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## Abstract

## Full Text

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# TRANSITION FROM METAL HYDRIDES TO $\pi$-ALLYL COMPLEXES AND INITIATION OF THE PROCESS OF STEREOSPECIFIC POLYMERIZATION OF BUTADIENE

It is well known that various cobalt and nickel compounds in combination with $R_2AlCl$ are effective catalysts for the polymerization of butadiene with formation of a cis-1,4-polymer. The catalytic nature of the process is illustrated by the fact that a single active center causes the formation of a large number of polymer molecules ([1]). It has recently been shown that $\pi$-allyl complexes of nickel, in particular $\pi$-crotylnickel chloride, are also catalysts for the cis-polymerization of butadiene ([2,3]). $\pi$-Crotylnickel chloride may be regarded as a compound modeling the active end of a growing polymer chain.

In studying the process of polymerization of butadiene under the influence of a cobalt catalytic system, it was established that the molecular weight of the polymer decreases sharply with increasing process temperature ([1]), and that acts of termination of the polymer chain, accompanied by regeneration of active centers, lead to the appearance of conjugated double bonds at the chain end ([4]). Termination of this type may proceed both as a result of chain transfer to monomer and as a result of spontaneous decomposition of the catalytic complex, accompanied by formation of a transition-metal hydride. In the case of polymerization under the influence of nickel crotyl chloride, the latter reaction may be represented as follows:

$$[\text{schematic } \pi\text{-allyl nickel complex}] \xrightarrow[\text{chain termination}]{1} CH_2{=}CH{-}CH{=}CHR + HNiCl \xrightarrow[\text{regeneration of the active center}]{+C_4H_6 \quad 2} [\text{schem}$$

where $R$ is a polymer radical.

The results of the present investigation showed that nickel hydrides initiate the cis-polymerization of butadiene through the stage of formation of $\pi$-crotyl complexes.

The so-called stoichiometric nickel hydrides were obtained by us according to the method described in the literature, by the interaction of an organomagnesium

compound with anhydrous $NiCl_2$ in an atmosphere of hydrogen ([5–7]). It is assumed that this reaction proceeds according to the following scheme:

$$NiCl_2 + RMgX \begin{cases} \longrightarrow RNiCl \xrightarrow{H_2} HNiCl + RH, \\ \longrightarrow R_2Ni \xrightarrow{2H_2} NiH_2 + 2RH. \end{cases}$$

Nickel hydrides may also be formed in the interaction of metallic nickel, arising upon decomposition of an unstable organonickel compound, with hydrogen:

$$R_2Ni \rightarrow R_{-H} + R_{+H} + Ni; \qquad Ni + H_2 \rightarrow NiH_2.$$

The interaction of the nickel hydrides obtained with butadiene should lead to the transfer of nickel into solution as a result of the formation of nickel-crotyl complexes soluble in hydrocarbon solvents:

$$HNiCl + C_4H_6 \rightarrow C_4H_7NiCl;$$

$$NiH_2 + 2C_4H_6 \rightarrow Ni(C_4H_7)_2.$$

We carried out the reaction as follows. Into a "trained" flask equipped with a stirrer we introduced 0.03 mole of anhydrous $NiCl_2$ and 100 ml of absolute diethyl ether, cooled the mixture to 0°, and saturated the ether with purified dry hydrogen. After this, 0.03 mole of ethylmagnesium bromide in ether solution was slowly added from a dropping funnel over 4 hours, with continuous stirring of the mixture and passage of a stream of hydrogen. After separation from the solution of the unreacted ethylmagnesium bromide, the precipitate obtained, containing nickel hydride, unreacted $NiCl_2$, and magnesium salts, caused polymerization of butadiene in benzene to give a polymer in which the amount of cis units was about 90%. When a solution of butadiene in a benzene–ether mixture in a ratio of 1 : 1 was added to the precipitate (the ether was introduced to suppress the polymerization process), the solution immediately acquired the dark-brown coloration characteristic of nickel crotyl derivatives. A measured volume of the solution was decomposed with 20% $H_2SO_4$. The gas evolved was analyzed on a KhL-4 chromatograph, and the nickel content in the aqueous solution was determined trilonometrically (8). In various experiments the amount of nickel that passed into the benzene–ether solution was about 20%, calculated on the reacted ethylmagnesium bromide. The gaseous products evolved during decomposition of the nickel crotyl derivatives consisted of a mixture of butenes with predominance of $\alpha$-butene (up to 70%). The total yield of butenes was more than 1 mole per mole of organonickel compound.

The solution of the nickel-crotyl derivative, after ether had been distilled off from it, caused polymerization of butadiene only after additional introduction

of $NiCl_2$ into the system, which is indirect evidence that the compound obtained is bis-($\pi$-crotyl)nickel. It was shown earlier that $\pi$-crotylnickel chloride initiates cis-polymerization of butadiene in the absence of metal halides (3).

We also carried out stereospecific polymerization of butadiene with formation of cis-1,4 polymer on nickel catalysts used for hydrogenation.* As catalysts we used nickel on kieselguhr (industrial samples) and Raney nickel. Before use, nickel on kieselguhr was activated in a stream of hydrogen at 400° for 1 hour. The results of the experiments are presented in Table 1.

From the data of Table 1 it is evident that the nature of the metal in the Lewis acid does not affect the microstructure of the polymer chain. The polymerization process proceeds with equal efficiency both in benzene solution and in heptane solution.

Taking into account the data presented above on the conversion of nickel hydrides (upon interaction with butadiene) into $\pi$-crotyl derivatives, it may be assumed that analogous reactions develop on the surface of nickel catalysts. Activation of a nickel catalyst by Lewis acids is analogous to the action of the same acids in systems with bis-($\pi$-crotyl)nickel (3).

It is known that in catalytic systems of the Ziegler type molecular hydrogen is a regulator of the length of the polymer chain (10, 11). The essence of this phenomenon apparently consists in the fact that hydrogen reacts at the C—Me bond with formation of a transition-metal hydride, the reaction of which—

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* Similar results were obtained by Japanese researchers (9).

Table 1

Polymerization of butadiene on nickel catalysts in the presence of various additives

Temperature 32-34°; duration 3 h; solvent benzene, heptane*; butadiene concentration in solution 45 vol. %

| No. | Catalyst | Amount of catalyst, g | 2nd component | Amount of 2nd component, mol. % of Ni | Polymer yield, % of the amount of monomer introduced | Polymer yield, g/g catalyst | Unsaturation of polymer, % of theory | 1,4-cis | 1,4-trans | 1,2 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Ni on kieselguhr | 2 | — | — | 49.5 | 1.4 | 95 | 95 | 2.2 | 2.8 |
| 2 | Same | 0.5 | $TiCl_4$ | 5 | 53 | 5.8 | 95 | 94 | 3.5 | 2.5 |
| 3 | » » | 0.5 | $VCl_4$ | 10 | 30 | 3.1 | 97.5 | 95 | 3 | 2 |
| 4 | » » | 0.5 | $AlCl_3$ | 6.6 | 23 | 2.2 | 92 | 95 | 2.5 | 2.5 |
| 5* | » » | 0.5 | — | — | 8.5 | 0.8 | — | — | — | — |
| 6* | » » | 0.5 | $TiCl_4$ | 5 | 45 | 4.9 | — | 95.8 | 2.6 | 1.6 |
| 7** | Ni-Raney | 0.56 | $TiCl_4$ | 5 | 61.5 | 4 | 100 | 94 | 4 | 2 |

* Heptane was used in experiments Nos. 5 and 6.
** Temperature 27°, duration 72 h.

with the monomer leads to regeneration of the active center. In this connection it is interesting to note that soluble Ziegler catalysts of polymerization, in the presence of excess hydrogen, begin to play the role of catalysts for the process of hydrogenation of double bonds ([12]).

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