

### Kinetic Studies on Copolycondensation Processes. III. Kinetic Studies on Copolycondensation of Terephthaloyl Chloride with Bisphenols in Solution

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#### Synopsis

Kinetics of copolycondensation of terephthaloyl chloride with 2,2-bis(4-hydroxyphenyl)propane and 2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane in  $\alpha$ -chloronaphthalene solution was examined. The extent of the reaction data obtained experimentally was compared with theoretical values, calculated on the basis of theoretical dependence derived previously. A satisfactory agreement of experimental results with theory was observed.

#### INTRODUCTION

In a recent paper<sup>1</sup> we have given the kinetic equation of the copolycondensation reaction in solution for the reaction between such three bifunctional monomers A, B, and C that the functional groups of monomer A are able to react with B and C, while the functional groups of monomers B and C do not react with each other. Our considerations were made assuming the equal reactivity of both functional groups of each monomer, independent of whether the other functional group has reacted or not. We have assumed that the reactions between the A and B as well as A and C monomers are irreversible, parallel reactions of the second order. We found that in the case of copolycondensation of 2,2-bis(4-hydroxyphenyl)propane (monomer B) and 2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane (monomer C) at a ratio of 1:1 with the equimolar amount of terephthaloyl chloride (monomer A) in  $\alpha$ -chloronaphthalene at 220°C, a good agreement of the experimental data with the dependence reported by us is observed.

In the present paper, the examination of the same monomer system is carried on in order to check the possibility of application of the obtained equation for the initial mixture of monomers with different compositions. Moreover, due to the numerical solution of the kinetic equation, one obtained the possibility of the indirect comparison of the theoretical and experimental dependence of the extent of reaction on time.

## EXPERIMENTAL

### Materials

Terephthaloyl chloride produced by the firm Merck-Schuchardt was crystallized twice from *n*-hexane and then distilled in vacuo. The purified product had a melting temperature of 81–82°C.

2,2-Bis(4-hydroxyphenyl)propane, a product of the firm T. Schuchardt G.m.b.H., was crystallized three times from chlorobenzene. The melting temperature of purified monomer B was 157°C.

2,2-Bis(3,5-dichloro-4-hydroxyphenyl)propane was obtained by chlorination of monomer B.<sup>2</sup> The obtained product was crystallized several times from benzene solution. The melting temperature of monomer C was 131–132°C.

### Procedure

All the copolycondensation reactions were carried out at 220° ± 0.1°C in  $\alpha$ -chloronaphthalene in nitrogen. The initial concentrations of the functional groups of monomers A and B + C were in all experiments 0.2 mole/l., while the concentration ratio of monomers B:C was 1:3, 1:1, and 3:1, respectively. The extent of the reaction was evaluated by measuring the amount of hydrogen chloride as by-product. Hydrogen chloride was absorbed in the solution of NaOH (0.1 *N*). The excess of NaOH was titrated with 0.1 *N* HCl in the presence of bromothymol blue.

The rate constants of the homopolycondensation reaction of terephthaloyl chloride with 2,2-bis(4-hydroxyphenyl)propane ( $k_{AB} = 52.4 \times 10^{-4}$  l./mole-sec) and with 2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane ( $k_{AC} = 8.64 \cdot 10^{-4}$  l./mole-sec) were determined by us previously<sup>1</sup> on the basis of the investigations of homopolycondensation kinetics.

## RESULTS AND DISCUSSION

Assuming an equimolar ratio of the reagents in the initial mixture of monomers,

$$c_{A0} = c_{B0} + c_{C0} \quad (1)$$

where  $c_{A0}$ ,  $c_{B0}$ ,  $c_{C0}$  the initial concentrations of the functional groups of the monomers A, B, and C, respectively, the derived kinetic equation had the following form:

$$\frac{dp}{dt} = (1 - p)[k_{AB}(c_{B0} - c_{BK}) + k_{AC}(c_{C0} - c_{CK})] \quad (2)$$

where  $p$  is the extent of the reaction;  $k_{AB}$ ,  $k_{AC}$  are the kinetic constants of the homopolycondensation reactions of the monomers A+B and A+C, respectively; and  $c_{BK}$ ,  $c_{CK}$  are the concentrations of the reacted functional groups of monomers B and C, respectively.

Two unknown quantities  $c_{BK}$  and  $c_{CK}$  appear in eq. (2). Between these quantities, there is the dependence given by Straichman<sup>3</sup> and Tyuzyo<sup>4</sup>:

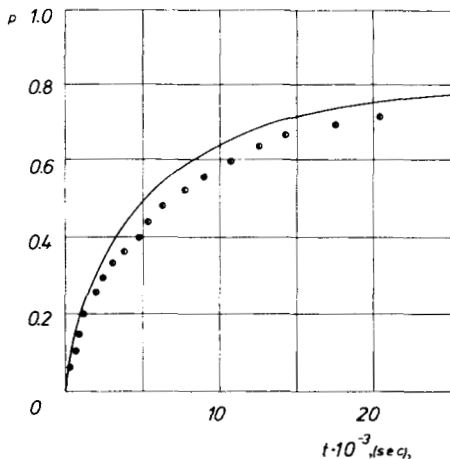


Fig. 1. Relationship between extent of reaction and time of copolycondensation. Theoretical curve and experimental points. Initial concentrations of functional groups:  $c_{A0} = 0.2$  mole/l.;  $c_{B0} = 0.05$  mole/l.;  $c_{C0} = 0.15$  mole/l.

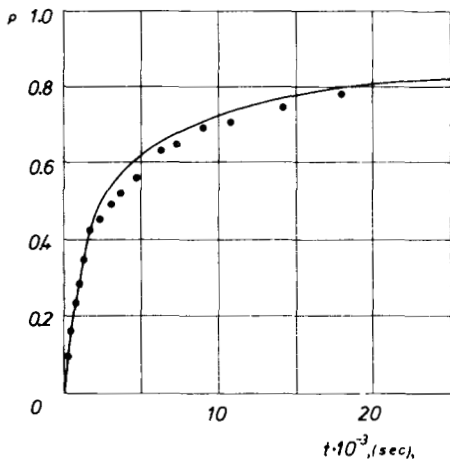


Fig. 2. Relationship between extent of reaction and time of copolycondensation. Theoretical curve and Experimental points. Initial concentrations of functional groups:  $c_{A0} = 0.2$  mole/l.;  $c_{B0} = C_{C0} = 0.1$  mole/l.

$$\log \frac{c_{B0}}{c_{B0} - c_{BK}} = \frac{k_{AB}}{k_{AC}} \log \frac{c_{C0}}{c_{C0} - c_{CK}} \tag{3}$$

It is impossible to solve the system of eqs. (2) and (3) in an analytical way, and thus a ZAM 41 computer was used to determine the theoretical curve illustrating the relation between the extent of the reaction and time. These curves and the experimental points are shown in Figures 1-3.

As can be seen from the results shown in Figures 1-3, there is no full agreement between the theoretically expected and the real course of copolycondensation. There are a few possible reasons accounting for these not very significant discrepancies. The experimental reasons should be mentioned first: even the smallest inaccuracy in determining the amount of hydrogen chloride being isolated directly affects the  $p$  value. This mainly refers to the initial

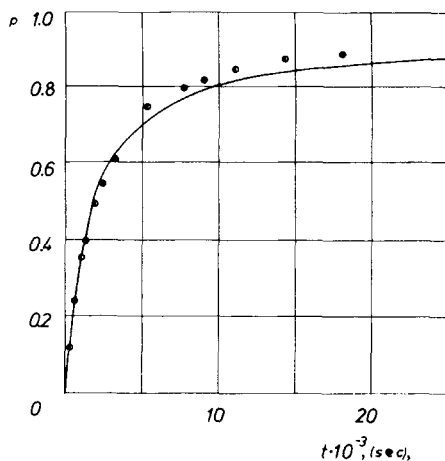


Fig. 3. Relationship between extent of reaction and time of copolycondensation. Theoretical curve and experimental points. Initial concentrations of functional groups:  $c_{A0} = 0.2$  mole/l.;  $c_{B0} = 0.15$  mole/l.;  $c_{C0} = 0.05$  mole/l.

reaction stage, in which the rate of isolating HCl from the reaction medium is the highest. On the other hand, the theoretical dependence of the reaction extent on time is burdened with the inexactitudes resulting from the accepted simplifying assumptions concerning the irreversibility of the reaction and the equal reactivity of the first and second functional groups of the reacting monomers. However, by taking into account the above-mentioned conditions, one would considerably complicate the kinetic equation, which in the given simple form, eq. (2), is quite a satisfactory illustration of the real course of the investigated copolycondensation process in a solution.

This work was carried out as part of the general research program "Studies on Synthesis, Structure, and Modification of Polymers" and was financed by the Polish Academy of Sciences.

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Received December 3, 1974

Revised September 9, 1975