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Abstract

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ON THE ROLE OF π-COMPLEXES IN THE COORDINATION-IONIC POLYMERIZATION OF BUTADIENE

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Recently published literature data make it possible to take a critical approach to consideration of the question of the necessity of participation of a metal-carbon σ bond in the processes of stereospecific polymerization of dienes.

Catalysts based on titanium halides should be assigned to systems of the coordination-anionic type ([1,2]). In this case, growth of the polymer chain takes place at the metal-carbon σ bond, and the radical of the organometallic compound becomes part of the polymer ([3]).

Catalytic systems based on cobalt and nickel compounds evidently act by another mechanism ([2,4–6]). According to Natta, in this case the polymer chain contains no radicals of the organoaluminum compound ([7]).

We have investigated, in the process of butadiene polymerization, catalysts based on transition-metal compounds and Lewis acids which, in their mechanism of action, are apparently similar to typical "cobalt" systems (Table 1).

Table 1

Catalytic systems for the polymerization of butadiene

Catalytic system	cis-1,4	trans-1,4	1,2
$CoCl_2 + AlCl_3 + C_6H_6$	70	27	3
$CoCl_2 + WCl_6 + C_6H_6$	80	16	4
$NiCl_2 + WCl_6 + C_6H_6$	79	17	4
$CoCl_2 + AlCl_3 + Al + C_6H_6$ ([7])	>90	–	–
$VCl_4 + AlCl_3 + Al + C_6H_6$	89	8	3
$Ni(CO)_4 + AlCl_3 + C_6H_6$*	89	8	3
$Ni(CO)_4 + TiCl_4 + C_6H_6$	87	10	3
$Ni(CO)_4 + MoCl_5 + C_6H_6$ ([8])	>85	–	–
$Mo(CO)_6 + VOCl_3 + C_6H_6$*	–	–	69
$Mo(CO)_6 + TiCl_4 + C_6H_6$*	–	9	50
$Co_2(CO)_8 - MoCl_5 + C_6H_6$	–	–	100

* The polymers were characterized by a reduced content of double bonds.

These catalytic systems are formed in the absence of organometallic compounds and do not contain metal-carbon σ bonds.

It should be emphasized that all the catalysts listed in Table 1 belong to one class of compounds—arene complexes of transition metals—and differ from one another only in the valence state of the metal in the complex.

The reactions leading to the formation of catalysts in the presence of the reducing agent aluminum are based on methods, studied in detail by a number of authors, for the synthesis of arene complexes of univalent metals:

$$\mathrm{VCl_4 + Al + Arene \xrightarrow{AlCl_3} [V^{I}(Arene)_2]AlCl_4} \quad (9),$$

$$\mathrm{CoCl_2 + Al + Arene \xrightarrow{AlCl_3} [Co^{I}(Arene)_2]AlCl_4} \quad (10).$$

Catalysts obtained by the interaction of cobalt or nickel chlorides with a Lewis acid without a reducing agent belong to arene com-

complexes of divalent metals:

$$\mathrm{CoCl_2 + 2AlCl_3 + Arene \longrightarrow [Co^{II}(Arene)_2](AlCl_4)_2}. \tag{10}$$

Complexes formed from metal carbonyls contain the metal in the zero-valent state:

$$\mathrm{Ni(CO)_4 + AlCl_3 + Arene \longrightarrow [Ni^{0}(Arene)_2](AlCl_3)_{\mathit{n}}}. \tag{11}$$

The stereospecificity of the action of the catalytic systems studied is determined, first of all, by the nature of the transition metal in the arene complex; the nature of the metal in the Lewis acid has no influence on the structure of the polybutadiene formed.

Irrespective of the valence state of the transition metal in the arene complex, nickel- and cobalt-based catalysts lead to the formation of 1,4-polybutadiene with a predominant content of cis-1,4 units. As the valence state of the transition metal decreases, the activity of the catalyst increases and the content of cis-1,4 units in the polymer rises somewhat.

Systems obtained from carbonyls of molybdenum and cobalt polymerize butadiene predominantly in the 1,2 position. Similar results with a catalyst containing cobalt carbonyl were recently published by Otsuka (8).

The catalytic system $Ni(CO)_4 + MoCl_5$ was used for the polymerization of isoprene. The polyisoprene obtained contained 6% 3,4 units, 35% cis-1,4 units, and 59% trans-1,4 units.

We believe that the activity of the catalysts studied is connected with their π-complex nature and must be determined by the strength of the bonds between the metal and the ligand. As is known, the stability of arene complexes increases with an increase in the number of alkyl substituents in the benzene ring, i.e., with an increase in electron density.

According to van de Kamp (12), in the polymerization of butadiene the activity of the "cobalt" system depends on the nature of the aromatic compound employed. In the presence of hexamethylbenzene, which forms very stable arene complexes, the polymerization of butadiene is practically suppressed.

In our opinion, catalytic "arene" systems are a special case of a broader class of stereospecific polymerization catalysts that can be obtained on the basis of π-complexes of transition metals.

In this connection, the so-called π-allyl complexes are of particular interest. In a very recent communication by Natta (13), bis-(π-allylnickel bromide) was used as a catalyst for the stereospecific polymerization of butadiene.

At present it is known that complexes of butadiene and other diolefins with certain transition metals (Ni, Co, Pd, etc.) have a π-allyl structure (14).

It may be supposed that, in the polymerization of dienes in the presence of catalysts that do not contain metal-carbon σ-bonds, the initiation stage consists in the formation of a π-allyl complex. It is highly probable that, in the case of such catalysts, the growing polymer chain is bound to the transition metal by means of a π-allyl grouping. This to a considerable extent explains the data obtained by a number of authors in studying the polymerization of butadiene on "cobalt" systems (2,4–6), and makes immaterial the question of the sign of the charge at the end of the growing chain.

Taking into account the comparative stability of π-allyl complexes with respect to polar reagents (in particular, water), one may suppo-

that the polymerization of butadiene in an aqueous medium under the influence of compounds of Group VIII metals [15,16] also proceeds by a π-allyl mechanism.

I. A. Zarova and I. M. Lapuk took part in carrying out the experiment.

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