Reports of the Academy of Sciences of the USSR

B. D. BABITSKY, Academician B. A. DOLGOPLOSK, V. A. KORMER,

1965

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1965. Volume 161, No. 3

CHEMISTRY

B. D. BABITSKY, Academician B. A. DOLGOPLOSK, V. A. KORMER,
M. I. LOBACH, E. I. TINYAKOVA, V. A. YAKOVLEV

STEREOSPECIFIC POLYMERIZATION OF BUTADIENE BY CATALYTIC SYSTEMS BASED ON π-ALLYL NICKEL COMPLEXES

The mechanisms proposed by various authors for the polymerization of dienes with controlled chain growth are certainly not universal, since they reliably describe only certain details of this complex process. The enormous amount of experimental, sometimes contradictory, data relating to one or another polymerization process increasingly testifies to the diversity of the phenomena underlying stereospecific synthesis. The most reliable hypotheses at present should be considered those in which the dominant role is assigned to the nature of the transition metal, its valence state, and the nature of the ligands stabilizing this valence state.

The role of ligands may be played both by organometallic compounds and by other substances with a pronounced electron-donor character, capable of forming π-bonds with the *p*- or *d*-orbitals of transition metals.

A significant stabilizing effect is achieved in π-complexes of transition metals in the reduced state when organic compounds with multiple carbon-carbon bonds are used as ligands (aromatic hydrocarbons, cyclic dienes, ethylene and acetylene hydrocarbons, etc.).

In this connection, elucidation of the role of π-complexes in processes of stereospecific polymerization is of undoubted interest.

We have previously shown the possibility of using π-allyl nickel complexes in combination with metal halides in the process of synthesis of cis-1,4-polybutadiene ([1]).

The study of the behavior of π-allyl complexes of metals is of particular importance because these complexes possess appreciable stability and because structures of this type are realized in the course of the process of stereospecific polymerization of dienes.

In the present work, data are given on the synthesis of π-allyl nickel complexes and their use for the stereospecific polymerization of butadiene.

Bis-(π-crotyl)-nickel was obtained from crotylmagnesium chloride* and anhydrous nickel chloride in diethyl ether or in an ether–toluene mixture (1 : 5 by volume) at a temperature of $-10 \div -15°$ (molar ratio magnesium/nickel = 0.5). The solution was separated from the precipitate by filtration. The ether was distilled off, and the residue, after dissolution in toluene, was analyzed for Ni, Mg, and Cl content. The yield of bis-(π-crotyl)-nickel was 75–80% of theory. The resulting solutions contained only traces of magnesium and chlorine.

---

* Crotylmagnesium chloride was obtained from crotyl chloride and magnesium in ether (^{2}). The ratio $RMgCl/R_2Mg$ was equal to 6.

Bis-(π-crotyl)-nickel by itself is not an initiator of butadiene polymerization. According to Wilke [3], bis-(π-allyl)-nickel causes cyclic trimerization of butadiene.

Effective catalysts for butadiene polymerization were obtained by adding metal halides to bis-(π-crotyl)-nickel (Table 1).

Table 1

Catalytic systems based on bis-(π-crotyl)-nickel*

Metal halide	Polymerization temperature, °C	Time, h	Polymer yield, %	1,2	trans-1,4	cis-1,4
$NiCl_2$	50	8	78	2	3	95
$NiCl_2$	50	6.5	62	2	5	93
$NiCl_2$	20	48	50	1	4	95
$TiCl_4$	20	15.5	90	2	28	70
$AlCl_3$	20	40		2	12	86
$SnCl_4$	20	40	83	2	6	92

* Amount of butadiene 0.25 mol; concentration of butadiene in solution 2.5 mol/L.

Polymerization was carried out in benzene solution: the ratio between bis-(π-crotyl)-nickel and the metal halides was 2. Nickel chloride was introduced into the system in solid form; the other halides, as benzene solutions.

Catalytic systems based on bis-(π-crotyl)-nickel, irrespective of the nature of the second component, lead to the formation of 1,4-polybutadienes with a predominant content of cis-1,4 units (up to 95%).

Table 2

Catalytic systems based on bis-(π-allyl)-nickel bromide*

$(C_3H_5NiBr)_2$, mmol	Metal halide	Molar ratio $(C_3H_5NiBr)_2$ / metal halide	Polymerization temperature, °C	Time, h	Polymer yield, %	1,2	trans-1,4	cis-1,4
0.26	–	–	50	14	20	3	53	46
0.13	$AlBr_3$	1.0	5	40	46	2	5	93
0.13	$TiCl_4$	1.0	5	17	20	3	5	92
0.13	$TiCl_4$	1.0	30	17	50	3	5	92
0.13	VCl_4	0.5	50	17	17	3	16	82
0.13	$MoCl_5$	1.0	50	17	100	4	6	90
0.20	WCl_6	1.0	5	17	33	2	6	92
0.10	WCl_6	1.0	50	16	72	3	7	90
0.13	$SnCl_4$	1.0	50	17	27	3	9	88
0.13	$VOCl_3$	0.5	50	11	23	3	3	94

* Amount of butadiene 0.25 mol; concentration of butadiene in solution 2.5 mol/L.

The most effective catalysts are formed in the presence of titanium tetrachloride.

The catalytic activity of these systems is associated with exchange reactions between the components of the catalyst, in particular with transfer of the halogen atom to nickel. The validity of this proposition is confirmed by the results obtained when bis-(π-allyl)-nickel halides were used as initiators of butadiene polymerization.

Bis-(π-allyl)-nickel bromide $(C_3H_5NiBr)_2$ and bis-(π-crotyl)-nickel chloride $(C_4H_7NiCl)_2$ were prepared by the method described by Fischer [4], from nickel carbonyl and the corresponding allyl and crotyl halides in benzene solution. After filtration of the solution and distillation of the benzene, the reaction products in some cases were subjected to sublimation in high va-

in vacuo. Special experiments showed that the catalytic activity of the nickel complexes obtained without sublimation is analogous to the activity of the sublimed products.

In contrast to bis-(π-crotyl)-nickel, the bis-(π-allyl)-nickel halides themselves are catalysts for the polymerization of butadiene (Tables 2 and 3).

Table 3

Catalytic systems based on bis-(π-crotyl)-nickel chloride*

$(C_4H_7NiCl)_2$, mmol	Metal halide	Molar ratio $(C_4H_7NiCl)_2$ / metal halide	Polymerization temp., °C	Time, h	Polymer yield, %	Microstructure of polymer, %: 1,2	Microstructure of polymer, %: trans-1,4	Microstructure of polymer, %: cis-1,4
0.3	–	–	30	40	40	1.5	5	93.5
0.3	–	–	50	19	50	2	6	92
0.15	$TiCl_4$	1.0	30	17	100	2	8	90
0.15	$TiCl_4$	0.5	20	1	81	3	5	92
0.15	$SnCl_4$	1.0	30	17	63	2	11	87
0.15	BCl_3	1.0	30	17	38	2	10	88

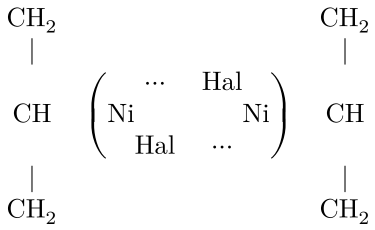
* Amount of butadiene: 0.25 mole; butadiene concentration in solution: 2.5 mol/l.

In the case of bis-(π-allyl)-nickel bromide, polymers are formed that contain approximately equal amounts of cis and trans units and practically no 1,2-units. Bis-(π-crotyl)-nickel chloride has greater activity in the polymerization process and leads to the formation of polybutadiene with a content of cis-1,4 units above 90%.

The addition of metal halides to bis-(π-allyl)-nickel bromide and to bis-(π-crotyl)-nickel chloride causes a marked increase in their catalytic activity; moreover, in the case of bis-(π-allyl)-nickel bromide this increase is accompanied by a change in the stereospecificity of the catalyst action.

The polybutadienes formed contain up to 92% cis-1,4 units. The nature of the metal halide has practically no effect on the structure of the polymer.

The catalytic activity of the systems studied is apparently connected with their complex nature. It is known that π-allylnickel halides exist in solution as dimeric complexes with bridge bonds through halide atoms (^{4}):



In the case of two-component systems, the possibility is not excluded of the formation of complexes of a similar type with the participation of atoms of two different metals.

It is known that catalytic systems involving nickel and cobalt salts and organoaluminum compounds are used for the stereospecific polymerization of butadiene (synthesis of cis-polybutadiene). The results obtained in the present work point to a possible role of π-allyl complexes in these processes.

All-Union Scientific Research Institute
of Synthetic Rubber named after S. V. Lebedev

Institute of Petrochemical Synthesis named after A. V. Topchiev,
Academy of Sciences of the USSR

Received
30 XI 1964

CITED LITERATURE

1. B. D. Babitskii, B. A. Dolgoplosk et al., *Vysokomolek. soed.*, **6**, No. 12 (1964).
2. W. C. Young, M. Eisner, *J. Am. Chem. Soc.*, **63**, 2113 (1941).
3. G. Wilke, *Angew. Chem.*, **75**, No. 1, 10 (1963).
4. E. O. Fischer, G. G. Bürger, *Zs. Naturforsch.*, **16b**, 77 (1961).

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