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Corresponding Member of the Academy of Sciences of the USSR V. V. Korshak and S. V. Vinogradova

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Abstract

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ON CERTAIN REGULARITIES OF THE POLYCOORDINATION REACTION

In recent years a number of works have been published on the preparation of coordination polymers. However, in most cases these polymers had a low molecular weight—of the order of 2000-4000 ([1]-[3]).

On the basis of a study of the regularities of the polycoordination reaction, we succeeded in finding synthesis conditions under which coordination polymers with molecular weights above 100,000 can be obtained. For the successful execution of this work it was necessary that the coordination polymer obtained be a soluble substance. Earlier Korshak and Krongauz ([2]) had shown that certain coordination polymers of 4,4′-bis-(acetoacetyl)-phenyl ether are soluble in organic solvents. We therefore decided to choose this tetraketone as the starting ligand.

The literature contains no data on the regularities of the formation of coordination polymers. It is not difficult to note, however, that the process of polycoordination in many respects resembles the process of polycondensation. In both cases the synthesis of the polymer is effected through the interaction of two types of reactive groups and is accompanied, along with growth of the polymer chain, by the liberation of a low-molecular reaction product.

In the case of polycondensation this is water, alcohol, etc.; in polycoordination it is acetylacetone, acetic acid, etc.

It is well known that the process of polycondensation is an equilibrium process. Thus, earlier ([4]), using the example of a study of the regularities of polyester formation, we showed that an increase in the molecular weight of a polyester can be achieved by creating conditions that ensure a shift of the equilibrium toward formation of the polymer molecule, through removal of the low-molecular reaction product from the reaction sphere. Usually this can be achieved by carrying out the process for a long time at elevated temperature, sometimes applying heating of the reaction mixture in vacuum at a definite stage.

It was of interest to determine whether polycoordination, like polycondensation, is a reversible reaction. If the polycoordination process has an equilibrium character, the coordination polymer should be destructured by the low-molecular reaction product.

As the experiment carried out by us showed, the coordination polymer of 4,4′-bis-(acetoacetyl)-phenyl ether and beryllium, heated in a stream of nitrogen for 5 hours at 100° with acetylacetone (taken in an amount of 10 moles per mole of the repeating unit of the polymer), was completely destroyed. As a result, the initial ligand, 4,4′-bis-(acetoacetyl)-phenyl ether, was isolated in 87% yield.

We were also able to establish that the coordination polymer enters into exchange reactions not only with the low-molecular reaction product, but also with substances chemically close to coordination polymers.

···in nature. Thus, as a result of the interaction of the coordination polymer of 4,4′-bis(acetoacetyl) diphenyl ether and beryllium with copper acetylacetonate, we isolated the coordination polymer of 4,4′-bis(acetoacetyl) diphenyl ether and copper.

Consequently, coordination polymers, like polymers obtained by polycondensation, are capable of entering into exchange reactions.

On the basis of these data, it could be assumed that, in order to obtain coordination polymers of high molecular weight, it is necessary to carry out the polycoordination process under conditions ensuring the most complete possible removal of the low-molecular-weight product from the reaction sphere.

Since polycoordination can be carried out both in solution and in the melt, we investigated the influence of various polycoordination conditions on the yield and reduced viscosity of the polymer in these two variants.

As objects of study we chose the interaction of 4,4′-bis(acetoacetyl) diphenyl ether with beryllium and zinc acetylacetonates, and also with zinc acetate.

The polycoordination of 4,4′-bis(acetoacetyl) diphenyl ether with zinc acetate was carried out by us in a dimethylformamide solution in a stream of nitrogen at temperatures of 120 and 140°. It was found that the polymer yield in both cases, after 0.5 h from the beginning of the reaction, was 84–87%. The reduced viscosity of the polymer solutions in cresol did not change with an increase in the reaction time from 0.5 to 11 h and varied within the limits 0.06–0.09. In an effort to increase the reduced viscosity of the polymer, i.e., its molecular weight, we decided to carry out the polycoordination at a higher temperature. However, carrying out the polycoordination in a dinyl solution at 220° for 5 h led to the formation of a polymer very poorly soluble in cresol.

In connection with the poor solubility of the coordination polymer of the tetraketone with zinc, we carried out further work on beryllium polymers. Table 1 gives data on the influence of the concentration of the solution (solvent—dinyl, reaction temperature 200–240°) on the yield and reduced viscosity of the coordination polymers in chloroform.

Table 1

Influence of the concentration of solutions of the starting substances on the yield and reduced viscosity of polymer solutions in chloroform

No.	Solution conc., mol/l	With distillation of acetylacetone* reduced viscosity	With distillation of acetylacetone* yield, %	Without distillation of acetylacetone** reduced viscosity	Without distillation of acetylacetone** yield, %	No.	Solution conc., mol/l	With distillation of acetylacetone* reduced viscosity	With distillation of acetylacetone* yield, %	Without distillation of acetylacetone** reduced viscosity	Without distillation of acetylacetone** yield, %
1	0.05	0.17	65	0.18	59	4	0.74	0.29	97	0.37	88
2	0.10	0.16	80	0.16	80	5	1.00	0.23	92	0.28	quantit.
3	0.50	0.18	92	0.30	92	6	2.00	0.21	80	0.31	82

* In a stream of nitrogen for 2 h at 200° and 9 h at 240°.

** In a stream of nitrogen for 1.5 h from 20 to 240° and 5 h at 240°.

It is evident from Table 1 that coordination polymers of higher reduced viscosities are formed when polycoordination is carried out in more concentrated solutions (0.74–2.00 mol/l). Our data also clearly show that carrying out polycoordination under conditions ensuring the distillation of acetylacetone from the reaction medium leads to the formation of a polymer of higher reduced viscosity, i.e., of higher molecular weight.

We also investigated the influence on the reduced viscosity of the coordination polymer—when polycoordination is carried out in solution—

ratios of the starting substances. The data obtained in this case are given in Table 2.

It can be seen from them that the ratio of the starting substances has a large effect on the value of the reduced viscosity, i.e., on the molecular weight of the polymer formed. Thus, the polymer of the greatest molecular

Table 2

Effect of the ratio of the starting substances on the reduced viscosity of the polymer solution in chloroform

No.	Molar ratio: tetraketone : beryllium acetylaceto-nate	Reduced viscosity	No.	Molar ratio: tetraketone : beryllium acetylaceto-nate	Reduced viscosity
1	1:0.2	0.10	7	1:1.1	0.20
2	1:0.4	0.08	8	1:1.2	0.10
3	1:0.5	0.08	9	1:1.4	0.06
4	1:0.6	0.08	10	1:1.5	0.06
5	1:0.8	0.08	11	1:1.6	0.06
6	1:1.0	0.37	12	1:2.0	0.04

Note. Polycoordination was carried out in 40.5% dinitol solutions under conditions that ensure distillation of acetylacetone from the reaction mixture, in a nitrogen stream, for 1.5 h with a gradual temperature rise from 20 to 240° and for 5 h at 240°.

molecular weight is formed at an equimolecular ratio of the starting substances. Increasing the amount of one of the reaction components above the equimolecular amount causes a marked decrease in the reduced viscosity of the coordination polymer. In this case the greatest effect is exerted by a certain excess of one of the components. Thus, an excess of one of the reaction components of 0.2 mole causes a decrease in the reduced viscosity of the polymer by almost a factor of 4. With a further increase in the excess of one of the reaction components, the reduced viscosity of the polymer practically no longer changes.

Table 3

Polycoordination in the melt. Effect of reaction conditions on the reduced viscosity of the polymer solution in chloroform

No.	In a nitrogen stream: temp., °C	In a nitrogen stream: duration, h	In vacuum: temp., °C	In vacuum: duration, h	Reduced viscosity	No.	In a nitrogen stream: temp., °C	In a nitrogen stream: duration, h	In vacuum: temp., °C	In vacuum: duration, h	Reduced viscosity
1	200	1	—	—	0.06	5	200	5	200	8	0.26
2	200	5	—	—	0.06	6	200	5	260	5	0.44
3	200	5	200	2	0.13	7	200 — 260	4	—	—	0.11

No.	In a nitrogen stream: temp., °C	In a nitrogen stream: duration, h	In vacuum: temp., °C	In vacuum: duration, h	Reduced viscosity	No.	In a nitrogen stream: temp., °C	In a nitrogen stream: duration, h	In vacuum: temp., °C	In vacuum: duration, h	Reduced viscosity
4	200	5	200	4	0.19	8	200 — 260	10	—	—	0.22

As was noted earlier, we also carried out the polycoordination reaction in the melt. Table 3 gives data on the effect of the conditions for carrying out polycoordination in the melt on the reduced viscosity of the coordination polymer of 4,4′-bis(acetoacetyl)phenyl ether and beryllium. It can be seen from them that when polycoordination is carried out in a nitrogen stream at 200° during the very first hour of the reaction a polymer is formed whose reduced viscosity in chloroform solution is 0.06. With a further increase in the duration of the reaction at the same temperature to 5 h, the reduced viscosity of the polymer remains unchanged. The picture changes when polycoordination is carried out at a higher temperature and, especially, when in the second stage of the process the reaction mixture is heated in a vacuum of 1-2 mm Hg. Thus, when the reaction temperature is increased from 200 to 260°, the reduced viscosity of the polymer increases

almost twofold. The reduced viscosity of the polymer also increases with increasing reaction time at 260°.

The greatest increase in the reduced viscosity of the polymer is observed when the second stage of the reaction is carried out in vacuum. Thus, when the reaction was first carried out in a stream of nitrogen for 5 h at 200°, and then for 5 h in vacuum at 260°, a coordination polymer was obtained whose reduced viscosity in chloroform solution was 0.44. A coordination polymer synthesized under similar conditions in a larger quantity (the charge of tetraketone was 6 g instead of 0.5 g), but with a longer reaction time in vacuum (14 h at 260°) because of the larger charge, had a reduced viscosity in chloroform solution of 0.48. Fractionation of this polymer from chloroform solution with *n*-hexane gave three fractions: I—27.3%; II—28.2%; III—44.5%. The reduced viscosities of these fractions in chloroform were 1.2, 0.5, and 0.32, respectively. The molecular weight of fraction I, determined by osmometry, proved to be 126000.

These data clearly demonstrate the possibility of synthesizing coordination polymers of high molecular weight by the polycoordination reaction. The increase in the molecular weight of the coordination polymer with increasing reaction

temperature and when the reaction is carried out in vacuum can undoubtedly be explained by the equilibrium character of the process. Both raising the reaction temperature and applying vacuum facilitate removal from the reaction sphere of the low-molecular product, in this case acetylacetone, which can cause chemical destruction of the polymer, and thereby shift the equilibrium toward formation of the polymer molecule.

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