *a priori* evaluation of the stabilities of polyurethanes of similar structure is possible by comparing the reactivities of diisocyanates.

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