ELSEVIER

Dehydration of $LnCl_3 \cdot 6H_2O$ (Ln = Tb, Nd, Dy) in the reaction with $i\text{-}Bu_3Al$, Et_3Al, Et_2AlCl, $EtAlCl_2$ and formation of the complexes $LnCl_3 \cdot 3(BuO)_3PO$

Ramil G. Bulgakov [a],*, Sergei P. Kuleshov [a], Aleksei N. Zuzlov [a],
Ildar R. Mullagaleev [b], Leonard M. Khalilov [a], Usein M. Dzhemilev [a]

[a] *Institute of Petrochemistry and Catalysis,*
Bashkortostan Republic Academy of Sciences and Ufa Scientific Center Russian Academy of Sciences, Prospekt Oktyabrya, 141,
450075 Ufa, Russian Federation
[b] *Institute of Organic Chemistry, Ufa Scientific Center Russian Academy of Sciences, Prospect Oktyabrya, 71, 450054 Ufa, Russian Federation*

Dedicated to Academic Oleg M. Nefedov on his 70th birthday

Abstract

The dehydration of toluene insoluble salts $TbCl_3 \cdot 6H_2O$ (**1**), $DyCl_3 \cdot 6H_2O$ (**2**) and $NdCl_3 \cdot 6H_2O$ (**3**) in their reaction with organoaluminum compounds (R_nAlX_{3-n}): $i\text{-}Bu_3Al$, Et_3Al, Et_2AlCl, $EtAlCl_2$ and the influence of $(BuO)_3PO$ (TBP) on the process were studied. In the reaction of R_nAlX_{3-n} with the water of crystallization of salts **1**–**3**, aluminoxanes and the following gases are formed: $i\text{-}BuH$ for $i\text{-}Bu_3Al$, EtH for Et_3Al, EtH and HCl for Et_2AlCl and $EtAlCl_2$ as a result of the attack on the Al–C or Al–Cl bond independent of the presence of TBP. In the absence of TBP the salts **1**–**3** are dehydrated by R_nAlX_{3-n} to give insoluble products $LnCl_3 \cdot 0.5H_2O \cdot 0.5(R_2Al)_2O$, where R is alkyl for $i\text{-}Bu_3Al$ and Et_3Al, or R is alkyl and Cl for Et_2AlCl. The reaction of R_nAlX_{3-n} with **1**–**3** in the mixture of toluene–TBP at the ratio TBP/Ln $\geq$ 12:1 results in the complete removal of water from $LnCl_3 \cdot 6H_2O$ and leads to the formation of homogeneous solutions, containing aluminoxanes and $LnCl_3 \cdot 3TBP$ complexes. Homogeneous solutions, obtained after interaction in the system $NdCl_3 \cdot 6H_2O + TBP + PhMe + R_3Al$ were then activated with either $i\text{-}Bu_3Al$ or $(i\text{-}Bu_2Al)_2O$ and used as catalysts for polymerization of butadiene. All the catalysts were highly active for polymerization of butadiene, and produced a low-molecular polybutadiene. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Organoaluminum compounds; Dehydration of crystalline hydrates of lanthanide thriclorides

1. Introduction

The compounds consisting of R_nAlX_{3-n} and anhydrous complexes $LnCl_3 \cdot 3L$ where L is $(BuO)_3PO$, R_2SO and ROH are used as heterogeneous catalysts for the polymerization of dienes [1,2]. The complexes $LnCl_3 \cdot 3L$ may be obtained by removing the water of crystallization from $LnCl_3 \cdot 6H_2O$ either by azeotrope distillation or through chemical reaction with dehydrating agents [3,4].

The reaction of $LnCl_3 \cdot 6H_2O$ with R_nAlX_{3-n} was not studied previously. It is known that R_nAlX_{3-n} readily interacts with water to give aluminoxanes [5]. This work reports on the possibility of obtaining homogeneous compositions, consisting of soluble anhydrous lanthanide complexes and aluminoxanes obtained by a one-pot synthesis by mixing $LnCl_3 \cdot 6H_2O + R_nAlX_{3-n} + (BuO)_3PO$ in toluene. The reaction products in the system $LnCl_3 \cdot 6H_2O + R_nAlX_{3-n}$ and routes to their formation in the presence and absence of TBP were studied with the use of chemical and luminescence methods. The compositions thus obtained were tested for catalytic activity in the polymerization of butadiene.

* Corresponding author. Fax: + 7-3472-312750.
E-mail address: ink@anrb.ru (R.G. Bulgakov).

2. Results and discussion

2.1. $LnCl_3·6H_2O + PhMe + R_nAlX_{3-n}$ system

It is well known that the water of crystallization in $LnCl_3·6H_2O$ is bonded strongly with the Ln^{3+} ion [6]. The reaction of R_nAlX_{3-n} with salts **1**–**3** in the absence of TBP was studied in the first instance to check the dehydrating ability of R_nAlX_{3-n}. The salts **1**–**3** are insoluble in toluene. According to photoluminescence measurements the concentration of Ln in toluene is $< 10^{-7}$ M after 5 h of stirring, while at the same time ca. 1% of the water of crystallization is extracted to toluene from $LnCl_3·6H_2O$. The gas evolution is observed immediately after the addition of R_nAlX_{3-n} to the suspension of salts **1**–**3** in toluene or TBP and it is intensified at higher temperatures. The rate of gas evolution increases in the order $EtAlCl_2 > i\text{-}Bu_3Al > Et_2AlCl > Et_3Al$, this order being similar to the one observed for the reaction of these compounds with $CuSO_4·5H_2O$ [7]. The volume of gas evolved is not dependent on the ratio of $LnCl_3·6H_2O/R_nAlX_{3-n}$ in the range 1:12–50. The quantity of water removed as well as the rate of reaction is similar for all the Ln^{3+} ions. It can be accounted for by the similar crystal structure (monoclinic, space group $P2/c-C_{2h}$) for salts **1**–**3** [6]. The composition of the evolved gas and the time required for the completion of gas evolution depended on the nature of substituents in R_nAlX_{3-n}, i.e. $i\text{-}BuH$ for $i\text{-}Bu_3Al$ (30 min), EtH for Et_3Al (240 min), EtH and HCl for Et_2AlCl (190 min) and $EtAlCl_2$ (10 min). The vacuum distillation of the reaction mixture leaves a viscous colorless residue which has the characteristics of aluminoxanes [7–9]. It was a surprise for us to find the aluminum in the toluene-insoluble solids left after the reaction of salts **1**–**3** with R_nAlX_{3-n}. The evolution of gas upon the addition of HNO_3 (0.1 M) to the solids indicated that these samples contained Al–C bonds. In the IR spectra (KBr) of solids two new groups of absorption bands belonging to aluminoxanes [8,9] were observed at 680, 620, 1460 cm^{-1} (valence and deformation oscillations of CH_2 groups bonded to Al ion) and at 780–810 cm^{-1} (asymmetric deformation oscillations of Al–O bond) besides the band of the Ln–Cl group at 340 cm^{-1}. Moreover, the presence of Al–C bonds was indicated by the emission of light (chemiluminescence) observed on contact of O_2 with the surface of the solids. This emission was in fact
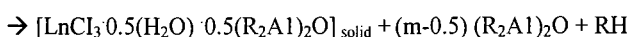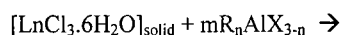
chemiluminescent and was not caused by the combustion of R_nAlX_{3-n}. Actually, the temperature of the samples in these experiments did not rise higher than 50–60 °C and spectral measurements indicated that electronic excited Ln^{3+} ions were the emitters of light in these systems. The efficiency of the chemiluminescence test for the Al–C bonds has been proved for a range of R_nAlX_{3-n} compounds [10].

The results obtained thus far led us to conclude that the solid phase had the composition $LnCl_3·0.5H_2O·0.5(R_2Al)_2O$ and thus the aluminum is present in the form of aluminoxane. The bonding of aluminoxanes in the form of adducts with water on the surface of solid inorganic materials (kaolin, tuff) has been described previously [11].

The maximum amount of water removed from salts **1**–**3** is independent of the nature of R_nAlX_{3-n} and temperature and is equal to 5.5 molecules. Both the photoluminescence intensity of Ln^{3+} and the lifetime of Tb^{3+} (τ) in the solid phase ($\tau = 80$ μs) are much lower than in the initial salts **1** ($\tau = 455$ μs), **2** and **3**. It may be concluded that soluble complexes of $LnCl_3$ with aluminoxanes are not formed during the reactions in the system studied since the Ln^{3+} ions were not observed in solution. The reactions of R_nAlX_{3-n} with $LnCl_3·6H_2O$ are illustrated in Scheme 1.

2.2. $LnCl_3·6H_2O + PhMe + (BuO)_3PO + R_nAlX_{3-n}$ system

It was shown by analytical methods that the same range of products are formed in the system $LnCl_3·6H_2O + PhMe + (BuO)_3PO + R_nAlX_{3-n}$ as in the system without TBP (see Section 2.1), i.e. ethane, i-butane, HCl, aluminoxanes. However, the dehydration of salts **1**–**3** in the presence of TBP occurred in a different way. Firstly, Ln^{3+} was observed to dissolve in toluene during the course of the reaction. Secondly, the interaction with Et_2AlCl and $EtAlCl_2$ was complicated by the side reaction of these compounds with TBP. It was established in control experiments that gas evolution and formation of a yellow viscous mass is observed immediately after the mixing of $EtAlCl_2$ and TBP solutions in the absence of other reagents. We have not studied this system in detail, however, it should be noted that the gas contained HCl as a component. Contrary to this, no gas evolution was observed on mixing toluene solutions of Et_2AlCl and TBP. At the same time, the kinetic curve of gas evolution for the reaction of Et_2AlCl with **1**–**3** had the form which is typical for an autocatalytic reaction (Figs. 1 and 2). The analysis of gas components indicated that during the first part of the kinetic curve (Fig. 2, section a) the water attacks the Al–C bond yielding EtH. Afterwards, the Al–Cl bond also becomes involved in the reaction and simultaneous evolution of both EtH and HCl is

$$[LnCl_3·6H_2O]_{solid} + mR_nAlX_{3-n} \rightarrow$$

$$\rightarrow [LnCl_3·0.5(H_2O)·0.5(R_2Al)_2O]_{solid} + (m-0.5)(R_2Al)_2O + RH$$

Scheme 1. Reagents and conditions: $LnCl_3$ (Ln = Tb, Dy, Nd); ($R_nAlX_{3-n} = i\text{-}Bu_3Al$, Et_3Al, Et_2AlCl, $EtAlCl_2$), $m = 12$), PhMe, 40 °C.
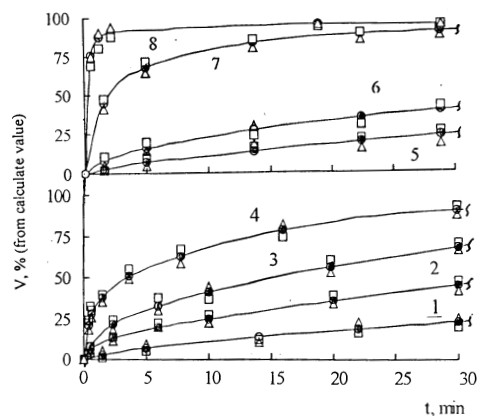
Fig. 1. Time dependencies of the volume of generated gas in the reaction of **1**–**3** (0.54 mmol) with R_nAlX_{3-n} (6.5 mmol) in toluene: 1–4 at interaction of **1**–**3** with Et_3Al without TBP: (1) 40 °C, (2) 50 °C, (3) 70 °C, (4) 90 °C; 5–8 at interaction (40 °C) of **1**–**3** with Et_3Al, Et_2AlCl, $(i\text{-}Bu)_3Al$, $EtAlCl_2$, respectively, without TBP; $-\bigcirc-$ Tb, $-\square-$ Dy, $-\triangle-$ Nd.
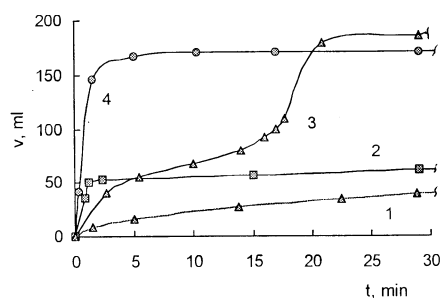

Fig. 2. Time dependencies of the volume of generated gas in the reaction of $EtAlCl_2$ (0.65 M) in toluene (40 °C): (1) with **1** (0.54 mmol); (2) with TBP (0.16 M); (3) with **1** (0.54 mmol) + TBP (0.16 M); (4) with **1** (0.54 mmol) and TBP (0.16 M) in the presence of HCl (0.3 M).

observed (Fig. 2, section b). The HCl formed reacts with initial Et_2AlCl to give $EtAlCl_2$ according to Eq. (1) and when the critical concentration of $EtAlCl_2$ is reached, the $EtAlCl_2$ reacts with TBP with the evolution of gas. The gas evolution is observed on the addition of HCl saturated toluene to the reaction mixture.

$$HCl + Et_2AlCl \rightarrow EtAlCl_2 + EtH \qquad (1)$$
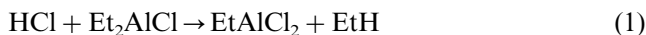
At $[HCl] = 3 \times 10^{-1}$ M the rapid gas evolution starts immediately after the contact of reagents (Fig. 2). Thus, both Et_2AlCl and $EtAlCl_2$ can be used to dehydrate the salts **1**–**3**, however, these reagents cannot be used to obtain anhydrous $LnCl_3$ complexes with TBP, due to the observed side reactions.

At high concentrations of TBP (TBP/Ln $\geq$ 12:1) the complete removal of water from the salts **1**–**3** and from the solution are observed for the $LnCl_3 \cdot 6H_2O$ + $PhMe + (BuO)_3PO + R_nAlX_{3-n}$ system, independent of the R_nAlX_{3-n} used. The water is removed during

the first 45 s of interaction with simultaneous dissolution of Ln^{3+} to form $LnCl_3 \cdot 3TBP$ complexes. The completeness of reaction with water is evidenced by the measurements of the volume of gas evolved and by Fischer titration, while the dissolution of Ln is indicated by the disappearance of the solid phase. The composition of $LnCl_3 \cdot 3TBP$ complexes, obtained at initial ratio TBP/Ln $\geq$ 12:1 was established by spectral methods as described below. The dissolution of Ln is also proved by the appearance of photoluminescence (Fig. 3) characteristic of lanthanide ions [12].

The appearance of TBP in the coordination sphere of Ln^{3+} instead of the water of crystallization is accompanied by the change of luminescence properties of Ln^{3+}, as compared to the initial salts **1**–**3**. The intensity of the known maxima in the luminescence spectra of $LnCl_3 \cdot 3TBP$ for Tb^{3+}, Dy^{3+} and Nd^{3+} are redistributed due to interaction as compared to hydrated salts. Thus for Tb salt which was studied in detail the most intense maximum at 545 nm is split into two new maxima at 547 and 552 nm, while the maxima at 488, 493 and 586, 591 nm undergo intensity redistribution and spectral shift to 490, 496 and 584, 596 nm, respec-
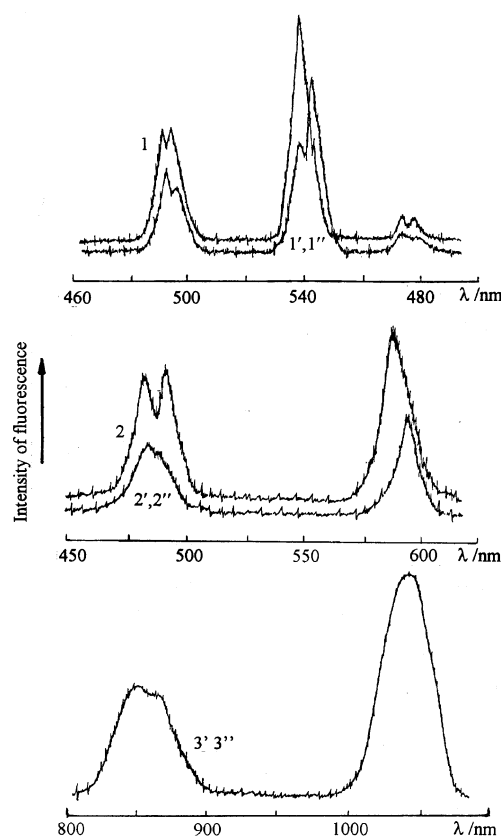
Fig. 3. Luminescence spectra (298 K): 1, 2 — $LnCl_3 \cdot 6H_2O$, Ln = Tb (1), Dy (2); the emission from $NdCl_3 \cdot 6H_2O$ was too weak to be detected. 1′, 2′, 3′ and 1″, 2″, 3″ — the solutions of $LnCl_3 \cdot 3TBP$ complexes and the solutions after reactions of $LnCl_3 \cdot 6H_2O$ (6.48 mmol) with Et_3Al (0.54 mmol) in toluene at TBP/Ln $\geq$ 12:1; Ln = Tb (1′, 1″), Dy (2′, 2″), Nd (3′, 3″). $\lambda_{excitation}$ (nm) = 365 (1,1′,1″), 352 (2,2′,2″), 337,1 (3′, 3″).

$$[LnCl_3.6H_2O]_{solid} + 12R_nAlX_{3-n} + zTBP \rightarrow$$

$$\rightarrow LnCl_3 \cdot 3TBP^- + 6 (R_2A1)_2O + RH + (z-3)TBP$$
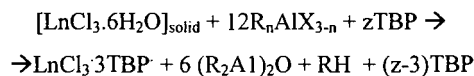
Scheme 2. Reagents and conditions: TBP/Ln $\geq$ 12:1; LnCl$_3$ (Ln = Tb, Dy), PhMe, 40 °C, 45 s; LnCl$_3$ (Ln = Nd), TBP, 40 °C, 45 s.

tively (Fig. 3). The reaction product obtained for the initial ratio of TBP/$\mathbf{1} \geq$ 12:1 shows photoluminescence spectra and lifetime and ^{13}C-NMR spectrum in toluene identical to TbCl$_3 \cdot$3TBP which was synthesized by the method described in Ref. [3]. It indicates that Tb in solution is present only in the form of the TbCl$_3 \cdot$3TBP complex. The lifetime of Tb^{3+}* (τ = 2800 μs) in the reaction solution is much higher than for the initial salt $\mathbf{1}$ (τ = 455 μs) and is equal to the lifetime observed for TbCl$_3 \cdot$3TBP in toluene at 300 K. The formation of a donor–acceptor bond for Ln^{3+} ion with the oxygen of a P=O group is indicated by the differences observed in the IR and ^{13}C-NMR spectra between the individual toluene solution of TBP and the solution obtained after the interaction of reagents in the system studied. Actually, a new IR band at 1225 cm^{-1} (P=O bond) appears after the end of the reaction and this band is shifted by 55 cm^{-1} from the more intense band at 1280 cm^{-1} observed for the individual TBP solution [3]. In the ^{13}C-NMR spectrum of an individual solution of TBP a doublet of CH$_2$O groups is registered at 66.5 ppm with a spin–spin constant $^2J(^{31}P-^{13}C)$ = 6 Hz. In the ^{13}C-NMR spectrum of the solution after reaction this doublet is transformed to the broad signal at 68.24 ppm with $\Delta W_{1/2}$ = 16 Hz. A similar signal at 68.30 ppm with $\Delta W_{1/2}$ = 16 Hz is observed in the specially prepared mixture TbCl$_3 \cdot$3TBP + 9TBP + 6(i-Bu$_2$Al)$_2$O in toluene. This signal can be ascribed to the free uncoordinated terminal BuO group.

We have also observed that besides the six molecules of the water of crystallization, additional water molecules (up to three) adsorbed by LnCl$_3 \cdot$6H$_2$O can be completely removed as a result of interaction in the system studied at TBP/Ln $\geq$ 12:1.

The salts $\mathbf{1}$–$\mathbf{3}$ are dehydrated in an equal period of time while their dissolution requires different times, which depends on the Ln used, e.g. Nd (1.5 week), Tb and Dy (45 s). These results are in accordance with the known [13] order of the ability of Ln^{3+} ions to form complexes with TBP: Nd $\ll$ Tb(Dy), which was established in other studies. The reactions of R$_n$AlX$_{3-n}$ with LnCl$_3 \cdot$6H$_2$O in the presence of TBP are illustrated in Scheme 2 [R$_n$AlX$_{3-n}$ = i-Bu$_3$Al, Et$_3$Al].

2.3. Butadiene polymerization results using homogeneous catalysts obtained in the reactions of NdCl$_3$· 6H$_2$O with i-Bu$_3$Al or Et$_3$Al in the presence of TBP

Homogeneous toluene solutions, containing LnCl$_3 \cdot$ 3TBP + aluminoxane and solid precipitates of the com-

position LnCl$_3 \cdot$0.5H$_2$O$\cdot$0.5(R$_2$Al)$_2$O may show catalytic activity in the polymerization and oligomerization of dienes and olefins. Herein, we wish to describe the preliminary test of the catalytic activity of the system in question in the polymerization of butadiene. The systems $\mathbf{4}$–$\mathbf{7}$ which had the following catalyst–cocatalyst content were tested for the polymerization of butadiene: $\mathbf{4}$ — [NdCl$_3 \cdot$3TBP + nTBP + 6(i-Bu$_2$Al)$_2$O]–i-Bu$_3$Al; $\mathbf{5}$ — [NdCl$_3 \cdot$3TBP + 29TBP + 6(Et$_2$Al)$_2$O]–i-Bu$_3$Al; $\mathbf{6}$ — [NdCl$_3 \cdot$3TBP + 6(i-Bu$_2$Al)$_2$O]–(i-Bu$_2$Al)$_2$O; $\mathbf{7}$ — [NdCl$_3 \cdot$3TBP]–i-Bu$_3$Al. The results for the polymerization of butadiene with catalysts $\mathbf{4}$–$\mathbf{6}$ are shown in Tables 1–3. The catalysts $\mathbf{4}$ and $\mathbf{5}$ were obtained in the reactions of NdCl$_3 \cdot$6H$_2$O with i-Bu$_3$Al or Et$_3$Al in the presence of TBP while catalyst $\mathbf{6}$ was prepared by mixing toluene solutions of NdCl$_3 \cdot$3TBP and (i-Bu$_2$Al)$_2$O. Moreover, the known heterogeneous catalyst $\mathbf{7}$ [1b] was prepared for comparison. The catalysts $\mathbf{4}$–$\mathbf{6}$ show no activity in the polymerization in the absence of cocatalysts. For all the polymerization conditions studied, the catalysts $\mathbf{4}$–$\mathbf{6}$ activated with i-Bu$_3$Al or (i-Bu$_2$Al)$_2$O produce polybutadiene with high activity and low number-average molecular mass (M_n) = 2×10^3 (Tables 1–3). The ratio of the components is one of the major factors determining the yield and microstructure of polybutadiene. The enhancement of the catalyst activity was observed starting from the ratio (i-Bu$_3$Al)/Nd = 10 and reaching saturation at (i-Bu$_3$Al)/Nd = 40–50. A high content of TBP (TBP/Ln = 12) is required to observe the catalytic activity in the system studied (Tables 1–3). For example, in the case of catalyst $\mathbf{4}$ the yield of polybutadiene and the content of 1,4-*cis* units increase as the ratios of TBP/Nd and i-Bu$_3$Al/Nd are increased (Table 1). The ratio of M_w/M_n (M_w is weight-average) increases independent of the relation TBP/Nd as the ratio of i-Bu$_3$Al/Nd is enlarged. The polybutadiene obtained at the optimal ratio of the components of catalyst $\mathbf{4}$ had $M_n = 2 \times 10^3$ and M_w/M_n = 4–5. The relative rate constants for the reactions of chain transfer to i-Bu$_3$Al (k_r) (e.g. the ratio of the rate constant for the reactions of chain transfer to that of chain propagation, k_p) are increased from 1.4×10^{-2} for TBP/Nd = 6 to 2.5×10^{-2} for TBP/Nd = 17. The 1,4-*cis* units content for the polybutadiene obtained with catalyst $\mathbf{4}$ becomes lower at the higher concentrations of i-Bu$_3$Al as a result of the increased 1,4-*trans* units content. The 1,2 units content is about 1–2%. At the same time the activity of catalyst $\mathbf{7}$ which was studied for comparison is twice higher and it produces polybutadiene with the following parameters at the optimal conditions: $M_n = 2 \times 10^5$, the 1,4-*cis* units content is 93–94%, 1,4-*trans* units is 5–6% and 1,2 units is 1% (independent of the ratio i-Bu$_3$Al/Nd); M_w/M_n = 4–5 and $k_r = 5 \times 10^{-2}$. These results coincide with the known data [1a,b]. Contrary to the catalysts $\mathbf{4}$–$\mathbf{6}$ the activity of catalyst $\mathbf{7}$ is diminished on the

Table 1
Polymerization of butadiene with catalyst **4** activated with i-Bu$_3$Al

TBP/Nd	Al/Nd	Yield (%)	1,4-cis units (%)	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$
9	20	9	88	94	20
9	30	14	87	81	15
9	40	15	87	63	13
9	50	18	85	50	12
9	60	18	80	44	11
17	20	11	94	120	25
17	30	36	93	95	20
17	40	74	88	73	18
17	50	77	84	56	15
17	60	77	82	49	14
29	20	13	95	233	30
29	30	44	93	173	21
29	40	96	88	90	17
29	50	98	85	43	12
29	60	99	83	40	10

Conditions: [Nd], 2×10^{-3} M; [butadiene] = 1.5 M, 25 °C, t_p, 2 h.

addition of TBP and it shows the maximum activity at i-Bu$_3$Al/Nd = 30 [1b]. The value of M_n decreases as the ratio i-Bu$_3$Al/Nd is increased.

The catalyst **5** synthesized in the reaction of **3** with Et$_3$Al shows the activity comparable to **4**, but its cis-1,4 stereospecificity is lower (Table 2). The molecular mass of the polymers obtained using this catalyst is also lower at all ratios of i-Bu$_3$Al/Nd. The ratio M_w/M_n becomes higher at a higher ratio of i-Bu$_3$Al/Nd and the magnitude of k_r is also larger and is equal to 5.5×10^{-2}, e.g. close to the value of k_r observed for **7**. The results obtained for catalyst **6** indicate a possible formation of the low-molecular polymer with the small amount of TBP on adding aluminoxane (Table 3). This catalyst is less active and gives the polybutadiene with the higher molecular mass than catalysts **4** and **5**, but the relation M_w/M_n is the same. The small value of $k_r = 1.1 \times 10^{-2}$ indicates that the chain transfer to (i-Bu$_2$Al)$_2$O is less efficient than to i-Bu$_3$Al.

Thus, the differences between the catalysts **4** and **5** from **7** are less in the activity and cis-1,4-regulating stereospecificity than in the molecular mass of the polymers obtained. These differences indicate the different nature of the active centers of the catalysts. The detailed studies of the nature of the active centers of the catalysts **4–6** and the polymerization kinetics will be the subject of another paper. However, the results obtained so far allow to conclude that the generation of the Nd–C bond and the coordination of the lanthanide ion with both aluminoxane and TBP are required for the formation of the active centers of the catalysts **4–6**. Actually, the catalysts **4–6** show no activity in the absence of Bu$_3$Al or (i-Bu$_2$Al)$_2$O, and their addition is necessary for the formation of the Nd–C bond. When

polymerization with catalyst **7** is carried out at the ratio TBP/Nd = 29 the yield of the polymer is decreased to 0.1%, but the molecular mass of the polymer is increased to $M_n = 4 \times 10^5$. According to Ref. [1c] the yield of the polymer for the catalyst obtained in the reaction of NdCl$_3$·3i-PrOH with i-Bu$_3$Al, is decreased in the presence of (i-Bu$_2$Al)$_2$O at the ratio of (i-Bu$_2$Al)$_2$O/Nd = 2:1, without the change of the molecular mass of the polymer. Thus, the active catalytic centers generating the low-molecular polymer are not formed when aluminoxane and TBP are added separately.

Table 2
Polymerization of butadiene with catalyst **5** activated with i-Bu$_3$Al

(i-Bu$_3$Al)/Nd/Nd	20	30	40	50	60	80
Yield (%)	1.4	20	96	98	100	100
1,4-cis units (%)	84	83	84	83	84	84
$M_w \times 10^{-3}$	–	66	60	56	50	46
$M_n \times 10^{-3}$	–	15	13	8.5	7.7	5

Conditions: [Nd], 2×10^{-3} M; [butadiene] = 1.5 M, 25 °C, t_p, 2 h.

Table 3
Polymerization of butadiene with catalyst **6** activated with (i-Bu$_2$Al)$_2$O

(i-Bu$_2$Al)$_2$O/Nd	20	30	40	50	60	80
Yield (%)	28	47	65	66	67	67
1,4-cis units (%)	94	96	95	95	94	94
$M_w \times 10^{-3}$	247	174	154	145	110	95
$M_n \times 10^{-3}$	66	39	32	28	19	18

Conditions: [Nd], 2×10^{-3} M; [butadiene] = 1.5 M, 25 °C, t_p, 2 h.

3. Experimental

3.1. Materials and procedures

All manipulations were carried out under Ar with the use of Schlenk techniques. The salts **1**–**3** were commercial products described as 'Chemical Pure' and were used without further purification. The commercial 90% solutions of R_nAlX_{3-n} in petroleum were used to prepare the diluted solutions in toluene used in this work. Hexane, toluene and TBP were boiled and distilled over Na in Ar atmosphere. $TbCl_3 \cdot 3TBP$ and $(i\text{-}Bu_2Al)_2O$ were obtained as outlined in Refs. [3,7], respectively. The reactions of solutions of R_nAlX_{3-n} with **1**–**3** were carried out in toluene under Ar in a glass reactor equipped with a magnetic stir-bar and connected with a gas burette. The salts **1**–**3** and the complexes generated in the reactions of these salts with R_nAlX_{3-n} were analyzed for the contents of Ln^{3+} by complexon titration [14] and by luminescence spectroscopy [6]. Cl^- was determined by Folgard method [15], TBP — by the method described in Ref. [15], aluminum — by complexon titration [14], water — by Fischer titration [15] before and after gas evolution. EtH and i-BuH were analyzed by GC (Zwet 500M, column on zeolite C-22, 25% in hexadecane). HCl gas was titrated by passing it through a solution of NaOH (0.7 M). Aluminoxanes were analyzed as described in Refs. [7–9]. The UV and IR absorption spectra were recorded in Specord M-40 and Specord IR-75. Photoluminescence spectra were obtained in a Aminco-Bowman fluorimeter, and chemiluminescence spectra with the use of equipment described in Ref. [16]. A lifetime of Tb^{3+*} was measured using impulses generated by a LGI-23 nitrogen laser (337.1 nm). ^1H- (90 MHz) and ^{13}C- (22.5 MHz) NMR spectra were recorded on a JEOL FX 90Q spectrometer. C_6D_6 was used as an internal standard and solvent. Chemical shifts in ppm are reported relative to TMS.

3.2. Reaction of $LnCl_3 \cdot 6H_2O$ with R_nAlX_{3-n} in the absence of TBP

A solution of R_nAlX_{3-n} (6.48 mmol) in petroleum (0.9–2.0 ml) was added to a stirred suspension of **1**, **2** or **3** (0.54 mmol) in toluene (8.0–9.1 ml) for 20 min at different temperatures (40, 50, 70, 90 °C). The mixture was stirred for 20–240 min (depending on R_nAlX_{3-n}) until the completion of gas evolution. Afterwards the solution and a white solid were filtered off. The solvent was removed from the filtrate in vacuo, leaving a colorless liquid which was an aluminoxane (except that in the reactions of the salts with $EtAlCl_2$ a green suspension was formed).

3.2.1. $(Et_2Al)_2O$
Anal. Found: C, 52.55; H, 10.90; Al, 28.94. Calc.: C,

51.60; H, 10.83; Al, 28.98%. IR (cm^{-1}): $\nu_{AlOAl} = 734$, 753–770, 790–814, $\nu_{C-C} = 920$, 954, 984, $\nu_{Al-C} = 478$, 545, 652.

3.2.2. $(i\text{-}Bu_2Al)_2O$
Anal. Found: C, 64.94; H, 12.34; Al, 18.01. Calc.: C, 64.40; H, 12.16; Al, 18.08%. IR (cm^{-1}): $\nu_{AlOAl} = 748$–780, $\nu_{C-C} = 813$, 942, 95; $\nu_{Al-C} = 688$.

3.2.3. $(EtAlCl)_2O$
Anal. Found: C, 24.25; H, 5.12; Al, 27.18; Cl, 35.59. Calc.: C, 24.14; H, 5.07; Al, 27.12; Cl, 35.63%. IR (cm^{-1}): $\nu_{AlOAl} = 738$, 755–770, 780–811; $\nu_{C-C} = 927$; 954, 990, $\nu_{Al-C} = 543$, 672.

The solid was washed twice with toluene (10 ml) and dried under vacuum to afford (99%) $LnCl_3 \cdot 0.5H_2O \cdot 0.5(R_2Al)_2O$ (where R is alkyl for i-Bu_3Al and Et_3Al, or R is alkyl and Cl for Et_2AlCl) as a white powder. The ratio of Al–C groups to the total Al was estimated by measuring the volume of gas evolved and it was equal to 2 and 1 for Et_3Al, i-Bu_3Al and Et_2AlCl, respectively.

3.3. Reaction of $LnCl_3 \cdot 6H_2O$ with R_nAlX_{3-n} in the presence of TBP ($TBP/Ln = 12:1$)

TBP (6.48 mmol) (1.76 ml) was added to **1**, **2** or **3** (0.54 mmol), the mixture was stirred at 20 °C for 10 min, leaving a homogeneous solution. Addition of toluene (7.4–6.3 ml) to the solution formed a cloudy milky suspension, which was kept for 20 min at 40 °C. After adding a solution of R_nAlX_{3-n} (6.48 mmol) in petroleum (0.9–2.0 ml) the mixture obtained was stirred for 45 s until the completion of gas evolution, leaving a homogeneous solution (for **1** and **2**) or a suspension (for **3**), which was filtered off. The content of Nd in the filtrate was 50% from the initial. It was necessary to add a solution of R_nAlX_{3-n} to a solution of **3** in TBP without adding toluene for obtaining a homogeneous solution, containing 100% Nd from the initial.

3.4. Polymerization procedure and the polymer characterization

Butadiene (99.8%) was purified by passing through columns filled with KOH and calcined aluminum oxide. To prepare homogeneous catalysts **4** and **5**, TBP (6.48 mmol) was added to **3** (0.54 mmol) and the mixture was stirred at 20 °C for 10 min leaving a homogeneous solution. After addition of a solution of i-Bu_3A (for **4**) or Et_3Al (for **5**) in petroleum, the mixture obtained was stirred for 1 min at 20 °C. The homogeneous catalyst **6** was prepared by adding a solution of $(i\text{-}Bu_2Al)_2O$ (3.24 mmol) in toluene to a solution of $NdCl_3 \cdot 3TBP$ (0.54 mmol) in toluene. The known heterogeneous catalyst **7** was prepared by the addition of a solution of i-Bu_3A in petroleum to a solution of $NdCl_3 \cdot 3TBP$ (0.54 mmol) in

toluene according to Ref. [1b]. Butadiene polymerization was carried out in toluene at 25 °C in Ar atmosphere under anhydrous conditions [1]. The polymers were precipitated with a 1% solution of ionol in methanol and dried in vacuum at 40 °C. The polybutadiene microstructure was determined with a Specord M-80 spectrometer based on the IR spectra of the films cast from the benzene solution of polymers. The molecular mass (M_w and M_n) of polybutadienes was estimated with a Waters chromatograph using toluene as an eluent. The rate constant of chain propagation (k_p) and the rate constants for the reactions of chain transfer to the monomer (k_x) were calculated from the dependencies of the polybutadiene molecular mass on the polymerization time and concentrations of the monomer and cocatalyst, as described in Ref. [1b].

Acknowledgements

References

[1] (a) Yu.B. Monakov, G.A. Tolstikov, Katalititcheskaya polimerizatsiya 1,3-dienov, Moskva, Nauka, 1990, 221 pp;
(b) I.G. Savel'eva, Doctoral dissertation, Institute of Organic Chemistry, Ufa, Russia, 1982;
(c) V.C. Bodrova, E.I. Piskareva, L.Ph. Shelochneva, I.A. Poletaeva, Vysokomol. Soedin. Ser. A 40 (1998) 1741.

[2] M.N. Botchkarev, G.S. Kalinin, L.N. Zakharov, S.Ya. Khorshev, Organicheskie, proizvodnye redkozemel'nykh elementov, Moskva, Nauka, 1989, 232 pp.

[3] Yu.M. Murinov, Yu.B. Monakov, Z.G. Shamaeva, N.G. Marina, V.S. Kolasnitsin, Yu.M. Nikitin, S.R. Raphikov, Izv. Akad. Nauk SSSR Ser. Khim. 12 (1977) 2790.

[4] V.K. Lakatos Osorio, A.M. Passos, Inorg. Chim. Acta 19 (1976) 245.

[5] N.N. Korneev, Khimiya i tekhnologiya alyumini'organitcheskikh soedinenii, Moskva, Khimiya, 1979, 256 pp.

[6] V.T. Panyushin, Yu.A. Aphanas'ev, E.I. Khanaev, A.D. Garnovskii, Lantanoidy. Prostye i kompleksnye soedineniya, Rostov na Donu, Izd. Rostovskogo universiteta, 1980, 296 pp.

[7] G.A. Razuvaev, Yu.A. Sangalov, Yu.Ya. Nel'kenbaum, K.S. Minsker, Izv. Akad. Nauk SSSR Ser. Khim. 11 (1975) 2547.

[8] A. Storr, K. Jones, A.W. Laubengayer, J. Am. Chem. Soc. 90 (1968) 3173.

[9] M. Boleslawski, J. Serwatowski, J. Organomet. Chem. 254 (1983) 159.

[10] R.G. Bulgakov, V.P. Kazakov, G.A. Tolstikov, J. Organomet. Chem. 387 (1990) 11.

[11] Z.G. Gorelik, L.A. Shesterina, A.D. Emel'yanova, L.Ph. Borisova, E.A. Phushman, V.Sh. Berner, N.N. Korneev, Zh. Obshch. Khim. 55 (1985) 2506.

[12] G.R. Choppin, D.R. Peterman, Coord. Chem. Rev. 174 (1998) 283.

[13] K.B. Yatsemirskii, N.A. Kostromina, Z.A. Sheka, N.K. Davidenko, E.E. Kriss, V.I. Ermolenko, Khimiya kompleksnykh soedinenii redkozemel'nykh elementov.

[14] K.G. Miesserov, E.I. Tinyakova, B.A. Dolgoplosk, Zh. Obshch. Khim. 12 (1984) 2828.

[15] G. Sharlo, Metody analititcheskoi khimii. Kolitchestvennyi analiz neorganitcheskikh soedinenii, Khimii, Moskva-Leningrad, 1965, 893 pp.

[16] R.G. Bulgakov, V.P. Kazakov, G.A. Tolstikov, Khemiluminestsentsiya metalloorganitcheskikh soedinenii, Moskva, Nauka, 1989, 220 pp.