Kinetic and stereospecific manifestations of a set of active centres in butadiene polymerization under the action of a catalytic system based on $NdCl_3$·3TBP

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The unusual dependence of butadiene conversion and polymer microstructure on the ratio Mg/Nd or Al/Nd during the polymerization of butadiene under the action of $NdCl_3$·3TBP–$AlBu^i_3$–$MgBu(i\text{-}C_8H_{17})$ can be explained by the formation of a set of active centres in the catalytic system.

Lanthanide Ziegler–Natta catalysts allow the synthesis of polydienes with high content of *cis*-1,4-units and other improved properties. Therefore, a great number of studies were devoted to the mechanism of diene polymerization with lanthanide catalytic systems.[1,2]

During the formation of a catalytic system based on $NdCl_3$·3TBP (where TBP is tributylphosphate), the addition of a cocatalyst (for example, an organoaluminium component) leads to the production of a set of compounds such as R_nNdCl_{3-n} and their complexes with organic compounds of non-transition metals, which can be the active centres (ACs) of diene polymerization. It seems reasonable that these ACs differ in both reactivity and stereospecificity. A change of the nature of the cocatalyst should affect the activity and stereospecificity of the catalytic system. This can be traced during diene polymerization under the action of 'mixed' catalytic systems containing a lanthanide component and two cocatalysts based on organic compounds of various non-transition metals, for example, organoaluminium and organomagnesium compounds.

The purpose of this work was to study the activity and stereospecificity of two catalytic systems: (**I**) $NdCl_3$·3TBP–$AlBu^i_3$ doped with $MgBu(i\text{-}C_8H_{17})$, and (**II**) $NdCl_3$·3TBP–$MgBu(i\text{-}C_8H_{17})$ doped with $AlBu^i_3$.†

The butadiene polymerization under the action of catalytic system **I** exhibited unusual extreme dependence of the system efficiency on a ratio of Mg/Nd: the polymer yield decreases with increasing ratio Mg/Nd up to 25, but a further increase of the ratio Mg/Nd leads to a growth in the of polymer yield (Figure 1). Thus, there is a small decrease in the *cis*-1,4-unit content at the expense of growth of *trans*-1,4-unit content of the polymer (Table 1). The increase of contact duration of organomagnesium compounds with $NdCl_3$·3TBP–$AlBu^i_3$ (from 1200 to 3600 s) reduces its activity (a general view of the curve is constant) in the entire range of Mg/Nd ratios. Thus, the *cis*-1,4-unit content of polybutadiene also decreases (Table 1).

Another behaviour was observed during butadiene polymerization in the presence of system **II**. The butadiene conversion slowly grows from 11 to 21% with the ratio Al/Nd (from 0 to 50) in the investigated range of the additives $AlBu^i_3$ (Table 2). Without the additives of $AlBu^i_3$, the $NdCl_3$·3TBP–$MgBu(i\text{-}C_8H_{17})$ catalytic system is *trans*-regulating (~90% *trans*-1,4-units). There is a monotonic increase of the catalytic system activity and a decrease of *trans*-1,4-unit content at the expense of an increase in *cis*-1,4-units with increasing Al/Nd ratio (a ratio of Mg/Nd being constant) (Table 2).

Table 1 Dependence of the polybutadiene microstructure on the ratio Mg/Nd in polymerization under the action of the $NdCl_3$·3TBP–$AlBu^i_3$ with $MgBu(i\text{-}C_8H_{17})$ additives. Al/Nd = 30, $[C_4H_6]$ = 1.77, $[NdCl_3\cdot 3TBP] = 1.2\times10^{-3}$ mol dm^{-3}; τ_{cont} is the time of contact between $MgBu(i\text{-}C_8H_{17})$ and the 'precipitated catalyst'; polymerization time is 3600 s.

Molar ratio Mg/Nd	τ_{cont}/s	Content of units (%)		
		cis-1,4-	*trans*-1,4-	1,2-
5	1200	94.4	4.5	1.1
25	1200	92.7	6.0	1.3
40	1200	90.4	7.8	1.8
40	3600	87.3	10.2	2.5
50	3600	87.2	10.0	2.8
80	3600	78.2	18.0	4.0

A precipitate was formed on mixing $NdCl_3$·3TBP with $AlBu^i_3$. The precipitate ('precipitated catalyst') is active in polymerization (the supernatant is inactive). It can contain compounds like $NdRCl_2$, NdR_2Cl and NdR_3 and their combinations with organoaluminium compounds. It is known that compounds like $NdRCl_2$ and $NdRCl_2$–AlR_3 are *cis*-regulative, and centres like NdR_3 are *trans*-regulative.[1,3] The stereospecificity of the compounds NdR_2Cl and NdR_2Cl–AlR_3 is not established. The content of AC such as NdR_3 in this catalytic system is low, and their contribution to the polymer microstructure can be neglected. The results on the interaction of organoaluminium compounds with $NdCl_3$ supported this assumption.[4] It is most probable that mono- and diisobutylneodimium chlorides are formed during the interaction of $LnHal_3$ (where Hal is a halogen) with AlR_3 (at Al/Nd = 15); the formation of completely alkylated compound $NdBu^i_3$ is improbable.[4]

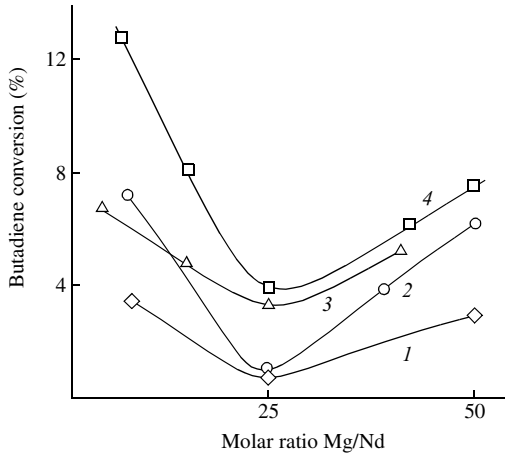

Figure 1 Butadiene conversion as a function of the ratio Mg/Nd during polymerization under the action of the $NdCl_3$·3TBP–$AlBu^i_3$ catalytic system with $MgBu(i\text{-}C_8H_{17})$ additives. Reaction conditions: Al/Nd = 30 mol mol^{-1}, $[C_4H_6]$ = 1.77, $[NdCl_3\cdot 3TBP] = 1.2\times10^{-3}$ mol dm^{-3}; τ_{cont} = (*1*, *2*) 3600 and (*3*, *4*) 1200 s; τ_{pol} = (*1*, *3*) 3600 and (*2*, *4*) 10800 s; 25 °C; toluene.

† Butadiene polymerization was carried out at 25 °C in toluene in glass ampoules in conditions accepted for ionic-coordination catalytic systems. System **I** was prepared by mixing of $NdCl_3$·3TBP with $AlBu^i_3$ (in the ratio Al/Nd = 30), held for 1800 s, centrifuged and washed with toluene. The precipitate named as 'precipitated catalyst' is active in polymerization. Further, the certain portions of $MgBu(i\text{-}C_8H_{17})$ were added to the 'precipitated catalyst', and the mixture was allowed to stand for 1200 or 3600 s at 25 °C. System **II** was prepared by mixing $MgBu(i\text{-}C_8H_{17})$ with a solution of $NdCl_3$·3TBP (the ratio Mg/Nd = 11) and allowed to stand for 10800 s (precipitate was absent). The order of adding components during polymerization was the following: $AlBu^i_3$ was added to a toluene solution of butadiene, and then the mixture of $NdCl_3$·3TBP and $MgBu(i\text{-}C_8H_{17})$ was added to the solution. The microstructure of polybutadiene was studied by IR spectroscopy.

Table 2 Dependence of the conversion and microstructure of polybutadiene on the ratio Al/Nd in polymerization under the action of the $NdCl_3 \cdot 3TBP$–$MgBu(i\text{-}C_8H_{17})$ catalytic system with $AlBu^i_3$ additives. $[C_4H_6] = 1.41$, $[NdCl_3 \cdot 3TBP] = 1.2 \times 10^{-3}$ mol dm^{-3}; polymerization time is 1.72×10^5 s.

Molar ratio Al/Nd	Conversion (%)	Content of units (%)		
		cis-1,4-	*trans*-1,4-	1,2-
0	10.9	0	96.2	3.8
10	11.0	17.7	78.4	3.9
20	11.8	48.9	48.1	3.0
30	13.0	53.1	44.1	2.8
40	14.2	54.3	43.1	2.6
50	21.9	59.5	37.9	2.6

Thus, we may believe that there are AC in the 'precipitated catalyst' formed from compounds like $NdRCl_2$ and NdR_2Cl and also their possible complexes with organic compounds of non-transition metals (AlR_3, $AlClR_2$, $AlCl_2R$ and $AlCl_3$). These AC can undergo association (through chlorine or mixed bridges); therefore, an amorphous catalytic deposit occurs. The AC of the 'precipitated catalyst' are *cis*-regulating because polybutadiene formed in this case contains up to 97% *cis*-1,4-units.

The following processes are possible in the preparation of catalytic system **I**, when $MgBu(i\text{-}C_8H_{17})$, which is a stronger alkylating agent than $AlBu^i_3$,[4] is added to $NdCl_3 \cdot 3TBP$–$AlBu^i_3$. First, there is further alkylation of already existing *cis*-regulating centres (with transforming $NdRCl_2$ and NdR_2Cl to compounds such as NdR_3) to increase the content of *trans*-1,4-units. Thus (because the reactivity of the *trans*-regulating centres is lower than that of the *cis*-regulating centers[3]), the general (total) activity of the system decreases. Second, there is the alkylation of non-alkylated $NdCl_3$ molecules. Because they are associated through chlorine bridges, it is believed that the alkylation reaction will occur not so effectively and quickly (as in case of individual $NdCl_3$ molecules) but in a slowed-up way. In the beginning, new *cis*-regulating AC should occur, which further become *trans*-regulating AC with deeper alkylation. The occurence of *cis*-regulating AC promotes an increase in the total activity of the system; however, their transition to *trans*-regulating centres causes a decrease in the total activity of the catalytic system. Note that in a three-component system (as district from the initial binary system), the deposit can contain compounds such as $NdRCl_2$, NdR_2Cl, NdR_3 and their complexes with not only organoaluminium but also organomagnesium compounds. It is impossible to exclude that AC distinguishing by the nature of non-transition metals (for example, $NdRCl_2$–AlR_3 and $NdRCl_2$–$MgRR'$) can differ in the reactivity.

The rate of formation of new *cis*-regulating centres and of transition of (both new and already existing) *cis*-regulating centres to *trans*-regulating centres depends on the concentration of $MgRR'$ (Mg/Nd ratio). As a result of these processes, the concentrations of *cis*- and *trans*-regulating centres (and also their total concentration) can be complicatedly related to the ratio Mg/Nd. Note that it is impossible to take into account the existence of only two types of the centres (*cis*- and *trans*-regulating) in an analysis of this phenomenon. It follows from the above results and published kinetic data on the AC in lanthanide catalytic systems[5,6] that four to six types of AC occur in two-component *cis*-regulating lanthanide–aluminium catalytic systems, which differ in both the kinetic activity and the stereospecificity of action (in general, multi-central distribution of Ziegler catalytic systems becomes a matter of common knowledge). The number of AC types can be even more in case of the use of three-component systems. Generally, the total rate of polymerization (W) is expressed by the equation

$$W = (\sum k_i^{cis} C_i^{cis} + \sum k_i^{trans} C_i^{trans}) C_M,$$

where k_i^{cis}, k_i^{trans} are the reaction rate constants of formation of *cis*- (*trans*-) units on ith (jth) AC, respectively; C_i^{cis}, C_i^{trans} are the concentrations of *cis*- (*trans*-) regulating AC, respectively; C_M is the monomer concentration.

In this connection, resulting curves for the total activity and the concentrations of different units in polybutadiene as functions of ratio between components of the catalytic system can have complex shapes (*e.g.*, see Figure 1). Nevertheless, the activity of the system should be lowered at any Mg/Nd ratios with time, and the content of *trans*-units should increase; this was observed experimentally (Table 1). The validity of this hypothesis was also supported by the fact that an increase of a ratio of Mg/Nd up to 80 and contact time up to 1.72×10^5 s (with intense stirring of the 'precipitated catalyst') leads to a decrease of the *cis*-1,4-unit content in polymer from 94 to 78% and to an increase of *trans*-unit content from 4 to 18% (Table 1).

During the preparation of system **II**, when $MgBu(i\text{-}C_8H_{17})$ was added to $NdCl_3 \cdot 3TBP$, the alkylation reaction resulted in the formation of completely alkylated forms such as NdR_3. The identity of the polybutadiene microstructure, formed under the action of $NdCl_3 \cdot 3TBP$–$MgBu(i\text{-}C_8H_{17})$ with the microstructure of polymers formed under the action of LnR_3 also supported this assumption.[1] Moreover, the examples of the complete replacement of chloride ions with hydrocarbon radicals in reactions of *f*-element chlorides with organomagnesium compounds are well known.[7,8] The addition of triisobutylaluminium to the $NdCl_3 \cdot 3TBP$–$MgBu(i\text{-}C_8H_{17})$ system resulted in 'dilution' of the strong alkylating agent $MgBu(i\text{-}C_8H_{17})$ by weaker $AlBu^i_3$. Because the catalytic system $NdCl_3 \cdot 3TBP$–$MgBu(i\text{-}C_8H_{17})$ is homogeneous an equilibrium is established in the course of exchange reactions of alkylating and re-alkylating between components of solution. As a result, the occurence of less alkylated forms of active centres such as $NdRCl_2$, NdR_2Cl and their complexes with AlR_3 and $MgRR'$ is possible in the system. Because chlorine atoms occur at centres such as $NdRCl_2$ and NdR_2Cl, it is possible to assume that they are *cis*-regulating. Thus, it is possible to expect that the activity of catalytic system **II** should increase with the Al/Nd ratio, and the concentration of *cis*-1,4-units in the formed polybutadiene should increase at the expense of a decrease in the fraction of *trans*-1,4-units, as this was observed in experiments (Table 2).

Thus, during butadiene polymerization under the action of a lanthanide catalytic system, a set of various AC different in the reactivity and stereospecificity of action is formed. The concentration and contribution of each of these centres to the microstructure of formed polymers depends on the nature and concentration of alkylating agent, which is an organic compound of a non-transition metal.

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