Luminescent probing of the Tb—C bond in a catalyst of diene polymerization based on $TbCl_3 \cdot 3(Bu^nO)_3PO+Bu^i{}_3Al$

S. P. Kuleshov, R. G. Bulgakov,* G. L. Sharipov, G. G. Bikbaeva, L. A. Safonova, A. A. Gavrilova, and L. I. Sharapova

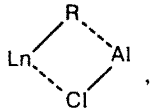
Institute of Petrochemistry and Catalysis, Academy of Sciences of Republic Bashkortostan,
141 prosp. Oktyabrya, 450071 Ufa, Russian Federation.
Fax: +7 (347 2) 31 2750

The application of chemiluminescence and photoluminescence methods is shown to be promising for studying the mechanism of diene polymerization on Ziegler—Natta catalysts based on organolanthanide and organoaluminum compounds.

Key words: catalysis, lanthanides, chemiluminescence, photoluminescence.

The main area of the application of organolanthanide derivatives is catalytic processes, in particular, stereospecific polymerization of conjugated dienes.[1] Different lanthanide compounds are catalytically active in these reactions, and the systems of the Ziegler—Natta type (LnX_3—R_3Al) are the most efficient.

It is assumed that the polymerization of dienes on these catalysts involves the insertion of a monomer into the Ln—C bond followed by the growth of the polymer chain on bridge complexes of the type



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which play a role of catalytically active centers (CAC). In these processes, R_3Al acts as a component alkylating lanthanides.[1–4] However, no direct experimental proof for this particular mechanism of catalysis has been obtained yet,[1,4] despite the application of all the known "dark" physicochemical methods, such as electron spectroscopy, NMR, ESR, *etc.*[1] Emission spectroscopy, chemiluminescence (CL), and photoluminescence (PL) have been of very limited utility to date. Meanwhile, it is mentioned in reviews[5,6] devoted to the study of CL in reactions of organometallic compounds (OMC) and, in particular, organolanthanides, that CL and PL provide valuable information on the change in the ligand surrounding, the oxidation state of a metal, and the formation of unstable intermediates in reactions of OMC of all types with oxidants of various chemical characters. We have recently shown that the application of CL and PL probes is promising for monitoring the formation and transformations of catalytic compositions of two types based on $TbCl_3 \cdot 3(Bu^nO)_3PO$ + $Bu^i{}_3Al$ [7] and Ph_3CLnCl_2 + $Bu^i{}_3Al$.[8]

The present work is devoted to the further development of the suggested approach to the study of the mechanism of catalysis on the Ziegler—Natta systems and testing the Ln—C bond as the main element of CAC based on luminescence analysis.

Experimental

Toluene and $Bu^i{}_3Al$ (TIBA) were purified by the known procedures.[9,10] Catalytic compositions were synthesized[11] by mixing toluene solutions of TIBA with $LnCl_3 \cdot TBP$, where TBP is tributyl phosphate, Ln = Tb, Nd, and Ce (hereinafter the compositions will be designated as **1**, **2**, and **3**, respectively). The ratio Ln : Al in **1**—**3** after washing off excess TIBA was 1 : 1.

CL was recorded at constant temperature (298 K) in a quartz CL-cell after the addition of aliquots of toluene solutions of TIBA or compositions **1**—**3** to toluene through which dry air or O_2 was continuously bubbled. The procedures of measurement of CL [5] and polymerization* of piperilene[11] were described previously. CL spectra were recorded on an MUM-2 monochromator, and PL spectra were recorded on MPF-4 Hitachi and on home-made spectrofluorimeters based on an MDR-23 monochromator. All the procedures (synthesis, polymerization, and preparation of solutions for oxidation) were carried out in an atmosphere of dry argon or nitrogen.

Results and Discussion

The oxidation of solutions of composition **1** with oxygen is accompanied by CL, whose intensity is $5.0 \cdot 10^7$ photon s^{-1} mL^{-1} at a maximum of the kinetic curve at [**1**] = $4 \cdot 10^{-2}$ mol L^{-1} (Fig. 1). For systems **2** and **3**, the intensity of CL under similar conditions is 75—80 % lower and close to that of the luminescence in the

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* The authors are grateful to N. V. Duvakina and Yu. B. Monakov for polymerization of several samples.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 2011—2015, August, 1996.

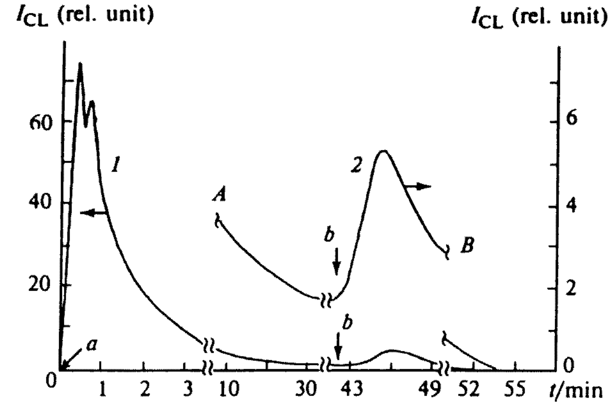


Fig. 1. Change in intensity of CL upon oxidation of a solution of **1** in toluene (10 mL) with oxygen (*1*) and upon addition of an aliquot of H_2O (0.5 mL) to the oxidizable solution (*2*). (*A—B* is the region of the curve in a larger scale). [**1**] = $4 \cdot 10^{-2}$ mol L^{-1}, T = 300 K. Arrows designate: *a*, beginning of O_2 bubbling; *b*, addition of H_2O.

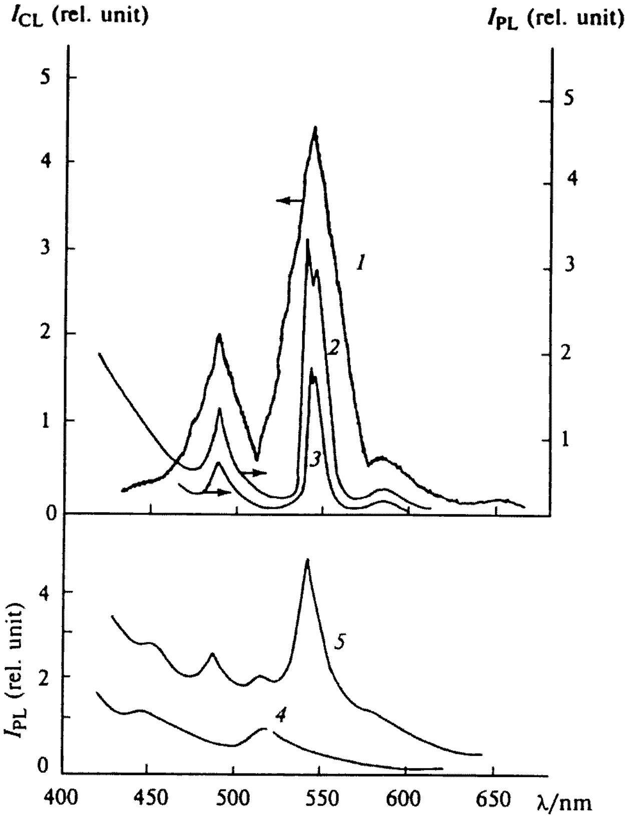


Fig. 2. Luminescence spectra: *1*, CL in oxidation of **1** with oxygen ([**1**] = $4 \cdot 10^{-2}$ mol L^{-1}, T = 300 K); *2*, PL of a solution of $TbCl_3 \cdot 3(Bu^nO)_3PO$ in toluene (300 K); *3*, PL of oxidized **1**; *4*, PL of a solution of $TbCl_3 \cdot 3(Bu^nO)_3PO$ + $Bu^i{}_3Al$ in toluene (300 K); *5*, PL of a solution of $TbCl_3 \cdot 3(Bu^nO)_3PO$ + $Bu^i{}_3Al$ in toluene (77 K). *4*, *5*: in the synthesis of **1**, the ratio Tb : Al = 1 : 20. *2—5*: λ_{exc} = 300 nm.

oxidation of TIBA. The oxidation also results in the formation of white precipitates, and the initial colored solutions (yellow for Tb and Ce and dark-brown for Nd) decolorize.

The CL spectrum in the oxidation of **1** (Fig. 2) exhibits three characteristic maxima (490, 545, and 585 nm), whose positions coincide with those of the maxima in the PL spectrum of solutions of $TbCl_3 \cdot 3TBP$ in toluene and the oxidized solution of **1**. Thus, the ions $(Tb^{3+})^*$ (transitions $^5D_4$—$^7F_6$, $^5D_4$—$^7F_5$, and $^5D_4$—$^7F_4$) are the emitter of CL in the oxidation of **1**.

Since Ce^{3+} and Nd^{3+} ions exhibit no characteristic luminescence bands in the visible region, the CL spectrum for **2** and **3** is a diffuse band at 400—600 nm. For samples of **2** and **3** prepared from TIBA triply distilled *in vacuo*, the CL spectrum transforms into a band in the range from 350 to 460 nm with a broad maximum at 420±15 nm. This spectrum is similar to the CL spectra recorded in the oxidation of TIBA and other individual alkylaluminum compounds[5,6] and is caused by the emission of aldehydes or ketones.

Since the contact of O_2 with $LnCl_3 \cdot 3TBP$ is not accompanied by CL, and excess TIBA (remaining after the syntheses of **1—3**) is washed off completely, it is the oxidation of metal—carbon bonds of compositions **1—3** that is the source of CL. This conclusion also follows from the fact that CL in the oxidation of the metal—carbon bond with O_2 is a common property of OMC.[5,6]

CL in the oxidation of **1—3** can appear due to the attack of O_2 on the metal—carbon (Al—C or Ln—C) bonds, where C is the carbon atom of the alkyl fragment of the bridged structure of CAC.

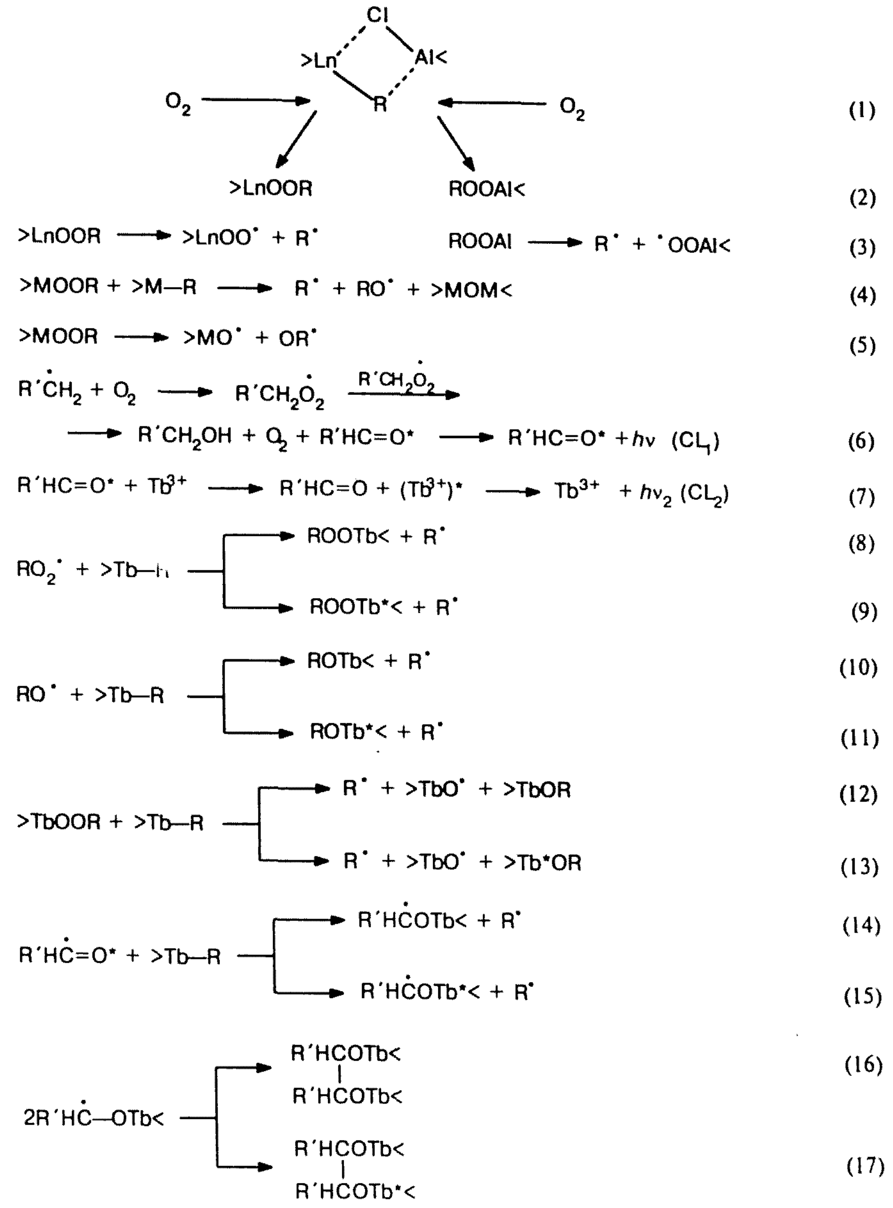
The mechanism of oxidation of complex compositions of the **1—3** type with oxygen is not documented. We found that this process has common features with the mechanism of oxidation of individual alkylaluminum compounds. In particular, intermediate organometallic peroxides (OMP) are formed. This is unambiguously evidenced from the "water test for OMP," which was developed previously in the study of autooxidation of individual OMC.[12]

In fact, the addition of an aliquot of water to the oxidizable solution of **1** at the instant of a decrease in the luminescence intensity results in a jump in the CL intensity (see Fig. 1, kinetic curve of CL from moment *b*) associated with the luminescence of the excited aldehyde, the product of the reaction of intermediate OMP with water.

Thus, the "dark" oxidation of **1—3** and the accompanying CL can be considered in the framework of the mechanism accepted for the oxidation of individual alkylaluminum compounds, in which the formation of OMP and their consumption are the most important stages of initiation and propagation of the chain process.[13,14]

Based on the data obtained in the study of the mechanism of CL in the oxidation of alkylaluminum

Scheme 1



M = Ln, Al; R = Bu^i; R' = Pr^i; R'CH$_2$ = R

compounds[6,14] and lanthanide cyclopentadienyl derivatives[5,6] and the experimental data presented above, we believe that CL in the oxidation of compositions **1**—**3** with oxygen can be caused by the two most probable emitters: the ion (Tb^{3+})* and the carbonyl fragment of aldehyde (R'HC=O*) (Scheme 1).

The CL spectra testify that R'HC=O* acts as an emitter in the oxidation of **2** and **3** (CL$_1$). No luminescence of R'HC=O* is recorded upon the oxidation of composition **1**, and the CL spectrum (see Fig. 2) contains only luminescence bands of (Tb^{3+})* (CL$_2$). However, this does not imply that R'HC=O* is not formed in the oxidation of **1**, because the absence of its luminescence can be due to the nonradiative deactivation of R'HC=O* by energy transfer to Tb^{3+} followed by the luminescence of (Tb^{3+})*. Similar energy transfer from the carbonyl fragment of ketones to lanthanide ions was observed for the first time in chemiluminescent reactions of hydrocarbon oxidation.[15] It is most reasonable to assign CL that appeared upon the attack of the Al—C bond of CAC to the emission of aldehyde R'HC=O* obtained from primary peroxy radicals by reaction (6) of Scheme 1 similar to the known[16] disproportionation of secondary radicals to form an excited ketone.

It is evident that R'HC=O* can be generated in the oxidation of all compositions **1**—**3** (reactions (1)—(6), the right branch of reactions (1)—(3) in Scheme 1). Formation of R'HC=O* by a similar pathway should also occur upon the attack of the Ln—O bonds by oxygen (reactions (1)—(6), the left branch of reactions (1)—(3) in Scheme 1). Based on the data[1] on the extremely high sensitivity of Ln—C bonds toward oxygen, we believe that the attack at this bond is preferable compared to that at the Al—C bond.

In spite of the fact that the mechanism of oxidation of alkyllanthanides with O_2 is not studied (because it is difficult to obtain these compounds in the individual state[1]), it can be assumed that this process is realized according to the mechanism typical of oxidation of many other alkylmetals of the Group III of the Periodic system[13] (see Scheme 1).

In addition to the luminescence (CL_1), excited aldehyde can transfer the energy to Ln^{3+} ions (7), among which only Tb^{3+} luminesces in the visible region and, hence, can act as a potential activator of luminescence (CL_2). However, Tb^{3+} ions that are components of the initial CAC cannot play the role of an activator, which follows from the disappearance of PL of terbium (300 K) after the addition of TIBA to $TbCl_3 \cdot 3TBP$ in the synthesis of **1** (see Fig. 2, curves *2* and *4*). The disappearance of the PL bands of terbium (see Fig. 2, curve *4*) is caused by quenching of $(Tb^{3+})^*$ by the alkylaluminum compound, which likely occurs according to the collision mechanism. This is indicated, in particular, by a considerable temperature dependence of the efficiency of quenching. In fact, when the solution is cooled to 77 K, PL of terbium is observed again (see Fig. 2, curve *5*). Thus, the oxidized forms (terbium oxide and peroxide compounds of the type >TbOR and >TbOOR) can serve as an activator. The form >TbOOR can exist only as an intermediate due to the extremely high instability of this peroxide (this is consumed mainly in reaction (4)), while >TbOR can be both an intermediate and a final product, *e.g.*, $Tb(OR)_3$. In any case, compound $Tb(OR)_3$ unambiguously possesses the ability of luminescence, which is evidenced by PL of terbium observed after the completion of the oxidation (see Fig. 2, curve *3*).

It is noteworthy that the contribution to the CL of the luminescence of terbium formed due to the energy transfer is not high. Thus, modeling the activation by the addition of a solution of $TbCl_3 \cdot 3TBP$ in toluene (V = 1 mL, $[TbCl_3 \cdot 3TBP] = 10^{-3}$ mol L^{-1}) to the oxidizable solution of **1** results in an increase in the intensity of CL by not more than 15—20 %, followed by a decrease according to the kinetic law observed in the absence of an activator.

It is of interest to consider processes (14)—(17). The suggestion on the reactions of types (14) and (16) for lanthanides is quite reasonable. It is based, on the one hand, on the results of the study[17] of reactions of alkylboron derivatives with excited acetone (generated photochemically) and, on the other hand, on a higher reactivity of the Ln—C bond than that of the B—C bond. Transformations (14) and (16) are similar to those that occurred in the case of alkylboron compounds. Thus, the Ln—C bond acts as a quencher of R'HC=O*, and a reaction similar to reaction (14) is likely the reason for the low intensity of CL_1 for compositions **2** and **3** based on Ce and Nd.

We believe that reactions similar to (14) and (16) can occur not only according to the known[17] "dark" route, but also with the formation of excited states of metals and, in particular, of terbium, according to Eqs. (15) and (17). Therefore, for the Tb-composition, the energy of R'HC=O* can transform by reaction (15) into the excitation of Tb^{3+}. In addition, $(Tb^{3+})^*$ can be formed at the next stage (17) in the recombination of R'HC$^{\cdot}$—OTb< radicals.

The process of excitation of terbium (15), unlike the known[15] physical process of energy transfer (7), can be called "chemical transfer of energy," because a chemical bond is formed between the energy donor (oxygen atom of the carbonyl group) and the acceptor (terbium ion).

Thus, the excitation of Tb^{3+} is mainly the result of chemical reactions such as (9), (11), (13), (15), and (17), and, as a consequence, the CL accompanied by the luminescence of terbium is a fine tool for probing Ln—C bonds in complex catalytic centers (for luminescing Ln).

A decrease in the concentration of the Tb—C bonds upon pretreatment of **1** with a dosed amount of O_2 or with argon saturated with H_2O decreases the luminous efficiency of CL (Σ_{CL}) emitted in subsequent oxidation with O_2 proportional to the duration of the treatment. When the luminous efficiency of CL and the concentration of the Tb—C bonds are proportional and there is a similar dependence between the yield of diene polymerization and the concentration of the same bonds, Σ_{CL} and the yield of polymerization catalyzed by **1** also should be proportional.

The results of the experiments on polymerization of piperylene in the presence of compositions **1** and **2**, which were performed in parallel with measurements of CL, are presented in Figs. 3 and 4. It is seen from Fig. 3 that for catalyst **1** the curves of the dependence of Σ_{CL} and the yield of polypiperylene (or conversion of piperylene, K) on the duration of exposure of **1** (before the addition to the reaction mixture) are parallel. When the interval from the moment of preparation of **1** to the moment of its addition to the reaction cell increases, the yield of the polymer and Σ_{CL} decrease. The observed decrease in the polymer yield for **2** does not correlate with almost unchanged Σ_{CL}. The curves of the change in Σ_{CL} in the autooxidation of **1** in toluene and the dependences of the polymer yield on the concentration of Tb^{3+} in **1** are presented in Fig. 4. It follows from the analysis of the shapes of the curves that a decrease in the concentration of **1** (and hence, of Tb^{3+} as well) results in a decrease in the yield of the polymer and a decrease in the amount of the emitted light. A similar result was obtained for the direct dilution of a solution of **1** with toluene (in a series of samples with various concentrations of Tb^{3+} and of M—C bonds) and in the autooxidation of a solution of **1**, through which O_2 was passed for 1—10 min.

Based on the suggested mechanism of CL, we explain the absence of the correlation between the yield of po-

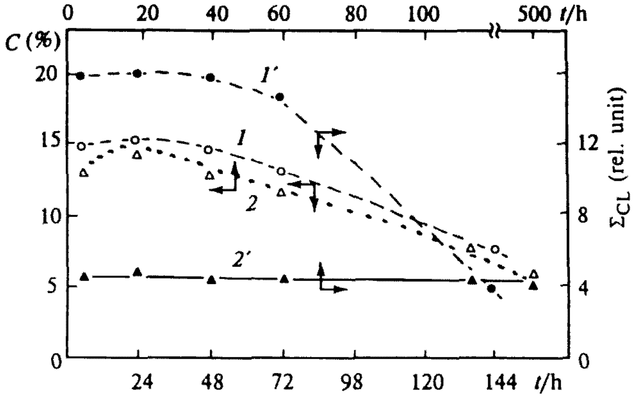


Fig. 3. Dependences of conversion of piperylene (*C*) (or yield of polypiperylene) (*1*, *2*) and luminous efficiencies of CL (*1'*, *2'*) on time of exposure of the catalyst in an inert atmosphere of the synthesis: *1* and *1'*, catalyst **1**; *2* and *2'*; catalyst **2**.

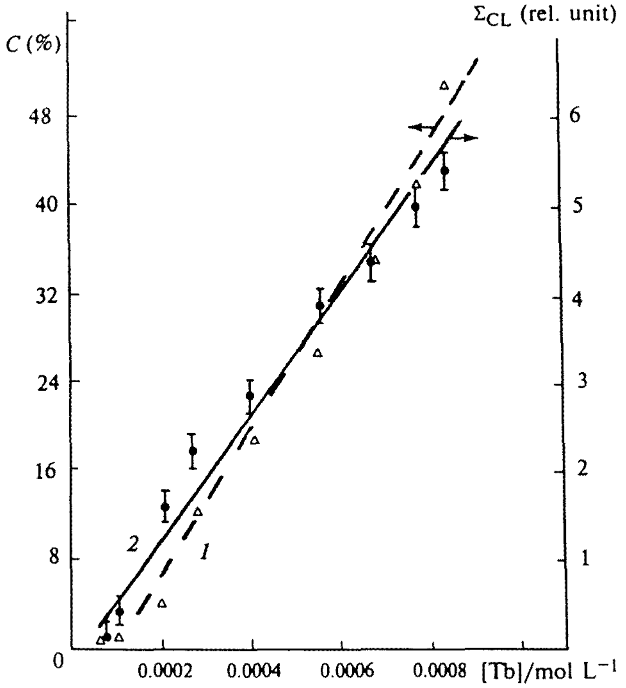


Fig. 4. Dependences of conversion of piperylene (*C*) (yield of polypiperylene) (*1*) and luminous efficiency of CL (*2*) on the concentration of Tb (or **1**).

lymerization and Σ_{CL} for catalyst **2** by the efficient quenching of CL due to the energy transfer from $R'HC{=}O^*$ to nonluminescing Ln. For **1**, this transfer onto Tb^{3+} is finished not with the quenching, but with the luminescence of terbium (this component of CL contributes 15 to 20 % to the overall luminous efficiency). Thus, the absence of the emission of a lanthanide in the case of oxidation of **2** and **3** makes it impossible to apply the CL method for probing these catalysts. However, the similarity of chemical properties of lanthanides determines the similar mechanism of catalysis for both luminescing and nonluminescing lanthanide compounds, which makes it possible to extend the conclusions on the mechanism of catalysis obtained for terbium-containing catalyst **1** by the methods based on luminescence to similar catalysts with other lanthanides.

The correlations of luminous efficiencies of CL with quantitative parameters of polymerization obtained are the experimental proof that it is Ln—C bonds that play the role of the main element of CAC in diene polymerization on lanthanide- and aluminum-containing Ziegler—Natta catalysts.

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Received August 1, 1995;
in revised form January 22, 1996