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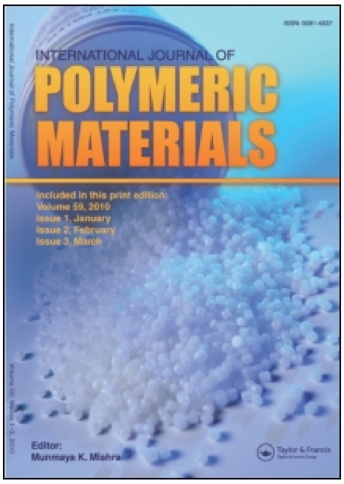

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Basic Stages of Microstructures Formation in Polydienes Upon Lanthanide Catalytic Systems*

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This review systematizes the studies on the various aspects of the stereoregulation mechanism in diene polymerization by the lanthanide catalytic systems. Quantum-chemical investigations of electronic and geometric structure of active centers and their complexes with monomers, and the analysis of the structural-kinetic scheme of propagation reaction were examined more thoroughly.

Keywords: Lanthanide catalytic systems; Active center of polymerization; Mechanism of stereoregulation; Microstructure of polydiene

INTRODUCTION

The main distinctive feature of lanthanide catalysts among other Ziegler–Natta catalysts is that they allow one to synthesize polydienes with a high content of *cis*-1,4-units. In most cases, lanthanides are used in the form of blends and concentrates. About 50% of the lanthanides consumed worldwide, are used for the production of catalysts for various chemical processes. The number of these processes may be increased by use of lanthanide catalysts in the manufacture of synthetic rubbers. A great number of studies are devoted to

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polymerization of dienes with lanthanide catalytic systems. Many of these studies are concerned with problems related to the mechanism that controls the microstructure of polydienes. Although not all aspects of stereoregulation have been clarified, many problems were solved and possible explanations were offered for others [1–4].

The objective of this work was to review the basic results of research of diene (butadiene, isoprene, and piperylene) polymerization with the $\mathrm{LnHal_3} \cdot n\mathrm{L}\text{-}\mathrm{Al}R_3$ (Ln = lanthanide, Hal = halogen, L = tributylphosphate, $\mathrm{Al}R_3$ = triisobutylaluminum and diisobutylaluminum hydride) catalytic system and to analyze the role of such factors as the electronic and geometric structure of bimetallic active centers, *anti-syn* and $\pi-\sigma$-transitions of the terminal units of the growing polymer chains, and the nature of the lanthanide, diene, and organoaluminum components in the mechanism of stereoregulation.

PRINCIPAL GROUPS OF LANTHANIDE-BASED CATALYSTS

Thus far, the attention of researchers has mainly been focused on the family of ion-coordination lanthanide catalysts, by which *cis*-polydienes may be synthesized. These catalysts can be classified into several groups [3]: Catalytic systems of the type $\mathrm{LnHal_3} \cdot n\mathrm{L}\text{-}\mathrm{Al}R_3$ ($n \leq 3$) make up group **I**. The initial compound of the lanthanide can be obtained by reacting its halide with the corresponding organic base [5]. The research is usually carried out with complexes containing various electron donor ligands L, such as alcohols [6, 7], cyclic ethers [8], aliphatic esters of orthophosphoric acid [9–15], aliphatic, and cyclic sulfoxides [12, 14, 16]. Catalysts in which the initial lanthanide component $\mathrm{Ln}X_3$ does not contain a halogen make up group **II**. The catalysts of this type include octanoates [17, 18], stearates [19–23], naphthenates [13, 18], acetylacetonates of trivalent lanthanides [19], and salts of di-2-ethylhexyl phosphoric acid [19, 20, 23]. In addition to $\mathrm{Ln}X_3$ and $\mathrm{Al}R_3$, these catalytic systems must include halogen-containing components (one of the most frequently used compounds is $\mathrm{Al}R_2\mathrm{Cl}$), the role of which is to halogenate the lanthanide by exchange reactions. Catalysts in which the initial halogen-containing compound of lanthanide has the Ln—C bond form group **III**.

Cis-polymerization of dienes can be catalyzed , for example, by the system $R'\mathrm{LnHal_2}\cdot n\mathrm{THF}\text{-}\mathrm{Al}R_3$ [24–28]. The synthesis of lanthanide compounds of this type is usually performed in tetrahydrofurane by conducting the reaction of the oxidative addition of R'Hal (triphenylmethyl chloride, benzyl chloride, phenyl bromide, allyl iodide) to zero-valent lanthanides [24, 25, 27, 29]. Chloride of oligoisoprene neodymium, which is not bound *via* solvation bonds to tetrahydrofuran (THF/Nd < 3), catalyzes *cis*-polymerization of dienes even when no organoaluminum cocatalyst is present [30].

The use of the catalysts based on individual compounds of lanthanides of various structures may help to elucidate the nature of active centers. This explains the interest in the problems of synthesis and conversions of these compounds [31–40].

FACTORS AFFECTING THE ACTIVITY AND STEREOSPECIFICITY OF CATALYSTS

Chemical Nature of Lanthanide

The activity of lanthanide-based coordination catalysts is strongly influenced by the chemical nature of the lanthanide component. Depending on the conditions of polymerization, the relative activities of lanthanides can vary slightly. In all cases, however, with regard to the rates of polymerization of dienes, lanthanides form the following series: La < Ce < Pr < Nd > Gd > Tb > Dy > Ho > Er [11, 14]. In the reaction of polymerization of butadiene, the propagation rate constant changes as follows: for La – 10, for Ce – 40, for Nd – 140, for Gd – 130 and for Dy – 30 l/(mol min) [41]. A similar behaviour is observed for *cis*-polymerization of isoprene [18] and piperylene [42]. Although the propagation rate constant depends on the chemical nature of lanthanide, in the case of polymerization of butadiene, the degree of stereospecificity is approximately the same for all most active catalysts [41]. For polymerization of isoprene, the content of 3,4-units in the *cis*-polymer decreases with a rise in the atomic number of the lanthanide (from 2.5 to 1%), whereas *trans*-1,4-units are not formed at all. The reaction of the addition of *cis*-1,4-units in polymerization of isoprene can occur *via* three different mechanisms. The data of ^{13}C NMR indicate that only one of these mechanisms, namely, "head-to-head" addition, is realized. This conclusion is also corroborated by the results of ozonolysis [43]. Thus, lanthanides catalysts can be used to synthesize polyisoprene with molecules almost identical to those of natural rubber. In the case of polymerization of *trans*-isomer of piperylene, the microstructure of the polymer formed strongly depends on the nature of the lanthanide used as a catalysts [11].

It was found that for the lanthanides of the Ce subgroup, the content of *cis*-1,4-units in polypiperylene increases with increasing atomic number. In contrast, in the Y subgroup, the number of *cis*-1,4-units decreases with a decreasing atomic number. The most stereoregular polypiperylene is formed when the polymerization occurs on a gadolinium catalyst. For a neodymium catalyst, the polypiperylene chain consists 1,4- and 1,2-units. At the same time, a spectroscopic examination of polypiperylene synthesized on a neodymium catalyst gave no evidence of 3,4-units. The ozonolysis data show that 1,4-units in this polydiene form "head-to-tail" sequences [22].

The Nature of the Ligand

It is known that the microstructure of polybutadiene synthesized with the use of catalytic systems on the basis of halides of elements with *d*-electron orbitals depends strongly on the nature of the halogen. A special feature of catalysts on the basis of *f*-elements (lanthanides, uranium) is that they do not exhibit this dependence [44, 45]. Nevertheless, the effect of the chemical nature of the halogen on the reactivity of active centers was observed for lanthanide-based catalysts. In the case of butadiene polymerization, this was confirmed by the results of measurements of reaction rate constants [14]. For other types of polydienes, the influence of the nature of halogen can be seen from the microstructure of the polymers formed. In the series of catalysts containing chlorine, bromine, and iodine, the content of *cis*-1,4-units in polyisoprene slightly decreases, and the content of 3,4-units, correspondingly, increases [14]. The effect of nature of the halogen is the strongest in the polymerization of piperylene [11].

Varying the ligand L in the initial component $LnHal_3 \cdot 3L$ does not change the microstructure of the polybutadiene formed [14]. Nevertheless, the analysis of propagation rate constants shows that active centers are different in catalytic systems based on tributyl phosphate and diamyl sulfoxide complexes of the same halide of lanthanide [14].

The correlation between the nature of the halogen and its presence in the catalyst, and the functioning of the active centers of the latter is very complicated and depends mainly on the nature of the ligands attached to the lanthanide. Polymerization catalyzed by compounds containing Ln—Hal bonds yields polydienes with a high content of *cis*-units. It was even thought that in the absence of such bonds, lanthanide catalysts are not stereospecific.

Systems based on polynuclear complexes $[(C_6F_5)_3GeI_7M_2]Ln$ 3L-$Al(i\text{-}C_4H_9)_3$, where M is either mercury or cadmium and Ln is either praseodium or neodymium (in the trivalent state), are catalytically active in the polymerization of dienes [46]. For instance, at 25°C, these systems catalyze a formation of polybutadiene with up to 90% of *cis*-1,4-units. The products of ball-milling of lanthanide metals in aromatic hydrocarbons include active intermediates of carbene type [=CH—CH—CH=CH —CH —Ln —] and initiate *cis*-1,4-polymerization of butadiene and isoprene. It is assumed that the role of the electron acceptor ligand is played by the bulk of the metal or by its complex with a polyconjugated (polyacetylene) fragment. The latter is formed as a result of polymerization of the solvent [40].

Polybutadiene and polyisoprene with 76–95% of *cis*-1,4-units can be obtained by using a combination of triisobutylaluminum with alcoholate or carboxylate of lanthanide chemically bonded to finely divided silica gel, on the surface of which compounds like $[SiO_2]—O—Nd(OR)_2$ are formed [47].

When the lanthanide has no electron acceptor groups, the polymerization yields *trans*-polydienes. For instance, systems including alcoholate or carboxylate of lanthanide in combination with triisobutylaluminum have low activity, and give macromolecules with the content of *trans*-1,4-units up to 85% [48]. Organometallic derivatives of LnR_3 type catalyze *trans*-polymerization of dienes [30, 33, 36].

When butadiene and isoprene are polymerized on halogen-free ion-coordination catalytic systems on the basis of compounds of *d*-elements, polymers are obtained which contain 1,2- and 3,4-units, respectively. Lanthanide-based catalysts ensure "head-to-tail" addition of monomers, *i.e.*, formation of 1,4-units, even when the catalyst contains no halogen. These catalysts are characterized by high stereospecificity and, depending on the types of ligands bonded to the central atom, direct the polymerization reaction so that the resulting polymer contains a majority of either *cis*-1,4 or *trans*-1,4-units. The only known case of when a lanthanide-based catalysts gave polybutadiene and polyisoprene macromolecules, which contained a mixture of *cis*- and *trans*-sequences and a considerable amount of 1,2- and 3,4-units, was that of phenylcarbin neodymium [31, 33].

The Structure of the Organometallic Component of Lanthanide Catalysts

The polymerization of dienes occurs when the lanthanide catalyst contains an organometallic component (usually, trialkylaluminum or dialkylaluminum hydride). $LnHal_3 \cdot nL\text{-}AlR_2Hal$ systems do not show catalytic activity. Moreover, dialkylaluminum halide acts as catalytic poison when added to $LnHal_3 \cdot nL\text{-}AlR_3$ systems [49]. A similar effect was observed when the content of dialkylaluminum halide in catalysts of the second group exceeded a certain optimum value [19].

The rate of polymerization of dienes at 25°C strongly depends on the structure of the organoaluminum component of the catalyst. Increasing the polymerization temperature results in a levelling of the activities of such systems [14]. In addition, at a polymerization temperature of 25°C, the yield of polyisoprene on the catalysts of the type $LnCl_3 \cdot 3TBP\text{-}AlR_3$, where Ln is Pr or Nd, decreases in the series $Al(n\text{-}C_{10}H_{21})_3 > Al(n\text{-}C_6H_{13})_3 > Al(C_2H_5)_3$. Raising the temperature to 80°C reverses the order in this series. This may be explained by the decomposition of associates at a higher temperature. The result of this decomposition is that the cocatalytic activity of AlR_3 becomes consistent with its reactivity. Increasing the polymerization temperature removes the anomaly in the dependence of the yield of polydienes *versus* the Al : Nd ratio. This anomaly is observed when the polymerization is performed with organoaluminum cocatalysts that are able to form associates [49]. These facts show that only the monomeric form of AlR_3 can form active centers. The number of active centers in neodymium catalysts containing higher alkyls (6–8 carbons in the radical R) is about half that in catalysts with triisobutylaluminum [41, 50]. It was somewhat unexpected that the propagation rate constant depended on the nature of AlR_3 for both butadiene and isoprene [18, 50].

That the reactivity of lanthanide active centers depends on the nature of AlR_3 follows also from the microstructure of polydienes. Varying AlR_3 component results in changes in the relative number of *cis*- 1,4 and *trans*-1,4-units in polybutadiene. At the same time, the content of 1,2-units remains the same (about 0.6% at 25°C). The only exception is a catalyst with diisobutylaluminum hydride, in which case, approximately a threefold increase in the content of 1,2-units is observed. As the concentration of butadiene decreases ($<0.5\%$ mol/l) and the polymerization temperature increases (from 25 to 80°C) the dependence of the number of *cis*- 1,4-units in the polymer on the structure of AlR_3 becomes more pronounced [10].

When an organomagnesium compound $i\text{-}C_8H_{17}MgC_4H_9$ was used instead of the organoaluminum compound (triisobutylaluminum), all other conditions being the same, the activity of the catalyst markedly decreases [51].

To achieve reasonable conversions, the polymerization with catalyst $NdCl_33TBP\text{-}i\text{-}C_8H_{17}MgC_4H_9$ was conducted for several days the (compound $i\text{-}C_8H_{17}MgC_4H_9$ is catalytically inactive under these conditions). For this catalyst, the yield of the polymer depends on the ratio between the starting components with a sharply pronounced maximum at $Mg/Nd = 12 \div 13$, which is not characteristic of the lanthanide systems.

The fact that the replacement of trialkylaluminum by dialkylmagnesium in the *cis*-regulating halide-containing catalyst $NdCl_3 \cdot 3TBP\text{-}AlR_3$ leads to the inversion of the stereo specificity was also unexpected. At $Mg/Nd = 12 \div 13$, a highly stereoregular *trans*-polybutadiene is formed. This polymer contains 95% of *trans*-1,4-units and 5% of 1,2-units at a maximum activity of the catalyst $NdCl_3 \cdot 3TBP\text{-}i\text{-}C_8H_{17}MgC_4H_9$. As the Mg/Nd ratio increases and goes beyond the above range, not only does the yield of polydiene drop but its microstructure also changes: the share of 1,2-units increases and, when toluene is used as a solvent, *cis*- 1,4-units appear in the polymer. Therefore, polybutadiene of mixed structure is formed at $Mg/Nd = 60$ in this solvent (the amounts of *cis*- 1,4-, *trans*-1,4-and 1,2-units are 47, 44 and 9%, respectively).

Although the inversion of stereospecificity of the ion-coordination system under the action of the organometallic compound is not quite common, nevertheless, in our opinion, it is consistent with the regularities conventional for the lanthanide systems. The *trans*-regulating effect of the halide-containing system is apparently associated with the formation of a catalytically active halide-free alkyl derivative of neodymium of LnR_3 type by the reaction between the starting components of the catalyst because it is known that $RLnCl_2$ initiates the *cis*-polymerization of dienes, whereas R_2LnCl is catalytically inactive [28]. Complete replacement of chloride ions by hydrocarbon radicals in the reaction of *f*-metal chloride with organomagnesium compound was reported in the literature [52, 53]. This assumption is also supported by the fact that the microstructures of polybutadienes formed with the LnR_3 [30, 33, 36] and $NdCl_3 \cdot 3TBP\text{-}i\text{-}C_8H_{17}MgC_4H_9$ catalysts are similar.

The Nature of the Solvent

In all cases, the process rate is higher in aliphatic than in aromatic hydrocarbons. The data for *n*-heptane and toluene show that in these solvents, the propagation rates are different (Tab. I). A similar effect was observed earlier [28] for polymerization of isoprene in *n*-hexane [$K_p = 730$ l/(mol min)] and in toluene [$K_p = 240$ l/(mol min)] at 25°C on the catalytic system $(C_6H_5)_3CNdCl_2$ THF-$Al(i\text{-}C_4H_9)_3$. The reduction in the propagation rate constant under the effect of aromatic hydrocarbon is due to hydrocarbon and diene monomer competing for coordination at the active center. The effect of slowing down

TABLE I Polymerization of dienes in toluene and heptane at 25°C in the presence of the catalytic system $NdCl_3 \cdot 3TBP\text{-}Al(i\text{-}C_4H_9)_3^3$

Monomer	*Solvent*	*Cis*-1,4-*units*(%)	K_p, *l*/(*mol min*)	C^*_{ac} * (%)
Butadiene	Toluene	95	140	7
	Heptane	95	470	6
Isoprene	Toluene	95	80	9
	Heptane	95	120	8
Piperylene	Toluene	64	14	9
	Heptane	78	70	6

* C^*_{ac} – concentration of active centers.

the polymerization reaction is due to the fact that the aromatic hydrocarbon forms an arene complex with the lanthanide atom. The higher the π-electron-donating ability of the aromatic hydrocarbon, the lower the rate constant for polydiene chain propagation . Thus, the rate of polymerization of dienes decreases in the series benzene > toluene > xylene [11, 14, 26, 28].

THE STRUCTURE OF ACTIVE CENTERS AND MECHANISM OF STEREOREGULATION IN THE POLYMERIZATION OF BUTADIENE

The main parameters of diene polymerization with lanthanide-based catalytic systems are similar to those of polymerization with ion-coordinated catalysts on the basis of *d*-metals. This can be seen from the following facts: polymerization of dienes has an anionic coordinated character [18]: at polymerization temperatures from 20 to 25°C, the reaction is of first order with respect to the monomer and catalyst (this property is independent of the natures of catalyst and hydrocarbon solvent, the only exception to this rule being the system considered in reference [18]) for most of catalysts studied [18, 21, 26, 28, 41] and, the apparent activation energy of the polymerization reaction of dienes is of the order of 33.5 kJ/mol [20, 41]. For lanthanide catalysts, the concentration of active centers is somewhat higher than for conventional Ziegler–Natta catalysts, *e.g.*, for neodimium-based catalysts their content varies from 6–10% [12, 41, 42, 50] to 15–20% [55, 57].

It is generally accepted that, in the polymerization of dienes on lanthanide catalysts, the growing chain is attached to the transition metal by π-allyl bond and that the chain growth occurs by incorporation of the monomer *via* the metal-carbon σ-bond. In the case of neodymium catalysts, the delocalized π-allyl type structure of the terminal unit has been observed by spectroscopic methods [8, 26, 28, 58–60]. The results reported in these works show that the relative contents of *cis*-1 4 and *trans*-1,4-units in polydienes depend on the type of solvent used, the polymerization temperature, structure of diene monomer, and the composition of lanthanide-based catalysts. These data can be interpreted in terms of the concept of isomerization equilibrium between *anti-* and *syn-* forms of π-allyl terminal unit. One of the arguments in favor of the existence of this of isomerization equilibrium is that the content of *cis-* 1,4-units in polydienes decreases concomitantly with an increase in the content of *trans*-1,4-units when the concentration of the monomer is reduced [10, 28, 54, 61 – 64]. More detailed information on the structure of the initial, terminal-, and penultimate unit of polydiene chains, and, correspondingly, information on the mechanism of the formation of chains, can be derived from the results of investigations of polymer structure by NMR. Works in this field are, however, not very numerous [65].

With regard to the operation of lanthanide catalytical systems, one of the most important questions is that of the nature of the bond responsible for the growth of the polymer chain. Both the traditional Ziegler – Natta catalysts and lanthanide catalysts contain bridge bonds (of either chlorine, alkyl, or hydride type) between the metal atoms [64 – 69]. In view of this, it is usually assumed that the addition of molecules to the growing polymer chain occurs either *via* the metal-carbon σ-bonds (monometallic model of active center) or *via* the bridge bond (bimetallic model of active center). In the second model, the question arises as to whether the organoaluminum fragment constitutes a part of the active center or not. Direct experimental investigation of the structure of active sites is extremely difficult. Therefore, attempts have been made to analyze it indirectly. To this end, the effect of the structure of active centers on the kinetics of the corresponding reactions was investigated [70 – 72]. For the polymerization of butadiene with $NdCl_3 \cdot 3TBP\text{-}AlR_3$ catalytic system, the reactivity of active centers and the dependence of the reactivity on the mechanism of introduction of AlR_3 were studied [70] using "precipitated" catalyst (precipitate of catalytic system multiple-wash with purified toluene). It was found that the reactivity K_p and the stereoregulating properties of active centers in the system $NdCl_3 \cdot 3TBP\text{-}AlR_3$ vary as the structure of AlR_3 is changed. The reactivity of these centers is similar to the reactivity of active centers initially prepared in the presence of the organoaluminum compound, which is added to the "precipitated" catalyst (Tab. II). This result (in combination with the data on the effect of the structure component of the catalyst on the microstructure of polydienes and the asymmetry of active centers and reactivity ratios [16, 18, 50]) suggests that the

TABLE II Reactivity of active centers and microstructure of polymer in butadiene polymerization with the precipitated catalyst with AlR'_3 additives (starting system, $NdCl_3 \cdot 3TBP$-butadiene-AlR_3; $[NdCl_3 \cdot 3TBP] = 1 \times 10^{-3}$, $[AlR'_3] = 1.5 \times 10^{-2}$, [butadiene] = 1.5 mol/l, toluene, 25°C

Starting catalytic system	*Additional* AlR'_3	K_p, *l/(mol min)*	*Cis*-1,4- (%)	*Trans*-1,4- (%)	1,2- (%)
starting $NdCl_3 \cdot 3$ TBP-butadiene-$Al(i\text{-}C_4H_9)_3$	–	220	94.3	5.1	0.6
	$Al(i\text{-}C_4H_9)_3$	210	94.5	4.8	0.7
precipitated $NdCl_3 \cdot 3TBP\text{-}Al(i\text{-}C_4H_9)_3$	$Al(i\text{-}C_4H_9)_2H$	45	93.5	4.8	1.7
starting $NdCl_3 \cdot 3TBP$-butadiene-$Al(i\text{-}C_4H_9)_2H$	–	50	93.4	4.8	1.8
	$Al(i\text{-}C_4H_9)_3$	200	94.3	4.9	0.8
precipitated $NdCl_3 \cdot 3TBP\text{-}Al(i\text{-}C_4H_9)_2H$	$Al(i\text{-}C_4H_9)_2H$	50	93.5	5.0	1.5

organoaluminum compounds constitutes a part of lanthanide active center and that, in the catalytic system, there occurs an exchange reaction, which results in the substitution of the initial organoaluminum fragment (ligand) of the active center by a new one.

The assumption about the bimetallic bridge structure of lanthanide catalytic systems was made in many works [66–69]. Nevertheless, the possibility must not be ruled out that the active centers contain both types of bonds (π-allyl and σ-bridge). It is important that these bonds may differ dramatically in reactivities. In order to answer the question concerning the possible coexistence of two types of bonds, the polymerization of butadiene on catalytic systems $NdCl_3 \cdot 3L\text{-}AlR_3$ (where R is $i\text{-}C_4H_9$; Ln is Nd or Tb; L is tributyl phosphate) prepared in the presence of a small amount of butadiene and piperylene [71, 72] was investigated (Tab. III). It was shown that the initial reactivity of active centers in $LnCl_3 \cdot 3L$-butadiene-AlR_3 (System 1) and in $LnCl_3 \cdot 3L$-piperylene-AlR_3 (System 2) in polymerization of butadiene is different. Addition prior to polymerization of a small amount of butadiene ([diene] : [neodymium] = 10) to system 2 and of the same amount of piperylene to System 1, and aging the system for certain time, results in that the systems "forget", as the residence time increases, what dienes were present during the preparation (formation) period. The reactivities of active centers of the two systems interchange (Tab. IV). These changes in the reactivities can be due to the fact that active centers have bimetallic structure and include two metal-carbon bond, Ln—C (π-allyl) and Ln—CAl (σ-bridge), *via* which the reaction of insertion of the monomer into the chain occur.

TABLE III Dependence of K_p in butadiene polymerization on the time of aging of catalytic Systems 3 and 4 (that is, after adding the second portion of diene)

Time of aging catalyst t, min	K_p, *l/(mol min), System* 3	K_p, *l/(mol min), System* 4
*	330(1)	220(2)
12	290	240
30	230	
90		260
120	230	
180		280
240	220	
360	220	
1440	220	300

System 1: $NdCl_3 \cdot 3L$-piperylene-AlR_3; System 2: $NdCl_3 \cdot 3L$-butadiene-AlR_3; System 3: System 1 + butadiene; System 4: System 2 + piperylene; [Al]/[Nd] = 30; [Nd] = 2, t_{prep} = 120 min, $AlR_3 = Al(i\text{-}C_4H_9)_3$, toluene, 25°C.

*The values of rate constants for the starting Systems 1 and 2.

TABLE IV Electron bond populations in model complexes *cis*-C_4H_7-*syn*-$C_4H_7NdCl_2$-$Al(CH_3)_3 + C_4H_6$

Complex on figure	*Electron bond populations*					
	$Nd—C_1$	$Nd—C_2$	$Nd—C_3$	$Nd—C_4$	$Nd—C_\alpha$	$C_\alpha—C_4$
1c	0.011	0.014	0.007	0.0	0.286	0.0
1d	0.043	0.047	0.030	0.008	0.096	0.235
1f	0.104	0.108	0.101	0.0	0.0	0.846

These bonds differ greatly in reactivity. The experimentally observed dependence of the reactivity of active centers of catalytic systems on the residence time can be explained by two reasons: (1) slow rate of chain growth in the case when the propagation occurs *via* the least reactive bond, and (2) equilibrium reaction (*e.g.*, migration of organoaluminum fragment in the active center) resulting in the bridge bond (Ln—Al—C) between the endgroup and the lanthanide conversion to π-allyl bond and *vice versa* [71, 72].

We also note that some individual organometallic (or hydride) compounds of the type $RLnCl_2$ lead to the formation of *cis*-polydienes even when the organoaluminum component is absent. However, these catalysts are much less active than $LnCl_3 \cdot nL\text{-}AlR_3$ [30, 38]. Complexes of these compounds with THF do not catalyze the polymerization of dienes. At the same time, the addition of AlR_3 gives an effective catalyst [24–28]. As evidenced by IR spectra, the addition of

$Al(i\text{-}C_4H_9)_3$ to $(C_6H_5)_3CNdCl_2$ THF (Al : Nd = 3–5) results in that molecules of THF migrate from neodymium to the coordination sphere of aluminum atom [26–28]. In the reaction between $LnCl_3 \cdot nL$ and AlR_3, alkylation of lanthanide should occur prior to the shift of the ligand coordination bond from L to AlR_3, otherwise alkylation would be prohibited. It is of interest that compounds of the type R_2LnCl do not exhibit catalytic activity. This property remains whether AlR_3 is present or not [24, 26, 28].

Active centers of lanthanide catalyst probably differ in reactivity. This conclusion was made on the basis that polydienes obtained with lanthanide catalysts have a broad molecular mass distribution [50, 55], the polydispersity index being on the order of three even when the reactions of chain termination and transfer do not occur [57].

Quantum-chemical calculations of the electronic structure of mod el active centers and analysis of their geometry was presented in references [70, 73–77]. It was established that *anti*-conformation of the model centers is less favorable (from the point of view of the total electron energy) than *syn*-conformation. The total energy of centers with σ-bonds is smaller than the total energy of centers with π-bonds. The fact that a particular isomeric form of the active center exerts little influence on the electron density on the $Ln—C_\alpha$ bond (it is *via* this bond that the growth of polymer chain occurs) suggests that the reactivities of different isomeric forms of the active centers are about the same. In the lanthanide series, the variation of the electronic structures of active centers is very small.

The calculation of the structure of complexes formed by active center with monomer showed that, for all lanthanides, the complexes which include *cisoid* conformers of dienes are energetically more favorable. In the lanthanide series, the preference for complexes with *cisoid* conformers with respect to similar complexes with *transoid* conformers (we measure the preference in terms of the difference in the total energy of formation of the corresponding complexes) changes from 4 to 7 kJ/mol. This means that, for *cisoid* conformers, the energy of complexation is from 19 to 23 kJ/mol larger than for *transoid* conformers.

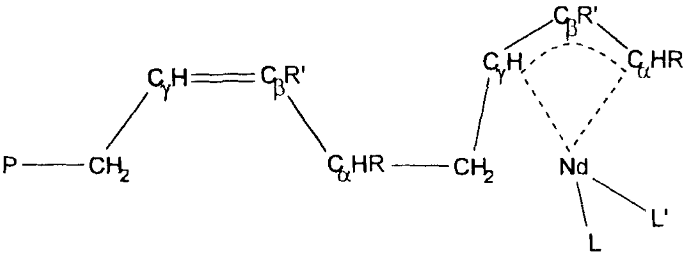
The results of quantum-chemical calculations also show that isomerization transitions of active centers, *anti*-conformation-*syn*-conformation, are possible, in principle [73–77].

If the insertion reaction occurs only in the σ-type complexes (*i.e.*, only by the metal-carbon σ-bond), one should take into account the lifetime τ of those σ-form of the active center that allow insertion of the monomer. This time, which is determined by the kinetics of the processes occurring in the complex, should be compared to the characteristic time τ_1 of the elementary act of insertion. The role of the $\pi-\sigma$ rearrangment in the mechanism of stereoregulation has been investigated [78, 79]. It was established that in cases where the terminal unit of the growing polymer chain has the form of a stable π-allylic structure (*i.e.*, when the time spent by the terminal unit in σ-form is much shorter than the characteristic time of the elementary act of insertion), only the cisoid conformer of butadiene molecule can convert the terminal unit from π- to σ-form and then insert into the metal-carbon σ-bond. During the insertion, the active center remains in the σ-form. This result does not depend on the overall geometry of the active center (*i.e.*, whether it is octahedral, tetrahedral *etc.*) and is explained exclusively by the presence of a stable, long life π-allyl terminal unit. It has been assumed that it is the latter factor, *i.e.*, the presence of a long life π-terminal unit, that explains the fact that in some cases polydienes are formed with an exceptionally high content of *cis*-units [70, 79].

ROLE OF THE STRUCTURE OF DIENE IN THE MECHANISM OF REGIO- AND STEREOSELECTIVITY

The objective of this part of work was to study the role of the diene (butadiene, isoprene and piperylene) structure in the mechanism of regio- and stereoselectivity in polymerization with the lanthanide catalytic system $NdCl_3 \cdot 3TBP\text{-}Al(i\text{-}C_4H_9)_3$. To this end, we performed a quantum-chemical investigation of the electronic and geometric structures of the prereaction complexes of the dienes (butadiene, piperylene, and isoprene) with an active center and of the complexes that model the transition state in the reaction of insertion of dienes *via* the Nd—C σ-bond in the active centers [80]. All calculations were performed using the quasi-relativistic extended Huckel method [81].

It is known that in diene polymerization with *cis*-regulating systems the terminal units of the growing polymer chains have delocalized π-allylic structure [8, 68]. High regioselectivity of the lanthanide catalysts in the polymerization of nonsymmetric dienes implies that active centers of a single type, in which the delocalized terminal unit is linked to the penultimate unit according to "head-to-tail" type, are predominantly formed during the polymerization. This is shown for P-*cis*-$CH_2C_\gamma HC_\beta R'C\alpha HR$-*anti*-$CH_2C_\gamma HC_\beta R'C_\alpha HR$-NdLL′:



where P is the polymer chain, L and L′ are the ligands determined by the initial composition of the catalytic system: $R = CH_3$ and $R' = H$ in the polymerization of piperylene, $R = H$ and $R' = CH_3$ in the polymerization of isoprene, and $R = R' = H$ in polymerization of butadiene.

The active centers formed in the polymerization of dienes with the $NdCl_3 \cdot 3TBP\text{-}Al(i\text{-}C_4H_9)_3$ catalytic system were modeled by the compound that took into account the two terminal units of the polymer chain: $CH_2HC_\gamma HC_\beta R'C_\alpha HR\text{-}CH_2C_\gamma HC_\beta R'C_\alpha HR\text{-}NdCl_2 \cdot AlR_3$. The necessity of including the organoaluminum component in the composition of active centers was substantiated previously [3, 82].

Because the reaction of insertion can proceed only *via* the metal-carbon σ-bond, at the first stage, the calculations were aimed at finding the manner in which the coordinating diene can stabilize the σ-structure of the active center. The calculations of prereaction complexes showed that both piperylene and isoprene (like butadiene [79]) can stabilize the σ-form of the center if they occupy the coordination site in the Nd sphere (Fig. 1c), which becomes vacant upon the transition of the active center from the π- to σ-structure

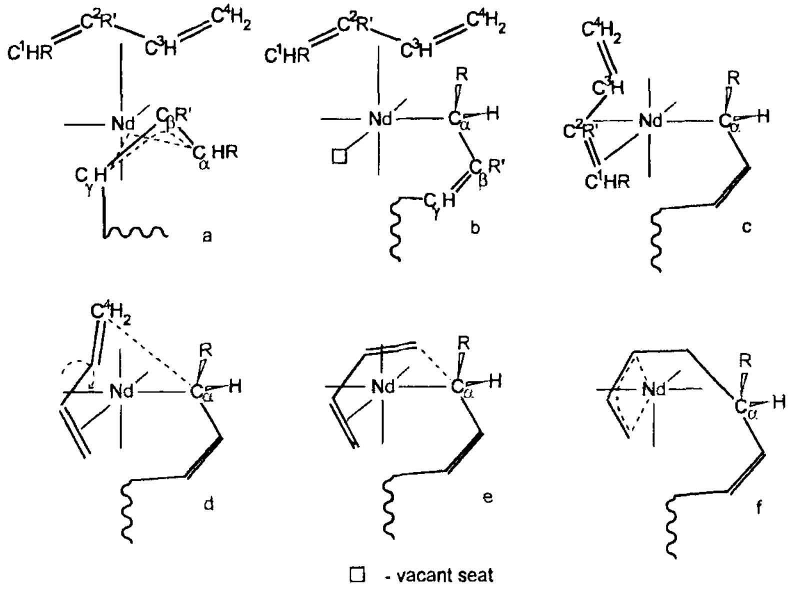


FIGURE 1 Basic stages of growing reaction by polymerization of butadiene ($R = R' = H$), isoprene ($R = H$ and $R' = CH_3$) and piperylene ($R = CH_3$ and $R' = H$) under the action of catalytic system $NdCl_3{\cdot}3TBF\text{-}Al(i\text{-}C_4H_9)_3$.

(Figs. 1a and 1b). The energies of this complex formation are 7.1, 8.5, and 9.2 kJ/mol for butadiene, isoprene, and piperylene, respectively. At the second stage, while retaining the center in the σ-form, the diene can isomerize from the *transoid* to the *cisoid* conformation (due to the rotation of the $—CH{=}CH_2$ double bond about the C—C ordinary bond). The driving force of isomerization is that, in the *cisoid* conformation, the $—C^3H{=}C^4H_2$ bond of the diene reacts with the $Nd—C_\alpha$ σ-bond. This is the beginning of the insertion of the diene into the chain (Fig. 1d). The energy expended to accomplish the isomerization is small and is equal to ~12–15 kJ/mol, depending of the structure of diene. The complexes of *cisoid* isomers formed upon isomerization have complex formation energies equaling 8.4, 9.7 and 10.5 kJ/mol, for butadiene, isoprene, and piperylene, respectively. Consideration of the possible structures of prereaction complexes shows that when the diene retains the *transoid* conformation, because of geometric reasons it cannot stabilize the σ-structure of the active center and participate in the insertion at the same time.

Thus, *cis*-stereospecificity results from π-allylic stabilization of the terminal unit of the growing polymer chain, when the lifetime of the terminal unit in the σ-state is not sufficient for the elementary event of insertion to take place. Otherwise, there is no need for σ-stabilization of the center by the formation of complex shown in Figure 1c, and the dienes directly attack the Nd—C_α bond with one of their double bonds. Naturally, the dienes take the conformation that is thermodynamically more advantageous in solution, that is, the *transoid* conformation.

The occurrence of the reaction of insertion in complex 1c necessitates that the diene further approaches the Nd atom; therefore, a certain energy is required to achieve the corresponding transition state. Taking into account that the structure of the active center in the polymerization of all dienes is similar and these complexes differ only by the presence and the arrangement of methyl substituents, the model structures of the transition states (Fig. 1e) were assumed to be similar. The calculations showed that the energy expended to form the transition states depends slightly on the structure of diene and is equal to 49, 54 and 57 kL/mol for butadiene, isoprene, and piperylene, respectively. The analysis of electronic populations of the bonds of the atoms of dienes and active centers (Fig. 1e, Tab. IV) indicates that the electronic structure of the transition complexes are characterized by delocalization of the $RHC^1{=}C^2R'$ double bond and by incorporation into the complex of the diene linked to the Nd atom by the three carbon atoms C^1, C^2 and C^3. The fourth carbon atom of the diene C^4 begins to form the bond (C^4—C_α) with the terminal carbon atom of the growing polymer chain. This implies that only a single double bond of the diene $C^3H{=}C^4H_2$ is involved in the insertion *via* the Nd—C_α bond. The second double bond $RHC^1{=}C^2R'$ reacts only with the Nd atom. This offers the possibility for the subsequent formation of a π-allylic bond with the Nd atom.

In fact, the calculation of complexes modeling the final state in the reaction of insertion (the length of the Nd—C_α bond is greater than 4.0Å; the plane of the molecule of the inserted diene was brought closer to a distance of 2.6Å, which corresponds to the equilibrium distance of the plane of the crotyl terminal group to the Nd atom) showed that the π-allylic bond of the newly forming terminal unit with the Nd atom takes place concurrently with the insertion.

Table IV shows that, in the final complex (Fig. 1f), the Nd—Cα bond does not exist any longer, a new C^4—Cα bond is formed, and the C^3—C^4 bond is ordinary (the population is 0.85). All these facts suggest that the insertion took place. The second double bond is delocalized (the electron populations of C^1—C^2 and C^2—C^3 bonds are close to 1.01) and the three carbon atoms C^1, C^2 and C^3 form a π-allylic bond with the Nd atom.

As for the regioselectivity, it is important to note that in the presence of lanthanide catalysts the dienes can enter insertion (upon isomerization from the *transoid* to *cisoid* conformation) only *via* the double bond containing no methyl group. The reactions for this phenomenon are different for piperylene and isoprene.

In the polymerization of piperylene, when the $CH_2{=}CH(CH_3)$ double bond of the diene comes closer to the Nd—C_α σ-bond, a steric repulsion appears between the methyl groups of the terminal unit and the piperylene molecule (Fig. 2a). Therefore, it is necessary to alter significantly the orientation of the terminal unit of the growing polymer chain, for example, to turn it about the Nd—C_α bond to decrease the repulsion of the methyl groups. Naturally, these changes are extended in time and need considerable expenditure of energy. In our opinion, it is this factor that is responsible for the participation of only the unsubstituted double bond of piperylene in the insertion and ensures the regioselectivity, that is, the addition of 1,4-units only according to the "head-to-tail" type.

As for the problem why the *cis*-isomers of piperylene are not polymerized with *cis*-regulating lanthanide catalysts, note that among the four possible isomers of piperylene (*cis-cisoid*, *cis-transoid*, *trans-cisoid*, and *trans-transoid*), the *cis-cisoid* isomer is the least advantageous (according to the total electron energy) and this isomer apparently does not occur in the racemic mixture in solution [83]. To take part in the reaction of insertion, piperylene must isomerize from the *transoid* to the *cisoid* conformation. In this case, the *cis-cisoid* conformation appears, which is the least advantageous for piperylene. Therefore, this isomerization may not take place. When the *cis-cisoid* isomer is involved in the insertion, steric hindrances may appear, because at any orientation the methyl substituent turns out to be directed inwards into the center (for example, see Fig. 2b).

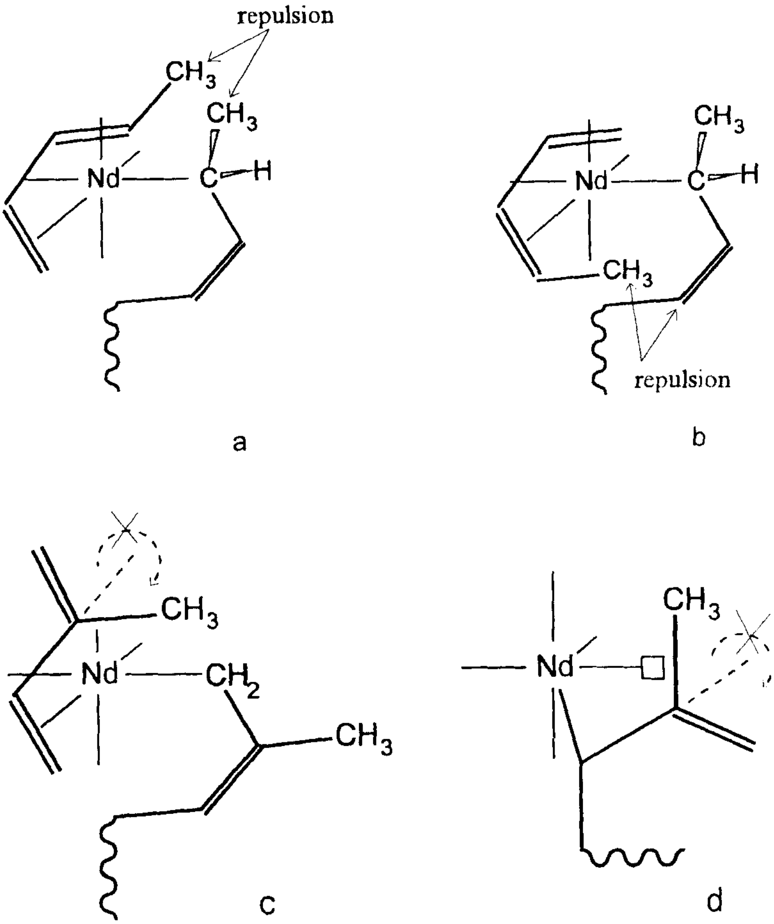


FIGURE 2 Appearance of steric hindrances by piperylene polymerization (a, b) and by isoprene polymerization (c, d).

All these facts predetermine the inactivity of the *cis*-isomer of piperylene in the polymerization with *cis*-regulating lanthanide catalysts. Naturally, in the polymerization initiated by the catalysts showing "mixed" stereospecificity or *trans*-stereospecificity, the transition of piperylene from the *transoid* to *cisoid* conformation is no larger necessary and, for example, the *cis-transoid* isomer can enter the polymerization.

Also note that, in accordance with the calculated data, the energies of the σ-form of the "piperylene" active center, in which the Nd atom is linked to the C_γ atom, and the σ-form of the center, in which the metal atom is bonded to the C_α atom, differ slightly. The corresponding value of ΔE is maximal when the terminal units are in the *trans-cisoid* conformation, and is as low as 4 kJ/mol. In the models of the "butadiene" centers, this difference is much greater (12.7 kJ/mol) [76], that is, in the polymerization of piperylene, the σ-structure of the active center with the NdC_γ bond is realized more often than in the butadiene polymerization. This accounts for why the total amount of 1,2- and *trans*-1,4-units must be greater in the polymerization of piperylene than in the polymerization of butadiene (due to insertion *via* the $Nd—C_\gamma$ bond and the *anti-syn* isomerization of the terminal unit). This was evidenced experimentally [82].

In the polymerization of isoprene, the arrangement of diene in the prereaction complex (as shown in Fig. 2c) requires that the transition from the *transoid* to *cisoid* conformation takes place *via* the rotation of the $C(CH_3){=}CH_2$ substituted bond. The fact that the methyl group and the double bond are aligned in the opposite directions with respect to the ordinary $C^2—C^3$ bond (contrary to piperylene, when they are situated on one side of the $C^2—C^3$ bond) hampers the isomerization. Upon rotation of the $—C(CH_3){=}CH_2$ group by 180°, either the methyl or the $={CH_2}$ group approaches the Nd atom too closely. This sharply increases the energy barrier (to 76 kJ/mol), in contrast to butadiene and piperylene, when the barrier to rotation is 11.9 and 14.9 kJ/mol, respectively. This explain why the double bond of isoprene, which bears a methyl substituent, cannot participate in the insertion. Therefore, regioselectivity appears and polyisoprene presumably does not contain the *trans*-units. In fact, upon insertion of isoprene, an active center is formed, whose σ-form (upon the formation of σ-bond with third carbon atom of the terminal unit) has a structure similar to that shown in Figure 2d. It is seen that, as in the case of complex 2c, the rotation of the $—C(CH_3){=}CH_2$ group is necessary for the isomerization to take place of the terminal unit from *cis* to *trans* conformation. It is the energy barrier of this isomerization that is responsible for the absence of *trans*-1,4-units in polyisoprene, in contrast to polypiperylene and polybutadiene prepared with the same *cis*-regulating catalysts.

Thus, the high stability of the terminal unit, which predominantly occurs in the π-allylic state, leads to the participation of only the *cisoid* isomers of dienes in the insertion reaction.

In the polymerization of piperylene regioselectivity (addition of 1,4-units according to "head-to-tail" type) is caused by the fact that only the double bond of diene bearing no methyl substituent can react with the metal-carbon σ-bond of the active center. Involvement of the double bond of piperylene bearing the methyl substituent in the insertion reaction is considerably hampered because of the steric repulsion between the methyl groups of the terminal unit of the growing chain and the diene. The smaller difference in energy between the two possible σ-forms of the terminal unit in the polymerization of piperylene (as compared to butadiene) is responsible for the increased lifetime of the active center in the σ-form, in which the Nd atom is linked to the C_γ atom. This results in an increased content of *trans*-1,2- and *trans*-1,4 units in polypiperylene.

In the polymerization of isoprene, high regioselectivity and the absence of *trans*-1,4-units in the polymer are related to the hampered rotation of the $C(CH_3){=}CH_2$ double bond of isoprene incorporated into the complex with the active center.

THE ROLE OF *ANTI-SYN* ISOMERIZATION OF THE TERMINAL UNIT OF THE GROWING POLYMER CHAIN

The possibility of the occurrence of *anti-syn* isomerization was qualitatively estimated from the experimental dependence of the relative content of *cis*- and *trans*-units in the polymer on the monomer concentration in polymerization with *cis*-regulating systems [4]. Similar dependence was also observed for lanthanide catalysts [84]. To obtain more detailed information on the isomerization reaction, we performed a quantitative estimation of the kinetic scheme of the propagation reaction, which includes *anti-syn*- isomerization, for the polymerization of butadiene and piperylene with the $NdCl_3 \cdot 3TBP$-$Al(i\text{-}C_4H_9)_3$ system [72, 77, 86–89]. According to the data of quantum-chemical studies, which indicates that the isomeric forms of active centers (in butadiene polymerization) must not markedly differ by their reactivity, the following reaction scheme was analyzed:

$$\begin{array}{lcl}
\wedge\wedge\wedge \mathrm{AS} + M & \underset{\mathrm{K}_{-1}}{\overset{\mathrm{K}_1}{\longrightarrow}} & \wedge\wedge\wedge \mathrm{AS}\cdot M \xrightarrow{\mathrm{K}} \wedge\wedge\wedge\, cis\text{-1,4-unit-AS+} \\
\mathrm{K}_3 \downarrow\uparrow \mathrm{K}_4 & & \mathrm{K}_5 \downarrow\uparrow \mathrm{K}_6 \\
\wedge\wedge\wedge \mathrm{AS}_t + M & \underset{\mathrm{K}_{-1}}{\overset{\mathrm{K}_1}{\longrightarrow}} & \wedge\wedge\wedge \mathrm{AS}_t\cdot M \xrightarrow{\mathrm{K}} \wedge\wedge\wedge\, trans\text{-1,4-unit-AS+}
\end{array}$$

where ∧∧∧AS is the *anti*-structure of active center, AS·M – is a complex of active center with monomer. The analogous designations are used for the *syn*-structure (AS_t) of active center., The meaning of the constants (K_1, K_{-1}, K_3, K_4, K_5 and K_6) can be deduced from the scheme. In accordance with the scheme it is possible to derive the following approximate expressions for chain propagation rate (V) and the ratio between *cis*-1,4- and *trans*-1,4-unit formation rates (V_{cis} and V_{trans}, respectively):

$$V = K_p C_\alpha [M] \tag{1}$$

$$V_{cis}/V_{trans} = \gamma + [M]/(\alpha_2[M] + \beta_2) \tag{2}$$

$$\text{where } K_p = 1/(\alpha_1[M] + \beta_1);$$

$$\gamma = \mathrm{K}_6/\mathrm{K}_5;\quad \beta_1 = (\mathrm{K} + \mathrm{K}_{-1})/\mathrm{K}\mathrm{K}_1;\quad \alpha_1 = 1/\mathrm{K};$$

$$\alpha_2 = \alpha_1 \mathrm{K}_5;\quad \beta_2 = \mathrm{K}_3[\alpha_2(1+\gamma) + \beta_1 \mathrm{K}_1]/\mathrm{K}_1 \tag{3}$$

This scheme takes into account that propagation is a two-stage reaction (coordination and insertion) and that *anti-syn* isomerization of the terminal unit of the growing chain can occur both prior to the diene coordination to the active center and after the formation of the complex between the diene and the active center.

The meaning of the constants is clear from the scheme. Formation of 1,2-units in polybutadiene was not taken into account because in all experiments, their content did not exceed 1 – 3%. The values of γ, α_2 and β_2 parameters were determined by minimizing the weighted sum of the squares of deviations of the experimental values of V_{cis}/V_{trans} from the theoretical values determined from expression (2). Table V list the experimental values of the constants for separate stages of chain propagation in butadiene polymerization with the $\mathrm{NdCl_3{\cdot}3TBP\text{-}Al(\mathit{i}\text{-}C_4H_9)_3}$ system.

TABLE V The value of rate constants for elementary stages of propagation reactions and their ratios in the polymerization of butadiene with the catalytic systems $NdCl_3 \cdot 3TBP\text{-}Al(i\text{-}C_4H_9)_3$ (I) and $NdCl_3 \cdot 3TBP\text{-}Al(i\text{-}C_4H_9)_2H$ (II)

Catalytic system	*Solvent*	$\beta_1 = KK_1/(K+K^{-1})$, *l/(mol min)*	$\alpha_1^{-1} = K$, *min*$^{-1}$	$\alpha_2 = K_6/K$	K_3, *min*$^{-1}$	K_6, *min*$^{-1}$	β_2^*, *mol/l*	γ
I	Heptan	2670	8000	0.08	22	660	0.01	0.98
	Toluene	900	–	0.04	80	–	0.09	0.97
II	Toluene	380	–	0.09	15	–	0.04	0.93

*$\beta_2 \approx K_3(2\alpha_2/K_1 + \beta_1)$.

As is seen, the nature of solvent most dramatically affects the stage of coordination (constant K_1 in toluene is ~3 times smaller than that in heptane) and the stage of isomerization (constant K_3 changes by ~4 times on going from toluene to heptane). This may be associated with the fact that in toluene, the active centers not complexed with the monomer form complexes (of the arene type) with aromatic hydrocarbon. The occurrence of aromatic hydrocarbon in the coordination sphere of Nd, first, hampers the coordination of the monomer (K_1 decreases) and, second, favors the activation of π-σ transitions (*i.e.*, increases the rate of *anti-syn* isomerization, which involved the σ-form of active center). This is reflected in an increase in the magnitude of K_3. For the centers complexed with the monomer, the isomerization constant (K_6) further increases, indicating that the monomer activates the π-σ transitions to a greater extent than the solvent. Thus, in heptane, the isomerization constant for the active centers complexed with the monomer (K_6) is 30 times larger than the isomerization constant for free active centers (K_3).

CONCLUSIONS

The suggested mechanism of *cis*-regulation takes into account in an explicit form the kinetic factor (time of occurrence of the terminal unit in the π- and σ-structures) and readily permits the following general conclusion to be drawn. In the case where the time of existence of the terminal unit in the π-structure exceeds the time τ_1 (reaction time), the stabilization (fixation) of the σ-structure of the active center by the diene molecule would be no longer neccessary and the diene molecule can participate in the reaction regardless of its conformation (*cis*- or *trans*-). Naturally, this should imply the loss of *cis*-stereospecificity of the active center. On the other hand, if the system does not possess *cis*-regulating properties (*i.e.*, the time of existence of the terminal unit in the σ-structure exceeds τ_1), the stabilizing π-structures (for example, by introduction of a halogenating agent) could lead to the emergence of *cis*-stereospecificity of active centers.

Thus, the major components of an active center (such as terminal unit, bridging bond, organoaluminum component, lanthanide atom and its ligands) can decisively affect its stereospecificity. The role of each element manifests itself through different factors, and the possible mechanisms of their influence were discussed above. The key point determining the value of one or another factor in the mechanism of stereoregulation is the relationship between the following characteristic times: lifetime of the terminal unit in the π-state, lifetime of the terminal unit in the σ-state, time of the elementary event of insertion, time of the elementary event of isomerization, time interval between two successive additions of diene molecules to polymer chain.

The above said shows how the interplay of these times can affect the microstructure of the resulting polydiene. Naturally, real active centers are markedly more complicated, and the mechanism of stereoregulation apparently includes many details, which are yet to be studied. However, an account of the characteristic times for different stages of the complicated reaction of chain propagation will undoubtedly always be a necessary stage for both the study of all diverse possibilities of lanthanide catalysts and the development of new catalytic systems.

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References

[1] Dolgoplosk, B. A. and Tinyakova, E. I. (1994). *Polymer Science*, **36A**(10), 1380–1403.

[2] Porri, L., Giarusso, A. and Ricci, G. (1994). *Polymer Science*, **36A**(10), 1421–1432.

[3] Monakov, Yu. B., Marina, N. G. and Sabirov, Z. M. (1994). *Polymer Science*, **36A**(10), 1404–1420.

[4] Dolgoplosk, B. A. and Tinyakova, E. I. (1985). *Metalloorganicheskii katalyz v protsessakh polimerizatsii* (*Organometallic catalysis in polymerization processes*), Moscow: Nauka, 2-nd edn., 536 pp.

[5] Murinov, Yu. I., Monakov, Yu. B., Shamaeva, Z. G. *et al.* (1977). *Izv. ANSSSR, Ser. Khim.*, No. 12, pp. 2790–2792.

[6] Eskina, M. V., Lovchikov, V. A., Khachaturov, A. S. *et al.* (1986). *Vysokomol. Soedin.*, **28B**(12), 887–890.

[7] Skuratov, K. D., Lobach, M. I., Khachaturov, A. S. *et al.* (1987). *Vysokomol. Soedin.*, **29A**(7), 1406–1412.

[8] Sanyagin, A. A. and Kormer, V. A. (1985). *Dokl. ANSSSR*, **283**(5), 1209–1211.
[9] Marina, N. G., Duvakina, N. V., Monakov, Yu. B. *et al.* (1985). *Vysokomol. Soedin.*, **27A**(6), 1203–1207.
[10] Monakov, Yu. B., Marina, N. G. and Tolstikov, G. A. (1988). *Chemia Stosowana*, **32**(3/4), 547–557.
[11] Monakov, Yu. B., Marina, N. G., Khairullina, R. M. *et al.*, *Inorg. Chim. Acta*, **142**(1), 161–164.
[12] Kozlov, V. G., Marina, N. G., Savel'eva, I. G. *et al.* (1988). *Inorg. Chim. Acta*, **154**(2), 239–245.
[13] Aksenov, V. I., Murachev, V. B., Ziborova, V. P. *et al.* (1988). *Vysokomol. Soedin.*, **30B**(6), 431–436.
[14] Monakov, Yu. B., Marina, N. G. and Tolstikov, G. A. (1989). *Polymery*, **34**(6–7), 263–270.
[15] Khairullina, R. M., Marina, N. G., Kozlova, O. I. *et al.* (1991). *Vysokomol. Soedin.*, **33B**(6), 463–465.
[16] Monakov, Yu. B., Marina, N. G., Kozlova, O. I. *et al.* (1987). *Dokl. ANSSSR*, **292**(2), 405–407.
[17] Lobach, M. I., Poletaeva, I. A., Khachaturov, A. S. *et al.* (1977). *Polymer*, **18**(11), 1196–1198.
[18] Bubnova, S. V., Tverdov, A. I. and Vasil'ev, V. A. (1988). *Vysokomol. Soedin.*, **30A**(7), 1374–1379.
[19] Rafikov, S. R., Monakov, Yu. B., Bieshev, Ya. Kh. *et al.* (1976). *Dokl. ANSSSR*, **229**(5), 1174–1176.
[20] Monakov, Yu. B., Bieshev, Ya. Kh., Berg, A. A. *et al.* (1977). *Dokl. ANSSSR*, **234**(5), 1125–1127.
[21] Monakov, Yu. B., Marina, N. G., Duvakina, N. V. *et al.* (1977). *Dokl. ANSSSR*, **236**(3), 617–619.
[22] Panasenko, A. A., Odinokov, V. N., Monakov, Yu. B. *et al.* (1977). *Vysokomol. Soedin.*, **19B**(9), 656–658.
[23] Berg, A. A., Monakov, Yu. B., Budtov, V. P. *et al.* (1978). *Vysokomol. Soedin.*, **20B**(4), 295–299.
[24] Markevich, I. N., Sharaev, O. K., Tinyakova, E. I. *et al.* (1983). *Dokl. ANSSSR*, **268**(4), 892–896.
[25] Yakovlev, V. A., Vollershtein, E. L., Cherezova, L. S. *et al.* (1983). *Dokl. ANSSSR*, **268**(6), 1422–1425.
[26] Avdeeva, O. G., Markevich, I. N., Sharaev, O. K. *et al.* (1986). *Dokl. ANSSSR*, **286**(3), 641–643.
[27] Gailyunas, G. A., Biktimirov, R. Kh., Khairullina, R. M. *et al.* (1987). *Dokl. ANSSSR*, **295**(6), 1385–1388.
[28] Avdeeva, O. G., Sharaev, O. K., Markevich, I. N. *et al.* (1990). *Vysokomol. Soedin.*, **32A**(2), 367–373.
[29] Dolgoplosk, B. A., Tinyakova, E. I., Markevich, I. N. *et al.* (1983). *J. Organomet. Chem.*, **255**(1), 71–79.
[30] Vollershtein, E. L., Glebova, N. N., Gol'shtein, S. B. *et al.* (1985). *Dokl. ANSSSR*, **284**(1), 140–142.
[31] Guzman, I. Sh., Chigir, N. N., Sharaev, O. K. *et al.* (1979). *Dokl. Akad. Nauk SSSR*, **249**(4), 860–862.
[32] Dolgoplosk, B. A., Tinyakova, E. I., Guzman, I. Sh. *et al.* (1980). *J. Organomet. Chem.*, **201**(1), 249–255.
[33] Chigir, N. N., Guzman, I. Sh., Sharaev, O. K. *et al.* (1982). *Dokl. ANSSSR*, **263**(2), 375–378.
[34] Vollershtein, E. L., Yakovlev, V. A., Tinyakova, E. I. *et al.* (1980). *Dokl. ANSSSR*, **250**(2), 365–366.
[35] Nikitin, A. B., Yakovlev, V. A. and Dolgoplosk, B. A. (1986). *Dokl. ANSSSR*, **291**(2), 393–395.

[36] Zavadovskaya, E. N., Sharaev, O. K., Borisov, G. K. *et al.* (1984). *Dokl. ANSSSR*, **274**(2), 333–334.
[37] Zavadovskaya, E. N., Sharaev, O. K., Borisov, G. K. *et al.* (1985). *Dokl. ANSSSR*, **284**(1), 143–144.
[38] Gol'shtein, S. B., Yakovlev, V. A., Bondarenko, G. N. *et al.* (1986). *Dokl. ANSSSR*, **289**(3), 657–660.
[39] Gol'shtein, S. B., Yakovlev, V. A., Mikaya, A. I. *et al.* (1989). *Dokl. ANSSSR*, **309**(5), 1129–1131.
[40] Dolgoplosk, B. A., Yakovlev, V. A., Tinyakova, E. I. *et al.* (1993). *Dokl. AN Russia*, **328**(1), 58–60.
[41] Monakov, Yu. B., Marina, N. G., Savel'eva, I. G. *et al.* (1982). *Dokl. ANSSSR*, **265**(6), 1431–1433.
[42] Rafikov, S. R., Kozlov, V. G., Marina, N. G. *et al.* (1982). *Izv. ANSSSR, Ser.Khim.*, No. 4, pp. 871–875.
[43] Kormer, V. A., Vasil'ev, V. A., Bubnova, S. V. *et al.* (1986). *Kauchuk i Rezina*, No. 1, pp. 5–8.
[44] Shen, Z., Ouyang, J., Wang, F. *et al.* (1980). *J. Polym. Sci., Part A: Polym. Chem.*, **18**(12), 3345–3357.
[45] Lugli, G., Mazzei, A., Poggio, S. (1974). *Makromol. Chem.*, **175**(7), 2021–2027.
[46] Marina, N. G., Gadeleva, Kh. K., Monakov, Yu. B. *et al.* (1985). *Dokl. ANSSSR*, **284**(1), 173–175.
[47] Chernenko, G. M., Yakovlev, V. A., Tinyakova, E. I. *et al.* (1989). *Vysokomol. Soedin.*, **31B**(8), 637–638.
[48] Chigir, N. N., Sharaev, O. K., Tinyakova, E. I. *et al.* (1983). *Vysokomol. Soedin.*, **25B**(1), 47–48.
[49] Marina, N. G., Gadeleva, Kh. K., Monakov, Yu. B. *et al.* (1984). *Dokl. ANSSSR*, **274**(3), 641–643.
[50] Kozlov, V. G., Nefed'ev, R. V., Marina, N. G. *et al.* (1988). *Dokl. ANSSSR*, **299**(3), 652–656.
[51] Marina, N. G., Duvakina, N. V., Sabirov, Z. M. *et al.* (1997). *Polymer Science*, **39B**(1–2), 34–35.
[52] Lugli, G., Marconi, W., Mazzei, A. *et al.* (1969). *Inorg. Chim. Acta*, **3**(2), 253–254.
[53] Thiele, K. H., Opitz, R. and Koehler, E. Z. (1977). *Z. Anorg. Allg. Chem.*, **435**(8), 45–48.
[54] Monakov, Yu. B., Marina, N. G., Savel'eva, I. G. *et al.* (1984). *Dokl. ANSSSR*, **278**(5), 1182–1184.
[55] Bodrova, V. S., Piskareva, E. P., Bubnova, S. V. *et al.* (1988). *Vysokomol. Soedin.*, **30A**(11), 2301–2306.
[56] Bubnova, S. V., Piskareva, E. P., Vasil'ev, V. K. *et al.* (1993). *Vysokomol. Soedin.*, **35B**(1), 18–21.
[57] Bodrova, V. S., Piskareva, E. P. and Kormer, V. A. (1987). *Dokl. ANSSSR*, **293**(3), 645–649.
[58] Hsieh, H. L. and Yeh, G. H. C. (1986). *Industr. Eng. Chem. Product. Developm.*, **25**(3), 456–463.
[59] Zhang, X., Pei, F., Li, X. *et al.* (1990). *Acta Polym. Sinica*, **8**(4), 391–398.
[60] Jin, Y., Zhang, X., Pei, F. *et al.* (1990). *Chinese J. Polym. Sci.*, **8**(2), 121–126.
[61] Wei, J. and Liao, Y. (1983). *Gaofenzi Tongxun*, No. 5, pp. 342–346.
[62] Jin, Y. T., Sun, Y. F., Liu, Z. *et al.* (1984). *Fenzi Kexue Yu Huaxue Yanjiu*, **4**(2), 247–252.
[63] Zhao, X. and Tian, F. (1982). *Kexue Tongbao*, **27**(12), 731–732.
[64] Zhao, X. and Wang, F. (1983). *Kexue Tongbao*, **28**(6), 776–778.
[65] Skuratov, K. D., Lobach, M. I., Shibaeva, A. N. *et al.* (1992). *Polymer*, **33**(24), 5202–5212.
[66] Jin, Y., Li, X., Sun, Y. *et al.* (1984). *Gaofenzi Tongxun*, No. 5, pp. 358–362.
[67] Jin, Y., Li, X., Sun, Y. *et al.* (1984). *Kexue Tongbao*, **30**(8), 1047–1049.

[68] Shan, C., Lin, Y., Ouyang, J. *et al.* (1987). *Makromol. Chem.*, **188**, 629–635.

[69] Throckmorton, M. C. (1969). *Kautsch. Gummi, Kunstst.*, **22**(6), 293–297.

[70] Monakov, Y. B., Marina, N. G., Sabirov, Z. M. *et al.* (1992). *Dokl. ANSSSR*, **327**(4–6), 524–527.

[71] Monakov, Yu. B., Sabirov, Z. M. and Minchenkova, N. Kh. (1993). *Mendeleev Commun.*, No. 3, pp. 85–87.

[72] Sabirov, Z. M., Minchenkova, N. Kh. and Monakov, Yu. B. (1991). *Vysokomol. Soedin.*, **32B**(2), 83–84.

[73] Sabirov, Z. M., Monakov, Yu. B. (1988). *Dokl. ANSSSR*, **302**(1), 143–145.

[74] Sabirov, Z. M., Monakov, Yu.B. and Tolstikov, G. A. (1989). *J. Mol. Catal.*, **56**(1–3), 194–202.

[75] Sabirov, Z. M. and Monakov, Yu. B. (1990). *Inorg. Chim. Acta*, **169**, 221–224.

[76] Sabirov, Z. M., Minchenkova, N. Kh. and Monakov, Yu. B. (1990). *Vysokomol. Soedin.*, **31A**(11), 803–804.

[77] Sabirov, Z. M., Minchenkova, N. Kh., Kazantseva, I. I. *et al.* (1991). *Teor. Eksp. Khim.*, **27**(6), 741–745.

[78] Sabirov, Z. M., Urazbaev, V. N. and Monakov, Yu. B. (1992). *Polymer Science*, **34A**(5), 379.

[79] Monakov, Yu. B., Sabirov, Z. M. and Urazbaev, V. N. (1993). *Dokl. AN* (*Russia*), **332**(1), 50–53.

[80] Sabirov, Z. M., Urazbaev, V. N. and Monakov, Yu. B. (1997). *Polymer Science*, **39B**(1–2), 22–25.

[81] Sabirov, Z. M. and Bagatur'yants, A. A. (1991). *Usp. Khim.*, **60**(10), 2065–2088.

[82] Marina, N. G., Monakov, Yu. B. and Tolstikov, G. A. (1994). *Chem. Rev.*, **18**(4), 1–45.

[83] Compton, D. A. G., George, W. O. and Maddams, W. F. (1977). *J. Chem. Soc., Perkin Trans. 2*, pp. 1311–1320.

[84] Monakov, Yu. B. and Tolstikov, G. A. (1990). *Kataliticheskaya polimerizatsiya* 1,3-dienov (*Catalytic polymerization of* 1,3-*dienes*), Moscow: Nauka, 211 pp.

[85] Sabirov, Z. M., Minchenkova, N. Kh., Urazbaev, V. N. *et al.* (1993). *J. Polym. Sci., Polym. Chem. Ed.*, **31**, 2419–2421.

[86] Sabirov, Z. M., Minchenkova, N. Kh. and Monakov, Yu. B. (1989). *Inorg. Chim. Acta*, **160**(1), 99–101.

[87] Sabirov, Z. M., Minchenkova, N. Kh., Vakhrusheva, N. A. *et al.* (1990). *Dokl. ANSSSR*, **312**(1), 147–150.

[88] Monakov, Yu., Sabirov, Z. M. and Marina, N. G. (1996). *Polymer Science*, **38A**(3), 232–240.

[89] Sabirov, Z. M., Urazbaev, V. N., Marina, N. G. *et al.* (1997). *Polymer Science*, **39B**(1–2), 14–17.