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POLYURETHANE FORMATION REACTIONS TESTED BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The processes of the reaction between oligomer diols and aromatic diisocyanate have been investigated by the means of isothermal DSC. The rate constants, activation energies and order of reaction have been determined. First-order reaction step has been determined in interaction of polyester diols and aromatic diisocyanate.

INTRODUCTION

The basic materials used for the preparation of isocyanate polymers = polyurethanes can be put into three groups:
polyols,
poly-isocyanates,
chain extender,
and polymers of various composition can be made depending on their chemical structure.

The elastomeric polyurethanes (PUR) are systems consisting of flexible "soft segments" of low Tg and highly polar, relatively "hard segments". The soft segments are formed in the reaction of a polyester or polyether polyol and the polyisocyanate, and the hard segments from the interaction of the chain extender with polyisocyanate 1 .

LITERATURE

Various methods are suitable for the kinetic investigation of the isocyanate polymer formation, and only general rules can be concluded. From among the factors influencing the rate of the PUR formation, the following should be mentioned:

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- chemical structure of isocyanate [2,3]
- role of H-donors [4]
- influence of catalysts [5]
- influence of the reaction conditions [2,6]

For describing the reaction in terms of time, the relationship

$$\frac{d\alpha}{dt} = k \cdot J(\alpha)$$

is true where is the transformed part, t is time, k is rate constant depending on the given process and temperature and $J(\alpha)$ is a function of the transformed part. The constant rate described by the Arrhenius equation can be calculated by the equation

$$k = A \cdot e^{-E/RT}$$

where E means the activation energy of the whole process. For $J(\alpha)$ function, the empiric relationship

$$J(\alpha) = (1 - \alpha)^n \quad [8\text{-}12]$$

is often true.

EXPERIMENTAL

The basic materials used for the synthesis are summarized in Table 1. The reaction of the equimolar composition of the starting materials has been observed by an isothermal DSC method using a thermal analyser equipped with Du Pont 990 measuring cell. 4.99-5.00 mg samples of the reaction composition were heated at a rate of 50 K/min^{-1} in nitrogen flow to the required temperature and - after the melting of the system - it was held at this temperature till the completion of the reaction.

The integration of the resulted curves was carried out manually, using the Simpson formula.

RESULTS AND DISCUSSION

In Figure 1 an isothermal DSC curve of PEG:MDI system is illustrated. Similar curves were obtained for the other systems.

investigated; at constant temperature the variation in time of the signal proportional to the transformed part was registrated as it can be seen in Figure 2.

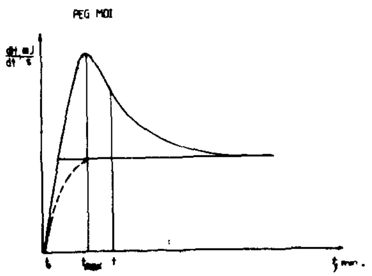


Figure 1

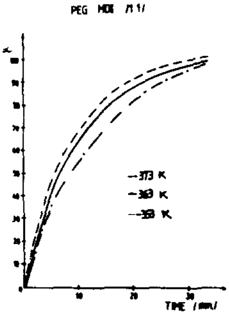


Figure 2

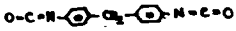
SAMPLE		FORMULA	MASS EQ
POLYOL	Poly(ethylene-glycol)-adipate PEG	$HOOC-[(CH_2)_4-CO-O-(CH_2)_2-O-]_n-H$	1000
	Poly(buthylene-glycol)-adipate PBG	$HOOC-[(CH_2)_4-CO-O-(CH_2)_4-O-]_n-H$	1000
	Poly(hexylene-glycol)-adipate PHG	$HOOC-[(CH_2)_4-CO-O-(CH_2)_6-O-]_n H$	1000
4-4'diphenyl-methane-diisocyanate MDI		 O=C=N-⟨⟩-CH_2-⟨⟩-N=C=O	125

Table 1

Then, assuming a first-order reaction, the relationship ln(1 -α) - t was plotted as it can be seen in Figure 3. The formation of the polymer proceeds in one step.

The data calculated from Figure 3 are summarized in Table 2.

It can be concluded from the results that the rate of the reaction increasing with rising the temperature of the reaction in the case of all oligomer diols.

At the same temperature, the rate of the reaction is increasing in the order of PEG PBG PHG, which is in good correlation with the results obtained for the reaction rate relations of small molar mass alcohols 13 .

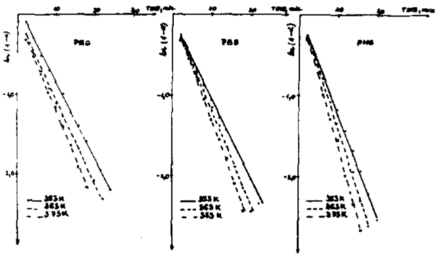


Figure 3

SAMPLE	TEMP, K	k_1, min^{-1}	A_1	E_1, KJmol^{-1}
PEG·MDI	353	9,36 10^{-2}	2,07	350
	363	10,57·10^{-2}		
	373	11,83 10^{-2}		
PBG MDI	353	9,65 10^{-2}	1,85	398
	363	11,83·10^{-2}		
	373	13,88 10^{-2}		
PHG·MDI	353	12,40 10^{-2}	1,40	604
	363	15,00 10^{-2}		
	373	20,00 10^{-2}		

Table 2

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