HETEROCHAIN POLYESTERS

COMMUNICATION 57. KINETICS OF THE POLYCONDENSATION OF CHLORIDES OF AROMATIC DICARBOXYLIC ACIDS WITH MONOHYDRIC ALIPHATIC ALCOHOLS

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It was demonstrated earlier [1-3] that mixed polyarylates containing residues of polyhydric aliphatic alcohols, such as, for example, trimethylolpropane and trimethylolethane, are thermoreactive polymers, capable both of thermostetting and of hardening on account of the interaction of free hydroxyl groups with various cross-linking agents, for example, diisocyanates. Such mixed polyarylates may be of interest for the manufacture of thermostable coatings, foam plastics, glues, etc. However, polyarylates with free hydroxyl groups in the chain should possess a definite complex of properties for the preparation of a number of objects: low molecular weight, fusibility and solubility. The content of free hydroxyl groups in the polymers should not exceed definite limits. The synthesis of such polyarylates is hindered, since the original dihydric phenols and polyhydric aliphatic alcohols differ substantially in their reactivity.

The kinetics of the polycondensation of chlorides of terephthalic and isophthalic acids with 4,4'-dihydroxydiphenyl-2,2-propane (diane) and other dihydric phenols was studied earlier [4]. This work was aimed at studying the kinetics of the polycondensation of the acid chlorides indicated above with such polyhydric alcohols as trimethylolpropane (1,1,1-trimethylolpropane) and trimethylolethane (1,1,1-trimethylolethane), which is of interest not only from the standpoint of studying the principles of the polycondensation of dicarboxylic acid chlorides with aliphatic monohydric alcohols, but also because these kinetic data may be used to determine the necessary system of polycondensation of mixed polyarylates containing free hydroxyl groups in the chain.

EXPERIMENTAL

The kinetics of the polycondensation of terephthalyl and isophthalyl chlorides with trimethylolethane and trimethylolpropane was investigated according to the evolution of hydrogen chloride during the reaction. Polycondensation was conducted in diniyl medium in a stream of dry nitrogen, freed of oxygen, the rate of delivery of which was controlled according to a rheometer. The kinetics of the polycondensation was studied within the temperature interval 110-150°. In all the experiments, the amount of the starting materials and their condensations were strictly constant, while the ratio was equimolar. Polycondensation was conducted in a two-necked flask, equipped with a thermometer and tube for delivery of nitrogen, as well as narrow outlet for the removal of nitrogen and of the hydrogen chloride evolved during the reaction. Hydrogen chloride was absorbed in two systems connected in parallel, each of which consisted of four traps, filled with a 0.5 N NaOH solution. The systems for absorption of hydrogen chloride were connected alternately. After the absorption, the alkaline solutions were titrated with 1 N H₂SO₄.

A calculation of the rate constants of the polycondensation of dicarboxylic acid chlorides with trimethylolethane and trimethylolpropane according to the equations of first-, second-, and third-order reactions indicated that only the rate constant of the reaction, determined according to the equation of a second-order reaction, retains a constant value to a degree of completion of the reaction ~0.5, i.e., polycondensation of chlorides of aromatic dicarboxylic acids with trimethylolethane and trimethylolpropane at the first
stage of the process (up to a degree of conversion ~0.5) obeys the principles of a bimolecular process. At the following stage of the polycondensation, the reaction order gradually changes, and most likely possesses a fractional value. Figure 1 graphically presents the change in the dependence of \(1/a - x\) (where \(x\) is the amount of hydrogen chloride evolved at a given moment of the reaction, \(a\) is the amount of hydrogen chloride that should be evolved in the case of 100% occurrence of the reaction) on the time. From it, it is evident that the linear dependence of \(1/a - x\) on the time is retained only up to a degree of completion of the reaction of 0.5-0.6 (for low temperatures, up to somewhat higher degrees of completion). Within the limits of the indicated degrees of conversion, the experimental points fit satisfactorily on straight lines. Subsequent deviation from the straight lines indicates that the polycondensation of chlorides of aromatic dicarboxylic acids with aliphatic triols occurs at the second stage according to a more complex mechanism, which also leads to a change in the reaction order. Evidently at the first stage of the reaction, the original polyhydric alcohol behaves as a bifunctional compound; as the process continues, the third hydroxyl group is also involved in the polycondensation, which leads ultimately to an increase in the viscosity of the system and to gel formation. Premature cross-linking of the polymer chains and the formation of a polymer with a three-dimensional structure lead to the fact that the degree of completion of the reaction, even after prolonged conducting of the process, practically does not exceed 0.8. We should mention that when the polycondensations conducted at low temperatures (100, 115, 120, and partly 130°), a number of the first points on the straight line (see Fig. 1) drop out, which may be explained by the fact that the conditions of the reaction had not yet become established at the very beginning of the process. At higher temperatures, for which the degree of completion of the reaction reaches a value of 0.5-0.6 in ~1 h, a steady-state reaction is established very rapidly, and the initial experimental points fit well on straight lines. The results that we obtained are in good agreement with the data of [5], devoted to a study of the process of polycondensation of adipyl chloride with 2,2-dimethylpropanediol-1,3 (neopentyl glycol) and trimethylolethane in tetrachloroethane medium. In the case described, the process also obeyed the principles of a second-order reaction up to a degree of conversion of 0.6. Then the second-order reaction rate constant decreased sharply. The authors explain this by premature gel formation on account of the third hydroxyl group of trimethylolethane and shielding (capture — "buried groups") of reactive groups within the gel. This was confirmed by treating the gel isolated with low-molecular alcohols (methanol, ethanol, etc.), which penetrate within the gel, giving rise to interaction of these alcohols with the free chloride groups.

The slope of the straight lines depicted in Fig. 1 gives the rate constant of the reaction of the corresponding temperature. Table 1 presents the reaction rate constants and the degree of its completion at various temperatures. From the data in Table 1, we may conclude that the rate constants differ negligibly from one another, both from one dicarboxylic acid chloride to another (with the same triol) and from one triol to another (with the same dicarboxylic acid chloride). However, the picture is substantially changed when the rate of interaction of terephthalyl and isophthalyl chlorides with trimethylolethane, trimethylolpropane, and with diane are compared. At 150°, the rate constant of the polycondensation of diane with terephthalyl chloride is 2.99 · 10⁻⁵ liter/mole·sec, i.e., at 150° terephthalyl chloride interacts with the