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S. V. VINOGRADOVA and Corresponding Member of the
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Abstract

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S. V. VINOGRADOVA and Corresponding Member of the Academy of Sciences of the USSR V. V. KORSHAK

KINETICS OF THE POLYCONDENSATION OF DICARBOXYLIC ACID CHLORIDES WITH DIHYDRIC PHENOLS*

The reaction of exchange decomposition, one example of which is the interaction of dicarboxylic acid chlorides with diols, has until now represented the least studied case of a polyesterification reaction. In the literature there are only a few references to the preparation of polyesters by this route (1–6).

In a previous communication (7) we presented data on polyesters of aromatic dicarboxylic acids and dihydric phenols. The aim of the present work was a kinetic study of the formation reaction of these polyesters, proceeding according to the following equation:

$$\mathrm{HOArOH} + \mathrm{ClOCArCOClarrowHCl} + \cdots - \mathrm{OArOOCArCO} - \cdots$$

The kinetics of polycondensation was studied by us using, as an example, the interaction of isophthaloyl and terephthaloyl chlorides with n,n'-dioxydiphenylpropane in the temperature range 150-210°, terephthaloyl chloride with o,o'-dioxydiphenyl, resorcinol, and hydroquinone at 170°, and also sebacoyl chloride with n,n'-dioxydiphenylpropane at 150°. The reaction was carried out in a diphenyl solution in a stream of dry purified nitrogen, with an equimolecular ratio of the starting substances. In most experiments, 200 ml of diphenyl, 2.67 g of aromatic acid chloride, and the corresponding amount of diol were taken for the reaction. The course of the reaction was monitored by determining the amount of hydrogen chloride evolved during the interaction. In some experiments, samples were withdrawn from the reaction mixture during the reaction in order to determine in them the amount of polymer and its viscosity.

Determination of the reaction order by the van ’ t Hoff method (8) for the interaction of isophthaloyl chloride with n,n'-dioxydiphenylpropane showed that the reaction proceeds by a bimolecular mechanism. The rate constants of this and other reactions, calculated from the equation for a second-order reaction, retained a constant value during the reaction, which also confirmed that the reaction proceeds by a bimolecular mechanism.

Table 1 gives data on the rate constants and degrees of completion of the reactions of acid chlorides with diols.

The change in the rate constants of the reactions of n,n'-dioxydiphenylpropane with terephthaloyl and isophthaloyl chlorides proceeds in accordance with the Arrhenius equation, as can be seen in Fig. 1. Treatment of the experimental data by the least-squares method for these two reactions gave the Arrhenius equations in the following form: $\lg K = 7.13 - 4963/T$ and $\lg K = 5.81 - 4308/T$, respectively. According to these equations, the activation energy of the interaction of isophthaloyl chloride with n,n'-dioxydiphenylpropane is 19,700 cal at a probability factor— nity $0.646 \cdot 10^6$. The activation energy of the reaction of terephthalic acid chloride with n,n'-dioxydiphenylpropane is 22700 cal, with a probability factor of $0.135 \cdot 10^8$. The higher value of the probability factor for the interaction of terephthalic acid chloride with n,n'-dioxydiphenylpropane can apparently be explained by a spatial effect.

Table 1

Starting substances	Reaction temperature, °C	Rate constant, $l/mol \cdot sec \cdot 10^5$	Degree of completion of the reaction after 7 h
$HO{-}C_6H_4{-}C(CH_3)_2{-}C_6H_4{-}OH + ClOC{-}C_6H_4{-}COCl$	150	5.72	0.17
$HO{-}C_6H_4{-}C(CH_3)_2{-}C_6H_4{-}OH + ClOC{-}C_6H_4{-}COCl$	170	10.7	0.26
$HO{-}C_6H_4{-}C(CH_3)_2{-}C_6H_4{-}OH + ClOC{-}C_6H_4{-}COCl$	180	17.99	0.38
$HO{-}C_6H_4{-}C(CH_3)_2{-}C_6H_4{-}OH + ClOC{-}C_6H_4{-}COCl$	200	50.3	0.63
$HO{-}C_6H_4{-}C(CH_3)_2{-}C_6H_4{-}OH + ClOC{-}C_6H_4{-}COCl$	210	92.0	0.72
$HO{-}C_6H_4{-}C(CH_3)_2{-}C_6H_4{-}OH + ClOC{-}C_6H_4{-}COCl$	150	2.99	0.09
$HO{-}C_6H_4{-}C(CH_3)_2{-}C_6H_4{-}OH + ClOC{-}C_6H_4{-}COCl$	170	6.56	0.17
$HO{-}C_6H_4{-}C(CH_3)_2{-}C_6H_4{-}OH + ClOC{-}C_6H_4{-}COCl$	180	14.3	0.33
$HO{-}C_6H_4{-}C(CH_3)_2{-}C_6H_4{-}OH + ClOC{-}C_6H_4{-}COCl$	190	30.4	0.46
$HO{-}C_6H_4{-}C(CH_3)_2{-}C_6H_4{-}OH + ClOC{-}C_6H_4{-}COCl$	210	79.6	0.64
$HO{-}C_6H_4{-}C(CH_3)_2{-}C_6H_4{-}OH + ClOC(CH_2)_8COCl$	150	344	–
$C_6H_4(OH){-}C_6H_4(OH) + ClOC{-}C_6H_4{-}COCl$	170	6.9	0.16
$HO{-}C_6H_4{-}OH + ClOC{-}C_6H_4{-}COCl$	170	7.06	0.19
$HO{-}C_6H_4{-}OH + ClOC{-}C_6H_4{-}COCl$	170	11.7	0.27

The location of the reactive groups in isophthalic acid chloride in the meta position creates greater obstacles to the approach of a second molecule than in the case of their para position in the aromatic ring.

Fig. 1. Dependence of the rate constants on temperature for the interaction

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[*] V. S. Artemova and D. T. Morozova took part in the experimental work.

Fig. 1. Dependence of rate constants on temperature for the interaction of n,n′-dioxydiphenylpropane: a—with terephthalic acid chloride; b—with isophthalic acid chloride

Figure 1: Fig. 1. Dependence of rate constants on temperature for the interaction of n,n′-dioxydiphenylpropane: a—with terephthalic acid chloride; b—with isophthalic acid chloride

of n, n'-dioxydiphenylpropane: a—with terephthalic acid chloride; b—with isophthalic acid chloride.

This also reduces the frequency of collisions of acid-chloride groups with hydroxyl groups in the formation of the polyester of isophthalic acid. From the graphical dependence of the change in the rate constant on temperature for the reactions of n, n'-dioxydiphenylpropane with the chlorides of terephthalic and isophthalic acids, the temperature coefficients of the reaction were calculated; these are given in Table 2.

To clarify the influence of the structure of the starting substances on the reaction rate, it is useful to compare the rate constants of the different reactions given in Table 1. As is evident from the data of Table 1, isophthalic acid chloride reacts with n, n'-dioxydiphenylpropane at a higher rate than terephthalic acid chloride. Replacing the chloride of an aromatic acid by the chloride of an aliphatic acid greatly increases the rate of the reaction. Thus, sebacic acid chloride at a temperature of 150° reacts with n, n'-dioxy-

diphenylpropane at a rate approximately 60 times greater than the rate of interaction of isophthalic acid chloride and 115 times greater than the rate of interaction of terephthalic acid chloride.

The reaction rate also depends on the structure of the dihydric phenol used. At a reaction temperature of 170°, n, n'-dioxydiphenylpropane, resorcinol, hydroquinone, and o, o'-dioxydiphenyl, in their rate of reaction with terephthalic acid chloride, are arranged as follows: hydroquinone > resorcinol > o, o'-dioxydiphenyl > n, n'-dioxydiphenylpropane. It should be noted that the differences in the reaction rates of the last three diols are small.

Table 2

Starting substances	160/150	170/160	180/170	190/180	200/190	210/200
$HO-C_6H_4-C(CH_3)_2-C_6H_4-OH + ClOC-C_6H_4-COCl$	1.36	1.4	1.68	1.68	1.65	1.82
$HO-C_6H_4-C(CH_3)_2-C_6H_4-OH + ClOC-C_6H_4-COCl$	1.36	1.62	2.18	2.13	1.76	1.48

Ratio of temperatures in °C

Fig. 2. Kinetics of polycondensation of isophthalic acid chloride with n, n'-dioxydiphenylpropane at 220°: 1 —change in the amount of hydrogen chloride evolved in the course of the reaction; 2 —change in the amount of polymer in the reaction mass; 3 —change in the amount of starting substances and low-molecular-weight polyester in the reaction mass; 4 —change in the reduced viscosity of the polyester.

Figure 2: Fig. 2. Kinetics of polycondensation of isophthalic acid chloride with n, n'-dioxydiphenylpropane at 220°: 1 —change in the amount of hydrogen chloride evolved in the course of the reaction; 2 —change in the amount of polymer in the reaction mass; 3 —change in the amount of starting substances and low-molecular-weight polyester in the reaction mass; 4 —change in the reduced viscosity of the polyester.

Table 1 gives data on the degree of completion of the reactions after they had proceeded for seven hours. It is evident from these data that, as the reaction temperature increases, the degree of completion of the reaction increases. However, even when the reaction is carried out at 210°, the degree of completion of the reaction in the interaction of n, n'-dioxydiphenylpropane with isophthalic acid chloride is only 0.72, i.e., the reaction proceeds only to 72%.

Determination, in this case, of the change during the reaction in the reduced viscosity of the polymer in cresol showed that it is small and, from 2 to 10 hours of reaction, practically does not change, remaining equal to ~ 0.18. In order to increase the degree of completion of the reaction, we investigated the interaction of n, n'-dioxydiphenylpropane with isophthalic acid chloride at a higher temperature (220°) and at a higher initial concentration of the reacting substances (5 g of diol and 4.45 g of acid chloride were taken per 100 ml of dinyl). It was found that by the 7th hour of the reaction the degree of completion of the reaction had increased considerably and amounted to 0.975.

Fig. 2. Kinetics of polycondensation of isophthalic acid chloride with n, n'-dioxydiphenylpropane at 220°: 1 —change in the amount of hydrogen chloride evolved in the course of the reaction; 2 —change in the amount of polymer in the reaction mass; 3 —change in the amount of starting substances and low-molecular-weight polyester in the reaction mass; 4 —change in the reduced viscosity of the polyester.

Figure 2 graphically presents the change, in the course of this reaction, in the composition of the reaction mixture and in the reduced viscosity of the polyester. It is evident from Fig. 2 that, as the reaction continues, a continuous increase is observed in the reduced viscosity of the polyester, i.e., in its molecular weight. The fact that the amount of polymer changes very little after 3 hours of reaction, while the amount of low-molecular-weight fraction by this time is already very much

insignificant, undoubtedly indicates that the growth of the polymer chain after 3-4 hours of the reaction proceeds mainly through the reaction of polymer molecules with one another.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.

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