Structure of Active Centers, Their Stereospecificity Distribution, and Multiplicity in Diene Polymerization Initiated by NdCl$_3$-Based Catalytic Systems

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ABSTRACT: On the basis of quantum-chemical calculations, it was shown that among six types of active centers (ACs) that can form during the polymerization of butadiene with lanthanide-based catalytic systems, five types (containing electron-accepting chlorine atoms in the coordination sphere of a lanthanide) exhibit a π-allyl binding of the terminal unit of a growing polymer chain to a lanthanide atom and function as *cis*-regulating. The sixth type of ACs is characterized by a σ-alkyl structure and shows a *trans*-stereospecificity. This results was used to interpret the data on the microstructure of polybutadiene prepared using NdCl$_3 \cdot$ 3TBP-Al(iso-C$_4$H$_9$)$_3$, NdCl$_3 \cdot$ 3TBP-Mg(n-C$_4$H$_9$)(iso-C$_8$H$_{17}$) catalytic systems and their combinations (TBP is tributyl phosphate). © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 601–603, 2003

INTRODUCTION

The multiplicity of active centers (ACs) may exist in lanthanide catalytic systems,[1,2] that is, several types of ACs initiating polymerization may be present in the reaction medium. However, no comprehensive theoretic investigations have been reported on the structure of ACs and their stereospecificity.

Here, the object is to perform the quantum-chemical study of the electronic structure and geometry of the potential ACs, to estimate their steoreospecificity, and to interpret the data on the microstructure of polybutadiene (PB) prepared in the presence of NdCl$_3 \cdot$ 3TBP-Al(iso-C$_4$H$_9$)$_3$, NdCl$_3 \cdot$ 3TBP-Mg(n-C$_4$H$_9$)(iso-C$_8$H$_{17}$); NdCl$_3 \cdot$ 3TBP-Al(iso-C$_4$H$_9$)$_3$-Mg(n-C$_4$H$_9$)(iso-C$_8$H$_{17}$), and NdCl$_3 \cdot$ 3TBP-Mg(n-C$_4$H$_9$)(iso-C$_8$H$_{17}$)-Al(iso-C$_4$H$_9$)$_3$.

RESULTS AND DISCUSSION

Recently it was reported[3] that, to a first approximation, six types of ACs may be distinguished in the lanthanide catalytic system NdCl$_3 \cdot$ 3TBP-AlR$_3$. These centers differ by the amount of Cl and C atoms occurring in the nearest environment of Nd atom (Fig. 1). The possibility of existence of these six types of ACs does not imply that all these types occur simultaneously. In reality, the fraction of each type of ACs depends on specific conditions used to prepare a catalytic system and the nature of a nontransition–metal organometallic compound (Al or Mg).

During the polymerization of dienes initiated by lanthanide catalysts, the terminal unit of a growing polymer chain may be linked to a lanthanide through a π- or σ-bond. Formerly we have demonstrated that the *cis*-stereospecificity and regioselectivity are independent of the geometry of the ACs as a whole.[4] The major manifestation of *cis*-stereospecificity is that π–σ-equilibrium is displaced to the π-state so that the lifetime of the AC in the σ-state does not provide the occurrence of the elementary act of insertion via this bond. In this case, *cis*-stereospecificity and regioselectivity develop. Factors favoring an increase in the lifetime of the σ-state (e.g., the introduction of electron–donor additives or substituents) will lead to the depression of the *cis*-regulating ability of CAs and will bring about the loss of regioselectivity.

Distinct information on the ratio of the lifetimes of ACs occurring in π- and σ-states may be derived by comparison of the full energies of these structures. Therefore, we performed quantum-chemical calculations of the geometry and electronic structure of π- and σ-states of six ACs. Six types of ACs that may be present in the NdCl$_3 \cdot$ 3TBP-Al(iso-C$_4$H$_9$)$_3$ catalytic system are schematically shown in Figure 1.

The terminal unit of a growing polymer chain was modeled by CH$_3$CH=CHCH$_2$—CH$_2$CH=CHCH$_2$, while Al(iso-C$_4$H$_9$)$_3$ was substituted by Al(CH$_3$)$_3$. For each kind of ACs, two π-structures (anti- and syn-) and two σ-structures (*cis*- and *trans*-) (a lanthanide atom forms a Nd–C$_\alpha$H$_2$-bond), and one more σ_γ-structure, in which the lanthanide atom is linked to the C$_\gamma$
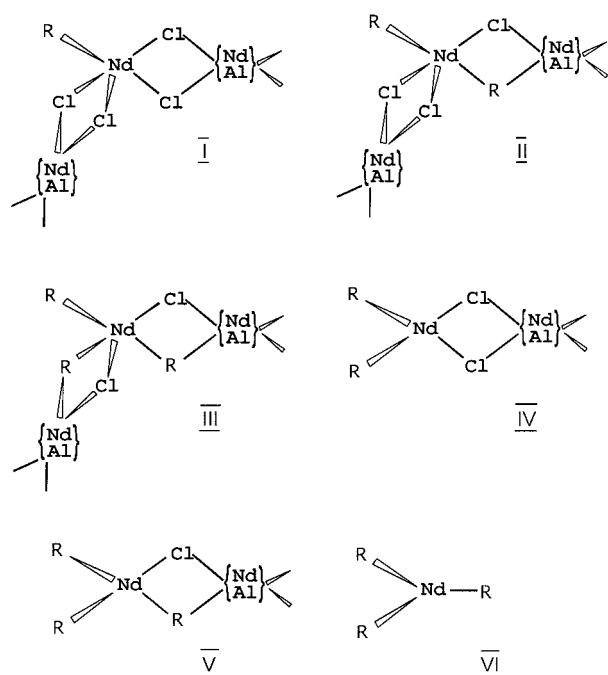
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Figure 1 Six types of active centers that may be present in the $NdCl_3 \cdot 3TBP\text{-}Al(iso\text{-}C_4H_9)_3$ catalytic system. Nd and Al atoms in braces indicate that either Nd or Al atom may reside in this place.

atom of the terminal unit of the growing polymer chain were calculated (Table I).

Results of quantum-chemical calculations show that the π-structure is energetically more preferable for the ACs of type I (by 44.8 kJ/mol compared to the σ-state). The difference in the energies ΔE between the most energetically favorable π- and σ-structures for the other types of centers are 40.2, 26.4, 16.0, 13.2, and -13.3 kJ/mol for structures II–VI, respectively. Thus, for the ACs of types I–V, delocalized π-structures are more favorable energetically, while for the ACs of type VI, this is true of the localized σ-structure. Therefore, it may be supposed that centers I–V are *cis*-regulating, while center VI possesses a *trans*-regulating ability. It may be expected that on passing from the ACs of type I to that of type VI, *cis*-stereospecificity will decrease, while *trans*-stereospecificity will increase.

Distinct support for this assumption is provided by experimental data that show that the interaction of $NdCl_3$ with AlR_3 produces (as a result of alkylation reaction) $RNdCl_2$ and R_2NdCl derivatives; according to ref. [5], no R_3Nd is produced.[5] This means that the ACs of types I–V may generate in the $NdCl_3 \cdot TBP\text{–}AlR_3$ catalytic system.

The substitution of AlR_3 by a stronger alkylating agent (e.g., Mg*RR'*) should bring about the appearance of R_3Nd centers and, consequently, the development of *trans*-stereospecific ACs. The complete replacement of chloride by hydrocarbon radicals in the reaction of f-metal chloride with organomagnesium compound was disclosed in ref.[6]. Actually, the use of dilakylmagnesium $Mg(n\text{-}C_4H_9)(iso\text{-}C_8H_{17})$ instead of trialkylaluminum in a *cis*-regulating (the content of cis-units is 93–97%) halide-containing catalyst $NdCl_3 \cdot 3TBP$ leads to the inversion of its stereospecificity (95% 1,4-*trans* units and 5% 1,2 units[7]).

The ratio between different types of ACs may be affected by a change in the alkylating ability and the concentration of a nontransition–metal organometallic compound, so we studied the effect of $Mg(n\text{-}C_4H_9)(iso\text{-}C_8H_{17})$ and $Al(iso\text{-}C_4H_9)_3$ additives on the stereospecificity of $NdCl_3 \cdot 3TBP\text{–}Al(iso\text{-}C_4H_9)_3$ and $NdCl_3 \cdot 3TBP\text{–}Mg(n\text{-}C_4H_9)(iso\text{-}C_8H_{17})$ catalytic systems (systems A and B, respectively).

It was found that, in the polymerization of butadiene catalyzed by system A, a slight monotonic reduction in the content of 1,4-*cis* units at the expense of the content of 1,4-*trans* units was observed (Table II). As the duration of contact between the organomagnesium compound and the "precipitant" catalyst becomes longer (from 1200 to 3600 s), its activity drops within the whole range of the studied Mg:Nd ratios. In this case, the content of 1,4-*cis* units in PB also drops (Table II).

During the polymerization of butadiene initiated by system B, an increase in the Al:Nd ratio from 0 to 50 causes a reduction in the content of 1,4-*trans* units due to the appearance of 1,4-*cis* units (Table II).

As was noted above, a set of ACs varying from I to V, which are *cis*-stereoregulating, may form in system

TABLE I
Full Energies E_n for the Structures of Active Centers[a]

Structures	E_n (kJ/mol) for structures					
	I	II	III	IV	V	VI
π-(anti-)	-46.3	-40.2	-25.9	-16.9	-6.5	0.0
π-(syn-)	-59.11	-51.4	-40.5	-31.7	-24.9	-12.6
σ^α-(cis-)	-5.4	-4.7	-8.3	-4.7	-4.9	-19.0
σ^α-(trans-)	-14.3	-11.2	-14.1	-15.7	-11.7	-25.9
σ^γ-	0.0	0.0	0.0	0.0	0.0	-14.4

[a] The energy of the least favorable structure is taken as the zero value.

TABLE II
Variation in the Microstructure of Polybutadiene with Mg:Nd and Al:Nd Ratios in Polymerization Catalyzed by A and B Systems

Mt:Nd (mol/mol)	Content of units, %		
	1,4-*cis*-	1,4-*trans*-	1,2-
System A (Mt—Mg)			
5	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
50	87.2	10.0	2.8
80	78.2	18.0	4.0
System B (Mt—Al)			
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

Note. $[NdCl_3 \cdot 3TBP] = 1.2 \times 10^{-3}$ mol/L. System A: $NdCl_3 \cdot 3TBP-Al(iso-C_4H_9)_3$ with $Mg(n-C_4H_9)(iso-C_8H_{17})$ additives; polymerization conditions:
Al:Nd = 30, $[C_4H_6]$ = 1.77 mol/L; the time of contact between $Mg(n-C_4H_9)(iso-C_8H_{17})$ and the "precipitate" catalyst is 1200 s for the first three ratios and 3600 s for the subsequent ones; the time of polymerization is 3600 s. System B: $NdCl_3 \cdot 3TBP-Mg(n-C_4H_9)(iso-C_8H_{17})$ with $Al(iso-C_4H_9)_3$ additives; the polymerization conditions: Mg:Nd = 11, $[C_4H_6]$ = 1.41 mol/L; the time of polymerization is 1.72×10^5 s; conversion is 11–22%.

A. Upon the addition of $Mg(n-C_4H_9)(iso-C_8H_{17})$, which is a stronger alkylating agent than $Al(iso-C_4H_9)_3$, a further alkylation reaction may take place that eventually produces the ACs of the R_3Nd type exhibiting *trans*-stereospecificity. Naturally, the content of *trans*-units in the resulting polymer grows.

As for the polymerization of butadiene catalyzed by system B, alkylation proceeds at the initial stage in the absence of $Al(iso-C_4H_9)_3$ additives. During this reaction in contrast to system A, equilibrium is shifted to the products of complete alkylation of R_3Nd. This assumption is proved by the fact that the microstructures of PB polymers produced using $NdCl_3 \cdot 3TBP-Mg(n-C_4H_9)(iso-C_8H_{17})$ and R_3Ln^8 catalysts are identical. The introduction of triisobutylaluminum into system B leads to the "dilution" of the strong alkylating agent $Mg(n-C_4H_9)(iso-C_8H_{17})$ by a weaker one. Because catalytic system B is homogeneous (no precipitate is formed upon the interaction of $Mg(n-C_4H_9)(iso-C_8H_{17})$ with $NdCl_3 \cdot 3TBP$), a new equilibrium is attained due to the occurrence of exchange alkylation reactions between the solution components. As a result, the appearance of less alkylated forms of ACs of the $RNdCl_2$ and R_2NdCl types, as well as their complexes with AlR_3 and MgRR′, becomes possible. In accordance with calculations, these ACs should be

cis-regulating. The content of 1,4-*cis* units in the resulting PB should increase at the expense of *trans*-1,4 units. This is indeed the case in experiments (Table II).

We also note that, upon the introduction of MgRR′ into the $NdCl_3 \cdot 3TBP-Al(iso-C_4H_9)_3$ catalytic system, a change in microstructure is not as pronounced as upon the addition of $Al(iso-C_4H_9)_3$ into the $NdCl_3 \cdot 3TBP-Mg(n-C_4H_9)(iso-C_8H_{17})$ catalytic system. Possibly, this is due to the fact that, in the $NdCl_3 \cdot 3TBP-Al(iso-C_4H_9)_3$ catalytic system (which is an amorphous precipitate), the alkylation reaction is hampered compared to the $NdCl_3 \cdot 3TBP-Mg(n-C_4H_9)(iso-C_8H_{17})$ system, which is a homogeneous catalyst.

Furthermore, the stereospecificity effects, the existence of a set of ACs in the polymerization system, should cause broadening of the molecular mass distribution of the resulting polydienes, as was demonstrated experimentally.[2] As follows from the molecular mass distribution data, a set of three or four ACs exists in the $NdCl_3 \cdot 3TBP-Al(iso-C_4H_9)_3$ lanthanide catalytic system. This fact may imply that either not all five types of *cis*-stereoregulating ACs are realized or several types of ACs have close reactivities.

By this means, six types of ACs may appear in the diene polymerization initiated by the lanthanide catalytic systems. Based on quantum-chemical calculations, it was shown that five types of ACs, containing electron-accepting chlorine atoms in the coordination sphere of lanthanide, feature the π-allyl binding of the terminal unit of the growing polymer chain to a lanthanide atom and exhibit *cis*-regulating ability. The sixth type of ACs, a compound of R_3Nd, has a σ-alkyl structure and functions as *trans*-regulating. Depending on conditions of preparing a catalytic system and on the nature of a nontransition–metal organometallic compound, one or another set of ACs forms; as a result, the stereospecificity of the used catalytic system may change.

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