Reports of the Academy of Sciences of the USSR

Corresponding Member of the Academy of Sciences of the USSR V. V. Korshak, T. M. Frunze, V. V. Kurashev, A. A. Izynéev

1963

SovietRxiv

Figure 1

Figure 1: Figure 1

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1963. Volume 149, No. 1

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR V. V. Korshak, T. M. Frunze, V. V. Kurashev, A. A. Izynéev

STUDY OF THE REACTION OF POLYBENZIMIDAZOLE FORMATION

A new class of polymers—polybenzimidazoles—has recently been obtained by Brinker and Robinson (1) through the interaction of bis-*ortho*-diaminophenyls with aliphatic dicarboxylic acids, and by Vogel and Marvel (2) with aromatic ones. It turned out that these polymers are distinguished by high chemical and thermal stability, especially the latter, which have a completely aromatic structure.

The aim of the present work was to elucidate certain regularities and the mechanism of this process. The object of study chosen was the polycondensation reaction of 3,3′-diaminobenzidine with diphenyl sebacinate. The polycondensation was carried out by heating the initial reagents in a stream of nitrogen, and in some cases additionally under vacuum.

Fig. 1. Thermographic analysis of polybenzimidazole obtained at 270° with a reaction time of 3 hours. **1** —change in the weight of the polymer during heating; **2** —increase in temperature with time; **3** —thermogram. At 630° the loss in weight of the polymer is 92.5%.

The polymers obtained in quantitative yields are yellow-brown glassy products, soluble cold only in concentrated sulfuric and formic acids. On heating they partially dissolve in dimethylformamide and glacial acetic acid; they do not dissolve in hydrochloric acid, cresol, or benzyl alcohol. For all polymers obtained, the viscosity of their 0.5% solutions in concentrated formic acid was determined, as was the elemental composition of the polymers; infrared and ultraviolet spectra, X-ray diffraction patterns, and thermomechanical curves were recorded.

Scheme I: reaction scheme for formation of polyaminoamide and polybenzimidazole

Figure 2: Scheme I: reaction scheme for formation of polyaminoamide and polybenzimidazole

Figure 1 gives the results of a thermographic study of poly-2,2′-(octamethylene)-5,5′-dibenzimidazole obtained by heating for 4 hours at 270°. The heating rate was 17° per minute. Curve **1**, representing the loss in weight of the polymer at high temperatures (21 mg), shows that this polymer decomposes only at 450-470°.

As the data obtained show, the reaction temperature is of great importance in the process of polycondensation of 3,3′-diaminobenzidine with diphenyl sebacinate. Raising the reaction temperature leads to a sharp increase in the molecular weight (solution viscosity) of the polymer formed (Fig. 2, **1**). At the same time, as is evident from Fig. 3, the duration of the reaction has different effects at different temperatures. At high temperatures (230, 270°) the process proceeds rapidly, leading to the formation of products with a fairly high solution viscosity, which can be further increased by increasing the duration of heating and by using

vacuum. Carrying out the reaction at 290° leads to the formation of insoluble products. At a temperature of 200° the viscosity of the solutions of the polymers formed is very low and decreases with increasing duration of heating. On the basis of the data obtained, the process of formation of polybenzimidazoles may be represented as a two-stage reaction proceeding according to Scheme I.

Scheme I

In the first stage, formation of the polyaminoamide takes place, and in the next stage closure of the imidazole ring occurs with elimination of water. The results of elemental analysis of polymers obtained at different

Fig. 2 Fig. 3

Fig. 2. Dependence of the reduced viscosity of a solution of poly-2,2′-(octamethylene)-5,5′-dibenzimidazole in formic acid.
1 –on the polycondensation temperature (heating duration 3 h); 2 –on the amount of stearic acid added; 3 –on the amount of added α-naphthylamine.

Fig. 3. Dependence of the reduced viscosity of a polymer solution in formic acid on the duration of the reaction.
1 –at 270°, 2 –at 230°, 3 –at 200°; solid lines –polymers obtained under atmospheric pressure; dashed lines –under vacuum: a -10^{-2} mm Hg, b -10^{-3} mm Hg.

temperatures testify in favor of this mechanism. The elemental composition of the product obtained at 200° corresponds to a polyamide unit, while the elemental composition of the product obtained at 270° approaches the composition of the corresponding polybenzimidazole unit. Polymers obtained at intermediate temperatures contain, according to the elemental-analysis data, both kinds of units. At the same time, as the reaction temperature is raised from 230 to 270°, an increase in the content of imidazole rings is observed in the polymers formed. Evidently, closure of the imidazole rings is favored by a higher temperature. At low temperature the reaction proceeds mainly in the direction of formation of the polyamide chain.

Thus, the reaction product has in its macromolecule both amide and imidazole groups, the ratio of which changes in the course of the reaction:

$$\cdots\!-\!\mathrm{HNH_2N} \qquad \mathrm{NH_2}\!-\!\mathrm{NH}\!-\!\mathrm{C}(=O)\!-\!(\mathrm{CH_2})_8\!-\!\text{benzimidazole-containing unit}\!-\!(\mathrm{CH_2})_8\!-\!\mathrm{CO}\!-\!\cdots$$

In this case the decrease in the viscosity of polymer solutions during the reaction at 200° becomes understandable. The polymer formed under these conditions is an almost homogeneous polyamide. The decrease in its viscosity during heating is explained by its destruction by the phenol liberated in the course of the reaction, which at 200° is removed only very slowly from the reaction zone. Imidazole rings are considerably more stable and do not undergo destruction under these conditions. The formation of insoluble products when the reaction is carried out at 290° is evidently explained by crosslinking of macromolecules, which may proceed under these conditions through several reactions, the most probable of which are transamidation reactions between NH_2 groups and amide groups and the interaction of NH_2 groups with the formation of secondary amino groups. Reactions involving the NH groups of the imidazole ring may also occur.

Fig. 4. Effect of an excess of the initial reagents on the reduced viscosity of a solution of poly-2,2′-(octamethylene)-5,5′-dibenzimidazole in formic acid.

The process studied obviously cannot be assigned to the ordinary type of equilibrium polycondensation, i.e., polycondensation characterized by the presence of an equilibrium state established as a result of the direct processes of polycondensation and the reverse processes of destruction of the macromolecules formed.

The process of formation of polybenzimidazoles is distinguished by greater complexity. In the first stages, when aminoamide units are formed predominantly, the reaction is evidently an equilibrium one and obeys the regularities characteristic of equilibrium polycondensation. This applies, in particular, to the influence of an excess of reagents (Fig. 4) and of additions of monofunctional compounds (Figs. 2, 3, 4). In this case the interruption of chain growth usual for equilibrium polycondensation occurs ([3],[4]). On the other hand, both here and in the case of an excess of one of the starting reagents, processes of acidolysis and aminolysis of the polymer chains may evidently occur, since, as was shown above, they contain polyamide units to a greater or lesser extent.

At the later stages of the reaction, when the macromolecules contain mainly benzimidazole rings, the process evidently increasingly loses its equilibrium character, since the benzimidazole rings are very stable and are not destroyed under the reaction conditions.

The authors express their gratitude to I. F. Manucharova for carrying out the thermographic study of the polymers.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
6 XII 1962

References Cited

[1] K. C. Brinker, J. M. Robinson, Am. pat. 2895948 (1959).
[2] H. Vogel, C. S. Marvel, J. Polym. Sci., **50**, 511 (1961).
[3] V. V. Korshak, *Chemistry of High-Molecular Compounds*, Publishing House of the Academy of Sciences of the USSR, 1950, p. 294.
[4] V. V. Korshak, V. V. Golubev, Izv. AN SSSR, OKhN, 1946, 885.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.