CATALYTIC REACTION
MECHANISMS

Transition Metal Compounds in Combination with Alkylaluminoxanes as Catalysts for Olefin and Diene Polymerization

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Abstract—Catalytic systems based on Zr, Co, Ti, V, and Nd in combination with –(–RAlO–)–$_n$ alkylaluminoxanes, where R = Me or iso-Bu, were used for the polymerization of olefins and dienes. The structure of methylaluminoxane (MAO) was studied with the use of theoretical calculations and experimentally by vibrational spectroscopy. It was found that only *cis* and *trans* conformations of linear MAO oligomers actually occurred at the active centers of olefin polymerization. The stereospecificity of catalytic systems for diene polymerization depends on the nature of the substituent at aluminum, as well as on the nature of the transition metal and its ligand environment.

INTRODUCTION

The discovery of highly effective homogeneous catalysts based on zirconocene and methylaluminoxane (MAO) derivatives was an outstanding event in the chemistry of polyolefins [1, 2]. A great number of publications on the catalytic properties of systems of this kind in polymerization processes and on the mechanism of their action appeared in the past two decades [3–7]. In this case, the range of the systems was considerably extended by other transition metals or other transition metal compounds and by the use of MAO homologues. Previously [8, 9], catalytic systems with different ligand environments of a metal were compared. The use of metallocenes with various ligand environments provides an opportunity to obtain new types of polymers with technically important properties [6].
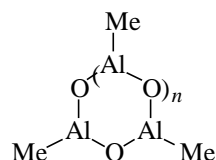
Based on NMR data for zirconocene dichloride/MAO complexes [10–12], we can assume that, in the interaction of bis(alkylcyclopentadienyl)ZrCl$_2$ with MAO, the $[(C_5H_5)_2ZrCH_3]^{\delta+}MAO^{\delta-}$ intermediate was initially formed with the subsequent hydride transfer and olefin coordination [6, 13]. An alkylated zirconocene dichloride was detected by ^{1}H and ^{13}C NMR spectroscopy upon the addition of MAO and then ethylene or 1-hexene [10].

The structure of propylene oligomers prepared on the zirconocene dichloride/MAO catalytic systems was studied [13–17]. It was found that the oligomers contained anomalous structures, (CH$_2$)$_n$ chains, where $n \geq$ 4; this suggests the possibility of the 1,3-insertion of propylene into a polymer chain.

The production of standardized MAO is of crucial importance in the successful polymerization of olefins in the presence of the metallocene catalysts under consideration.

In contrast to isobutylaluminoxane, the structure of which was determined by Mason *et al.* [18], it was noted that the complete characterization of MAO is difficult to perform because of high-temperature disproportionation reactions and association in solution with the formation of an oligomer mixture, that is, the occurrence of multiple equilibria. Moreover, X-ray diffraction analysis cannot be performed because it is impossible to prepare crystalline samples. Therefore, conclusions on the structure of MAO are currently drawn based on the analysis of MAO by physicochemical techniques and on the structural characteristics of related alkylaluminoxanes.

It is well known [19–23] that MAO prepared by the hydrolysis of trimethylaluminum (TMA) consists of linear (Me$_2$Al–[OAl(Me)]$_n$–OAlMe$_2$) or cyclic oligomers with n = 2–20:

$$\underset{Me}{\underset{|}{\overset{Me}{\overset{|}{Al}}}} \quad (O \quad O)_n \quad Al \overset{O}{\diagup} Al$$

Me   Me

The effect of synthesis conditions on the structure of MAO and the relationship between the structure and the catalytic activity of MAO in the polymerization of olefins were first reported in [20].

The aim of this work was to study the factors that affect the activity and stereospecificity of action of systems based on transition metal compounds in combination with alkylaluminoxanes and to examine the structure of the aluminum-containing component (MAO) using IR spectroscopy and the theoretical calculations of vibrational spectra.

Table 1. Activity of the zirconocene dichloride/MAO catalytic system in ethylene polymerization depending on MAO preparation conditions

MAO sample*	$[Zr] \times 10^6$, mol/l	[MAO], unit/l	Al/Zr, mol/mol	Polyethylene yield	
				g	kg (mol Cat)$^{-1}$ h^{-1}
1	7.0	0.0396	5700	2.45	39100
	2.5	0.0396	15840	2.64	58274
2	3.4	0.038	11176	3.27	25349
3	3.6	0.038	10555	Traces	–

Note: Polymerization conditions: $T = 70°C$; $P = 7$ atm; solvent, toluene.
  * (1) Direct hydrolysis of $Al(CH_3)_3$ with water; $T = -12°C$; $Al/H_2O = 2$ mol/mol.
    (2) From $Al_2(SO_4)_3 \cdot 18H_2O$ and $Al(CH_3)_3$ in toluene; $T = 20°C$; $\tau = 20$ h; $Al/H_2O = 1.5$ mol/mol.
    (3) From $Al_2(SO_4)_3 \cdot 18H_2O$ and $Al(CH_3)_3$ in toluene; $T = 50°C$; $\tau = 7$ h; $Al/H_2O = 1.5$ mol/mol.

EXPERIMENTAL

Preparation of the Catalytic System

$Ti(OBu)_4$ (Fluka) was vacuum distilled and kept under dry nitrogen. Cobalt diethyldithiocarbamate (DEDTC) was synthesized by the interaction of aqueous sodium diethyldithiocarbamate and $CoCl_2$ solutions. The resulting cobalt diethyldithiocarbamate precipitate was filtered off, washed with distilled water, and vacuum dried to a constant weight.

$V(OBu^t)_4$ was prepared according to a published procedure [24].

The synthesis of $All_2NdCl \cdot 2MgCl_2 \cdot 2THF$ (where All is allyl) was performed in two stages. At the first stage, 6 ml (0.062 mol) of allyl chloride in 10 ml of tetrahydrofuran (THF) was added to 1 g (0.041 mol) of Mg in 25 ml of THF, and the resulting mixture was refluxed for 1 h. After cooling and keeping it overnight, a 1 N Grignard reagent (AllMgCl) solution was obtained.

At the second stage, 3.2 ml of the 1 N AllMgCl solution (0.032 mol) in THF was slowly added to 3.64 g (0.045 mol) of $NdCl_3$ in 40 ml of THF on cooling to $0°C$ with stirring. After adding the first drops of the Grignard reagent, the solution turned light green from pale lilac. After the addition of AllMgCl, the temperature of the reaction mixture was increased up to $20°C$, and the mixture was left to stand overnight. The precipitate formed was filtered off and dried in a vacuum; 5.6 g (0.0094 mol) of a pale green substance of the composition $All_2NdCl \cdot 2MgCl_2 \cdot 2THF$ was obtained. Calculated (%): Cl, 29.77; Mg, 8.15. Found (%): Cl, 29.26; Mg, 8.48.

In the study of the structure of MAO, various procedures were used for the hydrolysis of TMA, in particular, the reactions of TMA with the crystal hydrates $CuSO_4 \cdot 5H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$ and the direct hydrolysis of TMA with water; in this case, the synthesis temperature was varied. The resulting samples of MAO were tested in the reaction of ethylene polymerization. Table 1 summarizes the reaction conditions.

The IR spectra of the MAO samples synthesized and tested for the catalytic activity were measured. The samples for IR-spectroscopic measurements were prepared as suspensions in Vaseline oil or as thin films in a box with a dry inert atmosphere. The spectra of the MAO samples, which were placed in hermetically sealed cells with CsI windows or between KBr plates, were measured on a Specord M-82 spectrophotometer over the region $200-4000$ cm^{-1}.

The most effective MAO samples (methyl-, ethyl-, and isobutylaluminoxanes) were used for diene polymerization. These samples were prepared by the direct hydrolysis of $Al(CH_3)_3$, $Al(C_2H_5)_3$, and $Al(iso-C_4H_9)_3$ at the ratio $AlR_3 : H_2O = 2$ and $-14°C$; the reaction time was 20 h. Toluene, which was washed with H_2SO_4 to remove unsaturated compounds and with water to a neutral reaction and dried with $CaCl_2$ for 24 h, was refluxed over Na for 5 h; next, it was distilled in a nitrogen atmosphere and stored over molecular sieves. Butadiene (99.5%; Voronezh Synthetic Rubber Plant) was used, which was additionally dried by passing through columns with Al_2O_3 and then over molecular sieves.

Butadiene Polymerization

Dry butadiene (13 ml; 0.149 mol) was condensed in a glass ampule in a vacuum at $-78°C$. Next, 1.5 ml of a cobalt diethyldithiocarbamate (1.5×10^{-5} mol) solution in toluene and 35 ml of a MAO solution in toluene were added in a flow of argon at the molar ratio $Al : Co = 800$. A 10-ml portion of dry toluene was added, and the ampule was sealed in a flow of argon. The polymerization of butadiene was performed under conditions specified elsewhere [25]. The resulting polymer was precipitated with methanol. Ionol was used as a stabilizing agent. The polymer was washed with methanol and dried in a vacuum to constant weight. The yield of the polymer was 56–83% depending on the conditions of polymerization.

Polymer Characterization

The characteristic viscosity of polymer solutions in toluene at $30°C$ was measured using an Ubbelohde viscometer [26].

The microstructure of polymers was evaluated using IR and NMR spectra. The IR spectra of polymers were measured on a Specord M-80 spectrophotometer over the wavenumber range 200–4000 cm^{-1}. The samples as films were prepared from solutions in benzene and toluene. The ^{1}H and ^{13}C NMR spectra of the samples were measured on a Bruker MSL-300 pulsed Fourier transform NMR spectrometer at a detector temperature of 25°C. CDCl$_3$ was used as a solvent; the concentration was usually equal to 10–15 wt %. The samples were placed in 10-ml ampules.
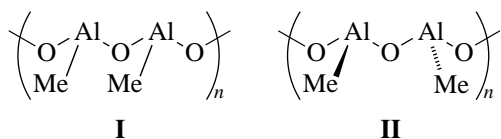
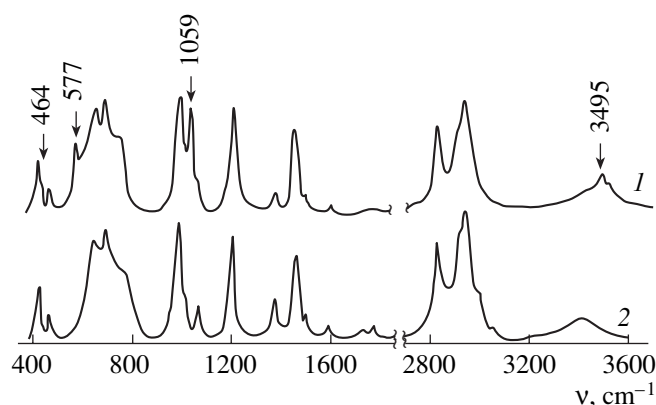## RESULTS AND DISCUSSION

Structure of MAO

The IR spectra of the samples of MAO (see the figure) that was the constituent of effective catalysts for ethylene polymerization (group *a*) exhibited significant differences form the spectra of the samples of MAO that were the constituents of inactive catalysts (group *b*) (Table 1 summarizes data on the activity of catalysts in ethylene polymerization). The spectra of group *a* samples exhibited a number of bands at 3495 (w), 1059 (vw), 577 (s), and 464 (w) cm^{-1}, which were absent from the IR spectra of group *b* samples. In addition, small (to within 5 cm^{-1}) shifts of absorption bands were observed at 490, 990–1015, and 2840–2950 cm^{-1}.

Note that the spectra of the samples of MAO that were the constituents of catalysts with low efficiencies occupied an intermediate position between the spectra of group *a* and *b* samples. That is, the above bands occurred in these spectra; however, their intensities were dramatically lower. Only a band at 3495 cm^{-1} in the spectra of MAO from group *a* can be interpreted as the stretching vibration ν(Al–OH); however, its low intensity is indicative of a very low concentration of these groups in the samples. The other most significant distinctive spectroscopic features of MAO samples from groups a and b can be explained only after the complete interpretation of bands in the vibrational spectra of various conformations of MAO oligomers. At the same time, these significant differences in the IR spectra of the samples of MAO effective and ineffective in the processes of ethylene polymerization directly suggest that the structure of MAO and its ability to form the active center of polymerization are interrelated.

To interpret the distinctive features of the spectra of various MAO samples, we performed theoretical calculations for the vibrational spectra of different structural models of MAO:

IR spectra of MAO samples: (*1*) active and (*2*) inactive in the polymerization of ethylene.

minoxane; it follows from the data obtained that this aluminoxane exhibits a cyclic structure. We calculated the vibrational spectra of a set of the following cyclic MAO structures:

In the calculations of the vibrational spectra of the cyclic MAO structures, we varied structural parameters (bond lengths, valence angles, and dihedral angles), force constants, and electrooptical parameters over wide ranges. With the use of the above sets, we failed to obtain a theoretical spectrum that at least vaguely resembled the experimental spectra of MAO. Therefore, we abandoned the idea of relating differences in the IR spectra of MAO to its cyclic or linear structure. Because of this, we believe that the analogy between the structures of MAO and *tert*-butylaluminoxane, studied by X-ray diffraction analysis, drawn by Mason *et al.* [18] is wrong.

Structures **I** and **II** simulate linear MAO oligomers with the numbers of elementary units (*n*) equal to 8, 12, and 16. The tetrahedral configurations of substituents occurred at each Al atom. Table 2 summarizes geometry parameters in the elementary units of MAO, which were used in the calculations.

Models **I** and **II** differ in the spatial arrangements of methyl groups at two neighboring Al atoms: in model **I**, methyl groups are arranged on one side with respect to
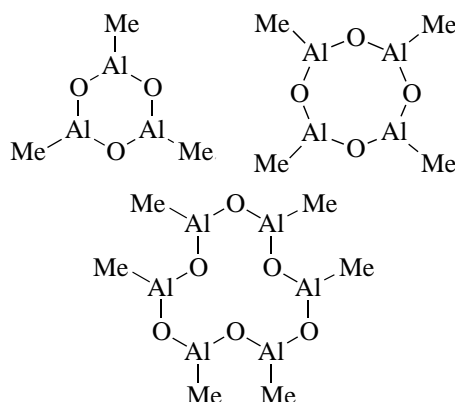
Consequently, only the models of linear MAO structures will be considered below. Mason *et al.* [18] performed the X-ray diffraction analysis of *tert*-butylalu-

Table 2. Main geometry characteristics (bond lengths and angles), force constants (K), and electrooptical parameters (dipole moments (μ) and derivatives of the dipole moments with respect to coordinate) used in the calculation of the vibrational spectrum of MAO

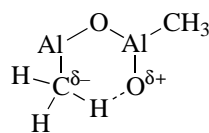| Bond	Length, Å	Angle, deg	$K \times 10^6$, cm^{-2}	μ, D	$d\mu/d\theta$, D/Å
Al–O	1.85	–	7.50	–0.5	–1.1
Al–C	1.98	–	4.55	–0.8	–1.1
C–H	1.09	–	7.80	0.305	0.8
O–Al–O	–	108	5.30	–	–
O–Al–C	–	122	3.65	–	–
Al–O–Al	–	110	2.75	–	–

the O–Al–O plane (*cis* form), whereas they are oriented in contrary directions with respect to this plane (*trans* form) in model **II**. For both of the models, vibrational spectra were calculated taking into account various conformations different in dihedral angles (θ) between two neighboring Al–O–Al planes. For each of the models, the angle θ was varied from 0° to 180° at 30° intervals, and the vibrational spectra of MAO oligomers were calculated for the conformations thus obtained. The code described by Gribov and Demen'ev [27] was used in the calculations; this code was adapted to the IBM PC. Table 2 summarizes the main force constants and electrooptical parameters, whereas Tables 3 and 4 summarize the results of a theoretical analysis of the vibrational spectra of different conformations as compared with the experimental IR spectra of various MAO samples.

The calculations of the vibrational spectra of all the above linear MAO conformations resulted in three types of theoretical spectra, which are denoted by *A*, *B*, and *C* in Table 3. The theoretical spectra of the *C* type exhibit a frequency set which is inconsistent with all the experimental IR spectra of MAO shown in the figure. These spectra were obtained for the *cis* form of MAO with the angles θ = 0°, 30°, and 180° and for the *trans* form with the angles θ = 60°, 90°, 150°, and 180°.

Moreover, the structural analysis of these conformations demonstrated the impossibility of their real occurrence because distances between the hydrogen atoms of methyl groups at neighboring Al atoms are very short.

The theoretical spectra of the *B* type are comparable to the experimental spectra of MAO catalyst samples that did not initiate the polymerization of olefins. These spectra were obtained for only two conformations (θ = 60° and 90°) of the *cis* form of MAO. The experimental IR spectra of the samples of MAO that are constituents of highly efficient catalysts for olefin polymerization are consistent with the theoretical spectra of the *A* type (Table 3) obtained for two conformations (θ = 120° and 150°) of the *cis* form and for three conformations (θ = 0°, 30°, and 180°) of the *trans* form of MAO. Note that the same set of force constants and electrooptical parameters was used for deriving all these theoretical spectra. The structural analysis of MAO models that give a theoretical spectrum of the *A* type demonstrates that these models have short distances (from 2.3 to 1.65 Å) between the hydrogen atoms of a methyl group at Al and the oxygen atom of a neighboring unit. The MAO models that give a theoretical spectrum of the *B* type exhibited no short distances between unbound atoms.

Thus, a combination of experimental data and theoretical calculations of vibrational spectroscopy allowed us to establish that only some conformations of linear MAO oligomers really occur. Moreover, the structure of MAO oligomers that are efficient catalysts for olefin polymerization differs from the structure of MAO oligomers that do not initiate this polymerization in the occurrence of short distances between unbound hydrogen atoms of the methyl group and the oxygen atom of a neighboring unit. These short distances can result in intramolecular association like hydrogen bonding, which is responsible for the appearance of an excessive negative charge at the carbon atom of the methyl group and a positive charge at the oxygen atom:

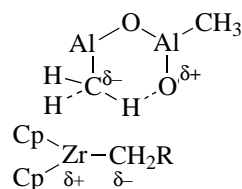**Table 3.** Types of the theoretical spectra of various MAO conformations

θ angle, deg	Type of the theoretical spectrum			
	cis-form **I**	short distances between unbound atoms, Å	*trans*-form **II**	short distances between unbound atoms, Å
0	C	H…H = 1.15	A	O…H = 1.75
30	C	H…H = 0.93	A	O…H = 1.68
60	B	–	C	H…H = 1.34
90	B	–	C	H…H = 0.91
120	A	0…H = 2.3	C	H…H = 0.84
150	A	O…H = 1.65	C	H…H = 1.52
180	C	H…H = 0.78	A	O…H = 1.75

Table 4. Comparison between the experimental and theoretical spectra of MAO

Experimental spectrum, group a; ν, cm^{-1}	Theoretical spectrum A		Experimental spectrum, group b; ν, cm^{-1}	Theoretical spectrum B		Assignment
	ν, cm^{-1}	$I*$		ν, cm^{-1}	$I*$	
437 m	429	1.36	437 m	430	1.85	δ(C–Al–O)
464 w	458	0.12	–	–	–	δ(O–Al–O, Al–O–Al)
497 m	488	1.43	486 m	485	1.46	δ(O–Al–O, Al–O–Al)
577 s	578	2.15	–	–	–	δ(O–Al–O), ν(Al–C)
637 vs	633	2.43	641 s	638	1.65	δ(Al–C–H), ν(Al–C)
–	658	0.45	–	–	–	δ(Al–C–H), ν(Al–C)
688 vs	680	2.56	690 vs	685	2.62	ν(Al–C), δ(O–Al–C)
778 sh	768	1.86	783 sh	778	0.61	δ(Al–C–H)
825 sh	826	0.95	829 sh	833	1.03	ν(Al–O), δ(Al–C–H)
989 vs	987	3.05	990 vs	987	7.07	ν(Al–O)
1015 sh	1024	0.75	1048 w	1046	0.65	ν(Al–O), δ(O–Al–O)
1059 vs	1065	8.30	1085 m	1078	1.85	ν(Al–O), δ(O–Al–O)
1203 vs	1196	8.50	1206 s	1200	3.60	δ(Al–C–H), δ(H–C–H)
1303 w	1295	0.71	1308	1298	0.15	δ(H–C–H)
1383 w	–	–	–	1379 w	–	Impurity
1460 m	1464	1.60	1460 m	1460	1.48	δ(H–C–H)
–	–	–	1770 w	–	–	–
–	–	–	1802 w	–	–	–
2854 s	2848	10.05	2856 s	2848	10.6	ν(C–H)
2897 sh	2890	3.20	–	–	–	ν(C–H)
2931 vs	2925	14.50	2928 vs	2938	13.80	ν(C–H)
2954 vs	2947	16.70	2956 sh	2953	12.90	ν(C–H)
3495 w	–	–	–	–	–	–

* I is the band intensity $\times 10^{-8}$, cm^2 molecule^{-1} s^{-1}.
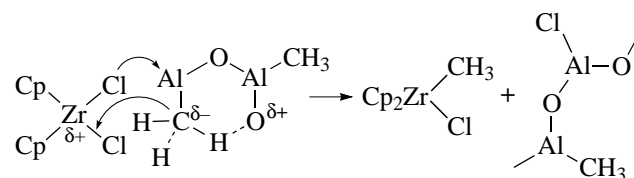
This charge polarization at certain sites of an MAO oligomer chain on coordination to aluminoxane can stabilize the active center of the zirconocene dichloride/MAO catalytic system, which has a strongly polarized M–C bond:

This coordination can result in an optimum charge distribution over the Zr–C bond for providing an act of chain propagation.

Moreover, the intramolecular association in MAO oligomers should increase the alkylating ability in the alkylation reactions of a transition metal compound and the formation of an M–C bond, which is active in polymerization catalysis.

The reaction scheme proposed for the alkylation of zirconocene dichloride with MAO does not exclude the hypothesis [28] that the impurity of TMA in MAO participates in the acts of formation of Zr–CH$_3$ bonds, which are active in olefin polymerization catalysis. Unfortunately, vibrational spectroscopy did not allow us to evaluate unambiguously the presence of a small amount of TMA in MAO because of the interference of the main absorption bands of these compounds. How-

Table 5. Butadiene polymerization in the presence of catalytic systems based on Co, Ti, V, and Nd compounds and aluminoxanes: Characterization of the test materials

1,4-*cis*-PB					1,2-PB				
No.	Catalyst	T_{pol}, °C	$[\eta]$, dl/g	Concentration of 1,4-*cis* units, wt %	No.	Catalyst	T_{pol}, °C	$[\eta]$, dl/g	Concentration of 1,2-units, wt %
1	Co(DEDTC)$_2$/MAO	–20	3.7	95	1	Co(DEDTC)$_2$/isobutyl-aluminoxane	16	4.0	82
2	″	0	2.2	95	2	″	23	2.0	73
3	″	16	1.4	95	3	Co(captax)$_2$/isobutylaluminoxane	20	4.8	75
4	″	40	0.9	95	4	″*	20	4.7	84
5	Ti(OBu)$_4$/MAO	20	2.0	95	5	Ti(OBu)$_4$/isobutylaluminoxane	20	9.1	83
6	Co(ethylhexanoate)$_2$/MAO	0	0.3	95	6	"Japan Synthetic Rubber"	–	1.0	93
7	V(OBu^t)$_4$/MAO	20	1.7	55	7	Co(naphthenate)$_2$**/isobutylaluminoxane	18	0.9	90
8	All$_2$NdCl · 2MgCl$_2$ · 2THF/MAO	25	–	98	8	V(OPr-*iso*)$_4$/isobutylaluminoxane	20	2.6	68

Note: Polymerization conditions: 10 ml (0.115 mol) of butadiene; 46.5 ml of toluene; the amount of a transition metal compound was [M] = 1.5×10^{-5} mol; Al : M = 10–800; η is the characteristic viscosity.
  * With phenanthroline additives.
  ** With triphenylphosphine additives.

ever, the proposed reaction scheme explains an increase in the alkylating ability of MAO in the reaction with a transition metal compound due to the intramolecular association of MAO.

The structural analysis of MAO oligomers that simulate aluminoxane active in polymerization processes suggests that short distances by no means occur in each pair of neighboring units. No more than three hydrogen-bonded oxygen atoms were observed in an oligomer containing 24 elementary units. This circumstance can be used for explaining high Al/Zr ratios (1000 : 1 or higher), which are commonly used for preparing an effective catalyst for olefin polymerization.

The tendency of oxygen atoms in MAO to form hydrogen bonds with methyl groups can be used for explaining the mechanism of unusual propylene 1,3-insertion in polymerization on zirconocene dichlorides in combination with MAO [13, 29]. The coordination of propylene at the active center of a catalyst can occur so that the methyl group of the propylene molecule becomes bound to the MAO oxygen atom that is free of intramolecular association. The act of insertion, which follows the act of this coordination, results in the unusual 1,3-addition of propylene.

Thus, the use of the experimental and theoretical techniques of vibrational spectroscopy for studying the structure of MAO, which is an efficient cocatalyst in olefin polymerization processes, uncovers new approaches to study the structure of active centers and

the mechanism of olefin polymerization stereoregulation.

Stereodirection in Diene Polymerization

Recently, attention has been focused on catalytic systems based on transition metal compounds and aluminoxanes for the polymerization of conjugated dienes. Previously [30, 31], we found that polyisoprene (PI) with a high concentration of unsaturated side groups (96%) can be prepared in a high yield (90%) under mild conditions using a catalytic system based on vanadium tetrabutoxide and MAO. The polymerization of butadiene on the above catalytic system resulted in a mixed-structure polymer (PB).

The use of vanadium acetylacetonates in place of vanadium alkoxides in combination with the same MAO under analogous conditions resulted in PB with the concentration of 1,4-*trans* units equal to 93% [31] or higher [32], whereas PI with the 1,4-*cis*/1,4-*trans* structure was obtained. In the copolymers of isoprene with butadiene on the above catalytic system, PI occurred solely as the 1,4-*trans* polymer [33]. It was reported [25, 34–37] that catalytic systems based on titanium and cobalt compounds in combination with MAO make it possible to obtain 1,4-*cis*-PB with a 95% concentration of 1,4-*cis* units. The results of studies of the structure, phase composition, and temperature behavior of PB were also given in the cited publica-

tions; these results were obtained using IR and ^{13}C NMR spectroscopy, DSC, and XRD analysis.

Table 5 summarizes the Co, Ti, V, and Nd compounds used in this work in combination with alkylaluminoxanes for butadiene polymerization and the experimental results obtained. It can be seen in Table 5 that, in addition to steric hindrances and donor–acceptor interactions due to the ligand environment of a transition metal, the nature of the metal also affects the stereospecificity of the catalytic system. In accordance with the ideas of Furukawa [38], if the distance between two neighboring positions for diene coordination is shorter than 2.42 Å, the structure of the active center is preferential for the production of a 1,2-polymer. This distance depends on the mutual arrangement of transition metal and aluminum atoms; as the distance between them decreased, the structure of the resulting polymer changed in the following order: *cis*, *trans*, and 1,2-polymer. It is likely that the difference in the stereoregulating ability of Co/MAO and Co/isobutylaluminoxane systems can be explained by the fact that the radius of the isobutyl radical is greater than that of methyl; because of this, the distance between transition metal and aluminum atoms is shorter. This behavior was found for transition metal ions with small radii (Ti, Ni, and Co). The situation changed in the case of lanthanide ions. The Nd^{3+} ion has a much greater radius than that of Ti, V, and Co ions; because of this, it can exhibit greater coordination numbers. This special feature of the Nd^{3+} ion, as well as other lanthanide ions, significantly increases the possibility of η^4-*cis* diene coordination, which requires two coordination sites and results in a 1,4-*cis*-polymer, as distinct from η^2-*trans* coordination (one coordination site), which results in a 1,4-*trans*-polymer.

Because of the great ionic radii of lanthanides, a diene molecule can undergo either η^2-*trans* or η^4-*cis* coordination; in both cases, this results in a 1,4-polymer. For example, a 1,4-*cis*-polymer was obtained with the use of either the Nd/MAO or the Nd/isobutylaluminoxane catalytic system. The $All_2NdCl \cdot MgCl_2 \cdot 2THF$/MAO system allowed the synthesis of 1,4-*cis*-PB with a 98% concentration of 1,4-*cis* units, whereas special additives, such as $(CH_3)_2SiCl_2$ or $(C_4H_9)_2AlCl$, are required for lanthanide catalytic systems with isobutylaluminoxane in order to reach a higher stereospecificity.

Thus, the efficiency of olefin polymerization processes and the stereodirection of diene polymerization under the action of catalysts containing aluminoxanes essentially depend on both the nature of the metal and its ligand environment and the nature and structure of the aluminoxane.

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