

# The Influence of the Nature of Organoaluminum Compound on Kinetic Heterogeneity of Active Sites in Lanthanide-Based Diene Polymerization

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Received 6 April 2001; accepted 15 February 2002

**ABSTRACT:** The influence of organoaluminum compound on kinetic heterogeneity of active sites in lanthanide-based diene polymerization was investigated. It was shown that heterogeneity of investigated catalytic systems was displayed in the existence of four types of active centers. They are formed at the beginning of the polymerization process and produce macromolecules with lengths that are definite for each type of active centers. The organoaluminum compound's nature greatly influences the kinetic activity of po-

lymerization centers. The method of analysis of the curves' maximum distribution on kinetic activity and the change of kinetic activity of every active centers' type were proposed, which permits the calculation of values of concentration for each type of active center separately. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 358–368, 2003

**Key words:** Ziegler-Natta polymerization; simulation

## INTRODUCTION

The study of diene polymerization on lanthanide catalytic systems showed<sup>1–4</sup> that the nature of organoaluminum compound (OAC) essentially had influence both on catalytic system activity and on properties of the received polydienes. It was established<sup>1,2</sup> that the use of various OAC-defined values of constants of transfer on OAC ( $k_t^{Al}$ ) reaction rate and the values of propagation chain reaction rate constants ( $k_p$ ) as well. The use of different OACs may influence the microstructure of formed polydienes.<sup>3</sup> Molecular characteristics of forming polydienes significantly depend on the OAC content and nature. It was shown that for the polybutadiene received on the  $NdCl_3 \cdot 3L$ -OAC (L-tributylphosphate) catalytic system, broad molecular weight distribution was typical. Form of the last one depends on synthesis conditions and OAC nature.<sup>4</sup> It was supposed that the reason for the broad molecular weight distribution was the existence of several types of active centers.<sup>5,6</sup>

By this connection, the influence of OAC nature on kinetic heterogeneity of active centers in lanthanide-based diene polymerization was investigated.

## EXPERIMENTAL

The butadiene polymerization was carried out at 25°C in the presence of the two-component lanthanide catalytic systems  $NdCl_3 \cdot 3L$ -OAC, where L was tributylphosphate.  $Al(i-C_4H_9)_3$ ,  $Al(C_2H_5)_3$ ,  $Al(C_6H_{13})_3$ , and  $Al(C_8H_{17})_3$  were used as organoaluminum compounds. The complexes were prepared according to the technique described in ref. 7. A complex was formed by an *in situ* procedure [i.e., the solutions of OAC ( $C_{Al} = 3 \times 10^{-2}$  mol/L) and  $NdCl_3 \cdot 3L$  were added sequentially into a toluene monomer ( $C_m = 1.5$  mol/l) solution at 25°C]. The ratio of Al/Nd was 30.

The 1,4-*cis*-units content was 90–95%; the content of 1,2-units was not less than 1%, and the 1,4-*trans* structures made up the remainder.

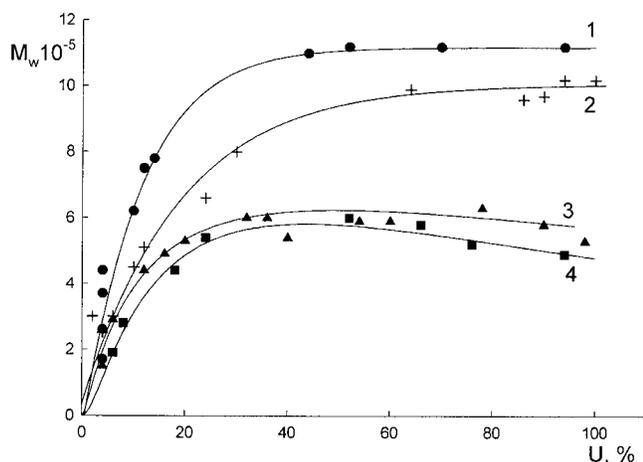
Molecular weights (weight-average,  $M_w$ ; number-average,  $M_n$ ) and the molecular weight distribution (MWD) of 1,4-*cis*-polybutadiene were estimated by gel permeating chromatography (chloroform, 1 mL/min, 25°C). Four Waters columns packed with  $10^6$ ,  $10^5$ ,  $10^4$ , and  $10^3$  Å  $\mu$ -styragel were used. The system of columns was calibrated under the standards with narrow MWD ( $M_w/M_n \leq 1.2$ ) by using the universal dependence of Benoit et al.<sup>8</sup> and an equation connecting the molecular weight of polydienes with characteristic viscosity.<sup>9</sup>

Chromatograms and the obtained values of molecular weights were corrected for instrumental spreading, as described in ref. 10.

The calculation of distribution function on kinetic heterogeneity of the  $NdCl_3 \cdot 3L$ -OAC catalytic system

Correspondence to: K. Gumargalieva.

Contract grant sponsor: Russian Foundation of Fundamental Investigations; contract grant number: N0 99-03-33437; Contract grant sponsor: "Leading Research Schools"; contract grant number: N0 00-15-97322.



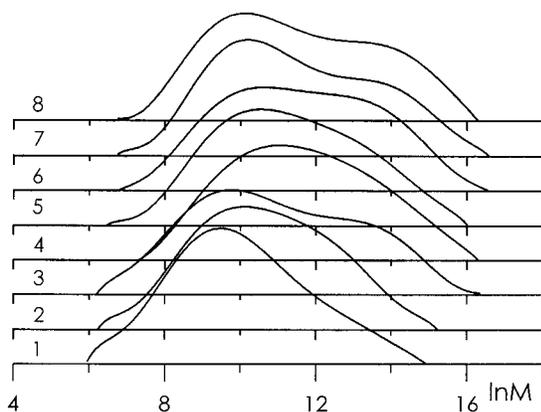
**Figure 1** The plots of  $M_w$  for polybutadiene versus the monomer conversion under polymerization on  $\text{NdCl}_3$  3L-OAC catalytic system. OAC: 1,  $\text{Al}(\text{i-C}_4\text{H}_9)_3$ ; 2,  $\text{Al}(\text{C}_2\text{H}_5)_3$ ; 3,  $\text{Al}(\text{C}_8\text{H}_{17})_3$ ; 4,  $\text{Al}(\text{C}_6\text{H}_{13})_3$ . Polymerization conditions: toluene,  $C_M = 1.5$ ;  $C_{Al} = 3 \times 10^{-2}$  mol/L;  $\text{Al}/\text{Nd} = 30$ ;  $T_{pm} = 25^\circ\text{C}$ .

was carried out by Tikhonov regularization method.<sup>11–14</sup> The minimum of the Tikhonov functional was reached at a regularization parameter of  $\alpha = 9.4 \times 10^{-5}$  at a quadratic average error of experiment,  $\delta^2 = 0.0001$ . The method and procedure used in this work permitted the modification of the error value in the choice of an integral equation kernel. Because the kernel representing the Shultz–Flory function was chosen as a model, we assumed that error  $h \rightarrow 0$ .

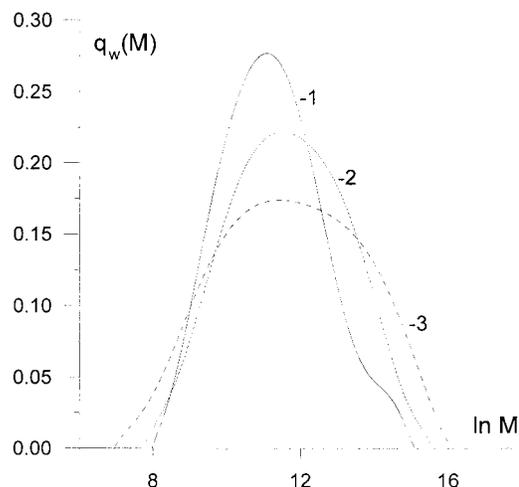
## RESULTS AND DISCUSSION

In a general view, the broad polymers MWD may be represented by:<sup>15</sup>

$$u = PSX \quad (1)$$



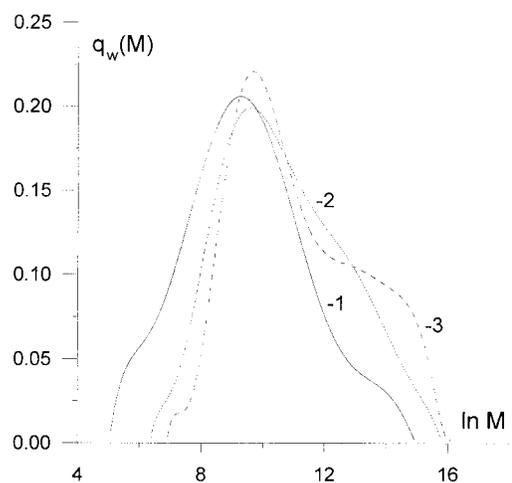
**Figure 2** Molecular weight distribution curves for polybutadiene, received on  $\text{NdCl}_3$  3L- $\text{Al}(\text{i-C}_4\text{H}_9)_3$  catalytic system. Polymerization conditions are given in Figure 1. Monomer conversion (%): 1, 3.61; 2, 6.8; 3, 11.1; 4, 17.4; 5, 25.6; 6, 37.3; 7, 55.6; 8, 67.8; 9, 87.9; 10, 88.8.



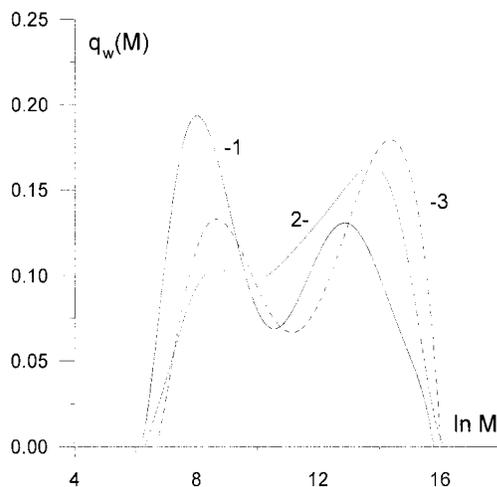
**Figure 3** Molecular weight distribution curves for polybutadiene, received on  $\text{NdCl}_3$  3L- $\text{Al}(\text{C}_6\text{H}_{13})_3$  catalytic system. Polymerization conditions are given in Figure 1. Monomer conversion (%): 1, 1.7; 2, 8.7; 3, 89.4.  $M_w/M_n$ : 1, 4.8; 2, 7.3; 3, 17.8.

where  $u$ , the polydispersity of polymer, is the magnitude equal to the ratio of  $M_w$  to  $M_n$ ;  $P$  is the measure of the correlation between polymerization reaction and diffusion limits;  $S$  is a factor depending on distribution of polymerization active centers ( $S \rightarrow 2$  in the case of homogeneity of active sites); and  $X$  is a function of particle size distribution.

As the butadiene polymerization process with lanthanide catalytic systems is homogeneous, it is possible to assume that  $P = 1$  and  $X = 1$ . The kinetic regularities of diene polymerization on these catalysts confirm this supposition. The polymerization reaction is characterized by the first-order organomagnesium monomer and catalyst. The chain transfer reactions

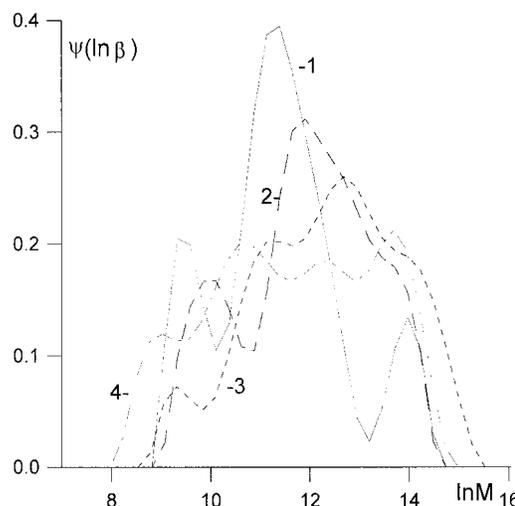


**Figure 4** Molecular weight distribution curves for polybutadiene, received on  $\text{NdCl}_3$  3L- $\text{Al}(\text{C}_8\text{H}_{17})_3$  catalytic system. Polymerization conditions are given in Figure 1. Monomer conversion (%): 1, 3.1; 2, 21.6; 3, 91.3.  $M_w/M_n$ : 1, 18.2; 2, 18.6; 3, 20.8.



**Figure 5** Molecular weight distribution curves for polybutadiene, received on  $\text{NdCl}_3 \cdot 3\text{L-Al}(\text{C}_2\text{H}_5)_3$  catalytic system. Polymerization conditions are given in Figure 1. Monomer conversion (%): 1, 3.2; 2, 9.6; 3, 88.0.  $M_w/M_n$ : 1, 28.3; 2, 42.2; 3, 55.2.

proceed under polymerization, but they do not result in the active center deactivation. These facts testify that the MWD of polydienes, obtained on these systems, should be close to the most probable Flory distribution with  $M_w/M_n \sim 2$ . However, in most cases, magnitude of polydispersity is significantly greater. Practically observed polydispersity of distributions on molecular masses for polydienes is significantly higher than that of the theoretically expected polydispersity, because active centers, differing in reaction ability, are involved in the polymerization process. There is some quasi-continuous distribution of active centers; each of them produces fractions distributed according to the law  $\beta_i e^{-\beta_i M}$ . Assuming that the law of catalytic centers distribution is described by some function  $\varphi(\beta)$ , the MWD will be

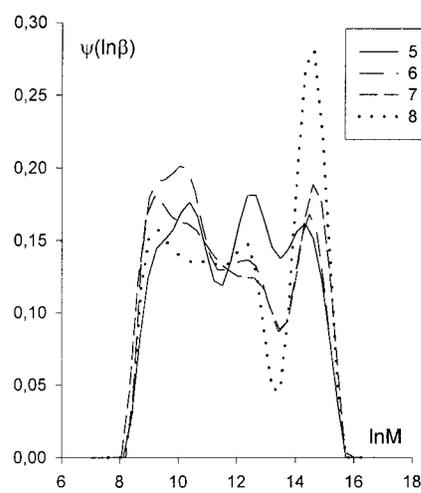
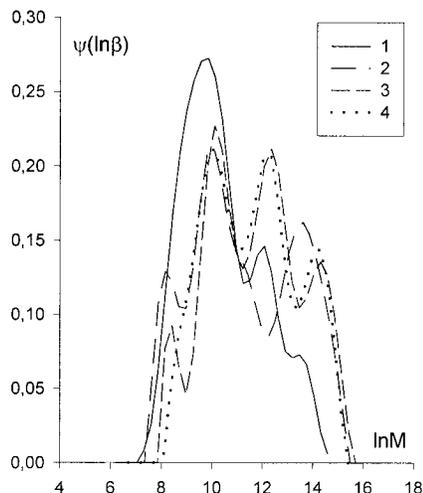


**Figure 7** Activity distributions of the  $\text{NdCl}_3 \cdot 3\text{L-Al}(\text{C}_6\text{H}_{13})_3$  catalytic system under butadiene polymerization; monomer conversions (%): 1, 1.7; 2, 8.7; 3, 26.2; 4, 72.0.

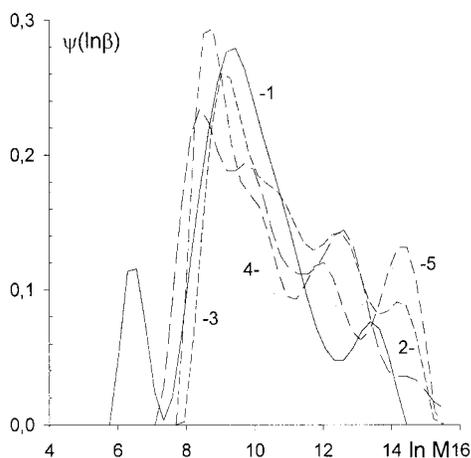
$$q_w(M) = \int_0^{\infty} \varphi(\beta) \beta^2 e^{-\beta M} d\beta \quad (2)$$

where  $\beta$ , the magnitude, is inverse to the average molecular weight  $M_n$ , characterizing probability of a chain transfer, and equals  $\beta = (1/m_0)(r_t/r_p)$  ( $r_p$  is the chain propagation rate;  $r_t$  is the summarized rate of chain transfer; and  $m_0$  is the molecular mass of the monomer).

As it follows from expression (2), the values of  $q_w(M)$  depend on an aspect of a cumulative distribution function on kinetic activity of catalytic system  $\varphi(\beta)$ . Suppose  $s = \ln \beta$  and  $x = \ln M$ ; then it is possible to show that  $Z(s) = e^{2s} \varphi(e^s)$ ,  $K(x, s) = \exp[x + s + \exp(x + s)]$ ,  $U_s(x) = q_w(M)$ , and eq. (2) is reduced to a classical equation of the Fredholm of the first sort:



**Figure 6** Activity distributions of the  $\text{NdCl}_3 \cdot 3\text{L-Al}(\text{i-C}_4\text{H}_9)_3$  catalytic system under butadiene polymerization; monomer conversions (%): 1, 3.61; 2, 11.1; 3, 17.4; 4, 25.6; 5, 55.6; 6, 67.8; 7, 87.9; 8, 88.8.



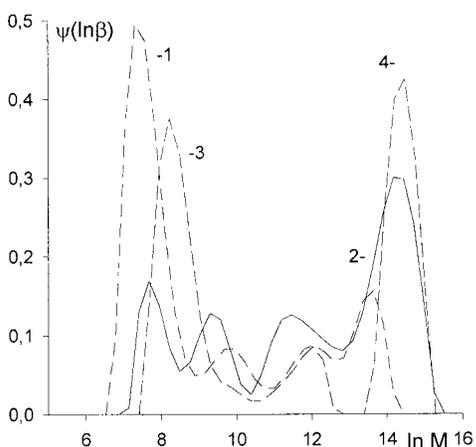
**Figure 8** Activity distributions of the  $\text{NdCl}_3$  3L- $\text{Al}(\text{C}_8\text{H}_{17})_3$  catalytic system under butadiene polymerization; monomer conversions (%): 1, 3.1; 2, 13.4; 3, 21.6; 4, 49.6; 5, 57.9.

$$U_\delta(x) = \int_0^\infty Z(s)K(x, s) ds \quad (3)$$

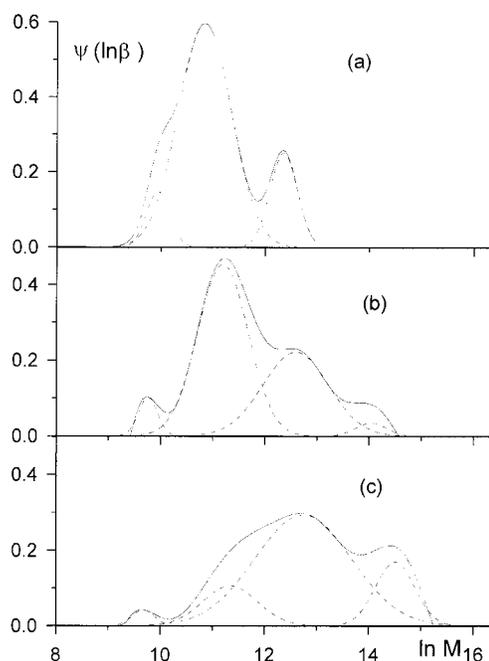
where  $K(x, s)$  is the kernel of an integral equation and  $Z(s) = e^{2s}\varphi(e^s)$ .  $Z(s)$  is the unknown function, and the index  $\delta$  in the left part of the equation specifies that the function, found from the experiment,  $U_\delta(x)$ , practically founded, is defined with an error  $\delta$ .

The complexity of calculating  $\varphi(\beta)$  from eq. (3) is in the fact that it has to do with the class of ill-posed problems.<sup>11-14</sup> Therefore, direct solution of such tasks because of an error of experimental data [the left part of eq. (3)] may even reduce to absurd outcomes.

For the wide MWD ( $M_w/M_n > 3$ ) numerical solution of an integral, eq. (3) is carried out by the Tikhonov method of regularization by a selection of regularization parameter  $\alpha$ , at which experimentally defined and calculated from eq. (2) functions  $q_w(M)$  coincide with



**Figure 9** Activity distributions of the  $\text{NdCl}_3$  3L- $\text{Al}(\text{C}_2\text{H}_5)_3$  catalytic system under butadiene polymerization; monomer conversions (%): 1, 3.2; 2, 9.6; 3, 40.2; 4, 88.0.



**Figure 10** Activity distributions of the  $\text{NdCl}_3$  3L- $\text{Al}(\text{i-C}_4\text{H}_9)_3$  catalytic system divided into separate peaks; monomer conversions (%): a, 2.6; b, 7.5; c, 53.4.

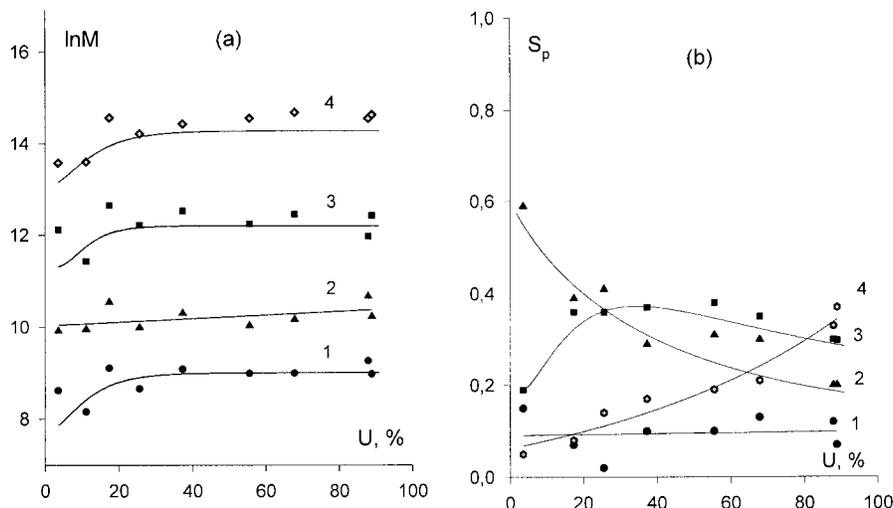
the given exactitude  $\delta$ . Besides the obtained solutions,  $\varphi(\beta)$  should satisfy a condition of normalization:

$$\int_0^\infty \varphi(\beta) d\beta = 1 \quad (4)$$

Because  $\beta$  is a magnitude inverse to molecular weight, the solution of eq. (3) in this work is represented as a plot of  $\varphi(\beta)$  in the  $\psi(\ln \beta) - \ln M$  coordinates, where  $\psi(\ln \beta) = \beta\varphi(\beta)$ .

The course of the polybutadiene molecular weight's dependence on monomer conversion is analogous for all used catalytic systems (Fig. 1). At the initial stage of polymerization,  $M_w$  grows; when the conversion achieves 20–40%, this growth ceases, and further conversion growth leads either to the constant values of molecular masses or to the small reduction of  $M_w$ . Such molecular mass change is typical for the ion-coordinated diene polymerization processes, and the invariable number of active centers, the occurrence of the chain transfer processes, and monomer reduction during polymerization cause it.

The highest polybutadiene molecular masses are observed under the  $\text{Al}(\text{i-C}_4\text{H}_9)_3$ ; then  $\text{Al}(\text{C}_2\text{H}_5)_3$ ,  $\text{Al}(\text{C}_8\text{H}_{17})_3$ , and  $\text{Al}(\text{C}_6\text{H}_{13})_3$  usage are observed under equal conditions (Fig. 1). As the conversion increases (Fig. 2), molecular weight distribution curves are displaced into the higher molecular weight region, and polydispersity of the polymer increases by this. The growth of polydispersity during polymerization is ob-



**Figure 11** Positions of maximum (a) and kinetic activity (b) of butadiene polymerization centers versus monomer conversion.  $\text{NdCl}_3$  3L- $\text{Al}(\text{i-C}_4\text{H}_9)_3$  catalytic system.

served for all investigated catalytic systems (Figs. 2–5). However, the form of polybutadiene MWD curves is changed under the use of various OAC. As it follows from the data of Figures 2 and 3, MWD curves of polybutadiene, received with the use of  $\text{Al}(\text{i-C}_4\text{H}_9)_3$  and  $\text{Al}(\text{C}_6\text{H}_{13})_3$ , are monomodal. Polymer synthesized on  $\text{NdCl}_3$  3L- $\text{Al}(\text{C}_2\text{H}_5)_3$  is characterized by bimodal distribution. MWD curves of polybutadiene were received with the  $\text{Al}(\text{C}_8\text{H}_{17})_3$  as OAC change their form under polymerization processing. Broadband appears on the curves in the region of molecular masses' high values at high monomer conversions.

Distributions on kinetic activity of investigated catalytic systems  $\text{NdCl}_3$  3L-OAC were received with the help of Tikhonov regularization method on the basis of MWD curves of polybutadiene obtained experimentally (Figs. 6–9).

All curves of distribution on kinetic activity are polymodal independently from the nature of using OAC, and four greatly expressive maximums appear with the conversion degree increase. It testifies that the polymerization process occurs on at least four types of active centers for all investigated systems. Moreover, multimodality of  $\psi(\ln \beta)$  curves is obtained even at very small monomer conversions. It indicates that different types of active sites are formed immediately, at the initial stage of the process (i.e., the catalytic system is primordial kinetically heterogeneous).

Every point on the distribution curves characterizes the active centers' part with the chain termination probability equal to  $\beta_1$  and produces macromolecules with molecular mass  $M_1$ . The fact of the presence of  $\psi(\ln \beta)$  distribution itself testifies about kinetic heterogeneity of catalytic system.

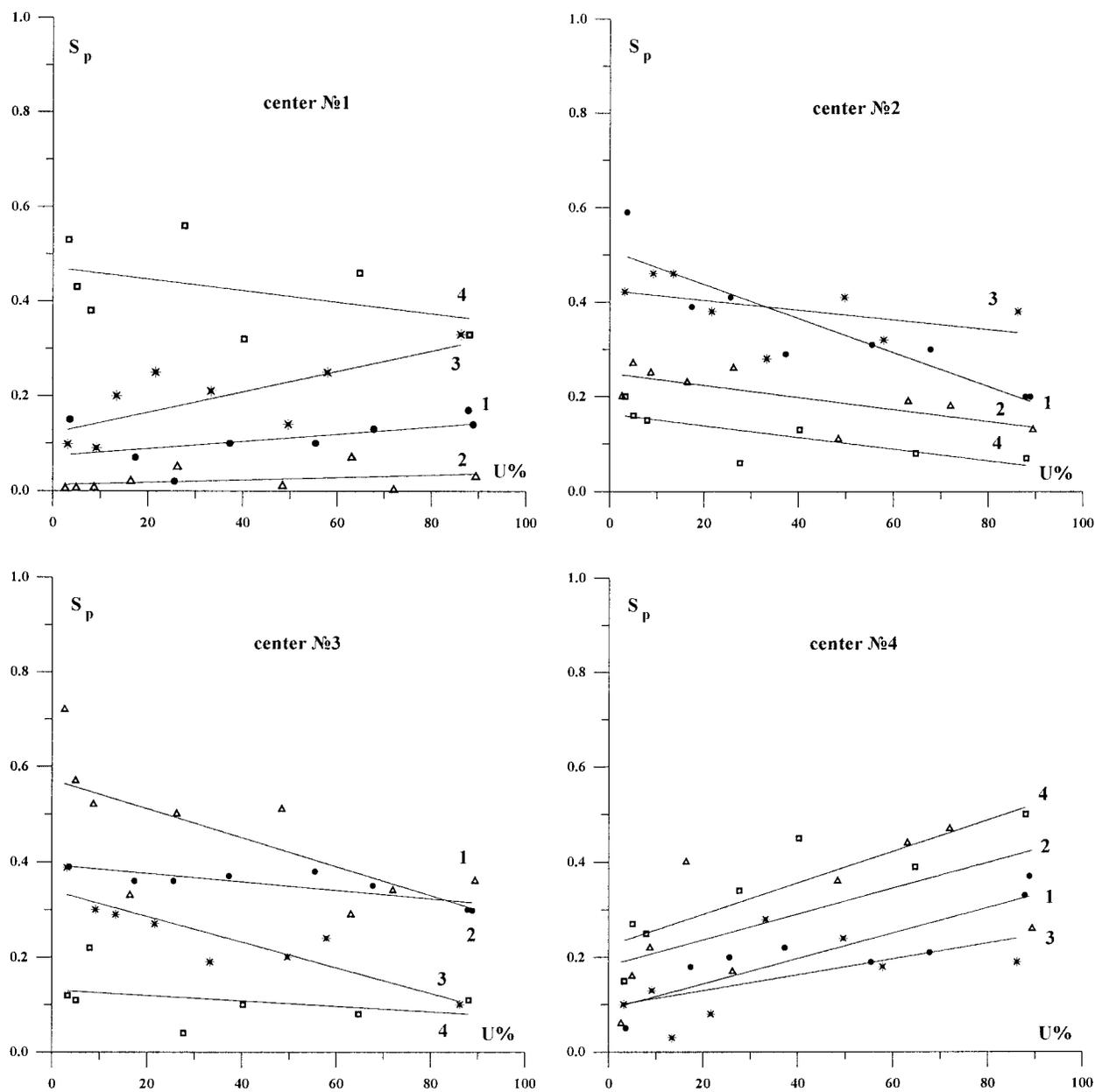
Distributions on kinetic activity of catalytic system  $\text{NdCl}_3$  3L- $\text{Al}(\text{C}_2\text{H}_5)_3$  (Fig. 9) differ from the  $\psi(\ln \beta)$

curves received in the presence of  $\text{Al}(\text{i-C}_4\text{H}_9)_3$ ,  $\text{Al}(\text{C}_6\text{H}_{13})_3$ , and  $\text{Al}(\text{C}_8\text{H}_{17})_3$ . For the system with  $\text{Al}(\text{C}_2\text{H}_5)_3$ , the presence of two clear maximums is characteristic. They correspond to the active centers that produce the very low molecular and the very high molecular polymer fractions. These two active center types produce the bulk of the polymer and the polymerization product fractions produced on every of active centers greatly differ in molecular mass—low molecular fraction  $10^3$ – $10^4$  and high molecular fraction  $\sim 10^6$ . The contribution of active centers that form macromolecules with intermediate values of molecular mass is not significant. Apparently, just in consequence of such unequal action of active centers of  $\text{NdCl}_3$  3L- $\text{Al}(\text{C}_2\text{H}_5)_3$  catalyst, the formed polybutadiene has bimodal MWD.

The received distributions may be divided into separate Gaussian functions, assuming that the deviations of active center from the maximum are statistical (Fig. 10). In this case, the area of every Gaussian curve will correspond to the numerical part of polymer, produced on the corresponding center. This allowed us to estimate a relative contribution of each active center type and to follow their changes.

Figure 11 presents the change of maximum positions, received by dividing the curve of kinetic activity distribution of catalytic system  $\text{NdCl}_3$  3L- $\text{Al}(\text{i-C}_4\text{H}_9)_3$  into separate peaks, dependent on the monomer conversion. One can say that maximum positions corresponding to the various types of active centers remain virtually unchanged throughout the polymerization process. That is, each active center seems to synthesize macromolecules of a certain length.

Besides, active centers of catalytic systems with  $\text{Al}(\text{i-C}_4\text{H}_9)_3$ ,  $\text{Al}(\text{C}_6\text{H}_{13})_3$ , and  $\text{Al}(\text{C}_8\text{H}_{17})_3$  produce fractions with identical molecular mass. Thus, the active center, that produces the highest molecular fraction, forms



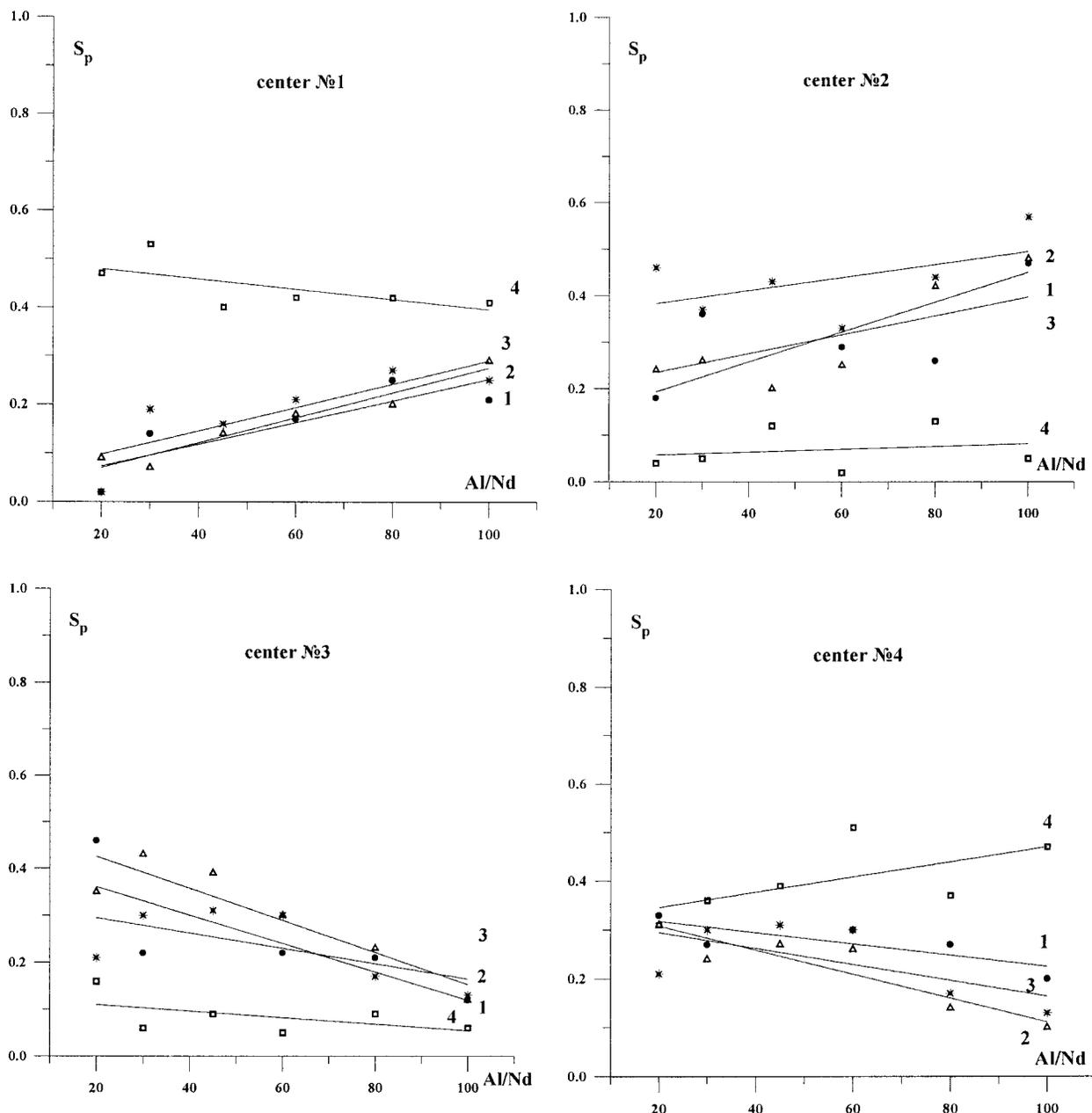
**Figure 12** The plots of kinetic activity of four types of butadiene polymerization active centers versus monomer conversion.  $NdCl_3 \cdot 3L-OAC$  catalytic system. [1,  $Al(i-C_4H_9)_3$ ; 2,  $Al(C_6H_{13})_3$ ; 3,  $Al(C_8H_{17})_3$ ; 4,  $Al(C_2H_5)_3$ ]. Polymerization conditions are given in Figure 1.

polymer with molecular mass  $\sim 10^6$ ; the first active center produces the lowest molecular mass,  $7-8 \times 10^3$ , the second and the third,  $2 \times 10^4$  and  $1.5 \times 10^5$ , respectively. For the system with  $Al(C_2H_5)_3$ , the position of the first (low molecular) peak differs slightly and the corresponding active center produces polymer with molecular mass  $\sim 3 \times 10^3$  (i.e., product with low molecular mass), compared with catalysts on the basis of  $Al(i-C_4H_9)_3$ ,  $Al(C_6H_{13})_3$ , and  $Al(C_8H_{17})_3$ .

The activity of centers determined by the area of this maximum on the curve of kinetic activity distribution is changed throughout the polymerization process. In

Figure 12, there are changes of kinetic activity of every active center under the butadiene polymerization process on the catalytic system  $NdCl_3 \cdot 3L-Al(C_2H_5)_3$ . It is obvious that active centers generating the lowest molecular fractions and corresponding to the first maximum on the distribution curve are characterized by very low activity, which is slightly increased in the course of polymerization.

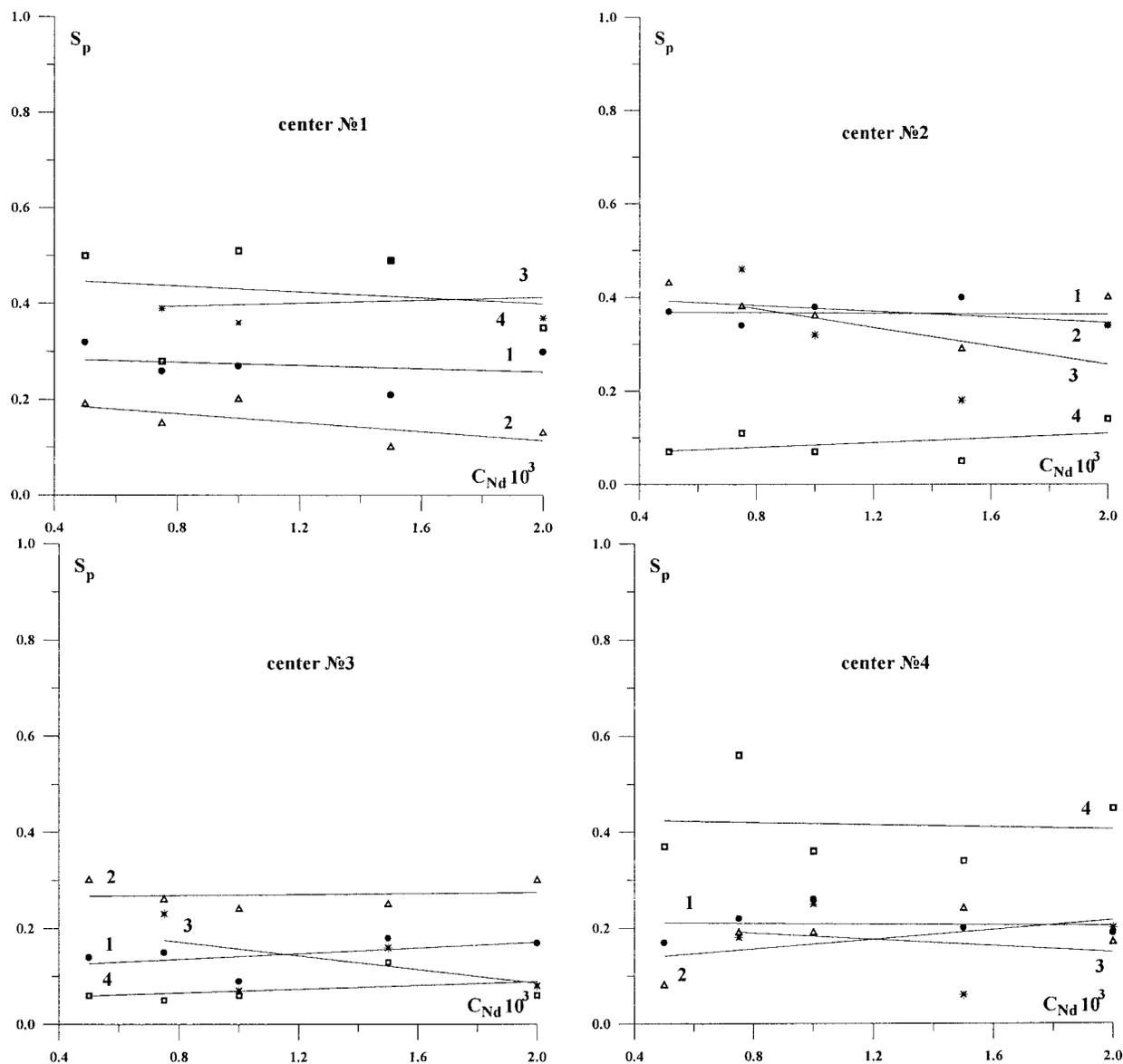
A reduction of activity is obtained for the second active center type; for the third, the growth with saturation, and a constant activity increase throughout the polymerization is obtained for the fourth type.



**Figure 13** Kinetic activity change of butadiene polymerization centers at various ratios of Al/Nd.  $\text{NdCl}_3$  3L-OAC catalytic system [1,  $\text{Al}(\text{i-C}_4\text{H}_9)_3$ ; 2,  $\text{Al}(\text{C}_6\text{H}_{13})_3$ ; 3,  $\text{Al}(\text{C}_8\text{H}_{17})_3$ ; 4,  $\text{Al}(\text{C}_2\text{H}_5)_3$ ].

Some disconnection of data is explained by the static nature of the polymerization process. It is difficult to prepare two polymer products with equal molecular masses, and consequently, with identical MWD in two different experiments. In turn, even insignificant deviations in MWD form lead to the essential changes in distributions on kinetic activity. However, one can estimate the tendency of the activity changes of various centers. Curves of the kinetic activity change of  $\text{NdCl}_3$  3L-OAC catalytic systems are separately grouped for every active center's type in Figure 13. It permits the tendency of kinetic heterogeneity change of catalytic systems, containing different organoalumi-

num compounds. It is obvious that under the use of  $\text{Al}(\text{i-C}_4\text{H}_9)_3$ ,  $\text{Al}(\text{C}_6\text{H}_{13})_3$ , and  $\text{Al}(\text{C}_8\text{H}_{17})_3$  as organoaluminum compounds, kinetic activity of all four center types is different in intensity, but is equally changed with monomer conversion. Active centers generating the lowest molecular fractions increase their activity in the course of polymerization. The activity of this center is decreased for the catalytic system with the use of  $\text{Al}(\text{C}_2\text{H}_5)_3$ . Activity of centers corresponding to the second and third maximums decreases for all used catalytic systems. There is the constant growth for the fourth type of active center, independent from using a catalytic system in the organoaluminum compound.



**Figure 14** Kinetic activity change of butadiene polymerization centers at various catalyst concentrations.  $NdCl_3$  3L-OAC catalytic system [1,  $Al(i-C_4H_9)_3$ ; 2,  $Al(C_6H_{13})_3$ ; 3,  $Al(C_8H_{17})_3$ ; 4,  $Al(C_2H_5)_3$ ].

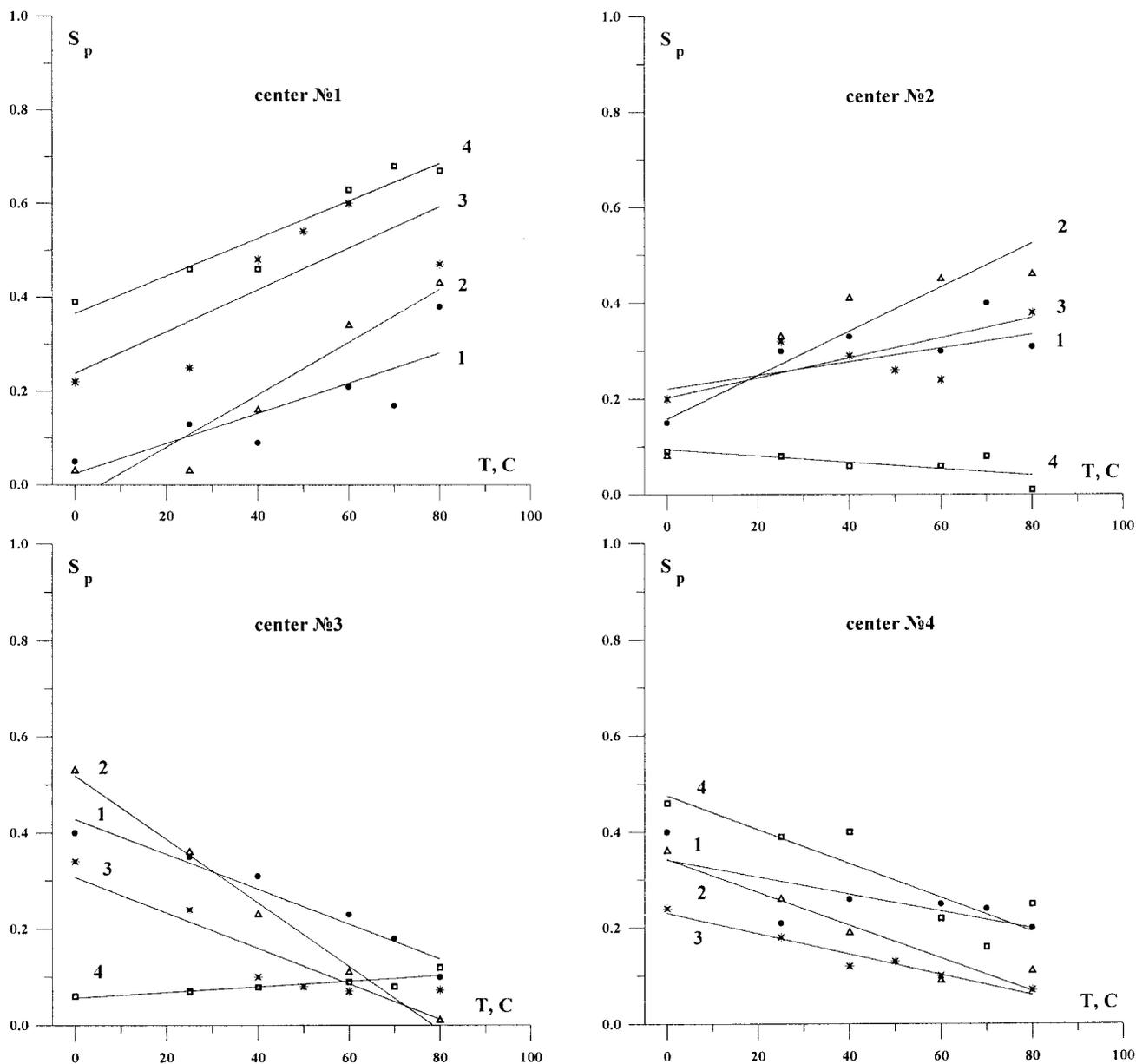
The low values of intensities of the second and the third peaks for  $NdCl_3$  3L- $Al(C_2H_5)_3$  catalytic system also must be noted.

The kinetic activity change of four active centers types of investigated catalytic systems at various ratios Al/Nd is depicted in Figure 14. It is obvious that the course of kinetic activity dependence on Al/Nd ratio practically coincides under the use of  $Al(i-C_4H_9)_3$ ,  $Al(C_6H_{13})_3$ , and  $Al(C_8H_{17})_3$ , as in the case of conversion curves. There are the increases of activity for the first and the second peaks and activity decrease is for the third and the fourth peaks with the growth of OAC content in catalytic system. In contrast to other investigated catalysts, for the catalytic system,  $NdCl_3$  3L- $Al(C_2H_5)_3$ , the first maximum has high activity values and slightly reduces

with the increase of the Al/Nd ratio. The change of the fourth peak intensity also differs from the rest of the catalytic systems. With  $Al(C_2H_5)_3$  content growth, its intensity increases.

As follows from Figure 15, the change of catalyst concentration in polymerization systems practically does not lead to the change of kinetic activity of polymerization centers.

The influence of butadiene polymerization temperature on the distributions of kinetic activity of investigated catalytic systems was also studied (Fig. 16). It is obvious that with the temperature increase, the intensity of the third and the second peaks, producing low molecular polymer, grows. Oppositely, centers responsible for generating high molecular fractions (peaks 3 and 4) decrease their activity. Obviously,



**Figure 15** Kinetic activity change of butadiene polymerization centers at various polymerization temperatures.  $\text{NdCl}_3$  3L-OAC catalytic system [1,  $\text{Al}(i\text{-C}_4\text{H}_9)_3$ ; 2,  $\text{Al}(\text{C}_6\text{H}_{13})_3$ ; 3,  $\text{Al}(\text{C}_8\text{H}_{17})_3$ ; 4,  $\text{Al}(\text{C}_2\text{H}_5)_3$ ].

active centers forming high molecular fractions are less thermostable than active centers, on which the low molecular polymer is formed. As for conversion dependences, the kinetic activity of centers corresponding to peaks 2 and 3 is very low when using  $\text{Al}(\text{C}_2\text{H}_5)_3$  as an organoaluminum component.

The magnitude  $S_i$ , area of peak, was received by dividing the activity distributions into separate Gaussian functions and, as it has been said earlier, characterizes the part of chains formed on the  $i$  active center.  $S_i$  is equal to the ratio of the quantity of chains received on  $i$  active center to the overall chains number  $Q_0$ :

$$S_i = \frac{Q_{oi}}{Q_0} \quad (5)$$

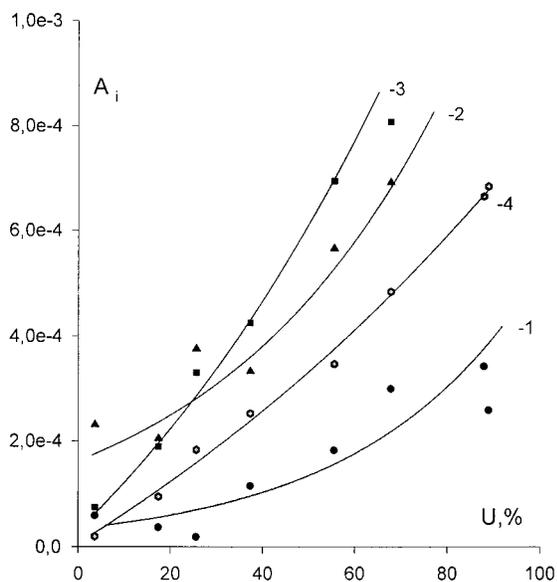
Suppose

$$\mu = C_{m0} \sum \frac{C_{ai}}{C_{ai}} x \quad (6)$$

is the part of monomer expended on  $i$  active center at conversion moment  $x$ , where  $C_{ai}$  is the  $i$  center concentration. Then, the magnitude

$$\frac{k_{mi}C_m + k_{Ali}C_{Al}}{k_{pi}C_m} \mu \quad (7)$$

is the number of dead chains formed on  $i$  center by transfer reactions to monomer and OAC at conversion



**Figure 16** The plot of  $A_i$  versus monomer conversion under butadiene polymerization on  $\text{NdCl}_3$  3L- $\text{Al}(\text{i-C}_4\text{H}_9)_3$  catalytic system.

moment  $x$ , where  $k_{mi}$  and  $k_{Al_i}$  are the rate constants for the reactions of chain transfer to the monomer and OAC, accordingly, and  $k_{pi}$  is the rate constant of chain propagation on the corresponding type of active centers.

The total number of macromolecules produced on the  $i$  center is

$$Q_{oi} = C_{ai} + \frac{k_{mi}C_m + k_{Al_i}C_{Al}}{k_{pi}C_m} \frac{C_{m0}C_{ai}}{\sum C_{ai}} x \quad (8)$$

where the first item  $C_{ai}$  characterizes the number of living chains.

The total number of chains is determined by the ratio of the quantity of reacted monomer and the number-average degree of polymerization  $P_n$

$$Q_o = \frac{C_{m0}}{P_n} x \quad (9)$$

with regard to eqs. (8) and (9); after noncomplicated transformations, expression (5) may be represented as:

$$\frac{S_i C_{m0} x}{P} = C_{ai} \left[ 1 + \frac{C_{m0} k_{mi}}{k_{pi} \sum C_{ai}} x + \frac{C_{Al} k_{Al_i} C_{m0}}{C_m k_{pi} \sum C_{ai}} x \right] \quad (10)$$

Then assume

$$\frac{S_i C_{m0} x}{P_n} = A_i$$

The position of maximum curve of distribution on kinetic activity characterizes the polymerization degree  $P_{ni}$  of polymer fractions formed on the corresponding active centers. The polymerization degree  $P_{ni}$  in its turn, is determined as a ratio of the monomer quantity  $\mu$ , reacted on  $i$  center, and number of chains,  $Q_{oi}$ , formed on it.

By using expression (6), one receives

$$P_{ni} = \frac{C_{m0} C_{ai}}{Q_{oi} \sum C_{ai}} x \quad (11)$$

Taking into account that conversion is determined as

$$x = 1 - e^{-\tau \sum k_{pi} C_{ai}}$$

for the initial polymerization moment, at  $\tau \rightarrow 0$ , one can assume

$$x \approx \tau \sum k_{pi} C_{ai} = \tau \langle k_p \rangle \sum C_{ai} \quad (12)$$

where  $\langle k_p \rangle$  is a generalized constant of propagation rate. With regard to eq. (12), eq. (11) may be represented as:

$$P_{ni} = C_{m0} \langle k_p \rangle \tau \quad (13)$$

As it follows from eq. (13), the angle of dependences of  $P_{ni}$  on  $\tau$  at  $\tau \rightarrow 0$  is a constant magnitude for all active centers and characterizes this catalytic system. Thus, the maximums' position shift in Figure 10 at the initial moment of polymerization is a natural phenomenon, and this effect must be observed in all cases under more detailed study of the polymerization process at low conversions.

One can receive the following expression for analysis  $P_{ni}$  by substituting eq. (8) into eq. (11):

**TABLE I**  
The Neodymium Catalytic Systems Active Centers Concentrations under Butadiene Polymerization

Catalytic system	$C_{ai} \times 10^5$ (mol/l)				$\sum C_{ai} \times 10^5$ (mol/l)	$\langle C_a \rangle 10^5$ (mol/l)
	$C_{a1}$	$C_{a2}$	$C_{a3}$	$C_{a4}$		
$\text{NdCl}_3$ 3L- $\text{Al}(\text{i-C}_4\text{H}_9)_3$	3.9	21.7	7.5	5.7	38.8	40.1
$\text{NdCl}_3$ 3L- $\text{Al}(\text{C}_6\text{H}_{13})_3$	0.05	0.9	1.5	0.8	3.3	3.0
$\text{NdCl}_3$ 3L- $\text{Al}(\text{C}_8\text{H}_{17})_3$	2.39	6.2	6.9	28.7	65.6	65.0
$\text{NdCl}_3$ 3L- $\text{Al}(\text{C}_2\text{H}_5)_3$	6.8	3.9	3.0	6.8	20.5	25.0

$$B_i = \frac{C_{m0}C_{ai}x}{P_{ni} \sum C_{ai}} = C_{ai} + \frac{k_{mi}C_m + k_{Al}C_{Al}}{k_{pi}C_m} \frac{C_{m0}C_{ai}}{\sum C_{ai}} \quad (14)$$

Expressions (10) and (14) permit the analysis of kinetic activity change of catalytic systems more clearly. The dependences of magnitude  $A_i$  on monomer conversion  $x$  are depicted in Figure 15. Extrapolation of this curve to zero conversion, according to eqs. (10) and (14), makes possible the determination  $C_{ai}$ , the concentration of every active center separately, and also the total concentration of polymerization centers  $\sum C_{ai}$ .

The values of concentrations of different active center types under butadiene polymerization on investigated catalytic systems are represented in Table I.  $\sum C_{ai}$  is the total concentration of all the active centers' types; values  $\langle C_a \rangle$  are also the total active centers concentration, but they were received by analysis of polymerization process kinetics by the equation:

$$W_p = k_p C_m \langle C_a \rangle$$

It is obvious that there is a coincidence of results of both calculation methods that confirm the adequateness of the used model.

## CONCLUSION

Thus, heterogeneity of the investigated catalytic systems was displayed in the existence of four types of active centers. They are formed at the beginning of the polymerization process and produce macromolecules with lengths that are definite for each type of active centers. Kinetic activity of polymerization centers depends on OAC concentration and nature and polymerization temperature. For the catalytic systems with  $\text{Al}(\text{i-C}_4\text{H}_9)_3$ ,  $\text{Al}(\text{C}_6\text{H}_{13})_3$ , and  $\text{Al}(\text{C}_8\text{H}_{17})_3$ , kinetic activity of polymerization centers equally changes in dependence on polymerization conditions and the change of monomer conversion. Maybe this is the consequence of identical structure of different active centers types of these catalytic systems.

The difference of distributions on kinetic activity and behavior of active centers of catalytic system with  $\text{Al}(\text{C}_2\text{H}_5)_3$  with similarity in behavior of systems with  $\text{Al}(\text{i-C}_4\text{H}_9)_3$ ,  $\text{Al}(\text{C}_6\text{H}_{13})_3$ , and  $\text{Al}(\text{C}_8\text{H}_{17})_3$  can be explained by the difference in association degree of free OAC molecules in the polymerization system. It is known that organoaluminum compounds with direct carbon chain are dimeric. Inclination to association is

greatly increased with the decrease of carbon radical length. Thus, dimmer molecules of  $\text{Al}(\text{C}_2\text{H}_5)_3$  are stable even in vaporous state and dissociate only at temperatures  $> 100^\circ\text{C}$ . In solutions,  $\text{Al}(\text{C}_2\text{H}_5)_3$  takes the monomer shape only under dilution to more than 0.1% concentration. Probably the bigger inclination to associate  $\text{Al}(\text{C}_2\text{H}_5)_3$  molecules in comparison with  $\text{Al}(\text{C}_6\text{H}_{13})_3$ ,  $\text{Al}(\text{C}_8\text{H}_{17})_3$ , and  $\text{Al}(\text{i-C}_4\text{H}_9)_3$  [ $\text{Al}(\text{i-C}_4\text{H}_9)_3$  is incapable of association, because it has the ramified structure of carbon radical] leads to the obtained differences in distributions of polymerization centers.

The method of analysis of curves' maximums of distribution on kinetic activity and the change of kinetic activity of every active center's type was proposed. It permits the calculation of the values of concentration for every type of active centers separately.

This work was supported by Russian Foundation of Fundamental Investigations (RFFI) N0 99-03-33437 and by the Grant "Leading Research Schools" N0 00-15-97322.

## References

1. Kozlov, V. G.; Marina, N. G.; Savel'eva, I. G.; Monakov, Yu. B.; Tolstikov, G. A. *Inorg Chim Acta* 1988, 154, 239.
2. Kozlov, V. G.; Sigaeva, N. N.; Nefedjev, K. V.; Savel'eva, I. G.; Marina, N. G.; Monakov, Yu. B. *J Polym Sci, Polym Chem Ed* 1994, 32, 1237.
3. Hsien, H. L.; Yeh, G. H. C. *Rubber Chem Technol* 1985, 58, 117.
4. Monakov, Yu. B.; Marina, N. G.; Khairullina, R. M.; Kozlova, O. I.; Tolstikov, G. A. *Inorg Chim Acta* 1988, 142, 161.
5. Sigaeva, N. N.; Usmanov, T. S.; Shirokova, E. A.; Budtov, V. P.; Spivak, S. I.; Monakov, Yu. B. *Dokl Phys Chem* 1999, 365, 83.
6. Sigaeva, N. N.; Usmanov, T. S.; Budtov, V. P.; Spivak, S. I.; Monakov, Yu. B. *Polym Sci B* 2000, 42, 753.
7. ĭurinov, Yu. I.; Monakov, Yu. B.; Shamaeva, Z. G.; Marina, N. G.; Kolosnitsyn, V. S.; Nikitin, Yu. E.; Rafikov, S. R. *Izv Ākad Nauk SSSR Ser Khim* 1977, 12, 2790.
8. Benoit, H.; Crubisic, L.; Rempp, P. A. *J Polym Sci, Part B: Polym Phys* 1967, 5, 753.
9. Berg, Ā. Ā.; Kozlov, V. G.; Budtov, V. P.; ĭonakov, Yu. B.; Rafikov, S. R. *Vysokomol Soed* 1980, 22, 543.
10. Provder, T.; Rozen, E. M. *Sep Sci* 1970, 5, 437.
11. Tikhonov, A. N.; Goncharov, A. V.; Stepanov, V. V.; Yagola, A. G. *Numerical Methods for the Solution of Ill-Posed Problems*; Kluwer: Dordrecht, 1995; ISBN 0-7923-3593-X.
12. Kochikov, I. V.; Kuramshina, G. M.; Yagola, A. G. *Surv Math Ind* 1998, 8, 63.
13. Yagola, A. G. *USSR Comput Math Phys* 1980, 20, 586.
14. Tikhonov, A. N.; Leonov, A. S.; Yagola, A. G. *Nonlinear Ill-Posed Problems*; Chapman and Hall: London, 1998; ISBN 0-412-78660-5.
15. Schmeal, W. R.; Street, J. R. *J Polym Sci, Polym Phys Ed* 1972, 10, 2173.