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# Polyesters Containing Sulfur. III. The Kinetics of Melt Polycondensation Diphenylmethane-4-4'-Di(methylthioacetic Acid) with Aliphatic Diols

Poliestry zawierające siarkę. III. Kinetyka polikondensacji w stopie kwasu 4-4'-Difenylometanodi(metylotiooctowego) z diolami alifatycznymi

### 1. INTRODUCTION

In the previous paper [1] the method of synthesizing new linear polyesters containing sulfur in the main chain with the use of a melt polycondensation from diphenylmethane-4,4'-di(methylthioacetic acid) and some aliphatic diols was described, and both physicochemical and thermal characteristics of these polymers was included.

Low-molecular weights, low-softening temperature, good solubility in organic solvents and good thermal stability are their characteristics.

Newly obtained thiopolyesters were used for the synthesis of new polyester-sulfur compositions with increased tensile strength and the problem was presented in the independent article [2].

Because of their good solubility and low-softening temperature, polyesters may also find use as modifiers and plasticizers of commercial polyesters, epoxy resins, poly(vinyl chloride), and the like. Polyesters ending with hydroxyl groups may be useful for the synthesis of polyurethanes.

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In further work on the synthesis, structure and properties of this new group of linear polyesters derivatives of various aliphatic-aromatic thiodicarboxylic acids it seemed useful to carry out kinetic investigations.

The melt polycondensation is the main method of synthesis of the highmolecular polyesters manufactured, as well as low- and medium-molecular ones such as polyesters for polyurethanes, unsaturated polyesters used for copolymerization with monomers or alkyd resins.

The subject of the present paper is the kinetic studies of melt polycondensation diphenylmethane-4,4'-di(methylthioacetic acid) with some aliphatic diols.

We were mainly interested in the later stages of the reaction (above 50–60% conversion) leading to polymers of molecular above approx. 600.

## 2. EXPERIMENTAL

#### MATERIALS AND METHODS

Diphenylmethane-4,4'-di(methylthioacetic acid), mp 166–167°C (after crystallization from ethanol) was obtained from 4,4'-di-(mercaptomethyl)diphenylmethane by condensation with monochloric acetic acid [3].

Commercial diols: 1,4-butanediol, bp 118°C and 2,2'-oxydiethanol, bp 128°C were purified by distillation under reduced pressure (at 10 mm Hg).

The kinetic measurements were carried out in an oil both-thermostated reactor equipped with a stirrer, a thermometer, a capillary for admitting a slow stream of nitrogen through the reaction mixture, and the system to remove water vapor with simultaneous returning of diol to reaction mixture. The temperature reaction was maintained with the accuracy  $\pm 0.5^{\circ}$ C.

Samples were removed at first after 15 min. then after every 0.5 h for 3–5 h, as appropriate, and then hourly. The samples taken in amount of 0.5–1.0 g, weighed with accuracy to 0.0002 g were dissolved in dioxane and titrated with 0.1 N alcoholic potassium hydroxide, using phenolphthalein indicator. The endpoint was very sharp.

#### RESULTS AND DISCUSSION

As is evident from the literature on the subject [4–10] the kinetics of the condensation polymerization of aliphatic dicarboxylic acids with aliphatic diols catalyzed by strong acids are of simple second order after an initial period in

which they are more complex, whereas uncatalyzed in most cases are of third order, or approximate to third order, considering autocatalytic function of carboxylic groups.

The basis of all the considerations when dealing with polycondensation is, experimentally confirmed, the rule of identical reactivity of functional groups at all the degrees of polymerization. Accepting the above assumption, kinetic dependencies of uncatalyzed polycondensation process of dicarboxylic acids with diols at equimolar use of reagents may be presented in a relatively simple form [6,11]:

$$2kt = 1/C^2 - 1/C_0^2, (1)$$

where k is the rate constant, C is the concentration of unreacted groups at the time t, and  $C_0$  is the initial concentration. If one neglects the effect on concentration of the decrease in volume due to loss of water then it may be assumed that  $C = C_0(1-p)$ , where p is the degree of conversion; and these equations may be replaced by:

$$2C_0^2 kt = 1/(1-p)^2 - 1.$$
 (2)

## DETERMINATION OF THE RATE CONSTANTS

To study the kinetics of the melt polycondensation, diphenylmethane-4,4'di(methylthioacetic acid) and 1,4-butanediol (BD) or 2,2'-oxydiethanol (ODE) were chosen as a model system. The investigations were carried out at equimolar relation of reagents at the 150, 160 and 170°C in the absence of catalyst.

The degree of conversion (p) was found by titration of the residual acid end groups [4].

The changes of degree of conversion (p) versus time (t) are shown in Figure 1 for examined reactions, as an instance for 150 and 170°C.

The order of reaction (*n*) was determined by a graphic method verifying the relationship between  $1/(1-p)^n$  and *t*. Linear relationship obtained in the case of expression  $1/(1-p)^2$  (Fig. 2) confirms that examined reactions of polycondensation are, after an initial period, a third order following equation (2) given above.

As shown in Figures 1 and 2, this equation is satisfied even for degree of conversion above 90%.

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Fig. 2. Plots of 1/(1-*p*) vs. time (*t*) for the polycondensation of diphenylmethane-4,4'di(methylthioacetic acid) with 1,4-butanediol (BD) and 2,2'-oxydiethanol (ODE).

The rate constants  $(k_3)$  were evaluated by the long-interval method [11] using equation (2).

The values of rate constants given in Table 1 show that the rate of polycondensation diphenylmethane-4,4'-di(methylthioacetic acid) with aliphatic diols depends on the nature of diol used and in the case of 1,4-butanediol is approx. twice grater than in the case of 2,2'-oxydiethanol due to the difference of nucleophilicity between starting diols.

Table 1. Rate constants of the polycondensation of diphenylmethane-4,4'-di(methylthioacetic acid) with 1,4-butanediol (BD) or 2,2'-oxydiethanol (ODE).

Temperature	Reaction Constant $(k_3 \cdot 10^4)$ [ $(dm^3)^2/(mole^2s)$ ]		
[K (°C)]	BD	ODE	
423 (150)	5.79	2.58	
433 (160)	8.04	3.69	
443 (170)	11.20	5.32	

 $[C_{acid}] = [C_{ODE}] = 2.338 \text{ mol/dm}^3$  $[C_{acid}] = [C_{BD}] = 2.344 \text{ mol/dm}^3$ 

## DETERMINATION OF ACTIVATION PARAMETERS

On the basis of the determined reaction rate constants the changes of Gibbs activation energy in the examined reactions of polycondensation were calculated from transformed Eyring's equation:  $\Delta G^{\#} = RT(23.764 - \ln k/T)$  and from equation:  $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$ , the changes of activation enthalpy and entropy [11].

The numerical data are given in Table 2.

Table 2. Activation parameters of the polycondensation of diphenylmethane-4,4'di(methylthioacetic acid) with 1,4-butanediol (BD) or 2,2'-oxydiethanol (ODE).

Diol	Contraction of the second	$\Delta G^{\#}$ [kJ/mole]		$\Delta H^{\#}$	$\Delta S^{\#}$	Correlation
	150	160 [°C]	170	[kJ/mole]	[kJ/mole]	coefficient
BD	131.0	133.0	135.0	46.4	-200	0.9999
ODE	133.9	135.9	137.7	53.6	-190	0.9995

## 3. CONCLUSIONS

The kinetics of the uncatalyzed melt polycondensation diphenylmethane-4,4'-di(methylthioacetic acid) with 1,4-butanediol as well as with 2,2'-oxydiethanol are of the third order in the wide range of degree of conversion from approx. 60 to approx. 90%. The rate of the polyesterification in the case of 1,4butanediol is approx. twice greater than in the case of 2,2'-oxydiethanol. Comparing reaction rate constants and activation parameters it is evident that the changes of enthalpy of the examined systems connected with energy forming and the cleavage of bonds during reaction have an important influence on the reaction rate.

Studies on the synthesis and properties of similar polyesters are in progress.

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## STRESZCZENIE

Badania kinetyczne tworzenia się poliestrów metodą polikondensacji w stopie były prowadzone w układzie: kwas 4,4'-difenylometanodi(metylotiooctowy) i 1,4-butanodiol (BD) lub 2,2'-oksydietanol (ODE) w temperaturze 150, 160 i 170°C. Stwierdzono, że badane reakcje są trzeciego rzędu przy wyższych stopniach przereagowania. Szybkość tych reakcji zależy od rodzaju użytego diolu i w przypadku 1,4-butanodiolu jest około dwukrotnie większa niż w przypadku 2,2'oksydietanolu. Na podstawie uzyskanych stałych szybkości określono zmiany energii aktywacji ( $\Delta$ G#), entalpii ( $\Delta$ H#) i entropii ( $\Delta$ S#).