

Kinetic Studies on Copolycondensation Processes.

I. Kinetic Equation of Copolycondensation in Solution

E. TURSKA, S. BORYNIEC, and L. PIETRZAK, *Technical University of Łódź, Institute of Synthetic Fibres, Łódź, Poland*

Synopsis

Based on the known composition equation of copolycondensation product, an equation was derived to describe the kinetics of the copolycondensation process. On the basis of the equation derived, a theoretical curve describing the course of the process was found. A satisfying agreement between the theoretical and experimental curves was observed.

INTRODUCTION

Recently, a growing interest in copolycondensation processes has been observed both from the theoretical and practical point of view. Numerous copolycondensable monomers are known and examined, and mostly a system of three bifunctional monomers A, B, and C is investigated where functional groups of monomer A are capable to react with groups of B and C, while no reaction is observed between functional groups of monomers B and C. Typical reactions are those between acid chloride (A) and two bisphenols (B and C), acid chloride (A), bisphenol (B), and diamine (C), etc.

Copolycondensation processes like homopolycondensation can be carried out by various methods. In the case of polycondensation in solution in homogeneous systems, kinetic relationships for the second-order reactions are applicable, hence theoretical considerations concerning composition of copolycondensation products are based on these relationships. Straichman¹ and Tyuzyo² have used known equations of the formal kinetics for the second-order simultaneous reactions, giving the integrated equation for the composition of copolycondensation products in the following form:

$$\log \frac{c_{B_0}}{c_{B_0} - c_{Bk}} = a \log \frac{c_{C_0}}{c_{C_0} - c_{Ck}} \quad (1)$$

where c_{B_0} and c_{C_0} are the original concentrations of functional groups of monomers B and C, respectively; c_{Bk} and c_{Ck} are the concentrations of reacted functional groups of monomers B and C; and $a = k_{AB}/k_{AC}$ is the rate constant of homopolycondensation of monomers A and B to the respective value for homopolycondensation of monomers A and C.

Another very significant question is the distribution of B and C units along the macromolecule chains of the copolycondensation products. The theoretical aspect of the problem has been considered by Case³ and Beste.⁴

EXPERIMENTAL

The results presented in this paper concern copolycondensation of terephthaloyl chloride (monomer A), 2,2-bis(4-hydroxyphenyl)propane (monomer B) and 2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane (monomer C). The process was carried out in α -chloronaphthalene 220°. The original concentrations of functional groups for monomers A, B, and C were: $c_{A_0} = 0.2$ mole/l., $c_{B_0} = 0.1$ mole/l., and $c_{C_0} = 0.1$ mole/l., respectively.

The extent of reaction was evaluated by measuring the amount of hydrogen chloride as by-product.

Homopolycondensations of monomers A and B and that of monomers A and C in equimolar proportions were also performed under the same conditions in order to find the rate constants k_{AB} and k_{AC} .

The course of homo- and copolycondensation is shown in Figure 1.

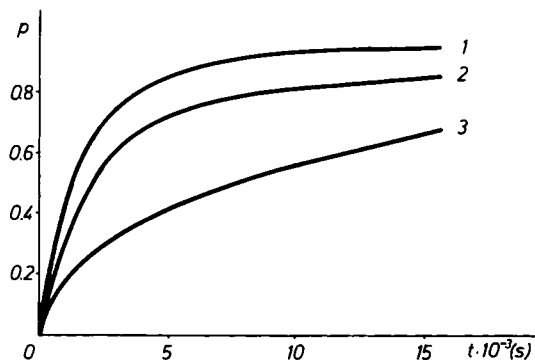


Fig. 1. Experimental curves of the relationship between the extent of reaction and time: curve 1, homopolycondensation A + B; curve 2, copolycondensation; curve 3, homopolycondensation A + C.

RESULTS AND DISCUSSION

The extent of the reaction, p , has been found by Flory⁵ as a ratio of the number of functional groups reacted to the number of functional groups present in the system prior to the process:

$$p = \frac{N_0 - N}{N_0} \quad (2)$$

where N_0 and N are the original number of functional groups and the number of unreacted functional groups, respectively.

Neglecting the volume variation in the reacting system caused by removal of low-molecular compound, eq. (2) for the system under investigation may become

$$p = \frac{c_{A_k}}{c_{A_0}} \quad (3)$$

where c_{A_k} is the concentration of the reacted functional groups of monomer A (calculated in terms of functional groups of monomer A), or also

$$p = \frac{c_{B_k} + c_{C_k}}{c_{B_0} + c_{C_0}} \quad (4)$$

where c_{B_k} and c_{C_k} are the concentrations of reacted functional groups of monomers B and C, respectively (calculated totally in terms of functional groups of monomer B and C) assuming equimolar ratio of the reacting functional groups

$$c_{B_0} + c_{C_0} = c_{A_0}. \quad (5)$$

For the assumed extent of the reaction, p , known concentrations c_{A_0} , c_{B_0} , and c_{C_0} and known rate constants k_{AB} and k_{AC} , the system of eq. (1) and eq. (4) can be solved by finding the values of c_{B_k} and c_{C_k} . These values allow the determination of molar fractions of bonds between A and B units and between A and C in the copolymer formed:

$$X_{A-B} = \frac{c_{B_k}}{c_{B_k} + c_{C_k}}, \quad X_{A-C} = \frac{c_{C_k}}{c_{B_k} + c_{C_k}}. \quad (6)$$

The total rate of copolycondensation consists of the rate of formation of bonds between A and B units equal to dc_{B_k}/dt and the rate of formation of bonds between A and C units equal to dc_{C_k}/dt .

Taking into account the designations introduced previously, the rates may be as follows:

$$\frac{dc_{B_k}}{dt} = k_{AB}(c_{A_0} - c_{A_k})(c_{B_0} - c_{B_k}) \quad (7)$$

$$\frac{dc_{C_k}}{dt} = k_{AC}(c_{A_0} - c_{A_k})(c_{C_0} - c_{C_k}). \quad (8)$$

Adding up the sides of eqs. (7) and (8), we obtain

$$\frac{dc_{B_k} + dc_{C_k}}{dt} = (c_{A_0} - c_{A_k})[k_{AB}(c_{B_0} - c_{B_k}) + k_{AC}(c_{C_0} - c_{C_k})]. \quad (9)$$

Dividing eq. (9) by eq. (5), we obtain

$$\frac{dc_{B_k} + dc_{C_k}}{(c_{B_0} + c_{C_0})dt} = \frac{c_{A_0} - c_{A_k}}{c_{A_0}} [k_{AB}(c_{B_0} - c_{B_k}) + k_{AC}(c_{C_0} - c_{C_k})]. \quad (10)$$

Taking into consideration eqs. (3) and (4), we may present eq. (10) as

$$\frac{dp}{dt} = (1 - p)[k_{AB}(c_{B_0} - c_{B_k}) + k_{AC}(c_{C_0} - c_{C_k})]. \quad (11)$$

Having the values of c_{B_k} and c_{C_k} calculated previously for the given extents of reaction, we may calculate respective values of dp/dt .

Such calculations were made for the system under investigation: terephthaloyl chloride (A), 2,2-bis(4-hydroxyphenyl)propane (B), and 2,2-bis(3,5-

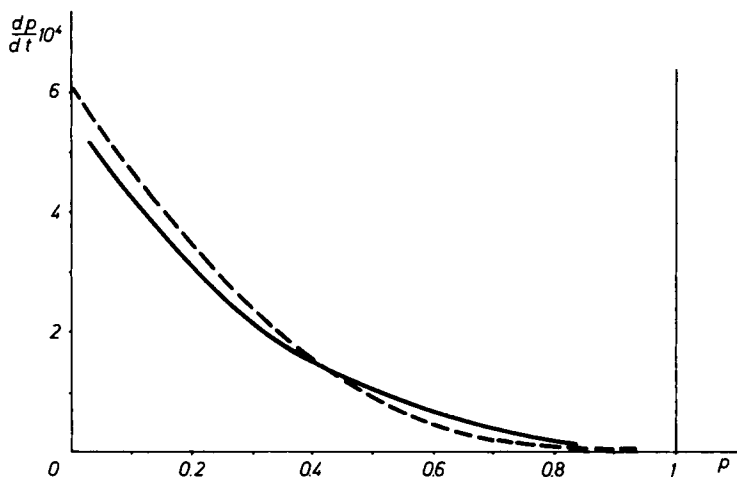


Fig. 2. Relationship between dp/dt and p . Dotted line - theoretical curve. Continuous line - experimental curve.

dichloro-4-hydroxyphenyl)propane (C), assuming for c_{A_0} , c_{B_0} , and c_{C_0} the same values as those used in the experiment.

The values of the rate constants found by us for homopolycondensation of monomer A and monomer B at 220°C and for homopolycondensation of monomer A and monomer C were $k_{AB} = 52.42 \times 10^{-4}$ l. mole⁻¹s⁻¹ and $k_{AC} = 8.64 \times 10^{-4}$ l. mole⁻¹s⁻¹, respectively.

Based on these calculations, the plot of dp/dt versus p was made which is shown in Figure 2 as a dotted line. The continuous line in Figure 2 illustrates the course of $dp/dt = f(p)$ as obtained by graphic differentiation of the experimental curve.

As follows from the data, eq. (11) gives a good picture of the real kinetic course of the process under investigation over a wide range of the extent of reaction.

It seems to us that the proposed procedure may be a convenient means to foresee the course of solution copolycondensation in homogeneous systems on the basis of calculations. It should be noticed, however, that in our considerations we accept silently a simplifying assumption of analogous reactivities of functional groups of monomer and macromolecule.

The differences in the reactivities existing in many cases should be taken into account in the calculations.

References

1. G. A. Straichman, *Zhur. Prikl. Chim.*, **32**, 673 (1959).
2. K. Tyuzyo, *J. Polym. Sci.*, **A3**, 3654 (1963).
3. L. C. Case, *J. Polym. Sci.*, **26**, 333 (1957).
4. L. F. Beste, *J. Polym. Sci.*, **36**, 313 (1959).
5. P. J. Flory, *Principles of Polymer Chemistry*, Wiley, New York, 1953.

Received July 5, 1973