

CATALYTIC REACTION MECHANISMS

Luminescence Monitoring of Lanthanide Catalysts for Diene Polymerization

R. G. Bulgakov*, S. P. Kuleshov*, A. N. Zuzlov*, R. R. Vafin*, S. V. Rusakov*, I. R. Mullagaliev**,
U. M. Dzhemilev*, and Yu. B. Monakov**

*Institute of Petrochemistry and Catalysis, Academy of Sciences of Bashkortostan, Ufa Scientific Center,
Russian Academy of Sciences, Ufa, 450075 Bashkortostan, Russia

**Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, Ufa, 450054 Bashkortostan, Russia
Received January 9, 2003

Abstract—Changes in the luminescence characteristics of Tb^{3+} and Ce^{3+} lanthanide ions in the interaction of $LnCl_3 \cdot 3(BuO)_3PO$ complexes with iso- Bu_3Al in the absence and presence of piperylene were studied. As a result, a new luminescence approach was proposed to study reaction mechanisms in the synthesis of lanthanide catalysts for diene polymerization.

INTRODUCTION

The luminescence of lanthanides (Ln) is widely used in chemistry and biology and in the development of scintillators and lasers [1–3]. In the scientific literature, this phenomenon is referred to as a rare earth luminescence probe. At the same time, only few examples concerning the use of rare earth luminescence probes for studying lanthanide Ziegler–Natta catalysts were published [4–6]. The composition formed by the interaction of $LnCl_3 \cdot 3TBP$ ($TBP = (BuO)_3PO$) complexes with iso- Bu_3Al [7] at a ratio of $R_3Al/Ln > 5$ is an efficient catalyst for the production of stereoregular polymers. Catalytically active centers of this catalyst are bridging structures that include Ln –iso- Bu – Al units [7, 8]. However, there is no direct experimental evidence that catalytic polymerization occurs by the insertion of monomer molecules into the Ln – C bond of lanthanide–aluminum-containing systems followed by polymer chain growth. Only indirect arguments in favor of the above mechanism were published [8, 9]. The mechanism of formation and the structure of active centers of lanthanide catalysts for diene polymerization are yet subjects for discussion [10]. Therefore, an urgent problem is to examine the capabilities of luminescence techniques for studying the mechanisms of reactions between $LnCl_3 \cdot 3TBP$ complexes and aluminum alkyls.

In this work, we first performed the luminescence monitoring of changes in the coordination environment of lanthanides in the $LnCl_3 \cdot 3TBP$ –iso- Bu_3Al –piperylene system ($Ln = Tb, Ce$) over a wide range of Al/Ln ratios, from homogeneous toluene solutions of the initial lanthanide complexes up to the formation of precipitates, which exhibited catalytic activity in the polymerization of dienes. We decided on Ce and Tb as lanthanides because of their relatively bright f – d and f – f luminescence, respectively, as well as because the

tributyl phosphate complexes of Ce and Tb in the presence of iso- Bu_3Al exhibited high catalytic activity in diene polymerization [7].

EXPERIMENTAL

Chemically pure $LnCl_3 \cdot 6H_2O$ were used in this study. Toluene and TBP were purified by refluxing and distillation from sodium metal, and argon was purified by passing through a gas absorbing apparatus. A commercial gasoline solution of iso- Bu_3Al (90%) was subjected to vacuum distillation [11]; the concentration of the alkoxy derivatives of aluminum in iso- Bu_3Al was no higher than 1% (according to 1H NMR data). The $LnCl_3 \cdot 3TBP \cdot H_2O$ complexes as syrupy liquids were synthesized in accordance with a published procedure [12] by the reaction of $LnCl_3 \cdot 6H_2O$ with TBP ($Ln/TBP = 1 : 3$) in toluene with the removal of water as an H_2O –toluene– $EtOH$ azeotrope. The subsequent dehydration of the complexes was performed with the use of molecular sieves 4 Å for 1–20 days. The $LnCl_3$ salts were prepared in according to a published procedure [13], and the $TbCl_3 \cdot 2TBP$ complex was prepared according to Korovin *et al.* [14] by dissolving $LnCl_3$ in a deficient amount of TBP. A solution of the $TBP \cdot (iso-Bu_3Al)$ complex was prepared by mixing TBP and iso- Bu_3Al ($TBP/iso-Bu_3Al = 1 : 3$) in toluene (300 K); the complex was identified by a comparison of the ^{13}C NMR spectra (toluene- d_8 ; δ , ppm; J , Hz) of a solution of the $TBP \cdot (iso-Bu_3Al)$ complex (69.8 (d, $^2J_{C-P} = 6$, $OCH_2(\alpha)$), 32.6 (d, $^3J_{C-P} = 7$, $CH_2(\beta)$), 18.8 $CH_2(\gamma)$; 13.6 (CH_3 , TBP), 25.8 ($Al-CH_2$), 26.7 (CH), 28.7 (CH_3 , iso- Bu_3Al)) and a solution of TBP (66.6 (d, $^2J_{C-P} = 6$, $OCH_2(\alpha)$); 32.4 (d, $^3J_{C-P} = 7$, $CH_2(\beta)$); 18.7 ($CH_2(\gamma)$); 13.4 (CH_3)).

Solutions of the $LnCl_3 \cdot 3TBP \cdot (H_2O)_x$ ($x = 0–0.3$) complexes and iso- Bu_3Al were prepared by dilution in

toluene. Piperylene was prepared by the rectification of a commercial product (98.3%, *trans*-to-*cis* isomer ratio of 60 : 40) according to a published procedure [15]. The water contents of $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{LnCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ were determined by the Karl Fischer method [16]. The reactions of $\text{LnCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ with iso- Bu_3Al in toluene were preformed in thermostatted Schlenk vessels (300 K) with stirring on a magnetic stirrer for 20 min (the reactions were performed at different ratios of $\text{Al/Ln} = 0\text{--}5$). Next, samples were taken using a syringe for the measurement of photoluminescence spectra in airtight quartz cells ($l = 0.1$ or 1 cm). To reduce the inner filter effect, the angle between the beams of exciting light and photoluminescence was equal to 45° . The shapes of spectra remained unchanged after keeping the samples for a day. The concentrations of Ln^{3+} and Al^{3+} in solutions and precipitates were determined by trilonometry [16].

The photoluminescence spectra were measured (with a resolution of 1.5 nm) on an original spectrofluorimeter based on an MDR-23 monochromator with the use of light from a DKSSh-150-2 xenon lamp for luminescence excitation; the exciting light was filtered with an MUM-2 monochromator. The ^1H NMR spectra (90 MHz) were measured on a JEOL FX 90Q NMR spectrometer. The lifetime (τ) of the excited terbium ion (Tb^{3+*}) was measured (in airtight quartz ampules) on a τ -metric unit using an LGI-21 nitrogen laser ($\lambda = 337.1$ nm) for photoluminescence excitation; the numerical value of τ was detected with a ChZ-39 frequency meter. In all cases, the photoluminescence intensity exhibited an exponential decay. The measurement error in τ was 10%, and the determination limit was 10 μs ; therefore, the measurement of the much shorter value of τ for Ce^{3+*} was impossible.

RESULTS

Luminescence Parameters of $\text{LnCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ ($x = 0\text{--}0.3$) Complexes

After keeping the solutions of $\text{LnCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ complexes in toluene over molecular sieves 4 Å for seven days, an insignificant amount ($x \leq 0.3$) of crystal water remained. To obtain anhydrous complexes ($x = 0$), keeping for a longer time (more than a week) over the molecular sieves was required. The photoluminescence spectrum of the $\text{CeCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ complex in toluene (Fig. 1) exhibits a diffuse maximum at 350 nm and a shoulder at 400 nm; this spectrum is similar to the photoluminescence spectrum of an aqueous CeCl_3 solution ($\lambda_{\text{max}} = 350.8$ nm and a shoulder at 365 nm [17]). The photoluminescence spectrum of the $\text{TbCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ complex in toluene (Fig. 2), which contains maximums at 490, 496, 547, 552, 584, and 596 nm, also differs only slightly from the photoluminescence spectrum of $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ ($\lambda_{\text{max}} = 488, 493, 545, 586, \text{ and } 591$ nm), and it is consistent with published data [6]. The value of τ for Tb^{3+*} in $\text{TbCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$

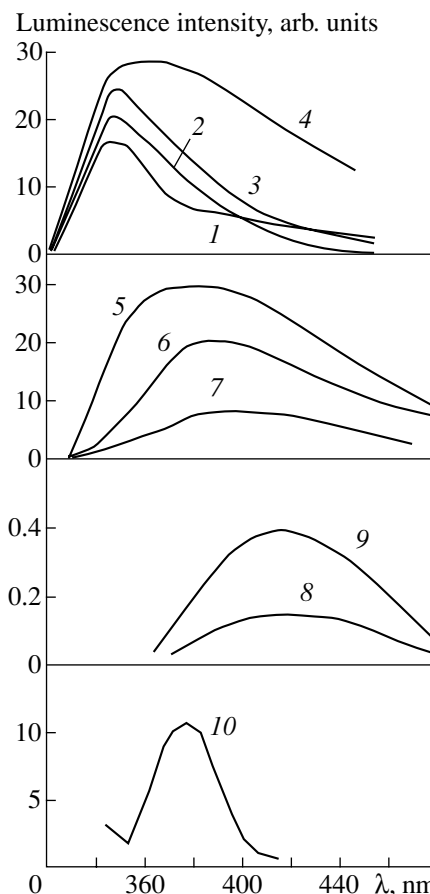


Fig. 1. Effect of iso- Bu_3Al on the photoluminescence spectra of solutions of the $\text{CeCl}_3 \cdot 3\text{TBP}$ complex in toluene: (1) in the absence of iso- Bu_3Al and in the presence of iso- Bu_3Al at Al/Ln ratios of (2) 1 : 1, (3) 2 : 1, (4) 3 : 1, (5) 4 : 1, (6) 5 : 1, (7) 6 : 1, and (8–10) > 6 ; (10) after bubbling O_2 . $[\text{CeCl}_3 \cdot 3\text{TBP}] = 5 \times 10^{-2}$ M; $T = (1\text{--}8, 10)$ 300 or (9) 77 K; $\lambda_{\text{excitation}} = 310$ nm.

complexes depends on the residual crystal water content and is equal to 2800 or 2500 μs at $x = 0$ or 0.3, respectively.

Effects of iso- Bu_3Al and Piperylene on the Luminescence Parameters of the Homogeneous Solutions of $\text{LnCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ Complexes

The addition of iso- Bu_3Al to the toluene solutions of $\text{LnCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ (300 K) resulted in complicated changes in Ln luminescence parameters. Thus, at $x = 0.3$ and an iso- $\text{Bu}_3\text{Al/Ln}$ (henceforth, Al/Ln) ratio of ≤ 0.3 (the amount of iso- Bu_3Al was equal to the crystal water content), an insignificant decrease (by 7%) in the intensity of Ce^{3+*} luminescence or an increase (by 5%) in the intensity of Tb^{3+*} luminescence was observed. The positions of maximums in the photoluminescence spectra of solutions remained the same as in the case of $\text{LnCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ solutions. Changes in the intensity of luminescence were not observed in anhydrous

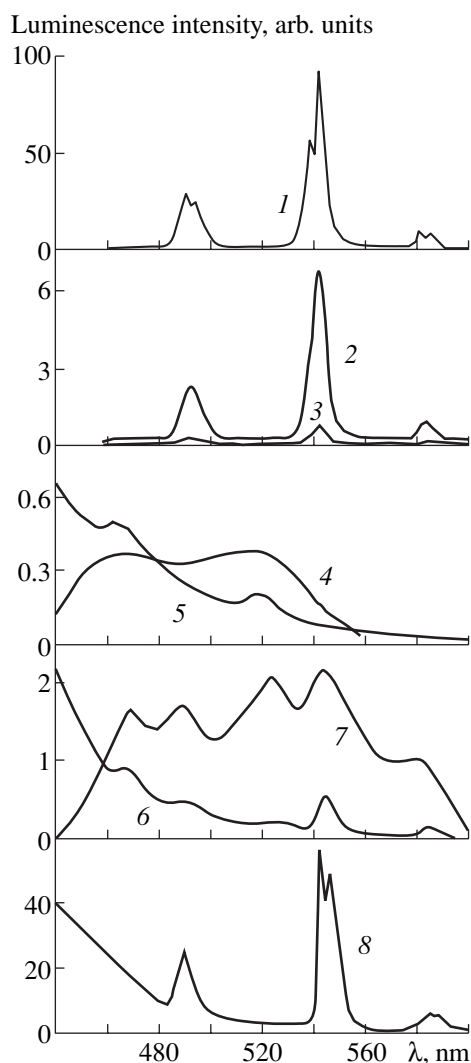


Fig. 2. Effect of $\text{iso-Bu}_3\text{Al}$ on the photoluminescence spectra of solutions of the $\text{TbCl}_3 \cdot 3\text{TBP}$ complex in toluene: (1) in the absence of $\text{iso-Bu}_3\text{Al}$ and (2–8) in the presence of $\text{iso-Bu}_3\text{Al}$ at Al/Ln ratios of (2) 2 : 1, (3) 3 : 1, and (4–8) > 5; (4, 7) in the presence of piperylene (piperylene/Tb = 5); (8) after bubbling O_2 . $[\text{TbCl}_3 \cdot 3\text{TBP}] = 0.1 \text{ M}$; $T = (4, 5) 300$ or (6, 7) 77 K; $\lambda_{\text{excitation}} = 313 \text{ nm}$.

complexes. The value of τ for Tb^{3+*} in $\text{TbCl}_3 \cdot 3\text{TBP}$ ($\tau = 2800 \mu\text{s}$) remained unchanged, whereas the corresponding value for $\text{TbCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ increased from 2500 to 2800 μs (Fig. 3).

The luminescence intensity of Ce^{3+*} (Fig. 1) or Tb^{3+*} (not shown in Fig. 1) increased with an increasing Al/Ln ratio up to 2. In this case, the positions of maximums in the photoluminescence spectra of the solutions remained unchanged; the luminescence shoulder of Ce^{3+*} at 400 nm disappeared (Fig. 1), and the value of τ for Tb^{3+*} insignificantly increased up to 2900 μs (Fig. 3).

At Al/Ln ratios of 2–3, the intensity of Ce^{3+*} luminescence increased with a simultaneous shift of a maximum from 350 to 380 nm (Fig. 1). In contrast, the

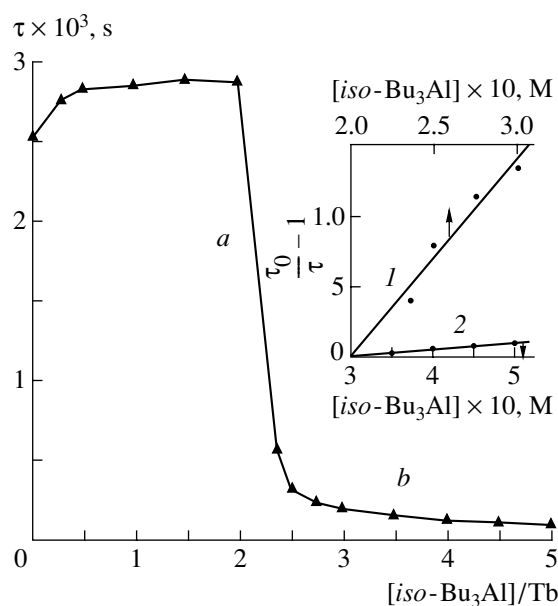


Fig. 3. Dependence of τ for Tb^{3+*} in a solution of the $\text{TbCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ complex in toluene on the concentration of $\text{iso-Bu}_3\text{Al}$. Insert: (1, 2) Stern–Volmer linear anamorphoses of portions *a* and *b*, respectively. $[\text{TbCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x] = 0.1 \text{ M}$; $T = 300 \text{ K}$; $\lambda_{\text{excitation}} = 337.1 \text{ nm}$.

intensity of Tb^{3+*} luminescence decreased (Fig. 2) and the photoluminescence spectrum of the solution became less structured and contained only three maximums at 490, 545, and 580 nm (Fig. 2) in place of five maximums at 490, 496, 547, 552, 584, and 596 nm, which were detected for $\text{TbCl}_3 \cdot 3\text{TBP}$. The value of τ for Tb^{3+*} also decreased (by more than one order of magnitude) and became equal to 200 μs (Fig. 3). The quenching of Tb^{3+*} with the aluminum alkyl (Fig. 3, portion *a*) obeys the Stern–Volmer relationship

$$\frac{\tau_0}{\tau - 1} = k_b \tau_0 [\text{iso-Bu}_3\text{Al}], \quad (1)$$

where τ_0 and τ are the lifetimes of Tb^{3+*} in the absence and in the presence of $\text{iso-Bu}_3\text{Al}$, respectively, and k_b is the bimolecular rate constant of quenching. The value of k_b was determined from the slope of the Stern–Volmer function (Fig. 3) to be equal to $(4.87 \pm 0.44) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (293 K).

As the concentration of $\text{iso-Bu}_3\text{Al}$ in solution was increased, a further shift of the luminescence maximum of Ce^{3+*} to the long-wavelength region up to 400 nm accompanied by a decrease in the intensity was observed (Fig. 1) over the range Al/Ln = 3–5. The intensity of Tb^{3+*} luminescence ($\lambda_{\text{max}} = 490, 545, \text{ and } 580 \text{ nm}$) also decreased (Fig. 2), whereas the value of τ for Tb^{3+*} decreased to 20 μs (Fig. 3). The quenching of Tb^{3+*} over this range of Al/Ln ratios also followed the Stern–Volmer relationship (Fig. 3) with $k_b = (24.90 \pm 0.71) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ (293 K). Note that at Al/Ln = 3 (initial portion of region *b* in Fig. 3), the $\text{TbCl}_3 \cdot 2\text{TBP}$

complex, which is characterized by $\tau_0 = 200 \mu\text{s}$, was the initial Tb species.

It is well known [18] that, in the preparation of lanthanide catalysts, a small amount of piperylene was initially added to an $\text{LnCl}_3 \cdot 3\text{TBP}$ complex solution ($\text{Ln}/\text{piperylene} = 1/5$); next, an aluminum alkyl was added. Therefore, it was of interest to study initially the effect of piperylene and then the combined effect of piperylene and $\text{iso-Bu}_3\text{Al}$ on the luminescence parameters of $\text{LnCl}_3 \cdot 3\text{TBP}$. Because piperylene and $\text{CeCl}_3 \cdot 3\text{TBP}$ luminesce in the same region of the UV spectrum, these experiments were performed with the complex of Tb. On the addition of piperylene to $\text{TbCl}_3 \cdot 3\text{TBP}$ in toluene, the intensity of Tb^{3+*} luminescence and the value of τ decreased. The constant k_b was determined from the slope of the Stern–Volmer straight line (Fig. 4) to be equal to $(20.13 \pm 0.14) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ($T = 293 \text{ K}$). At a ratio of piperylene/Tb = 5, τ for Tb^{3+*} was equal to $100 \mu\text{s}$. The addition of $\text{iso-Bu}_3\text{Al}$ to a solution containing $\text{TbCl}_3 \cdot 3\text{TBP}$ and piperylene (piperylene/Tb = 5) resulted in a further decrease in τ (Fig. 4); in this case, $k_b = (10.65 \pm 0.19) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ($T = 293 \text{ K}$). It is interesting to note that in this mixture the quenching of terbium by trialkylaluminum began immediately after the addition of $\text{iso-Bu}_3\text{Al}$, that is, even at the ratio $\text{Tb}/\text{iso-Bu}_3\text{Al} = 1 : 0.025$.

*Effects of iso-Bu₃Al and Piperylene
on the Luminescence Parameters of Precipitates
Formed by Reactions
in the LnCl₃ · 3TBP–iso-Bu₃Al System*

As well as Svetashev and Tsvirko [17], we observed the formation of precipitates on the addition of $\text{iso-Bu}_3\text{Al}$ to $\text{LnCl}_3 \cdot 3\text{TBP}$ solutions in toluene at a ratio of $\text{Al}/\text{Ln} > 5$. These precipitates [7, 8, 19] are diene polymerization catalysts (henceforth, they are referred to as catalysts). The luminescence intensity of the catalysts is lower than that of $\text{LnCl}_3 \cdot 3\text{TBP}$ complex solutions (Figs. 1, 2), and their photoluminescence spectra (300 K) contain diffuse maximums at $420 \pm 10 \text{ nm}$ for Ce^{3+*} (Fig. 1) and at 470 ± 1 and $520 \pm 5 \text{ nm}$ for Tb^{3+*} (Fig. 2). The value of τ for Tb^{3+*} in the catalyst is $\leq 10 \mu\text{s}$ (300 K). After freezing these precipitates (77 K), the luminescence intensity of both Ln increased. In this case, the positions of luminescence maximums for Ce^{3+*} remained unchanged (Fig. 1), whereas new maximums at 490, 545, and 580 nm appeared in addition to maximums at 470 and 520 nm for Tb^{3+*} (Fig. 2).

To demonstrate the formation of Ln–C bonds in the catalysts, we studied the action of oxygen on them. After bubbling O_2 through a suspension of the terbium catalyst in toluene (300 K), maximums at 470 and 520 nm disappeared from the photoluminescence spectrum (300, 77 K), whereas more structured maximums at 490, 545, 547, 585, and 590 nm were observed (Fig. 2). For the cerium catalyst, a maximum at 380 nm appeared in place of that at 420 nm (Fig. 1).

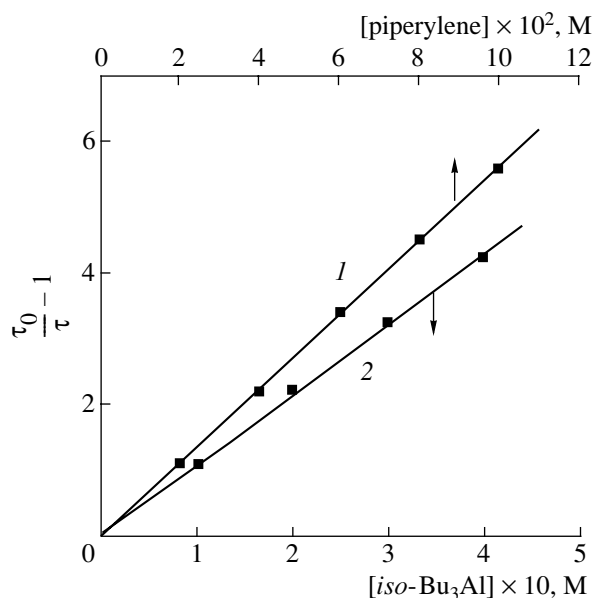
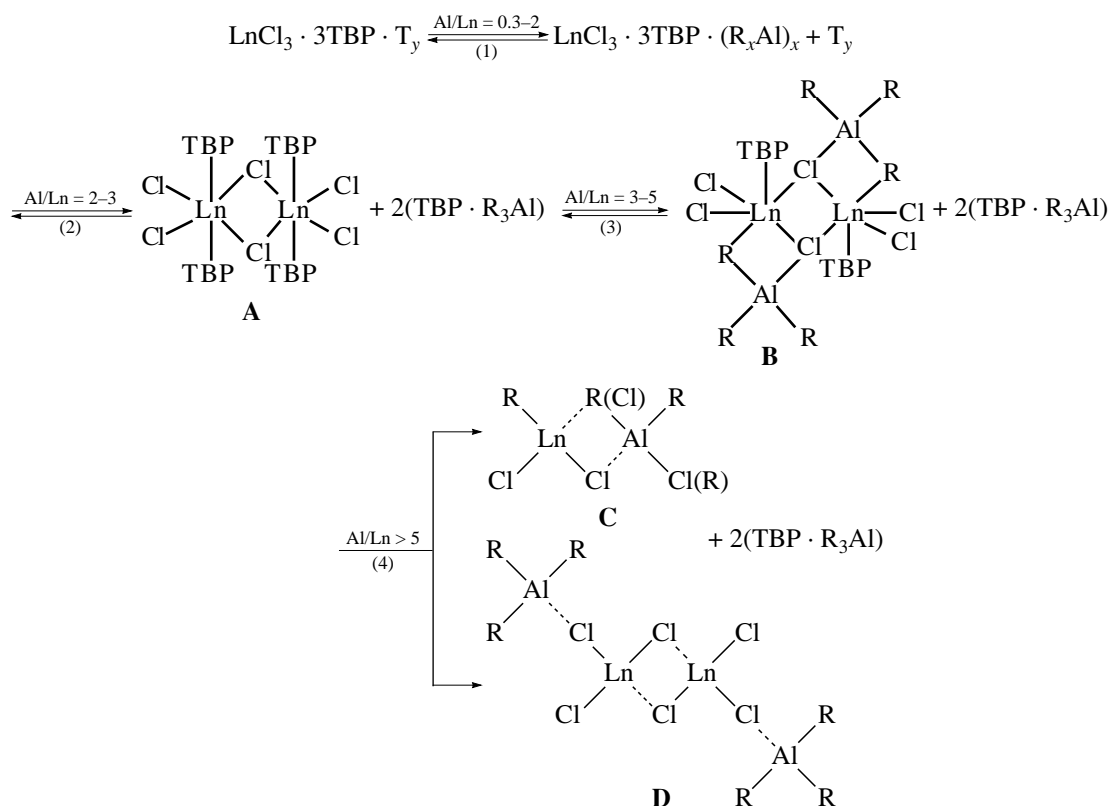


Fig. 4. Stern–Volmer linear anamorphoses of the quenching curves of the $\text{TbCl}_3 \cdot 3\text{TBP}$ complex: (1) quenching with piperylene and (2) quenching with $\text{iso-Bu}_3\text{Al}$ in the presence of piperylene at the ratio piperylene/Tb = 5. $[\text{TbCl}_3 \cdot 3\text{TBP}] = 0.1 \text{ M}$; $T = 300 \text{ K}$.

DISCUSSION

A comparison of the photoluminescence spectra of toluene solutions of $\text{CeCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ and an aqueous solution of CeCl_3 demonstrated that the photoluminescence of these complexes was due to transitions from the lower level 2D to the sublevels $^2F_{7/2}$ and $^2F_{5/2}$ [17, 20]. The photoluminescence spectrum of the $\text{TbCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ complex in toluene is different from the known photoluminescence spectrum [6, 20] of the crystalline hydrate $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ in fine structure. Nevertheless, the positions of the most intense maximums suggest that the photoluminescence of $\text{TbCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ and $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ resulted from the same f - f transitions characteristic of Tb^{3+*} ($^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, and $^5D_4 \rightarrow ^7F_4$ [20]). The difference in the values of τ for Tb^{3+*} in $\text{TbCl}_3 \cdot 3\text{TBP}$ and $\text{TbCl}_3 \cdot \text{H}_2\text{O}_x$ ($x = 0.3$) is indicative of the occurrence of two emitting Tb^{3+*} centers; one of these centers is associated with only the organic ligand TBP, whereas the other is associated with both TBP and the molecules of residual crystal water, which acts as a quencher. The $\text{LnCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ complexes occur in solution in the solvated form $\text{LnCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x \cdot \text{T}_y$ (T is toluene); this was supported by the occurrence of a shoulder at 400 nm in the photoluminescence spectrum of a $\text{CeCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ solution in toluene. The photoluminescence spectrum of a TBP solution of this complex exhibited no shoulder. A decrease in the luminescence intensity of Ce^{3+} for $\text{CeCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ and an increase in the luminescence intensity of Tb^{3+} for $\text{TbCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ over the range $\text{Al}/\text{Ln} = 0\text{--}0.3$ resulted from the removal of residual crystal water from



Scheme. Bridging structure **A** is a primary building block; on its basis, two solid-phase structures **C** and **D** are formed as a result of precipitation through the step of formation of intermediate structure **B** (which exists under conditions when a homogeneous solution is retained). Catalytically active structure **C** contains Ln–R–Al units, and it is characterized by anomalous lanthanide photoluminescence, the spectrum of which contains maximums at 420 ± 10 nm for Ce^{3+*} or at 470 ± 1 and 520 ± 5 nm for Tb^{3+*} . The above maximums of anomalous photoluminescence disappeared upon the contact of the precipitate with air. Catalytically inactive structure **D** is characterized by the occurrence of classical photoluminescence, the spectrum of which, in the case of terbium, contains maximums at 490, 545, and 580 nm, which are inert with respect to oxygen.

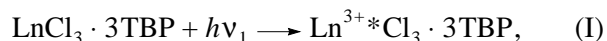
these complexes as a result of the interaction with iso- Bu_3Al [6] and from different effects of water on the yield of photoluminescence of these complexes. Indeed, in an aqueous solution of $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$, cerium exhibited a maximum yield of photoluminescence equal to unity [17]. Therefore, the addition of iso- Bu_3Al , which dehydrates [6] $\text{CeCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$, resulted in a decrease in the intensity of Ce^{3+*} luminescence. At the same time, water is a quencher of Tb^{3+*} because, on the one hand, the luminescence intensity of Tb^{3+} increased as a result of $\text{TbCl}_3 \cdot 3\text{TBP} \cdot (\text{H}_2\text{O})_x$ dehydration by iso- Bu_3Al additives and, on the other hand, this intensity decreased on the addition of water to a solution of $\text{TbCl}_3 \cdot 3\text{TBP}$ in toluene. After the complete removal of residual crystal water by iso- Bu_3Al additives, only a single form of terbium, $\text{TbCl}_3 \cdot 3\text{TBP}$, which is characterized by one value of $\tau = 2800$ μs , occurred in the solution.

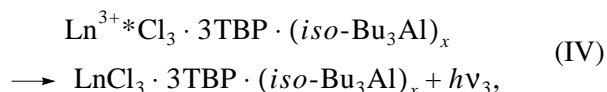
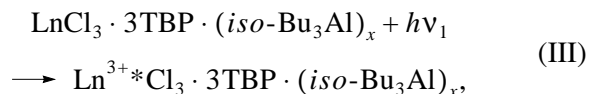
The subsequent changes in the test system during the interaction of $\text{LnCl}_3 \cdot 3\text{TBP}$ with iso- Bu_3Al can be described by the scheme given below. This scheme was drawn based on elemental analysis data published by Shamaeva *et al.* [19], who found that all the three TBP

molecules were removed from the coordination sphere of Ln.

We believe that an increase in the luminescence intensity of $\text{LnCl}_3 \cdot 3\text{TBP}$ solutions and in the value of τ for Tb^{3+*} (Fig. 3), as well as the disappearance of a shoulder from the photoluminescence spectrum of the $\text{CeCl}_3 \cdot 3\text{TBP}$ complex over the range $\text{Al/Ln} = 0.3-2$, resulted from the formation of more complicated complexes of $\text{LnCl}_3 \cdot 3\text{TBP} \cdot \text{T}_y$ with iso- Bu_3Al molecules by reaction (1) (see the scheme). As a result, three TBP molecules remained in the coordination sphere of Ln; however, toluene molecules were replaced by iso- Bu_3Al . Previously, the ability of iso- Bu_3Al to displace solvent molecules from the solvated forms of La complexes was demonstrated using the reaction with $\text{Ph}_3\text{CLnCl}_2(\text{THF})_x$ (THF is tetrahydrofuran) as an example [21].

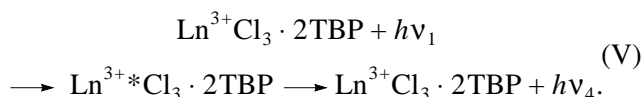
In the detection of photoluminescence over this range of Al/Ln ratios, the excitation and emission of Ln can be described by the following processes:





where $h\nu_i$ are the quanta of absorbed and emitted light.

We related the increase in the luminescence intensity and the shift of the luminescence maximum of Ce^{3+} , as well as the change in the fine structure and positions of Tb^{3+} luminescence maximums, which was accompanied by a decrease in the luminescence intensity and the value of τ for Tb^{3+} , observed within the range $\text{Al/Ln} = 2-3$ to the displacement of one TBP molecule from $\text{LnCl}_3 \cdot 3\text{TBP} \cdot (\text{iso-Bu}_3\text{Al})_x$. As a result of this, two new complexes, $\text{LnCl}_3 \cdot 2\text{TBP}$ and $\text{TBP} \cdot (\text{iso-Bu}_3\text{Al})_x$, were formed by reaction (2) (see the scheme). The formation of $\text{LnCl}_3 \cdot 2\text{TBP}$ under the specified conditions was evidenced by an agreement of the value of τ for Tb^{3+} (200 μs) at $\text{Al/Ln} = 3$ with the value of τ for Tb^{3+} measured in $\text{TbCl}_3 \cdot 2\text{TBP}$, which was independently prepared according to the published procedure [14]. We believe that the complexes $\text{LnCl}_3 \cdot 3\text{TBP} \cdot (\text{iso-Bu}_3\text{Al})_x$ and $\text{LnCl}_3 \cdot 2\text{TBP}$ (which are likely solvated by toluene) are the emitting centers of photoluminescence observed in the range $\text{Al/Tb} = 2-3$. In this case, the decay of Tb^{3+} luminescence intensity in accordance with an exponential law indicates that the time of rearrangement between equilibrium emitting Tb species is much shorter than τ . According to Ermolaev and Sveshnikova [1], the value of τ is the sum of τ for various rapidly changing complex lanthanide species. The excitation and emission of Ln can be described by processes (III)–(V).

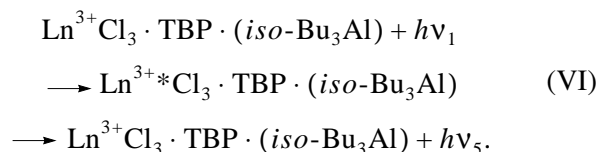


We related the difference in the direction of changes in the luminescence properties of Tb (a decrease in the luminescence intensity and τ of Tb, Fig. 2) and Ce (an increase in the luminescence intensity, Fig. 1) due to the removal of a TBP molecule from the coordination sphere of Ln to the detected effect of CeCl_3 quenching (in an aqueous solution) by TBP molecules. This is consistent with published data [22] on the high efficiency of Ce^{3+} quenching by other electron-donor ligands (dimethyl sulfoxide), whereas, on the contrary, the luminescence of Tb was enhanced in the presence of these ligands. It is well known [14] that $\text{LnCl}_3 \cdot 2\text{TBP}$ complexes in solution occur as structures **A** (scheme), in which Ln atoms are bound to each other through chlorine bridges. Because of, on the one hand, the coordination saturation of Ln in structures **A** and, on the other hand, the binding of $\text{iso-Bu}_3\text{Al}$ to form complexes

with TBP, $\text{LnCl}_3 \cdot 2\text{TBP}$ did not form complexes with $\text{iso-Bu}_3\text{Al}$, as distinct from $\text{LnCl}_3 \cdot 3\text{TBP}$.

We believe that structures **A** are primary building blocks, based on which well-known [8–10] catalytically active (**C**) and inactive (**D**) structures are formed. Thus, bridging structures begin to form before the formation of Ln–C bonds at low Al/Ln ratios, when catalytically active precipitates are not yet formed. It is likely that this preformation of bridging structures facilitates the subsequent formation of catalytically active structures that include Ln–alkyl–Al units. The molecules of TBP displaced by $\text{iso-Bu}_3\text{Al}$ from the coordination sphere of Ln form the toluene-soluble $\text{TBP} \cdot (\text{iso-Bu}_3\text{Al})_x$ complex of the 1 : 1 stoichiometry. Shamaeva *et al.* [19] detected this complex by IR spectra and calorimetrically by measuring the heat of formation of this complex in the $\text{TBP} \cdot (\text{iso-Bu}_3\text{Al})_x$ model system in toluene. A necessary condition for the identification of $\text{TBP} \cdot (\text{iso-Bu}_3\text{Al})_x$ is the presence of an excess of the aluminum alkyl in solution ($\text{iso-Bu}_3\text{Al}/\text{TBP} = 3$) [19]. We obtained new evidence for the occurrence of the $\text{TBP} \cdot (\text{iso-Bu}_3\text{Al})_x$ complex by comparing the ^{13}C NMR spectra (the spectra were characterized in Experimental) of free TBP and TBP bound in the above complex, in which the α -carbon atoms of butyl groups in TBP are significantly deshielded ($\Delta = -3.2$ ppm). The signals of the other carbon atoms did not undergo reliable changes.

We relate the decrease in the luminescence intensity of either Ln^{3+} and in the value of τ for Tb^{3+} observed over the wider range $\text{Al/Ln} = 3-5$ to the displacement of a second TBP molecule from $\text{LnCl}_3 \cdot 2\text{TBP}$, as a result of which $\text{LnCl}_3 \cdot \text{TBP}$ is formed. In $\text{LnCl}_3 \cdot \text{TBP}$, Ln is coordinatively unsaturated to a considerable extent; therefore, it adds $\text{iso-Bu}_3\text{Al}$ molecules. It is likely that the transfer of TBP molecules from the coordination sphere of Ln and the coordination of $\text{iso-Bu}_3\text{Al}$ to Ln occur as a single act of substitution in accordance with (3) (scheme). The shift of the maximum of Ce^{3+} luminescence from 380 to 400 nm (Fig. 1) suggests that two cerium complex species, which are in an equilibrium, occur in solution. We explain the lower luminescence intensity of either of the Ln^{3+} ions and τ for Tb^{3+} in $\text{LnCl}_3 \cdot \text{TBP} \cdot (\text{iso-Bu}_3\text{Al})_x$, as compared with $\text{LnCl}_3 \cdot 2\text{TBP}$, by two reasons. The first is the quenching of Ln^{3+} by the aluminum alkyl, which is a constituent of this complex. The second is the well-known [20] effect of a decrease in the intensity of lanthanide photoluminescence as a result of a decrease in the number of organic ligands in the coordination sphere of Ln, which is a constituent of a catalytically inactive structure (**D**, scheme). Excitation and emission over this range of Ln/Al ratios are represented by Eqs. (V) and (VI).



We relate the decrease in τ of Tb^{3+*} as a result of piperylene addition to a solution of $\text{TbCl}_3 \cdot 3\text{TBP}$ in toluene to the well-known [23] effect of Tb^{3+} deactivation by unsaturated organic molecules. We believe that Tb^{3+} quenching is a consequence of energy transfer to piperylene molecules, which displaced toluene and entered into the coordination sphere of Tb. We failed to find the energy of the triplet level (E_T) of the acceptor piperylene in the literature; however, we believe that it is close to the E_T of butadiene, which is equal to 2.58 eV [24]. This value is even somewhat lower than $E_T = 2.63$ eV of naphthalene [24], for which energy transfer from Tb^{3+} was unambiguously established [23]. We believe that piperylene enters the coordination sphere of Tb more easily than naphthalene for steric reasons. This was supported by a higher value of $k_b = 2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for Tb^{3+*} quenching by piperylene, as compared with naphthalene ($k_b = 7 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$). The value of k_b determined was close to $2.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, which was obtained by Rafikov *et al.* [4] for the photoluminescence quenching of the $\text{TbCl}_3 \cdot 3\text{DASO}$ (DASO is diamyl sulfoxide) complex by isoprene.

It is likely that a decrease in τ from 100 to 10 μs on the addition of iso- Bu_3Al to a toluene solution of a $\text{TbCl}_3 \cdot 3\text{TBP}$ –piperylene mixture (Fig. 4) is due to the incorporation of iso- Bu_3Al into the coordination sphere of Tb and the displacement of TBP molecules from it. If piperylene molecules were displaced, τ of Tb^{3+*} would increase because, as demonstrated above, the aluminum alkyl does not quench Tb^{3+*} in the range of iso- $\text{Bu}_3\text{Al}/\text{Tb} < 0\text{--}2$. The fact that terbium quenching by the aluminum alkyl in a $\text{TbCl}_3 \cdot 3\text{TBP}$ –piperylene–(iso- Bu_3Al) mixture begins immediately upon the addition of small amounts of iso- Bu_3Al (i.e., even at the ratio iso- $\text{Bu}_3\text{Al}/\text{Tb} = 0.025$) with a higher value of $k_b = 1.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, as compared with the $\text{TbCl}_3 \cdot 3\text{TBP}$ –(iso- Bu_3Al) system (iso- $\text{Bu}_3\text{Al}/\text{Tb} = 2\text{--}3$, $k_b = 4.87 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and iso- $\text{Bu}_3\text{Al}/\text{Tb} = 3\text{--}5$, $k_b = 24.90 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$), clearly indicates that the displacement of TBP by the aluminum alkyl occurs more easily in the presence of piperylene. This is most likely due to the fact that the coordination of piperylene to Ln weakens the bonds of TBP molecules with Ln. We found that the efficiency of Tb^{3+} quenching by the aluminum alkyl was different in the absence and in the presence of piperylene. This fact allowed us to understand and explain analogously the reason for the greater efficiency of catalysts for diene polymerization [18] prepared by the preaddition of small diene amounts (piperylene/Ln ≤ 5) together with R_3Al .

The even lower intensity of Ln^{3+*} luminescence (Figs. 1, 2) and the very short τ of Tb^{3+*} (Fig. 3) in precipitates formed by the addition of iso- Bu_3Al to $\text{LnCl}_3 \cdot 3\text{TBP}$ solutions at a ratio of $\text{Ln}/\text{Al} > 5$ are the consequence of the displacement of all the TBP molecules from the coordination sphere of Ln by iso- Bu_3Al . The diffuse luminescence maximums at 470 and 520 nm in the photoluminescence spectrum of a precipitate (300 K) obtained from $\text{TbCl}_3 \cdot 3\text{TBP}$ are not character-

istic of Tb^{3+*} luminescence, which is usually detected as much more narrower maximums in various Tb compounds [20]. However, photoluminescence maximums at 470 and 520 nm were observed in neither individual components of the test system (iso- Bu_3Al , TBP, toluene, and piperylene) nor possible variations of their mixtures in the absence of Tb from the system (300, 77 K). They were also not detected in the photoluminescence spectrum of a toluene solution of an $\text{LnCl}_3 \cdot 3\text{TBP}$ –piperylene mixture (300, 77 K). These results allowed us to unambiguously attribute the luminescence maximums observed at 470 and 520 nm to Tb^{3+} emission. Their unusual positions can be explained by the occurrence of a σ bond between the Tb^{3+} ion and a carbon atom in the Tb –(iso- Bu_3Al)–Al unit. We believe that the occurrence of a strong reductant [25] (an aluminum alkyl fragment) adjacent to the Tb^{3+} ion has a significant effect on the electronic structure of terbium. It is likely that this effect decreased the effective ionic charge, although the reduction of Tb^{3+} to a lower oxidation state did not take place. The oxidation state 3+ is most stable for Tb and other Ln. Nevertheless, it is well known [26] that the effective charge of an Ln central ion in halide complex compounds decreased from 3+ to 2.7–2.8. Therefore, it seems more reasonable that this effect manifests itself with an Ln ion in the neighborhood of an aluminum alkyl. We believe that the formation of Ln–C bonds results in the appearance of new 4f sublevels in the Tb^{3+*} ion; radiative transitions between these sublevels are responsible for this unusual luminescence of Tb in the catalytically active center of diene polymerization. Note that the luminescence of Ln compounds in which an ion of Ln is covalently bound to a carbon atom was not exemplified previously in the literature [20, 27].

The appearance of two groups of bands at 470 and 520 nm and at 490, 545, and 580 nm in the photoluminescence spectrum after freezing the precipitate (77 K) is indicative of the occurrence of two emitting Tb^{3+*} species, which are characterized by different coordination environments. According to Monakov *et al.* [7, 8], the concentration of Ln bound to the carbon atom (the concentration of active centers) in the precipitate is lower than 10%; that is, the major portion of Ln loaded occurs in a catalytically inactive form. We believe that luminescence maximums at 490, 545, and 580 nm in the photoluminescence spectrum of the frozen precipitate are due to the emission of Tb^{3+} , which is a constituent of the catalytically inactive form. It is most likely that this form consists of bridging groups containing Tb–Cl–Tb units, in which Tb is not bound to the carbon atom, that is, structures **D** (scheme). The occurrence of a catalytically active Ln–C bond in catalysts can be clearly tested by the disappearance of the luminescence maximums of Tb^{3+*} at 470 and 520 nm or Ce^{3+*} at 420 nm, which results from oxygen insertion into the Ln–C bond in the course of bubbling O_2 through a catalyst suspension in toluene. Chemiluminescence, which was detected previously [5] in the oxidation of a

terbium catalyst with O₂, additionally provides strong evidence of the occurrence of Ln–C bonds in these catalysts. In this case, the light sum of chemiluminescence and the yield of a polymer prepared with the use of this catalyst were directly proportional to the Tb content of the catalyst.

According to the scheme proposed, structure **B**, which was formed under conditions when a homogeneous solution was retained, was subsequently converted into catalytically active (**C**) and inactive (**D**) structures in the course of precipitate formation. In the catalytically inactive structure, chlorine atoms bound to a lanthanide should also be bound to Al atoms in order to obey the known [19] ratio Ln/Al = 1. Structure **C** resulted from the cleavage of donor–acceptor Ln–C bonds in structure **B**. Species **C** reflects the set of various structures proposed by Monakov *et al.* [7] based on quantum-chemical calculations.

In summary, note that the results of this study allowed us to conclude that a lanthanide luminescence probe can be efficiently used for examining the mechanism of formation of lanthanide Ziegler–Natta catalysts and the nature of catalytically active centers for diene polymerization. We believe that the measurement of lanthanide luminescence parameters directly in the course of a polymerization reaction can also provide valuable information on the mechanism of this reaction.

REFERENCES

1. Ermolaev, V.L. and Sveshnikova, E.B., *Usp. Khim.*, 1994, vol. 63, no. 11, p. 962.
2. Mirochnik, A.G., Gukhman, E.V., Karasev, V.E., and Zhikhareva, P.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, no. 6, p. 1030.
3. Zolin, V.F. and Koreneva, L.G., *Redkozemel'nyi zond v khimii i biologii* (The Rare-Earth Metal Probe in Chemistry and Biology), Moscow: Nauka, 1980, p. 350.
4. Rafikov, S.R., Tolstikov, G.A., Monakov, Yu.B., Vakhruшева, N.A., Afonichev, D.D., and Kazakov, V.P., *Dokl. Akad. Nauk SSSR*, 1980, vol. 251, no. 4, p. 919.
5. Kuleshov, S.P., Bulgakov, R.G., Sharipov, G.L., Bikbaeva, G.G., Safonova, L.A., Gavrilova, A.A., and Sharapova, L.I., *Izv. Akad. Nauk, Ser. Khim.*, 1996, no. 8, p. 1907.
6. Bulgakov, R.G., Kuleshov, S.P., Zuzlov, A.N., Mullagaleev, I.R., Khalilov, L.M., and Dzhemilev, U.M., *J. Organomet. Chem.*, 2001, vol. 636, p. 56.
7. Monakov, Yu.B., Sabirov, Z.M., and Marina, N.G., *Vysokomol. Soedin.*, A, 1994, vol. 36, no. 10, p. 1680.
8. Monakov, Yu.B., Sabirov, Z.M., and Marina, N.G., *Vysokomol. Soedin.*, A, 1996, vol. 38, no. 3, p. 407.
9. Bochkarev, M.N., Kalinina, G.S., Zakharov, L.N., and Khoroshev, S.Ya., *Organicheskie proizvodnye redkozemel'nykh elementov* (Organic Derivatives of Rare-Earth Metals), Moscow: Nauka, 1989, p. 232.
10. Monakov, Yu.B., Sabirov, Z.M., Urazbaev, V.N., and Efimov, V.P., *Kinet. Katal.*, 2001, vol. 42, no. 3, p. 346.
11. Korneev, N.N., *Khimiya i tekhnologiya alyuminiorganicheskikh soedinenii* (Chemistry and Technology of Organoaluminum Compounds), Moscow: Khimiya, 1979, p. 246.
12. Murinov, Yu.I., Monakov, Yu.B., Shamaeva, Z.G., Marina, N.G., Kolosnitsyn, V.S., Nikitin, Yu.E., and Rafikov, S.R., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, no. 12, p. 2790.
13. *Handbuch der Präparativen Anorganischen Chemie*, Brauer, G., d., Stuttgart: Ferdinand Enke, 1975.
14. Korovin, S.S., Galaktionova, O.V., Lebedeva, E.N., and Voronskaya, G.N., *Zh. Neorg. Khim.*, 1975, vol. 20, no. 4, p. 908.
15. Kovrizhko, L.F., Bryantseva, Yu.V., Raevskaya, V.I., and Agarkova, T.P., *Tr. laboratorii khimii vysokomolekulyarnykh soedinenii* (Collected Works of the Laboratory of High-Molecular Compounds), Voronezh: Voronezh Univ., 1964, no. 3, p. 78.
16. Charlot, G., *Les methodes de la chimie analytique*, Paris: Masson, 1961.
17. Svetashev, A.G. and Tsvirko, M.P., *Opt. Spektrosk.*, 1984, vol. 56, no. 5, p. 842.
18. Gadeleva, Kh.K., *Cand. Sci. (Chem.) Dissertation*, Ufa: Inst. of Organic Chem., 1985.
19. Shamaeva, Z.G., Marina, N.G., Monakov, Yu.B., and Rafikov, S.R., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, no. 4, p. 846.
20. Poluektov, N.S., Kononenko, L.I., Efryushina, N.P., and Bel'tyukova, S.V., *Spektrofotometricheskie i lyuminescentnye metody opredeleniya lantanidov* (Spectrophotometric and Luminescent Methods for Lanthanide Determination), Kiev: Naukova Dumka, 1989, p. 11.
21. Markevich, I.N., Sharaev, O.K., Tinyakova, E.I., and Dolgoplosk, B.A., *Dokl. Akad. Nauk SSSR*, 1983, vol. 286, no. 4, p. 892.
22. Ostakhov, S.S., Ableeva, N.Sh., Sharipov, G.L., and Kazakov, V.P., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, no. 8, p. 1932.
23. Sveshnikova, E.B. and Naumov, S.P., *Zh. Prikl. Spektrosk.*, 1978, vol. 29, no. 3, p. 539.
24. McWeeny, R. and Sutcliffe, B.T., *Methods of Molecular Quantum Mechanics*, London: Academic, 1969, p. 96.
25. Chirkov, N.M., Matkovskii, P.E., and D'yachkovskii, F.S., *Polimerizatsiya na kompleksnykh metalloorganicheskikh katalizatorakh* (Polymerization Induced by Complex Organometallic Catalysts), Moscow: Khimiya, 1976, p. 32.
26. Yatsimirskii, K.B., Kostromina, N.A., *et al.*, *Khimiya kompleksnykh soedinenii redkozemel'nykh elementov* (Chemistry of Rare-Earth Metal Complexes), Kiev: Naukova Dumka, 1966, p. 37.
27. Brittain, H.G., *Organometallics*, 1983, no. 2, p. 1661.