Relationship between the Stereospecificity of Lanthanide Catalysts and the Structures of Active Sites and Dienes, the Nature of a Cocatalyst, and Preparation Conditions

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Received September 18, 2000

Abstract—Several types of active sites can be formed during the polymerization of dienes in the presence of lanthanide catalytic systems. These sites differ in the nearest environment of a lanthanide atom (the numbers of chlorine and carbon atoms) and in the number of lanthanide–carbon bonds involved in chain growth. Quantum-chemical calculation shows that the π-allyl binding of the terminal unit of a growing polymeric chain with the lanthanide atom of an active site may be the reason for the *cis*-stereospecificity of the site. Therefore, the active sites containing electron-acceptor chlorine atoms that favor π-allyl binding can form *cis*-polydienes. Depending on the conditions of catalytic system preparation, primarily on the nature of an organic compound of a nontransition metal, one or another set of active sites is formed that can affect its stereospecificity. The quantitative analysis of kinetic data for diene polymerization shows that the *anti-syn* isomerization of terminal units of growing polymeric chains made a certain contribution to the formation of *trans*-1,4 units in the presence of *cis*-regulating active sites.

INTRODUCTION

Diene polymerization in the presence of lanthanide catalytic systems $LnX_3 \cdot 3L–AlR_3$ (where X is a halogen, L is an electron-donor ligand, and R is a hydrocarbon radical) results in polydienes enriched in *cis*-units [1–4]. Additionally, lanthanide catalysts are characterized by high regioselectivity depending on the diene structure. Thus, all possible types of chain units (*cis*-1,4; *trans*-1,4; and 1,2-units [5]) are present in polybutadiene, whereas 3,4-units are entirely absent from polypiperylene [6] and *trans*-1,4-units, from polyisoprene [7]. All 1,4-units are linked head-to-tail. It is interesting that *cis*-piperylene is not polymerized in the presence of *cis*-regulating lanthanide catalysts, although it is involved in polymerization under the action of some catalytic systems based on *d*-elements, for example, in the presence of VCl_3-AlR_3 [8]. A complete inversion of the stereospecificity of the catalytic $LnX_3–3L–AlR_3$ system from *cis* to *trans* after the substitution of an organomagnesium MgRR' compound for an organoaluminum compound AlR_3 [9] is also of interest. The formation of polymers with a broad molecular-weight distribution in the presence of lanthanide catalytic systems is specific of them [10]. Despite intensive research, a unified explanation for the above phenomena is lacking.

The goals of this paper are to find the relationship between the stereospecificity of $NdCl_3 \cdot 3TBP–Al(iso\text{-}C_4H_9)_3$ and $NdCl_3 \cdot 3TBP–Mg(n\text{-}C_4H_9) \cdot (iso\text{-}C_8H_{17})$ (TBP is tributyl phosphate) catalytic systems in the polymerization of dienes and to identify the structure of active sites, the nature of cocatalysts, and the conditions of the catalytic system preparation.

RESULTS AND DISCUSSION

The structure of active sites is one of the main factors that affect all the parameters of a catalytic system. The interaction of initial components of the $NdCl_3 \cdot 3TBP–AlR_3$ catalytic system starts with the partial or complete abstraction of TBP molecules from $NdCl_3$ because of the formation of TBP complexes of organometallic compound of a nontransition metal. The remaining molecules of $NdCl_3$ tend to associate via chlorine bridging bonds and to precipitate. However, until then, they can be alkylated to form the following lanthanides: $RNdCl_2$, R_2NdCl, and R_3Nd. These compounds together with initial molecules $NdCl_3$ and AlR_3 can associate with each other and with nontransition metal compounds $ClAlR_2$, Cl_2AlR, and Cl_3Al that can also be formed in the catalytic system. After all, many different compounds with complex structures containing one, two, or three lanthanide–carbon bonds may

appear in the system. These bonds can later be involved in the further growth of polymer chain.

The nearest environment of a lanthanide atom has the strongest effect on the electronic properties of these bonds. This allows us to roughly classify all possible structures of active sites according to the composition of the first coordination sphere of the lanthanide atom.

Six types of active sites can be distinguished by the number of Cl and C atoms in the nearest environment of the neodymium atom that forms the Nd–R bond. The number of Cl and C atoms in active sites varies from the maximal number of Cl atoms to the maximal number of C atoms (Fig. 1). The braces in the structures of active sites in Fig. 1 point to the place where either Nd or Al atom can be located.

Here, two remarks are necessary. First, the existence of σ-bonds in Nd–R as they are presented in Fig. 1 is barely probable. More likely, this bond is stabilized either by the coordination of aromatic solvent molecules or by weak carbon bridging bonds formed in the interaction of Nd–R and AlR₃, which we ignore in our approximation, or by the π-allyl binding of terminal units of a growing chain with Nd atom, if a catalyst was prepared in the presence of a small amount of monomer. Second, the possibility of six types of active sites does not mean that they all are present at the same time. In each particular catalytic system, some or other types of active sites can be formed and the fraction of any of them depends on the particular conditions of preparation of a given system.

In the polymerization of dienes in the presence of lanthanide catalysts, the terminal unit of a growing chain can be either π- or σ-bonded to a lanthanide atom. The delocalized (π-allylic) structure is the main form of active site existence in lanthanide catalytic systems [11, 12]. Nevertheless, most researchers followed the opinion that was presented in [8] and consisted in that diene was only inserted into the metal–carbon σ-bond. The π–σ equilibrium (Fig. 2) enabled the insertion of diene molecules into both σ^{α} bond of Nd–C^{α} with the formation of 1,4-units and σ^{γ} bond of Nd–C^{γ} with the formation of vinyl units.

The calculation of model precursor complexes showed that the mere coordination of diene to a lanthanide atom does not result in the stabilization of a σ-structure of an active site (a π-structure remains energetically preferable). Because diene can be inserted only into a metal–carbon σ-bond we first sought for a way by which the coordinated diene could stabilize an unstable σ-structure of active sites. For this purpose, we calculated the geometric and electronic structures of precursor diene complexes with π- and σ-structures of active sites (Fig. 3). Compounds with the general formula $CH_3HC^{\gamma}HC^{\beta}R'C^{\alpha}R–CH_2HC^{\gamma}HC^{\beta}R'C^{\alpha}R–NdCl_2 \cdot Al(CH_3)_3$ (R = CH₃ and R' = H in piperylene polymerization, R = H and R' = CH₃ in isoprene polymerization, and R = R' = H in butadiene polymerization) that corre-
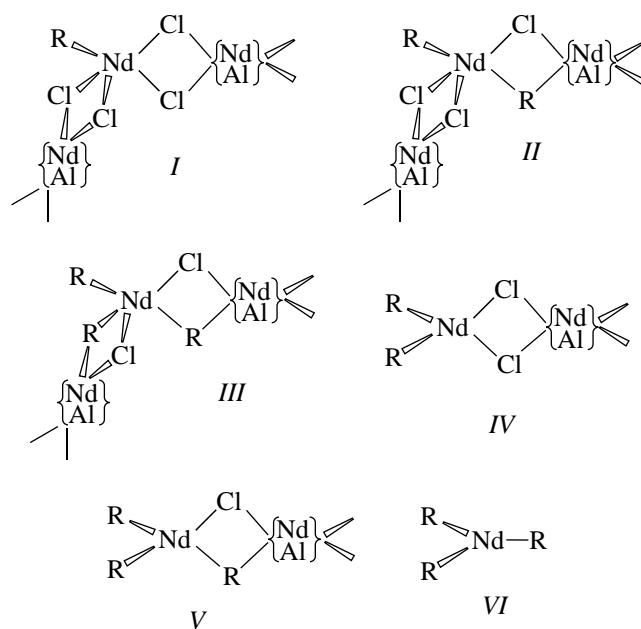
Fig. 1. Six types of active sites that may be formed in the NdCl₃ · 3TBP–Al(isoC₄H₉)₃ catalytic system.
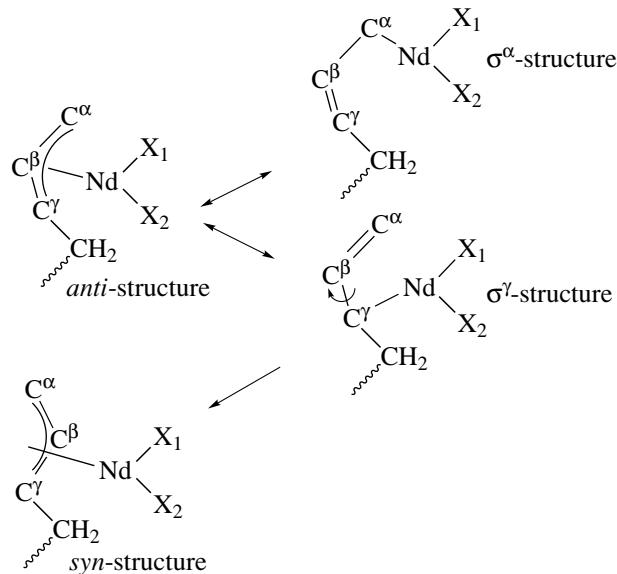
Fig. 2. Isomeric structures $(C_4H_7)NdX_1X_2$, models of the butadiene polymerization active site (X_1 and X_2 are two ligands that are coordinated to Nd atom and can form single or bridging bonds).

sponded to two terminal units of a growing chain were chosen as models of active sites. Diene molecules were found to be capable of stabilizing the active sites with a σ-structure when they occupied the coordination vacancy appeared in the sphere of Nd atom after active sites transformed from π- to σ-structure (Fig. 3C). The energies of diene complex formation were 7.1, 8.5, and
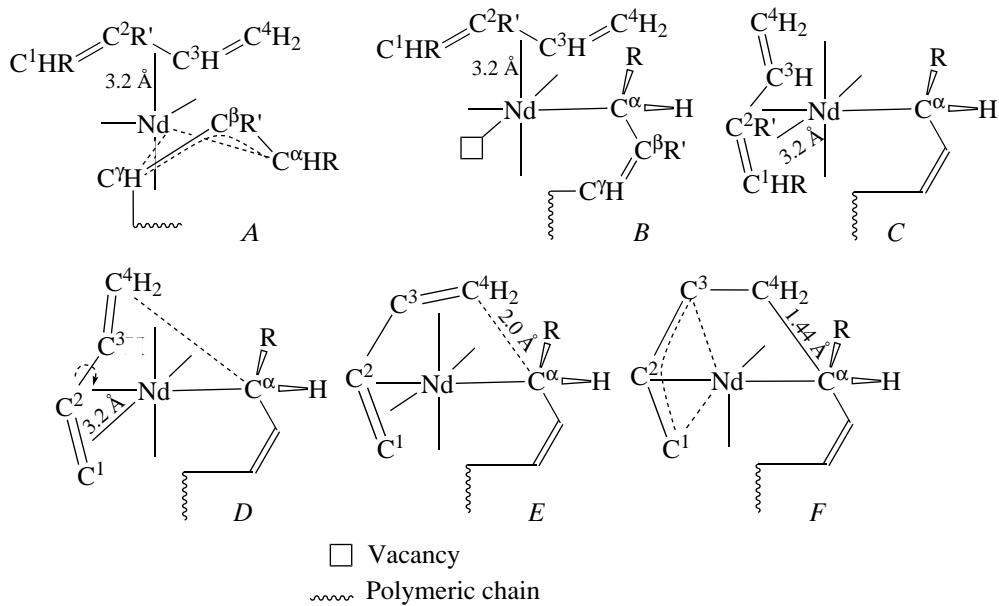
Fig. 3. Main steps of the chain growth in the polymerization of butadiene ($R=R'=H$), isoprene ($R=H$ and $R'=CH_3$), and piperylene ($R=CH_3$ and $R'=H$) in the presence of the $NdCl_3 \cdot 3TBP–AlR_3$ catalytic system: *A* is the coordination of the *trans* conformation of diene to the π-structure of active site; *B* and *C* are the coordination of the *trans* conformation of diene to the σ-structure of active site; *D* is the isomerization of diene from *trans* to *cis* conformation; *E* is the transition state in the insertion reaction; *F* is the final state.

9.2 kJ/mol for butadiene, isoprene, and piperylene, respectively. At the stage step, when σ-structure of active sites is retained, diene molecules isomerizes from *trans* to *cis* conformation after rotating the $-C^3H=C^4H_2$ double bond about the $C^2–C^3$ single bond (Fig. 3*C*). The energy barrier to rotation varied from 12 to 15 kJ/mol depending on the structure of diene. After isomerization, the resulting complexes of *cis*-dienes were characterized by complex formation energies of 8.4, 9.7, and 10.5 kJ/mol for butadiene, isoprene, and piperylene, respectively. In the course of isomerization, before the complete transformation of diene into *cis*-conformation, the $-C^3H–C^4H_2$ bond of diene already begins to interact with the σ-bond of $Nd–C^\alpha$ and starts the insertion of diene (Fig. 3).

The energies consumed in the attainment of the transition state (Fig. 3*E*) were 49, 54, and 57 kJ/mol for butadiene, isoprene, and piperylene, respectively. Analysis of electron population densities of the bonds in the transition complex showed that dienes are bound to an Nd atom with three carbon atoms C^1, C^2, and C^3. The corresponding electron population densities are 0.104, 0.108, and 0.101. The fourth carbon atom (C^4) begins to form the $C^4–C^\alpha$ bond with a terminal carbon atom of a growing polymeric chain (the electron population density of this bond is 0.846). It is important that only one $-C^3H=C^4H_2$ double bond of diene takes part in the insertion into the $Nd–C^\alpha$ bond. The second double bond is localized and interacts only with the Nd atom. This enables the subsequent formation of π-allyl bond

between newly formed terminal unit and the Nd atom simultaneously with the insertion reaction. The most important fact is that, while remaining in *cis*-conformation, dienes are unable to stabilize the σ-structure of active sites and simultaneously participate in the insertion reaction on mere geometrical grounds. This means that only *cis*-conformers of diene can be involved in the insertion reaction during the interaction with the delocalized structure of the active site. Thus, *cis*-stereospecificity is due to the short lifetime of the terminal unit in the σ-state that was not enough for the occurrence of the elementary act of insertion, because the π-state of the active site is preferred to its σ-state. Otherwise, there would be unnecessary to stabilize the σ-structure of active sites via the formation of the complexes of the types presented in Fig. 3*C*, and dienes could directly attack the $Nd–C^\alpha$ bond with one of their double bonds. Of course, dienes present in solution are in the most thermodynamically stable conformation (*cis*-conformation). A loss of *cis*-stereospecificity in the catalyst action should be accompanied by the deterioration of its regioselectivity.

The mechanism proposed for polymeric chain growth enabled the analysis of the relationship between the stereospecificity of catalyst active site action and the structure of diene. In the polymerization of piperylene, the participation of the double bond containing methyl substituent ($-C^2H=CH^1CH_3$) in the insertion reaction demanded considerable energy because of a strong steric repulsion between the methyl groups of

the terminal unit and piperylene molecule (Fig. 4*A*). As a result, only the nonsubstituted bond of piperylene takes part in the insertion reaction and provides regioselectivity, that is, the selective head-to-tail addition of 1,4-units. Similar effect is responsible for regioselectivity in isoprene polymerization (Fig. 4*B*). In this case, the rotation of $-C^2(CH_3)=C^1H_2$ group is required to isomerize the terminal unit from *cis* to *trans* conformation after the insertion of isoprene (Fig. 4*C*). The energy hindrance to this process resulted in the absence of *trans*-1,4 units from polyisoprene, as opposed to polypiperylene and polybutadiene that were obtained in the presence of the same *cis*-regulating catalysts.

Considering the reasons why the *cis*-isomers of piperylene failed to polymerize in the presence of *cis*-regulating catalysts, we note that, of four possible isomers of this hydrocarbon (*cis–cis*, *trans–cis*, *cis–trans*, and *trans–trans*), the *cis–cis* isomer is the most unfavorable from the viewpoint of total electron energy. The corresponding relative values of total energies were 53.91, 5.72, 1.59, and 0 kJ/mol (the energy of the *trans–trans* isomer was taken zero). Most likely, the *cis–cis* isomer was absent from the racemic mixture in the solution. To participate in the insertion reaction, the *cis–trans* isomer present in the solution should be isomerized to *cis*-conformation. This would again result in the most unfavorable *cis–cis* conformation; therefore, such isomerization does not take place. This is the reason for the inactivity of the *cis*-isomer of piperylene in polymerization under the action of *cis*-regulating lanthanide catalysts.

Thus, the *cis*-stereospecificity and regioselectivity of catalytic action are generally independent of the geometry of active sites. The main and determining factors are a shift in the π–σ equilibrium toward the π-state of active sites and the short lifetime of active sites in the σ-state that is insufficient for the elementary step of insertion to occur. These are the reasons for the *cis*-stereospecificity and regioselectivity of catalysts.

Of course, it is quite difficult to directly calculate or measure the lifetimes of active sites in the corresponding states. However, based on numerous experimental data, we assume that electron-acceptor atoms present in the coordination sphere of lanthanides favor the π-allyl binding of the terminal unit of a growing polymeric chain with a lanthanide atom. Then, *cis*-stereospecificity might be expected from the active sites of types *I–V* and *trans*-stereospecificity might be expected from *VI*-type sites (Fig. 1). This assumption was supported by the quantum-chemical calculations of the model active sites of types *II* and *VI*. It was found that, for the compound $CH_3HC^\gamma HC^\beta HC^\alpha H–CH_2HC^\gamma HC^\beta HC^\alpha H–NdCl_2 \cdot Al(CH_3)_3$ that simulated the sites of type *II*, the π-structure was energetically preferable (compared with the σ-structure, the gain in energy was
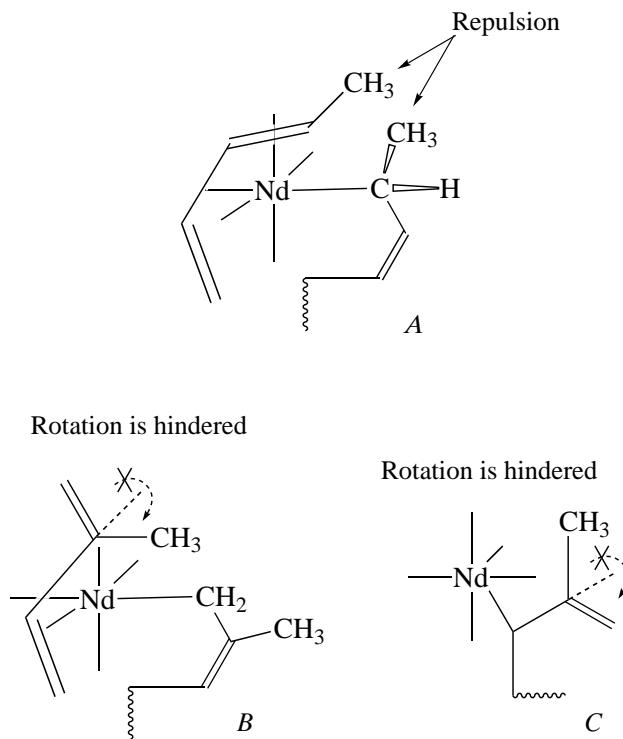
Fig. 4. Steric hindrance arising in the polymerization of (*A*) piperylene and (*B* and *C*) isoprene.

42.4 kJ/mol). For the compound $CH_3HC^\gamma HC^\beta HC^\alpha H–CH_2HC^\gamma HC^\beta HC^\alpha H–Nd(CH_3)_2$ (sites of type *VI*), σ-structure was more favorable (by 16.3 kJ/mol).

The experimental results indirectly confirmed the above assumption. It is known that $NdCl_3$ reacts with AlR_3 to give alkylated compounds $RNdCl_2$ and R_2NdCl, while compounds R_3Nd, most likely were not formed [13]. One might expect the appearance of active sites of all types from *I* to *V* in the catalytic system $LnCl_3 \cdot 3L–AlR_3$. Because *cis*-polydienes were formed in the presence of $NdCl_3 \cdot 3TBP–AlR_3$ catalytic system, we can assume that the active sites of types *I* to *V* are *cis*-regulating.

The *anti–syn* isomerization of the terminal unit of a growing polymeric chain bound with the lanthanide atom of the active site can play a role in the formation of the microstructure of polydienes. The dependence of the relative concentration of *cis* and *trans* units in the polymer on the concentration of a monomer served as a qualitative proof of possible *anti–syn* isomerization [14]. To obtain comprehensive information, we quantitatively evaluated kinetic data for chain growth, which involved the step of *anti–syn* isomerization, in the polymerization of butadiene and piperylene in the presence of $NdCl_3 \cdot 3TBP–Al(isoC_4H_9)_3$ system [15]. Preliminary quantum-chemical calculations of model active sites showed that the electron characteristics of the $Nd–C^\alpha$ bond into which diene was inserted insignifi-

cantly depends on the (*cis* or *trans*) conformation of the terminal unit of growing chain. This suggests that the isomer structures of active sites barely differed in reac-

tivity. In this case, the structural kinetic diagram of chain growth exemplified by piperylene polymerization can be written as follows:

$$\text{\small wwww}\ \pi\text{-}anti + M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{\small wwww}\ \pi\text{-}anti \cdot M \xrightarrow{k} \text{\small wwww}\ (1,4\text{-}cis)\text{units-}\pi\text{-}anti + \ldots$$

$$k_3 \updownarrow k_4 \qquad\qquad\qquad k_5 \updownarrow k_6$$

$$\text{\small wwww}\ \pi\text{-}syn + M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{\small wwww}\ \pi\text{-}syn \cdot M \xrightarrow{k} \text{\small wwww}\ (1,4\text{-}trans + 1,2)\text{units-}\pi\text{-}anti + \ldots$$
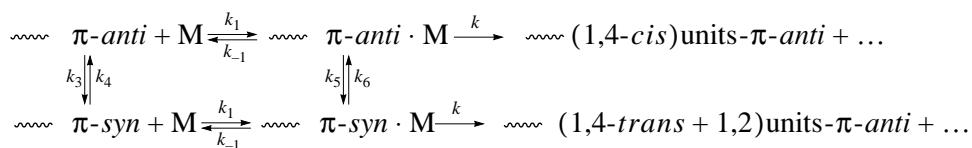
The meanings of constants are clear from the diagram. Note that the diagram takes into account the isomerization step of active sites incorporated into a complex with the monomer.

$$w_{cis}/(w_{trans} + w_{1,2}) = \gamma + [M]/(\alpha_2[M] + \beta_2), \quad (1)$$

where [M] is the monomer concentration, $\gamma = k_6/k_5$, $\beta_1 = (k + k_{-1})kk_1$, $\alpha_1 = 1/k$, $\alpha_2 = \alpha_1 k_5$, $\beta_2 = k_3[\alpha_2(1 + \gamma) + \beta_1 k_1]/k_1$.

Expression (1) derived from the rate laws described rather well the experimental dependence of the ratio of formation rates for *trans* and *cis* units in the polymer on the concentration of the monomer and quantitatively estimated rate constants of single steps of chain growth (Fig. 5). This enabled the quantitative evaluation of the effect of different factors (structure of diene, nature of solvent, temperature, and others) on the occurrence of elementary steps of chain growth [15].

It might be expected that the replacement of AlR_3 with a stronger alkylating agent (e.g., MgRR') will result in the appearance of R_3Nd sites and, therefore, in

trans-stereospecificity. The examples of the complete replacement of chloride ions with hydrocarbon radicals in the reaction of an *f*-metal chloride with an organo-magnesium compound are well known [16]. The comparison of microstructures of polydienes obtained in the presence of $NdCL_3 \cdot 3TBP–Al(iso\text{-}C_4H_9)_3$ and $NdCl_3 \cdot 3TBP–Mg(n\text{-}C_4H_9)(iso\text{-}C_8H_{17})$ systems led to the following findings. The substitution of dialkyl magnesium for trialkyl aluminum in the *cis*-regulating halogen-containing $NdCl_3 \cdot 3TBP–Al(i\text{-}C_4H_9)_3$ catalyst (the concentration of *cis*-units varied from 93 to 97%), that is, change-over to the system containing $Mg(n\text{-}C_4H_9)(iso\text{-}C_8H_{17})$ resulted in the inversion of stereospecificity. When the Mg-to-Nd ratio varied from 7 to 15, highly stereoregular *trans*-polybutadiene containing 95% *trans*-1,4-units and 5% 1,2-units was formed. In the copolymerization of butadiene and isoprene, as well as in the homopolymerization of butadiene, the replacement of organoaluminum component by organomagnesium component caused the entire inversion of stereospecificity in the lanthanide catalytic system. The copolymers obtained in the presence of $NdCl_3 \cdot 3TBP–Al(iso\text{-}C_4H_9)_3$ catalytic system predominantly contained *cis*-1,4 units, whereas the copolymers obtained in the presence of $NdCl_3 \cdot 3TBP–Mg(n\text{-}C_4H_9)(iso\text{-}C_8H_{17})$ system mainly contained *trans*-1,4 units (Table 1). In copolymerization performed in the presence of $NdCl_3 \cdot 3TBP–Al(iso\text{-}C_4H_9)_3$ catalytic system, the concentration of *trans*-1,4-units in the butadiene moiety increased and that of *cis*-1,4-units decreased, as the initial mixture of monomers was enriched with isoprene. Because isoprene is less reactive than butadiene, we believe that the observed effect was due to an increase in the contribution from the *anti–syn* isomerization of butadiene terminal units of growing polymeric chains.

It was of interest to trace how stereospecificity would change with the use of mixed catalytic systems $NdCl_3 \cdot 3TBP–Al(iso\text{-}C_4H_9)_3–Mg(n\text{-}C_4H_9)(iso\text{-}C_8H_{17})$ in the light of obtained results. We studied the effect of $Mg(n\text{-}C_4H_9)(iso\text{-}C_8H_{17})$ additions to the $NdCl_3 \cdot 3TBP–Al(iso\text{-}C_4H_9)_3$ catalytic system that was prepared by pouring together $NdCl_3 \cdot 3TBP$ and $Al(iso\text{-}C_4H_9)_3$ at Al/Nd = 30, keeping the mixture for 30 min, centrifuging, and washing it with toluene. The precipitate exhibited activity in polymerization. Then, particular portions of $Mg(n\text{-}C_4H_9)(iso\text{-}C_8H_{17})$ were added to this catalyst, and the mixture was kept for 20 or 60 min at
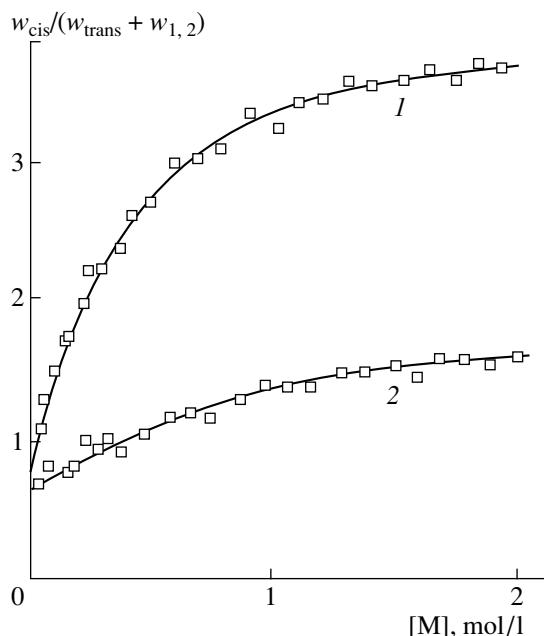
Fig. 5. Relative formation rates for *cis*-units in the polymerization of piperylene in (*1*) heptane and (*2*) toluene as functions of the monomer concentration. (Points show experimental data; lines correspond to theoretical calculation).

Table 1. Microstructure of copolymers of butadiene and isoprene obtained in the presence of the $NdCl_3 \cdot 3TBP$–Al(iso-$C_4H_9)_3$ and $NdCl_3 \cdot 3TBP$–Mg(n-C_4H_9)(iso-C_8H_{17}) catalytic systems

Polymer composition, mol %		Concentration of units, %					
		Butadiene moiety			Isoprene moiety		
butadiene	isoprene	cis-1,4-	trans-1,4-	1,2-	cis-1,4-	trans-1,4-	3,4-
$NdCl_3 \cdot 3TBP$–Al(iso-$C_4H_9)_3$							
100	0	94.7	4.8	0.5	–	–	–
87	13	93.1	6.1	0.8	98.5	–	1.5
80	20	92.3	7.0	0.7	98.1	–	1.9
72	28	92.9	6.5	0.6	98.0	–	2.0
64	36	94.1	5.7	0.2	97.7	–	2.3
55	45	91.3	7.7	1.0	97.1	–	2.9
40	60	90.7	8.5	0.8	96.4	–	3.6
30	70	90.2	9.8	–	96.3	–	3.7
20	80	87.6	12.4	–	95.3	–	4.7
0	100	–	–	–	94.8	–	5.2
$NdCl_3 \cdot 3TBP$–Mg(n-C_4H_9)(iso-C_8H_{17})							
100	0	–	96.0	4.0	–	–	–
94.4	5.6	–	95.8	4.2	–	100	0
90.5	9.5	–	96.1	3.9	–	100	0
89.4	10.6	–	96.0	4.0	–	100	0
82.8	17.2	–	96.6	3.4	–	100	0
74.6	25.4	–	96.8	3.2	–	100	0
70.2	29.8	–	97.7	2.3	–	97.7	2.3
53.7	46.3	–	98.5	1.5	–	96.2	3.9
43.1	56.9	–	100	0	–	92.7	7.3
25.0	75.0	–	100	0	–	92.3	7.7
0	100	–	–	–	–	91.7	8.5

25°C. It turned out that, in the polymerization of butadiene, the concentration of cis-1,4 units somewhat decreased with an extension of the exposure time from 20 to 60 min and with an increase in the Mg/Nd ratio from 5 to 40 (Table 2). During the polymerization of butadiene in the presence of the $NdCl_3 \cdot 3TBP$– Mg(n-C_4H_9)(iso-C_8H_{17}) system and Al(iso-$C_4H_9)_3$ additives, the concentration of trans-1,4 units decreased and that of cis-1,4 units increased as the Al/Nd ratio grew (Table 2).

It should also be noted that the simultaneous presence of several types of active sites in a catalytic system should, first of all, widen the molecular-weight distribution of polymers. This is in agreement with the results of recent research (see, for example, [10]), which demonstrated that a wide molecular-weight distribution of polydienes obtained in the presence of neodymium catalytic systems was due to the kinetic nonuniformity of the active site of neodymium catalysts. Regardless of the nature of organoaluminum

Table 2. Microstructure of polybutadiene as functions of the Mg/Nd and Al/Nd ratios in the polymerization of butadiene in the presence of $NdCl_3 \cdot 3TBP–Al(iso-C_4H_9)_3$ system with the additions of $Mg(n-C_4H_9)(iso-C_8H_{17})$ and in the presence of $NdCl_3 \cdot 3TBP–Mg(n-C_4H_9)(iso-C_8H_{17})$ system with the additions of $Al(iso-C_4H_9)_3$ ($[NdCl_3 \cdot 3TBP] = 1.2 \times 10^{-3}$ mol/l; polymerization time, 1 h in the first system, and 48 h in the second system)

Ratio of elements		Concentration of units, %		
Mg/Nd	Al/Nd	*cis*-1,4-	*trans*-1,4-	1,2-
$NdCl_3 \cdot 3TBP–Al(iso-C_4H_9)_3 + Mg(n-C_4H_9)(iso-C_8H_{12})$				
5	30	94.4	4.5	1.1
25	"	92.7	6.0	1.3
40	"	90.4	7.8	1.8
40*	"	87.3	10.2	2.5
$NdCl_3 \cdot 3TBP–Mg(n-C_4H_9)(iso-C_8H_{12}) + Al(iso-C_4H_9)_3$				
11	0	0	96.2	3.8
"	10	17.7	78.4	3.9
"	20	48.9	48.1	3.0
"	30	53.1	44.1	2.8
"	40	54.3	43.1	2.6
"	50	59.5	37.9	2.6

* The mixture was kept for 60 min (in the three previous cases, it was kept for 20 min).

component of neodymium catalysts used in the polymerization of dienes, four types of active sites were formed on which polydienes with different molecular weights were obtained. It was assumed that two of five possible active sites (see Fig. 1) exhibited almost equal reactivity.

CONCLUSION

Several types of active sites that differ in both the nearest environment of a lanthanide atom (the numbers of chlorine and carbon atoms) and the number of lanthanide–carbon bonds involved in chain growth may be formed during the polymerization of dienes in the presence of lanthanide catalytic systems. According to quantum-chemical study, the π-allyl binding of the terminal unit of a growing polymeric chain with the lanthanide atom of an active site may be the reason for the *cis*-stereospecificity of the site action. Therefore, the active sites containing electron-acceptor chlorine

atoms form *cis*-units in polydienes. Depending on the conditions of the catalytic system preparation, primarily on the nature of an organometallic compound of a nontransition metal, one or another set of active sites that can affect its stereospecificity is formed. The *anti-syn*-isomerization of terminal units of growing polymeric chains makes a certain contribution to the formation of *trans*-1,4 units in the polymerization of dienes in the presence of *cis*-regulating active sites.

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