YU. B. MONAKOV, N. G. MARINA, G. A. TOLSTIKOV

Institute of Chemistry, Bashkirian Research Centre
Ural Department of the USSR Acad. Sci.

The main regularities of diene polymerization with the lanthanide metal-complex catalysts

Summary — This contribution is concerned with a fragment of studies on homo- and copolymerization of dienes with catalytic systems formed from an organoaluminium compound and complexes of lanthanide metal halides (LnHal₃). 3L, where L is an organic electron-donating ligand and Ln — lanthanide. It has been found that activity of systems under study depends both on the catalyst composition and on the type of lanthanide used and that changes in catalyst composition have an effect on the polymer chain growth rate constant. Unexpectedly, it has also been found that polybutadiene microstructure depends on the AlR₃-structure, what gave rise to the assumption that organoaluminium component participates in the formation of active centre of butadiene polymerization. An analysis of the results of studies on the effect of monomer concentration, polymerization temperature and type of solvent on catalyst activity led to the conclusion that active centres in lanthanide metal-complex catalysts have π-allilic structure.

Great progress has been recently observed in research and application of the lanthanide compounds utilized for various catalytic processes and, in particular, for polymerizations. The main bank of data on the lanthanide catalysts of polymerization has been accumulated in the last few years only. The research workers of many countries (the U.S.A., China, Italy, the F.R.G., the U.S.S.R., etc.) have obtained valuable results in various aspects of stereospecific polymerization with lanthanide catalysts of dienes and, though to an appreciably less extent, of olefins. It is no mere chance that the lanthanide catalysts have given rise to the scientists' interest; great prominence is given to them due to their promising potentials.

Our studies have been carried out into the homo- and copolymerization of conjugated dienes with catalytic systems involving a complex of lanthanide halide LnHal₃·3L (where L — organic electron-donor ligand) combined with an organoaluminium compound.

It should be noted with regard to the most general kinetic characteristics of the process that irrespective of the lanthanide number, monomer structure, and solvent type the rate of polymerization is of first order to the monomer and catalyst concentrations, i.e. $W = k_p \cdot C_M^1 \cdot C_a^1$, where W — polymerization rate, k_p — chain propagation constant, C_M and C_a — concentration of monomer and active centres, respectively. At room temperature and above, an induction period is usually not observed with the above mentioned parameters varied and with either method of catalyst preparation (in situ or in advance). This serves as an evidence to high rates of the reaction between catalyst components resulting in alkylated lanthanide compounds as well as of the initiation reaction. The activation energy of polymerization is about 8 kcal/mole [1].

All these characteristics are usually observed in diene polymerizations with the classical Ziegler-Natta catalysts.

The effects of the composition of lanthanide catalytic system, the monomer structure, and polymerization conditions upon the catalytic activity of catalyst and properties of polydiene formed have been investigated.

THE TYPE OF LANTHANIDE

The activity of catalytic systems is strongly influenced by the atomic number of the lanthanide involved (Fig. 1). According to Table 1, under certain polymerization conditions, the activity series can slightly vary with the main tendency retained. This tendency can be summarized as follows. The highest polymerization rates for conjugated dienes are reached with neodymium containing catalysts. The activity of catalytic systems is growing with the increasing atomic number of lanthanide in the cerium subgroup, i.e. from lanthanum to neodymium, whereas a reversed dependence is observed in the yttrium subgroup (Fig. 1). The europium and samarium catalysts fail in polymerization and heavier lanthanides lose their characteristic properties because of the transition of these elements to their divalent state under the effect of an organoaluminium compound.

Table 1. CATALYST ACTIVITY SERIES FOR LnCl₃·3TBP-Al(iC₄H₉)₃*) (in situ)

Monomer	Solvent	Polymerization temperature, °C	Activity series of lanthanides
Butadiene	toluene	25	Nd > Gd > Pr > Tb > > Ce > Dy
		80	Nd > Gd ⩾ Pr > Ce > > Tb > Dy
Isoprene	toluene heptane	25	Nd > Pr > Ce > Gd > > Tb > Dy
Piperylene	toluene	25	Nd > Gd > Pr > Tb > > Ce > Dy

*) TBP — tributyl phosphate

The systems based of heavy lanthanides following erbium are really inactive. As known, with the increasing atomic number of lanthanide there takes place the deepening of f-orbitals, which is especialy pronounced in the yttrium subgroup, what results in their lowered involvement in the formation of chemical bonds. Due to f-degeneration, erbium and heavier lathanides lose their characteristic properties inherent to f-elements. It is the very peculiarity of heavy lanthanides that may be presumed to determine their actual zero-order catalytic activity.
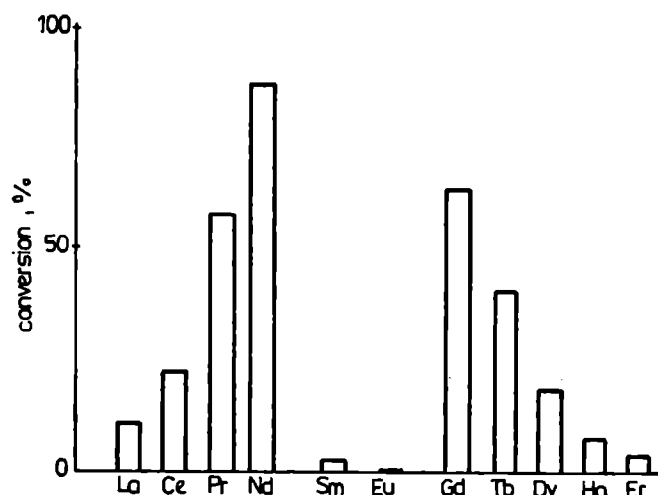

Fig. 1. The dependence of LnCl₃·3TBP—Al(iC₄H₉)₃ catalyst activity on the lanthanide used for butadiene polymerization, toluene, 25°C.

The value of chain propagation constant k_p increases with the growing atomic number of elements in the cerium subgroup and decreases in that of yttrium (Table 2). This dependence of C_a obeys a more simple tendency as C_a decreases with the growing atomic number of lanthanide.

Table 2. BUTADIENE POLYMERIZATION WITH $LnCl_3 \cdot 3TBP\text{-}Al(iC_4H_9)_3$ AS CATALYSTS (in situ, toluene, 25°C) [1]

Lanthanide	k_p l/mole · min	C_a, %
La	10	12
Ce	40	9
Pr	60	8
Nd	140	7
Gd	130	5
Dy	30	5

Therefore, the position of every lanthanide in the given activity series (Fig. 1, Table 1) is determined above all by the reactivity of active centres (k_p), while the factor of active centre concentration (C_a) is of secondary importance.

Though the chain propagation constant k_p is lanthanide dependent, the stereospecificity of the catalysts investigated is retained at 25°C on one level in polymerization of the simplest diene — butadiene (Table 3). Polymers with a high

Table 3. DIENE POLYMERIZATION WITH $LnCl_3 \cdot 3TBP\text{-}Al(iC_4H_9)_3$ AS CATALYSTS (toluene, 25°C) [2]

Lanthanide	cis-1,4-units, %		
	polybutadiene	polyisoprene	polypiperylene
La	95.4	—	—
Ce	94.7	94,7	57
Pr	95.1	94,7	62
Nd	94.6	95,0	64
Gd	95.2	95.9	70
Tb	95.0	96.0	69
Dy	93.7	96.0	66
Ho	92.2	—	—
Er	93.0	—	—

content of 1,4-cis-units are also formed in isoprene polymerization, while one should note a weak tendency to the lowered content of 3,4-units in polyisoprene with the growing atomic number of lanthanide rather strong dependence of catalyst stereospecificity on the lanthanide is observed in polymerization of piperylene as opposed to butadiene and isoprene. This tendency correlates to a certain extent with the studied lanthanide effect upon the catalyst activity where the content of 1,4-cis-units in polypiperylene increases in the subgroup of cerium and decreases in that of yttrium with the growing lanthanide atomic number. Under otherwise equal conditions the most stereoregular polypiperylene is formed with the gadolinium catalyst. Thus, the

highest activity and stereospecificity are not displayed one and the same lanthanide.

Although the polydiene molecular weight is influenced by the atomic number of lanthanide, this influence is considered appreciably low. However, one should mention that among active catalysts those of cerium are notable for the formation of the lowest molecular-weight polydienes which reveal, moreover, the widest molecular-weight-distribution (Fig. 2).

THE TYPE OF HALOGEN

The type of halogen has been known to exert a strong influence on the stereospecificity of the Ziegler-Natta catalysts based on titanium, cobalt, and nickel (Table 4). The absence of such an effect in butadiene polymerization

Table 4. BUTADIENE POLYMERIZATION WITH VARIOUS HALOGEN CONTAINING CATALYSTS OF THE ZIEGLER-NATTA TYPE [3]

Halogen	cis-1,4-units, %				
	Ti	Co	Ni	Nd	U
F	35	93	98	95.7	—
Cl	75	98	85	96.2	99.0
Br	87	91	80	96.8	98.5
I	93	50	10	96.7	98.5

is believed to be a peculiar property of the catalysts based on f-elements. However, the effect of halogen type on the reactivity of active centres is revealed for the lanthanide catalysts, too.

Thus, in the case of polybutadiene it is confirmed by the values of chain propagation constant (Table 5) and in that

Table 5. BUTADIENE POLYMERIZATION WITH $Ln\,Hal_3 \cdot 3TBP\text{-}Al(iC_4H_9)_3$ AS CATALYSTS (toluene, 25°C)

Ln Hal₃	k_p, l/mole · min	cis-1,4-units, %
$CeCl_3$	40	94.7
$CeBr_3$	60	94.5
$NdCl_3$	140	94.6
$NdBr_3$	150	94.8

of other polydienes — by their microstructure. In the series of chlorine, bromine, and iodine containing catalysts, there occurs a decrease in the content of 1,4-cis-units in polyisoprene with an increasing content of 3,4-units (Table 6).

Table 6. ISOPRENE AND PIPERYLENE POLYMERIZATIONS WITH $PrHal_3 \cdot 3TBP\text{-}Al(iC_4H_9)_3$ AS CATALYSTS (toluene and heptane, respectively, 25°C

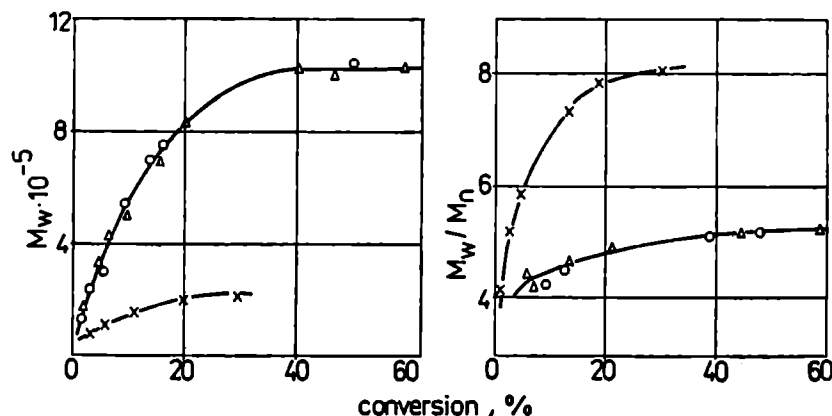| Halogen	Polyisoprene		Polypiperylene
	3,4-units, %	[η]	[η]
Cl	5.3	3.9	3.8
Br	7.2	4.1	3.4
I	11.0	0.4	1.1

Fig. 2. The dependence of polybutadiene molecular-weight characteristics on the lanthanide involved in catalyst $LnCl_3 \cdot 3TBP$— $Al(iC_4H_9)_3$, toluene, 25°C; × — cerium, ○ — neodymium, △ — gadolinium

The changes of stereospecificity in the said catalytic series become most obvious in piperylene polymerization (Table 7) and, besides, the chlorine- and bromine- containing catalysts are similar both in their stereospecificity and activity (Fig. 3). The iodine containing catalysts give much lower

Table 7. PIPERYLENE POLYMERIZATION WITH LnHal₃ · 3TBP-Al(iC₄H₉)₃ AS CATALYSTS (heptane, 25°C) [4]

Lanthanide	Halogen	Content of units, %		
		cis-1,4-	trans-1,4-	1,2-
Pr	Cl	71	9	20
	Br	73	9	18
	I	35	34	31
Gd	Cl	79	3	18
	Br	83	2	15
	I	69	11	20
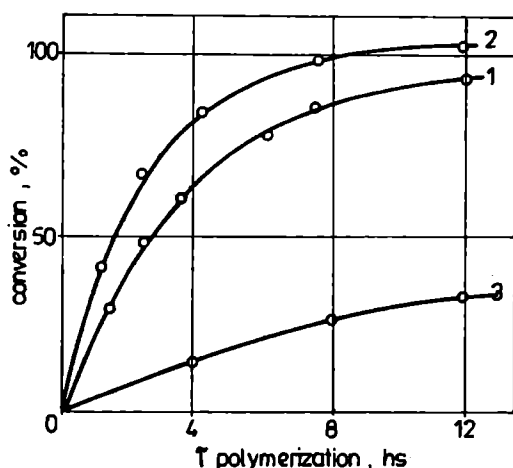
Fig. 3. The kinetics for piperylene polymerization with PrHal₃·3TBP—Al(iC₄H₉)₃ as catalysts, heptane, 25°C [4]; 1 — chlorine, 2 — bromine, 3 — iodine

polymerization rates and result in polypiperylene of inferior microstructure. Attention should be paid to a pronounced increase in the content of 1,4-trans-units as well as to the enhancement of stereospecificity dependence on the lanthanide type with the iodine containing catalysts which are also peculiar the formation of polydienes of lower molecular weight (Table 6).

THE TYPE OF ORGANIC LIGAND

With the organic ligand L varied in the lanthanide LnHal₃·3L component, the catalyst stereospecificity remains unchanged (Table 8) and the values of polymer molecular

Table 8. BUTADIENE POLYMERIZATION WITH NdCl₃ · 3L-Al(iC₄H₉)₃ AS CATALYSTS (toluene, 25°C)

Ligand L	Yield, %	cis,-1,4-units, %	[η]
Tributyl phosphate	92	94.6	5.7
2-Hexylthiophane sulfo-xide	77	94.3	5.5
Diamylsulfoxide	77	94.7	5.7
Dioctylsulfoxide	65	94.0	5.4
Didodecylsulfoxide	62	94.5	5.2

weight are also retained on one level. Sulphoxide complexes have been taken to illustrate decreasing polymer yields with the growing lengths of alkyl radicals in R₂SO. The reactivity of active centres has been found to depened on ligand L

Table 9. DIENE POLYMERIZATION WITH NdCl₃ · 3L-Al(iC₄H₉)₃ AS CATALYSTS (25°C)

Monomer	Solvent	kp, 1/mole · min	
		TBP*)	DASO**)
Butadiene	toluene	140	100
Isoprene	toluene	80	70
Piperylene	heptane	70	40

*) TBP — tributyl phosphate
**) DASO — diamylsulfoxide

(Table 9), the chain propagation constant k_p being lower for the catalysts based on sulphoxide complexes what indicates for their lower activity. These data give evidence to the formation of non-identical active centres in the catalytic systems based on tributylphosphate and diamyl-sulphoxide complexes. With regard to the higher electro--donor ability of sulphoxides, that non-identity can be explained by the assumption that the sulphoxide ligand is not completely removed from the lanthanide coordination sphere in reaction of the related lanthanide halide complex with an organoaluminium compound. Such an assumption is justified by the optically active polypiperylene prepared with the optically active sulphoxide used in the catalyst, that being the subject of further discussion.

The corresponding data have also been obtained to demonstrate the effect of ligand combination (halogen and organic electron-donor) on the reactivity of active centres. It turned out that the type of ligand L affects the dependence of chain propagation constant on he halogen type. As shown above (Table 5), $k_p(Cl) < k_p(Br)$ with the tributyl-phosphate complexes used. A reversed dependence has been observed with sulphoxide complexes (Table 10) what is another confirmation to the presence of sulphoxide ligand in active centres.

Table 10. BUTADIENE POLYMERIZATION WITH Ln Hal₃ · 3DASO-AL(iC₄H₉)₃ (toluene, 25°C)

Ln Hal₃	kp, 1/mole · min
PrCl₃	40
PrBr₃	20
NdCl₃	100
NdBr₃	40

THE STRUCTURE OF ORGANOALUMINIUM COCATALYST

The variation of an organoaluminium component involved into the Ziegler–Natta catalysts is considered a possible way to exert influence upon many characteristics of diene polymerization. We have studied the effect of structure of an organoaluminium compound involved into lanthanide
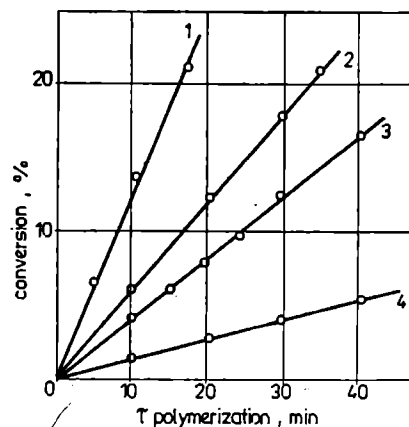

Fig. 4. The kinetics for butadiene polymerization with NdCl₃·3TBP—butadiene—AlR₃ as catalysts, toluene, 25°C; 1 — Al(iC₄H₉)₃, 2 — Al(C₂H₅)₃, 3 — Al(iC₄H₉)₂H, 4 — Al(nC₁₁H₂₃)₃

catalyst upon the main characteristics of polymerization and the properties of polydienes formed.

According to Fig. 4, the polymerization rate is appreciably dependent of AlR_3. Triethylaluminium and diisobutylaluminium hydride are known to occur in their associated states in hydrocarbon solutions. The degree of AlR_3 association decreases with the growing length of normal structure radicals at the aluminium atom and triisobutylaluminium exists in its monomeric form in solutions. This peculiarity of organoaluminium compounds is very likely responsible for their cocatalytic properties. Thus, an increase in the polymerization temperature favours the weaker dependence of the lanthanide catalyst activity on the structure of AlR_3 involved (Fig. 5) which is obviously a result of the decom-
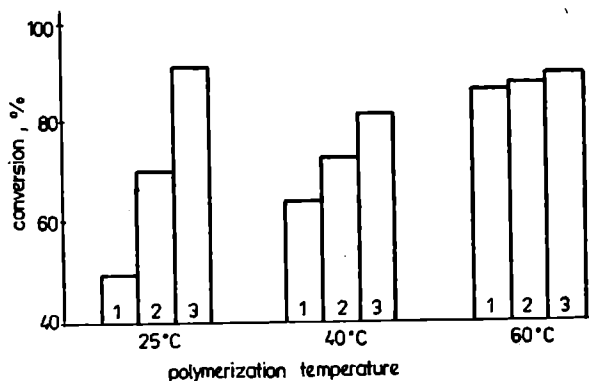

Fig. 5. The temperature effect on $NdCl_3 \cdot 3TBP$—AlR_3 catalyst activity with isoprene polymerized in toluene; 1 — $Al(C_2H_5)_3$, 2 — $Al(nC_6H_{13})_3$, 3 — $Al(iC_4H_9)_2H$

position of associates. Here too, the anomalous dependence of polydiene yield on the Al/Ln ratio disappears, that being observed with the AlR_3 capable of association at lower polymerization temperatures (Fig. 6).
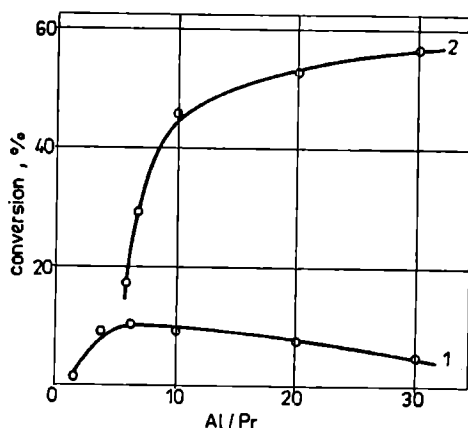

Fig. 6. The dependence of isoprene conversion on Al/Pr ratio with $PrCl_3 \cdot 3TBP$—$Al(C_2H_5)_3$ catalyst at polymerization temperatures of 25°C (1) and 80°C (2) [5].

With the employment of non-associated triisobutylaluminium, the polymerization rate steeply increases with the growing Al/Nd ratio from 5 to 20 and suffers only small changes (Fig. 7) at higher Al/Nd ratios. The obtained dependences (Fig. 7) allow to relate the rate changes for the varied Al/Nd ratio to different concentrations of similar active centres because k_p remains unchanged within the whole range of Al/Nd ratios studied, the polybutadiene microstructure being also retained. The cerium systems represent an exception where the values of k_p, polymerization rate, and content of 1,b-cis-units in polybutadiene decrease with the growing Al/Ce ratio above 20.

It has been found that an induction period occurs for the diisobutylaluminium hydride containing catalyst prepared in situ and in advance; still, it disappears with the catalytic complex aging in the presence of monomer additions (Fig. 8). The slowly proceeding initiation can be considered

indicative of the formation of active centres with Ln-H bonds. The structure of AlR_3 has been proved to affect the stability of lanthanide active centres. Thus, the increased temperature of preparation of $NdCl_3 \cdot 3TBP$-$Al(iC_4H_9)_3$ catalyst
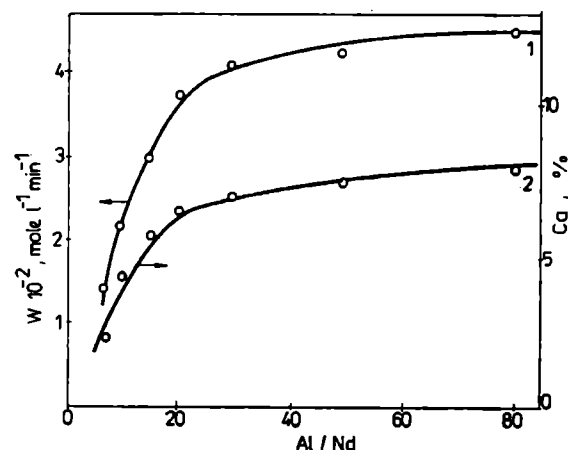

Fig. 7. The dependences of butadiene polymerization rate (1) and the number of active centres (2) on the Al/Nd ratio in $NdCl_3 \cdot 3TBP$—$Al(iC_4H_9)_3$ [1].
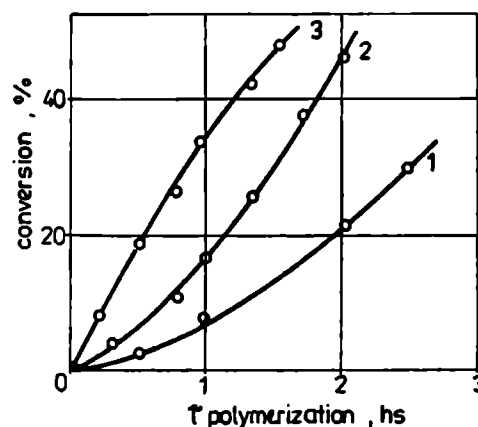

Fig. 8. The effect of the method of $NdCl_3 \cdot 3TBP$—$Al(iC_4H_9)_2H$ catalyst preparation on the kinetics of butadiene polymerization in toluene at 25°C; 1 — in situ, 2 — in advance, 3 — in advance, in the presence of monomer

results in the loss of active centres in their alkylated form, whereas a similar tridecylaluminium containing catalyst retains its activity almost unchanged for the temperature of its preparation ranging from 20 to 60°C (Fig. 9).
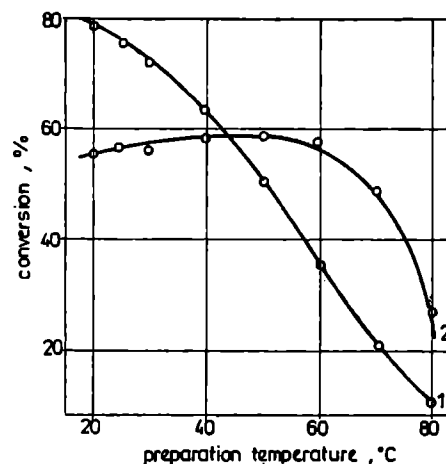

Fig. 9. The dependence of the activity of $NdCl_3 \cdot 3TBP$—AlR_3 catalysts on the temperature of their preparation in isoprene polymerization, toluene, 25°C [5]; 1 — $Al(iC_4H_9)_3$, 2 — $Al(nC_{10}H_{21})_3$

All these factors in total give the reason to assume a certain non-identity of active centres formed in the reaction of $LnHal_3 \cdot 3L$ with AlR_3 where AlR_3 is varied. Additional experimental data are in conformity with this assumption. Thus, the polydiene microstructures have been found dependent on the organoaluminium component in the catalyst (Tables 11, 12). With AlR_3 varied, the relation

Table 11. BUTADIENE POLYMERIZATION WITH $NdCl_3 \cdot 3TBP\text{-}AlR_3$ AS CATALYSTS (in situ, toluene, 25°C)

AlR_3	Content of units, %		
	cis-1,4-	trans-1,4-	1,2-
$Al(C_2H_5)_3$	89.0	10.3	0.7
$Al(iC_4H_9)_2H$	91.2	7.4	1.4
$Al(iC_4H_9)_3$	94.5	5.0	0.5
$Al(nC_6H_{13})_3$	92.1	7.3	0.6
$Al(nC_8H_{17})_3$	91.7	7.7	0.6

Table 12. PIPERYLENE POLYMERIZATION WITH $NdCl_3 \cdot 3TBP\text{-}AlR_3$ (in situ, toluene, 25°C)

AlR_3	Content of units, %	
	cis-1,4-	1,2-
$Al(C_2H_5)_3$	64	23
$Al(iC_4H_9)_2H$	59	22
$Al(iC_4H_9)_3$	64	25
$Al(nC_8H_{17})_3$	55	26

between cis-1,4- and trans-1,4-units content changes in polybutadiene, whereas the total content of 1,4-units is retained at one level with the exception of the catalyst containing diisobutylaluminium hydride (Table 11). These data reveal rather a striking phenomenon which can be presented as follows: at moderate polymerization temperatures the polybutadiene microstructure shows no response to the varied catalyst consumption by lanthanide, halogen, and organic ligand, while with the varied structure of AlR_3 in the catalyst it is changed, though slightly.

As has been stated above, the higher the temperature of polymerization the lower is the effect of AlR_3 structure on the activity of lanthanide catalysts while a reversed effect is observed with respect to their stereospecificity (Fig. 10). The effect of AlR_3 used on the catalyst stereo-
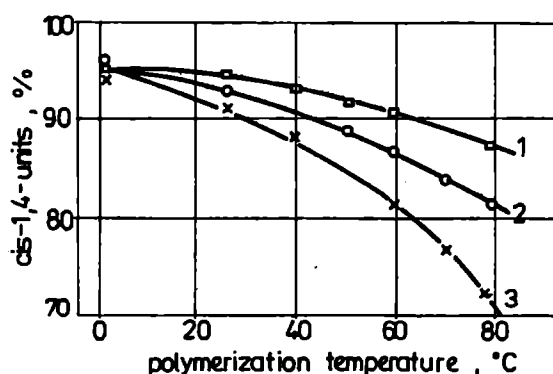

Fig. 10. The temperature effect of butadiene polymerization in toluene with $NdCl_3 \cdot 3TBP$—AlR_3 catalysts on the polymer microstructure; 1 — $Al(C_4H_9)_3$, 2 — $Al(nC_{11}H_{23})_3$, 3 — $Al(C_2H_5)_3$

specificity is more pronounced also at lower monomer concentration (Fig. 11). The reactivity ratios (Table 13) give evidence to the formation of non-identical centres for the varied AlR_3 structure.

Thus, there exist no grounds to confirm the formation of simple active organometallic derivatives of the $RLnCl_2$ type in reaction of $LnCl_3 \cdot 3L$ with AlR_3 because the R

changes should not be followed by such considerable alterations of the catalyst characteristics which have been found in fact.
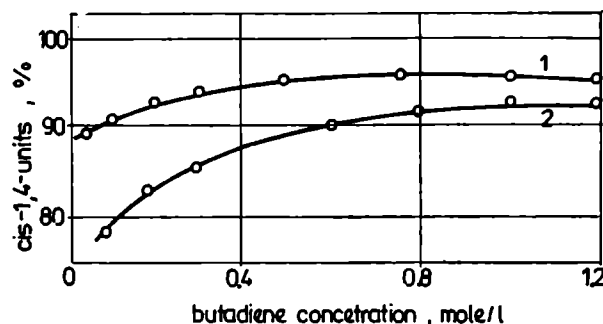

Fig. 11. The effect of monomer concentration in toluene on the polybutadiene microstructure with $NdCl_3 \cdot 3TBP$—AlR_3 catalysts, 25°C; 1 — $Al(iC_4H_9)_3$, 2 — $Al(iC_4H_9)_2H$

Table 13. REACTIVITY RATIOS FOR BUTADIENE (r_1) AND ISOPRENE (r_2) WITH $NdCl_3 \cdot 3TBP\text{-}AlR_3$ (toluene, 25°C

AlR_3	r_1	r_2
$Al(iC_4H_9)_2H$	1.94	0.53
$Al(iC_4H_9)_3$	1.29	0.67

Before considering the reasons of non-identity of active centres, one needs to determine the role of an organoaluminium component in lanthanide catalytic systems. The main role of AlR_3 in the conventional Ziegler-Natta catalysts is the reduction of a transition metal, its alkylation and complexation. In the catalysts based on halides of trivalent lanthanides, the organoaluminium compound is undoubtedly an alkylating agent and fails to be a reducer. Apparently, the complexation properties of an organoaluminium compound are responsible for the non-identity of active centres. Different arguments may be advanced for the occurrence of this non-identity. One of them is associated with the structure effect of AlR_3 and its electron-accepting properties on the extent of removal of the organic ligand from the lanthanide coordination sphere. The results obtained for the catalytic systems involving an optically active sulphoxide (Table 14) agree with the above statement. Indeed, the

Table 14. PIPERYLENE POLYMERIZATION WITH $NdCl_3 \cdot 3L^*\text{-}AlR_3$ AS CATALYSTS (in situ, toluene, 0°C) [6]

AlR_3	$[\alpha]_D^{20}$ (for polypiperylene)
$Al(iC_4H_9)_3$	−8.3
$Al(C_2H_5)_3$	−4.4
$Al(iC_4H_9)_2H$	0.0

L^* — sulphoxide of formula

$[\alpha]_D^{20}$ — 41°
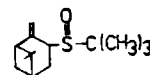
Table 15. PIPERYLENE POLYMERIZATION WITH $NdCl_3 \cdot 3L^*\text{-}Al(iC_4H_9)_3$ AS CATALYSTS (in situ, toluene) [6]

$t_{polymerization}$, °C	$[\alpha]_D^{20}$ (for polypiperylene)
0	−8.3
25	−5.4
40	−3.0
60	0.0

L^* — the same as in the Table 14

specific angle of rotation of polypiperylene depends on the organoaluminium component in the catalyst. In this case, the presence or the absence of the asymmetry effect of active centres may be accounted for the presence or absence

of ligand L* in those centres. With diisobutylaluminium hydride (DIBAH) used, the optical activity of polypiperylene is not observed evidently due to higher electron-accepting property of DIBAH and to a complete removal of L* from the neodymium coordination sphere as early as at 0°C. Similar result has been obtained with triisobutylaluminium at higher polymerization temperatures (Table 15) since the specific angle of rotation of polypiperylene decreases to zero at 60°C.

Consequently, if the presence or absence of the electron--donor ligand in active centres were a single argument for their non-identity with AlR_3 varied, the increasing polymerization temperature would have led to the similarity of catalytic systems under consideration of their stereospecificities, while experimental evidence has proved a reversed dependence (Fig. 10). Thus, one should assume the lanthanide active centre to contain an organoaluminium fragment the occurrence of which as a ligand in the lanthanide coordination sphere affects the reactivity of this centre.

The statement concerning changes of reactivity of lanthanide active centres due to the varied AlR_3 structure is in conformity with the molecular weight data obtained for polydienes. Thus, higher organoaluminium compounds are poor chain transfer agents (Fig. 12). Still, under certain
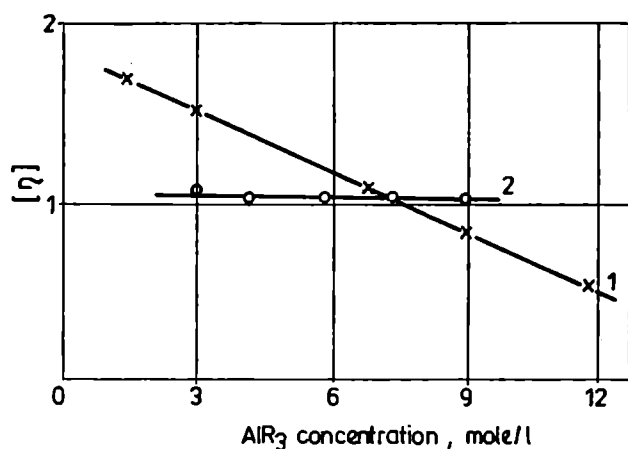
Fig. 12. The dependence of polyisoprene intrinsic viscosity on AlR_3 concentration with $NdCl_3·3TBP—AlR_3$ catalysts, toluene, 25°C; 1 — $Al(iC_4H_9)_3$, 2 — $Al(nC_{10}H_{21})_3$

conditions they promote the formation of lower molecular--weight polydiene than triisobutylaluminium. With the growing length of R radicals in AlR_3 the polydiene polydispersity and its dependence on the organoaluminium compound concentration become lower (Fig. 13), what is first of all due to a worse chain transfer to higher AlR_3.
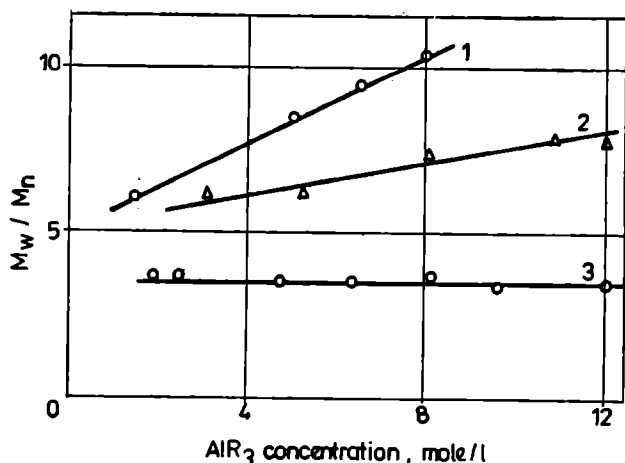
Fig. 13. The dependene of polyisoprene polydispersity on AlR_3 concentration with $NdCl_3·3TBP—AlR_3$ catalysts, toluene, 25°C; 1 — $Al(iC_4H_9)_3$, 2 — $Al(nC_6H_{13})_3$, 3 — $Al(nC_{10}H_{21})_3$

THE TYPE OF SOLVENT

A variety of solvents can be used to polymerize dienes with lanthanide catalysts. As shown in Fig. 14, the rate of polymerization is appreciably dependent on the solvent used. Polymerization proceeds much faster in aliphatic hydrocarbons than it does in aromatic ones.
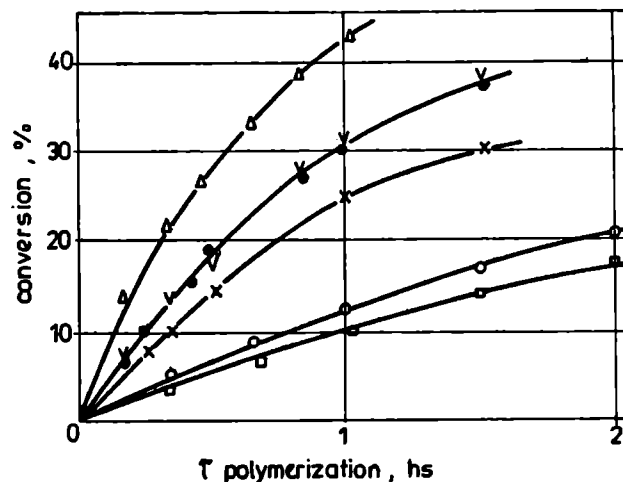
Fig. 14. The kinetics of isoprene polymerization in different solvents at 25°C with $NdCl_3·3TBP—Al(iC_4H_9)_3$ catalyst, 25°C; △ — chlorobenzene, ∨ — isopentane, ● — heptane, × — benzene, ○ — toluene, □ — xylene

The data obtained with n-heptane and toluene prove the formation of non-identical active centres in these media. It can be associated with the changed ligand environment of lanthanide due to the arene type complexes formed this results in a substantial decrease of the chain propagation constant in toluene as compared to heptane (Table 16). It is

Table 16. DIENE POLYMERIZATION WITH $NdCl_3·3TBP-Al(iC_4H_9)_3$ AS CATALYSTS (25°C) [1, 7]

Monomer	Solvent	cis-1,4-units, %	k_p l/mole·min	C_a, %
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

for this reason that the polymerization rate is higher in aliphatic hydrocarbons while in aromatic solvents the concentration of active centres is somewhat greater due to their stabilization. Under certain conditions the stereospecificity of catalysts is also determined by the solvent used. At temperatures close to room temperatures the polymerizations of butadiene and isoprene result in polymers with their microstructure being solvent independent. Under similar conditions the content of cis-1,4-units in polypiperylene is higher in aliphatic hydrocarbon solutions (Fig. 15). Besides, the increasing polymerization temperature makes the difference in microstructure of polypiperylene prepared in toluene and heptane still more profound (Fig. 16). An analogous effect of the solvent has also been found in butadiene polymerization under certain conditions. These conditions come either to the use of extremely diluted butadiene solutions (Fig. 17) or to an increase in temperature of the process (Table 17). The increased polymerization temperature with the concomitant low monomer concentration in toluene results in a highly deteriorated polybutadiene microstructure (Fig. 18). As follows from Fig. 18 and Table 17, for butadiene polymerized at 80°C the catalyst stereospecificity turns still more vividly dependent on the hydrocarbon solvent type as well as on the lanthanide type.
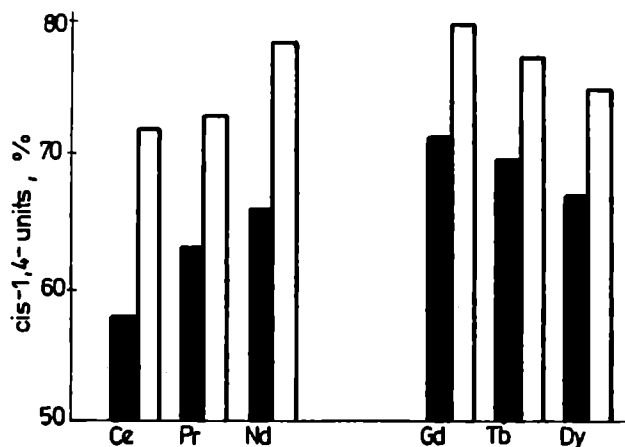
Fig. 15. The dependence of polypiperylene microstructure on the lanthanide involved in $LnCl_3 \cdot 3TBP$—$Al(iC_4H_9)_3$ catalysts, toluene (■), heptane (□), 25°C [4]

Fig. 18. The dependence of polybutadiene microstructure on the monomer concentration in toluene with $LnCl_3 \cdot 3TBP$—$Al(iC_4H_9)_3$ catalyst, 80°C; 1 — neodymium, 2 — gadolinium

Table 17. BUTADIENE POLYMERIZATION WITH $LnCl_3 \cdot 3TBP$-$Al(lC_4H_9)_3$ AS CATALYSTS (80°C)

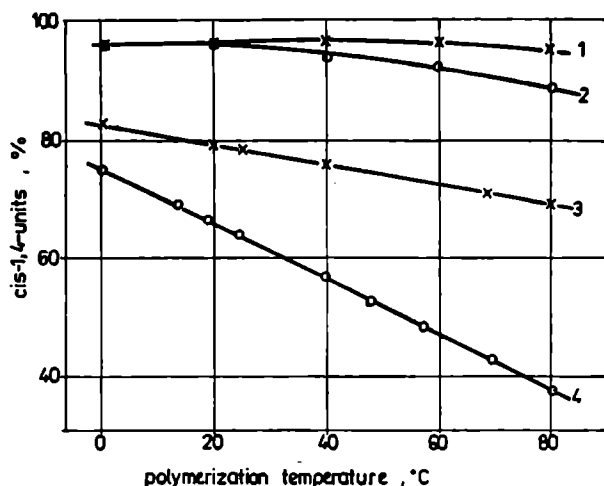| Ln	cis-1,4-units, %	
	toluene	heptane
Ce	86	93
Pr	85	93
Nd	88	92
Gd	90	93
Tb	89	90
Dy	83	88

Fig. 16. The dependence of polybutadiene (1, 2) and polypiperylene (3, 4) microstructures on the polymerization temperature in toluene (2, 4) and heptane (1, 3) with $NdCl_3 \cdot 3TBP$—$Al(iC_4H_9)_3$ catalyst [8]

Each diene monomer has its own temperature limit, i.e. that very temperature below which the microstructure of the related polydiene remains unchanged with different lanthanides in the same solvent. This temperature limit is shifted to the region of lower polymerization temperatures for more complicated diene structures. A similar shift is also observed of the temperature value below which the polydiene microstructure becomes independent of the solvent type (Fig. 16). Thus, in piperylene polymerization the stereospecificity of neodymium catalyst is solvent dependent within the whole range of temperatures studied (0—80°C), whereas in butadiene polymerization this dependence is observed at temperatures above 40°C only. The lanthanide type exerts its influence on the said temperature limit, e.g. for the gadolinium catalyst the microstructure of polypiperylene is solvent independent as early as at 0°C.

The molecular weights of polybutadiene and polyisoprene are determined by the solvent type in the initial stages of the process only due to the existing dependence of chain propagation constants on the solvent used, while the same level of the average molecular weight is reached at higher conversion (Fig. 19). The piperylene polymerization is
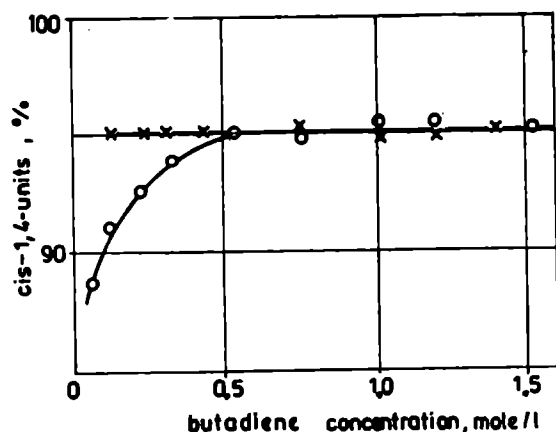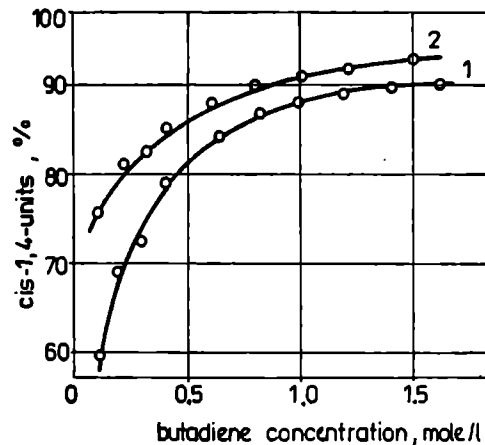

Fig. 17. The dependence of polybutadiene microstructure on the monomer concentration in toluene (○) and heptane (×) with $NdCl_3 \cdot 3TBP$—$Al(iC_4H_9)_3$ catalyst, 25°C [8]
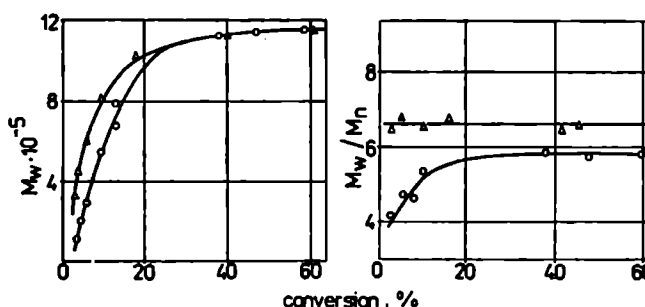

Fig. 19. The dependence of polybutadiene molecular-weight characteristics on the solvent used in polymerization with $NdCl_3 \cdot 3TBP$—$Al(iC_4H_9)_3$; ○ — toluene, △ — heptane

considered peculiar owing to the formation of much more lower-molecular-weight polymer in aromatic than in aliphatic hydrocarbon solution (Fig. 20). The polydiene molecular weight depends strongly on the polymerization temperature (Fig. 20).
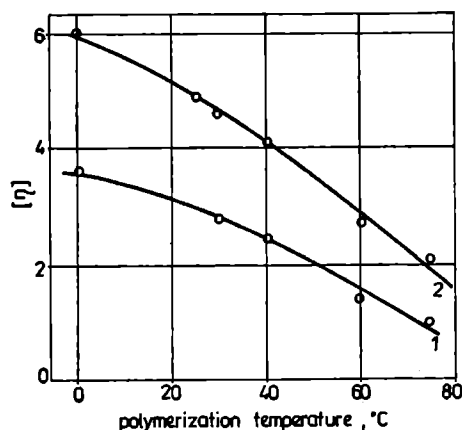

Fig. 20. The dependence of polypiperylene intrinsic viscosity on the polymerization temperature in toluene (1) and heptane (2) with $NdCl_3 \cdot 3TBP$—$Al(iC_4H_9)_3$ catalyst

THE STRUCTURE OF ACTIVE CENTRES

According to the up-to-date idea, in diene polymerization with ion-coordinative catalysts the propagating chain is connected to a d-metal by a π-allylic bond; thus, the anti-syn isomerization of this π-allylic compound is believed a decisive point in the formation of a polydiene chain at any ratio of 1,4-units of cis- and trans-configurations.

The obtained results are consistent with the idea of the π-allylic structure of active centres in the investigated catalysts based on lanthanides as f-elements [8]. The display of anti-syn isomerization of such active centres is first of all supported by a lowered content of cis-1,4-units due to an increasing amount of trans-1,4-units in polydienes with a decreasing monomer concentration (Fig. 17). As follows from Fig. 17, isomerization takes place to a much lower extent in aliphatic hydrocarbons to provide thus for a higher content of cis-1,4-units than it occurs in aromatic hydrocabons under otherwise equal conditions. Since the content of cis- and trans-1,4-units in the chain is determined by the ratio of propagation rate to anti-syn isomerization rate of active centres, one should take into accout the appreciably higher value of k_p in heptane as compared to those found for polymerization in toluene (Table 16). It is also necessary to pay attention to the possible solvent effect upon the anti-syn isomerization constant (k_i).

At temperatures close to room temperature, the absence or extremely poor display of anti-syn-isomerization of lanthanide active centres may serve as a possible explana-tion of one of the peculiar features of butadiene polymeriza-tion, namely of the discrepancy between the regularities of changes in the chain propagation constant and the catalyst stereospecificity with the varied lanthanide component and solvent type. As shown above, the changes of these para-meters influence the value of k_p with no concomitant alteration of cis-1,4-unit content in polybutadiene. The lowered monomer concentration and/or an increased poly-merization temperature are those factors which abolish the „insensitivity" of polybutadiene microstructure to the above parameters. In thise case, the k_p/k_i ratio is evidently changed.

The weak anti-syn isomerization of lanthanide active centres is followed by the formation of butadiene-isoprene copolymers with a high content of cis-units in both buta-dienic and isoprenic chain parts. The mutual effect of comonomers upon the microstructure is absent even for unequal copolymerization constants, $r_b > r_i$ (Table 13).

The value of k_p/k_i ratio is also dependent on the diene monomer itself because the content of cis- and trans-units in polypiperylene is not only different from that in polybuta-diene but also reveals its higher response to the varied poly-merization conditions, i.e. to solvent type, temperature, and monomer concentration. It should be noted that for a more complicated structure of the diene monomer, the lanthanide catalysts lose their high cis-stereospecificity, that being caused by the more expressed anti-syn-isomerization follow-ed by an increasing content of trans-1,4-units, on the one hand, and by a growing content of 1,2-(or 3,4-)-units (Table 18), on the other. This results from steric factors and their effect on the way of monomer insertion into the propagating polymer chain.

Table 18. POLYMERIZATION OF MONOMERS WITH $NdCl_3 \cdot 3TBP$-$Al(iC_4H_9)_3$ AS CATALYSTS (toluene, 25°C) [9]

Monomer	Content of units, %	
	1,4-	1,2-
Butadiene	99.5	0.5
Isoprene	95	5*)
Pentadiene-1,3	76	24
Octatriene-1,3,6	63	37
5-methylheptatriene-1,3,6	33	67

*) 3,4-units

Therefore, there have been discovered no principal diffe-rences between the lanthanide catalytic systems and the Ziegler-Natta catalysts based on d-elements in their formal compositions, the main polymerization rules, and in the assumed π-allylic structure of active centres. The main lanthanide catalysts, peculiarities resulting from the realiza-tion of their high cis-stereospecificity for the catalyst composition and polymerization conditions widely varied have been believed to originate from the low ability of active centres to anti-syn-isomerization.

REFERENCES

1. Monakov Yu. B., Marina N. G., et al.: *Dokl. AN SSSR* 1982, 265, No 6, 1431.
2. Murinov Yu. I., Monakov Yu. B.: *Inorg. Chim. Acta* 1987, 140, No 1—2, 25.
3. Marina N. G., Monakov Yu. B., et. al.: *Vysokomol. Soed.* 1984, 26(A), No 6, 1123.
1. Monakov Yu. B., Marina N. G., et al.: *Inorg. Chim. Acta* 1988, 142, No 1, 161.
5. Marina N. G., Gadeleva Kh. K., et al.: *Dokl. AN SSSR* 1984, 274, No 3, 641.
6. Monakov Yu. B., Marina N. G., et al.: *Dokl. AN SSSR* 1987, 292, No 2, 405.
7. Rafikov S. R., Kozlov V. G., et al.: *Izv. AN SSSR, Chem. Ed.* 1982, No 4, 871.
8. Monakov Yu. B., Marina N. G., et al.: *Dokl. AN SSSR* 1984, 278, No 5, 1182.
9. Marina N. G., Duvakina N. V., et al.: *Vysokomol. Soed.* 1985, 27(A), No 6, 1203.