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

N. N. Sigaeva,[1] T. S. Usmanov,[1] G. E. Zaikov,[2] Yu. B. Monakov[1]

[1]*Institute of Organic Chemistry Ufa Research Center, Russian Academy of Science, 71, pr. Oktyabrya, Ufa, 450054, Russia*
[2]*N. M. Emanuel Institute of Biochemical Physics, 4, Kosygin St., Moscow, 119991, Russia*

ABSTRACT: The influence of the organoaluminum compound on the kinetic heterogeneity of active sites in lanthanide-based diene polymerization was investigated. It was found that the heterogeneity of investigated catalytic systems was shown in the existence of four types of active centers. They were formed at the beginning of the polymerization process and produced macromolecules with lengths that were definite for each type of active center. The nature of the organoaluminum compound greatly influenced the kinetic activity of the polymerization centers. A method for analyzing the curves' maximums of distribution on kinetic activity and the change in kinetic activity of every type of active centers is proposed. This method allows calculating the concentration values for each type of active center separately. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 674–685, 2003

Key words: active site; polymerization; butadiene

INTRODUCTION

Studies of diene polymerization on lanthanide catalytic systems have shown[1–4] that the nature of the organoaluminum compound (OAC) had an essential influence both on catalytic system activity and the properties of the obtained polydienes. It has been established[1,2] that the use of various OACs define the values of constants of the reaction rate of transfer on OAC (K_t^{Al}) and the values of the reaction rate of the propagation chain as well. The use of different OACs may influence the microstructure of formed polydienes.[3] The molecular characteristics of forming polydienes depend significantly on the OAC content and nature. It was shown that for polybutadiene obtained on NdCl$_3$ṡ3L–OAC (L-tributylphosphate) catalytic system, a broad molecular-weight distribution was typical. The form depended on synthesis conditions and the nature of the OAC.[4] It was supposed that the reason for the broad molecular-weight distribution was the existence of several types of active centers.[5,6]

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

EXPERIMENTAL

Butadiene polymerization was carried out at 25°C in the presence of the two-component lanthanide catalytic system NdCl$_3$ṡ3L–OAC, where L is tributylphosphate. Al(i-C$_4$H$_9$)$_3$, Al(C$_2$H$_5$)$_3$, Al(C$_6$H$_{13}$)$_3$, and Al(C$_8$H$_{17}$)$_3$ were the organoaluminum compounds used. The complexes were prepared according to the technique described in Ref. 7. A complex was formed by an *in situ* procedure, that is, the solutions of OAC (C$_{Al}$ = 3 × 10^{-2} mol/L) and NdCl$_3$ṡ3L, were added sequentially into a toluene monomer (C$_m$ = 1.5 mol/L) solution at 25°C. The ratio Al:Nd was 30.

The 1,4-*cis* unit content was 90%–95%, the content of 1,2 units was not less than 1%, and the 1,4-*trans* structures were the rest.

The molecular weights (M_w, weight-average molecular weight, M_n, number-average weight) and 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 μ-styragel were used. The system of columns was calibrated under standards with a narrow MWD ($M_w/M_n \leq 1.2$) using the universal dependence of Benoit[8] and an equation connecting the molecular weight of polydienes with their characteristic viscosity.[9]

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

The calculation of the distribution function on kinetic heterogeneity of NdCl$_3$ṡ3L–OAC catalytic system was carried out using the Tikhonov regularization method.[11–14] The minimum Tikhonov function was reached at a regularization parameter of $\alpha = 9.4 \times 10^{-5}$ at a quadratic average error of experiment of $\delta^2 = 0.0001$. Because the kernel representing the Shultz–Flory function was chosen as a model, we assumed that error $h \to 0$.

RESULTS AND DISCUSSION

In a general view the broad polymers MWD may be represented by[15]

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

where u, the polydispersity of the polymer, is the magnitude equal to the ratio of the weight-average molecular weight to the number-average molecular weight; P is the measure of the correlation between the polymerization reaction and diffusion limits; S is a factor depending on distribution of polymerization active centers ($S \to 2$ for the 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 first-order organomagnesium monomer and catalyst. The chain transfer reactions proceed under polymerization, but they don't result in deactivation of the active centers. These facts lend support to the idea that the MWD of the polydienes obtained on these systems should be close to the most probable Flory distribution, with an M_w/M_n of about 2. However, in most cases the magnitude of polydispersity was significantly greater. The practically observed polydispersity of the distributions on molecular masses for polydienes was significantly higher than that theoretically expected because active centers that differed in reaction ability were involved in the polymerization process. There was some quasicontinuous distribution of active centers, each of which produced fractions distributed according to the law $\beta_i e^{-\beta_i M}$. Assuming that the law of catalytic centers distribution is described by the function $\varphi(\beta)$, the MWD will be:

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

where β minus the magnitude is inverse to the weight-average molecular weight, M_n, characterizing the probability of a chain transfer; β is $\beta = (1/m_0) \cdot (r_t/r_p)$ (r_p – 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 eq. (2), the values of $q_w(M)$ depend on an aspect of a cumulative distribution function on kinetic activity of the catalytic system $\varphi(\beta)$. Suppose $s = \ln \beta$ and $x = \ln M$, then it is possible to show, that $Z(s) = e^{2s}\varphi(e^s)$, $K(x,s) = \exp[x + s + \exp(x + s)]$, $U_\delta(x) = q_w(M)$, and eq. (2) is reduced to a classical Fredholm equation of the first kind:

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

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

Calculating $\varphi(\beta)$ from eq. (3) is complex in that it has to do with a class of ill-posed problems.[11–14] So direct solution of such tasks because of an error in the experimental data [the left part of eq. (3)] may even reduce to absurd outcomes.

For a wide MWD ($M_w/M_n > 3$), the numerical solution of an integral is carried out by the Tikhonov method of regularization by selecting a regularization parameter, α, at which, experimentally defined and calculated from eq. (2), functions $q_w(M)$ coincide within the given error (δ). In addition to the obtained solutions, $\varphi(\beta)$ should satisfy a condition of normalization:

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

Because β 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 polybutadiene molecular-weight dependence on monomer conversion is analogous for all used catalytic systems (Fig. 1). At the initial stage of polymerization M_w grows; when conversion reaches 20%–40%, this growth ceases, and further conversion growth leads either to constant values of molecular masses or to a small reduction of M_w. Such molecular mass change is typical for ion-coordinated diene polymerization processes and the invariable number of active centers; it is caused by the occurrence of chain
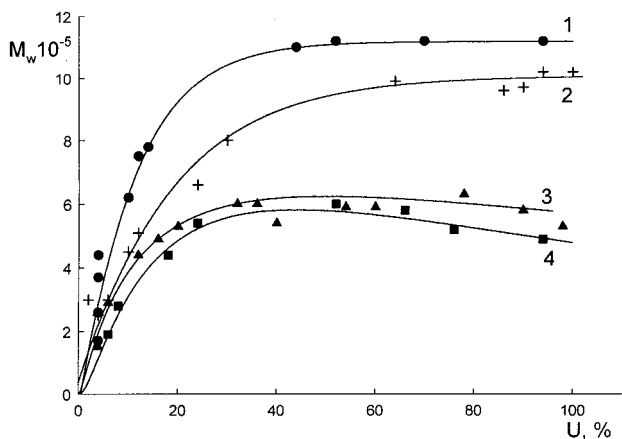
Figure 1 The plots of M_w for polybutadiene versus the monomer conversion under polymerization on NdCl$_3$ṡ3L–OAC catalytic system. OAC: 1—Al(i-C$_4$H$_9$)$_3$, 2—Al(C$_2$H$_5$)$_3$, 3—Al(C$_8$H$_{17}$)$_3$, 4—Al(C$_6$H$_{13}$)$_3$. Polymerization conditions: toluene—C_M = 1.5, C_{Al} = 3 × 10^{-2} mol/L, Al/Nd = 30, T_{pm} = 25°C.

transfer processes and monomer reducing during polymerization.

The largest polybutadiene molecular masses were observed under Al(i-C$_4$H$_9$)$_3$, then Al(C$_2$H$_5$)$_3$, Al(C$_8$H$_{17}$)$_3$, and Al(C$_6$H$_{13}$)$_3$ usage under equal conditions (Fig. 1). As the conversion increased (Fig. 2) molecular-weight distribution curves were displaced into the higher molecular-weight region. Polydispersity of the polymer increased by this. The growth of polydispersity during polymerization was observed for all investigated catalytic systems (Figs. 2–5). However, the form of polybutadiene MWD curves was changed when using various
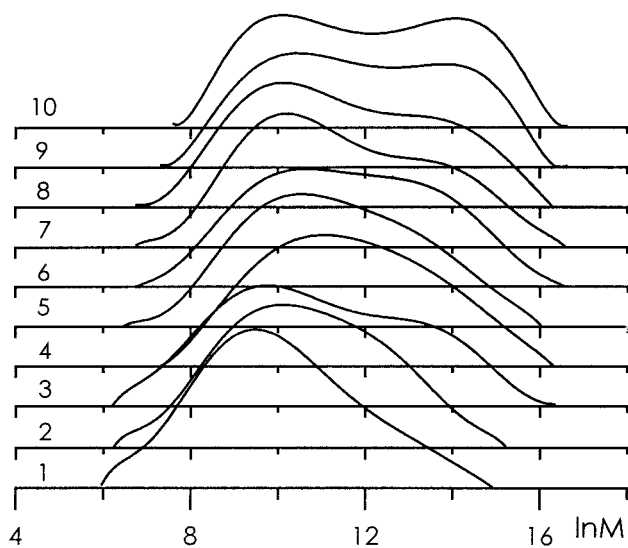

Figure 3 Molecular weight distribution curves for polybutadiene obtained on NdCl$_3$ṡ3L–Al(C$_6$H$_{13}$)$_3$ catalytic system. Polymerization conditions are given in Figure 1. Monomer conversion (%): 1—1.7; 2—8.7; 3—89.4. M_w/M_n: 1—4.8; 2—7.3; 3—17.8.

OACs. As follows from the data shown in Figures 2 and 3, the MWD curves of polybutadiene obtained with the use of Al(i-C$_4$H$_9$)$_3$ and Al(C$_6$H$_{13}$)$_3$ were monomodal. Polymer synthesized on NdCl$_3$ṡ3L–Al(C$_2$H$_5$)$_3$ was characterized by a bimodal distribution. The MWD curves of polybutadiene obtained with Al(C$_8$H$_{17}$)$_3$ as the OAC changed their form during the polymerization process. A broadband appeared on the curves in the region of

Figure 2 Molecular weight distribution curves for polybutadiene obtained on NdCl$_3$ṡ3L–Al(i-C$_4$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.
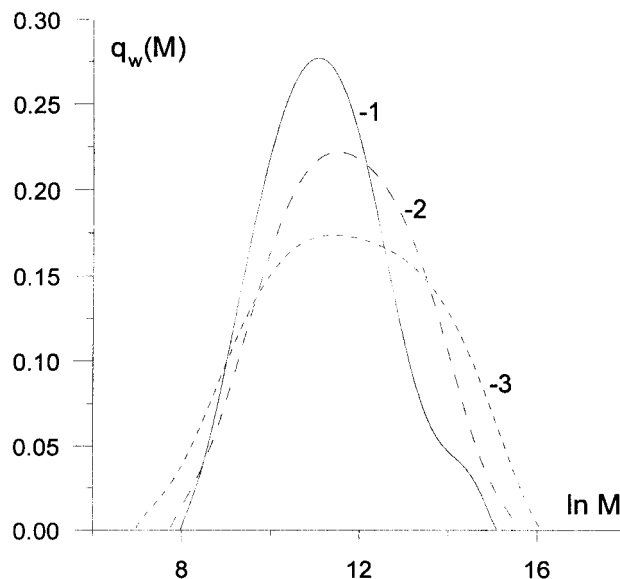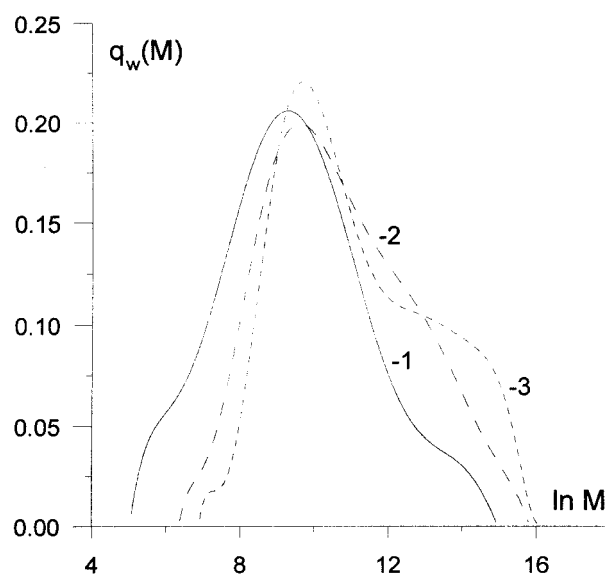

Figure 4 Molecular weight distribution curves for polybutadiene obtained on NdCl$_3$ṡ3L–Al(C$_8$H$_{17}$)$_3$ catalytic system. Polymerization conditions are given in Figure 1. Monomer conversion (%): 1—3.1; 2—21.6; 3—91.3. M_w/M_n: 1—18.2; 2—18.6; 3—20.8.
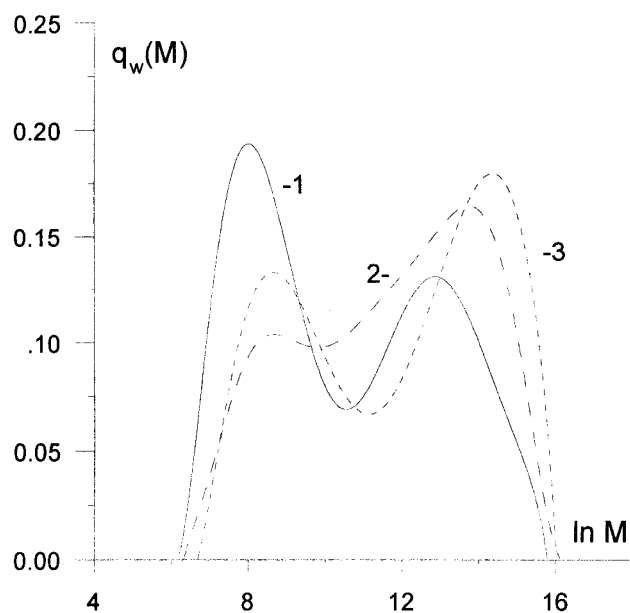
Figure 5 Molecular weight distribution curves for poly-butadiene obtained on $NdCl_3 \dot{s} 3L–Al(C_2H_5)_3$ catalytic system. Polymerization conditions are given in Figure 1. Monomer conversion (%): 1—3.2; 2—9.6; 3—88.0. M_w/M_n: 1—28.3; 2—42.2; 3—55.2.

molecular masses' high values at high monomer conversions.

Distributions of the kinetic activity of the investigated catalytic systems $NdCl_3 \dot{s} 3L–OAC$ were obtained with the help of the Tikhonov regularization method on the base of the MWD curves of the polybutadiene obtained experimentally (Figs. 6–9).

All curves of distribution on kinetic activity are polymodal independently of the nature of the OAC being used, and four greatly expressive maximums appear with an increase in the degree of conversion. This testifies to the polymerization process occurring on at least four types of active centers for all investigated systems. Moreover, multimodality of $\psi(\ln \beta)$ curves is obtained even with very small monomer
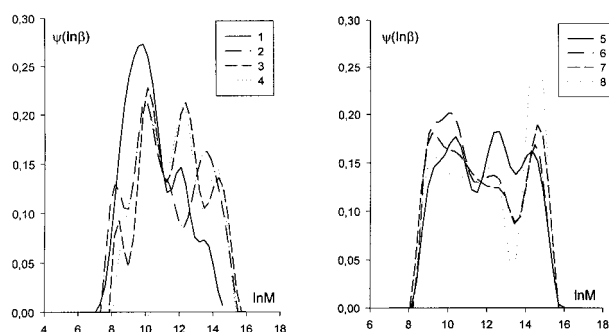

Figure 6 Activity distributions of the $NdCl_3 \dot{s} 3L–Al(i-C_4H_9)_3$ catalytic system under butadiene polymerization. Monomer conversions (%): 1—3.61; 2—11.1; 3—17.4; 4—25.6; 5—55.6; 6—67.8; 7—87.9; 8—88.8.
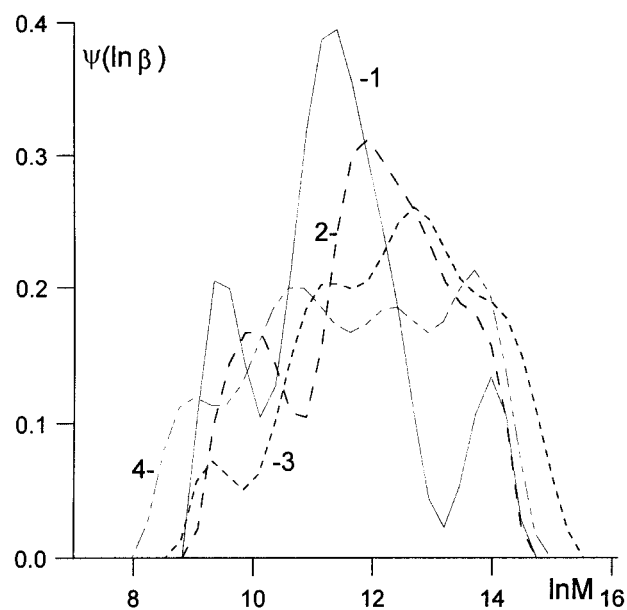

Figure 7 Activity distributions of the $NdCl_3 \dot{s} 3L–Al(C_6H_{13})_3$ catalytic system under butadiene polymerization. Monomer conversions (%): 1—1.7; 2—8.7; 3—26.2; 4—72.0.

conversions. This indicates that different types of active sites are formed immediately at the initial stage of the process, that is, the catalytic system is primordially kinetically heterogeneous.

Every point on the distribution curves characterizes the active centers' part in the chain termination probability equal to β_1 and produces macromolecules with molecular mass M_1. The presence of the $\psi(\ln \beta)$ distribution itself testifies to the kinetic heterogeneity of the catalytic system.
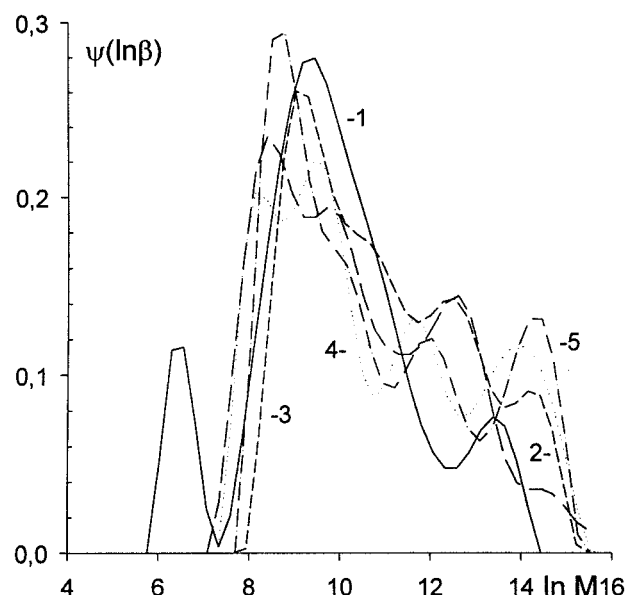

Figure 8 Activity distributions of the $NdCl_3 \dot{s} 3L–Al(C_8H_{17})_3$ catalytic system under butadiene polymerization. Monomer conversions (%): 1—3.1; 2—13.4; 3—21.6; 4—49.6; 5—57.9.

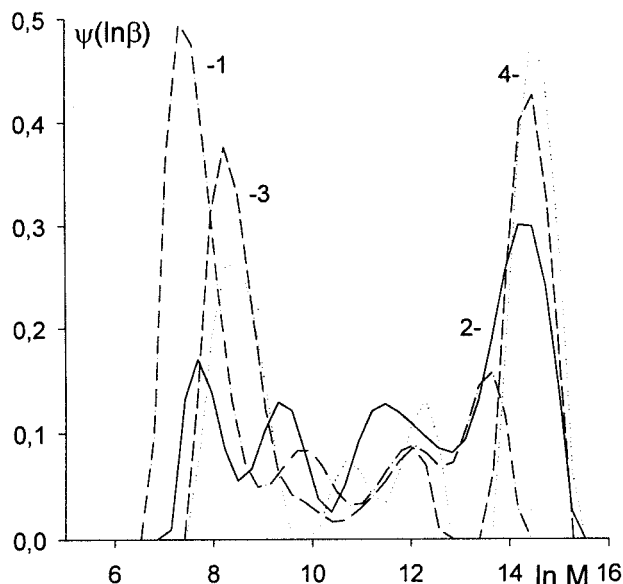**Figure 9** Activity distributions of the $NdCl_3\dot{s}3L-Al(C_2H_5)_3$ catalytic system under butadiene polymerization. Monomer conversions (%): 1—3.2; 2—9.6; 3—40.2; 4—88.0.

Distributions of the kinetic activity of the catalytic system $NdCl_3\dot{s}3L-Al(C_2H_5)_3$ (Fig. 9) differed from the $\psi(\ln \beta)$ curves, obtained by the presence of $Al(i-C_4H_9)_3$, $Al(C_6H_{13})_3$, and $Al(C_8H_{17})_3$. For the system with $Al(C_2H_5)_3$ the presence of two clear maximums was characteristic. They corresponded to the active centers that produced the very low molecular and the very high molecular polymer fractions. These two types of active centers produced the bulk of polymer, and the polymerization product fractions produced on every active center differed greatly in molecular mass—low molecular fraction ($10^3/10^4$) and high molecular fraction ($\sim 10^6$). The contribution of active centers that formed macromolecules with intermediate values of molecular mass was not significant. Apparently, as a consequence of such unequivalent action of the active centers of the $NdCl_3\dot{s}3L-Al(C_2H_5)_3$ catalyst, the formed polybutadiene had a bimodal MWD.

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

Figure 11 presents the change in positions of the maximums, obtained by dividing the curve of kinetic activity distribution of the catalytic system $NdCl_3\dot{s}3L-Al(i-C_4H_9)_3$ into separate peaks versus monomer conversion. It can be said that the positions of the maximums corresponding to the various types of active centers remained

virtually unchanged throughout the polymerization process. That is, each active center seemed to synthesize macromolecules of a certain length.

In addition, the active centers of the catalytic systems with $Al(i-C_4H_9)_3$, $Al(C_6H_{13})_3$, and $Al(C_8H_{17})_3$ produced fractions with identical molecular mass. Thus, the active center, which produced the highest molecular fraction, formed polymer with a molecular mass of about 10^6—the first active center producing the smallest molecular mass, $7/8 \times 10^3$; the second and the third, 2×10^4 and 1.5×10^5, respectively. For the system with $Al(C_2H_5)_3$, the position of the first (low molecular) peak differed slightly, the corresponding active center producing polymer with a molecular mass of about 3×10^3, that is, product with a low molecular mass, compared with catalysts on the base 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 was changed throughout the polymerization process. Figure 12 shows the changes in kinetic activity of every active center under the butadiene polymerization process on the catalytic system $NdCl_3\dot{s}3L-Al(C_2H_5)_3$. It is obvious that active centers generating the lowest molecular fractions and corresponding to the first maximum on the distribution curve are char-
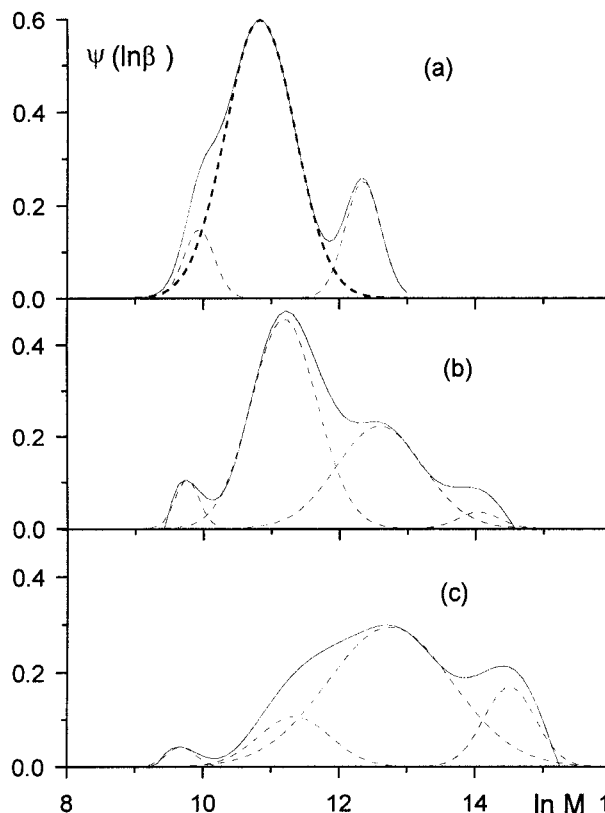

Figure 10 Activity distributions of the $NdCl_3\dot{s}3L-Al(i-C_4H_9)_3$ catalytic system divided into separate peaks. Monomer conversions (%): a—2.6; b—7.5; c—53.4.
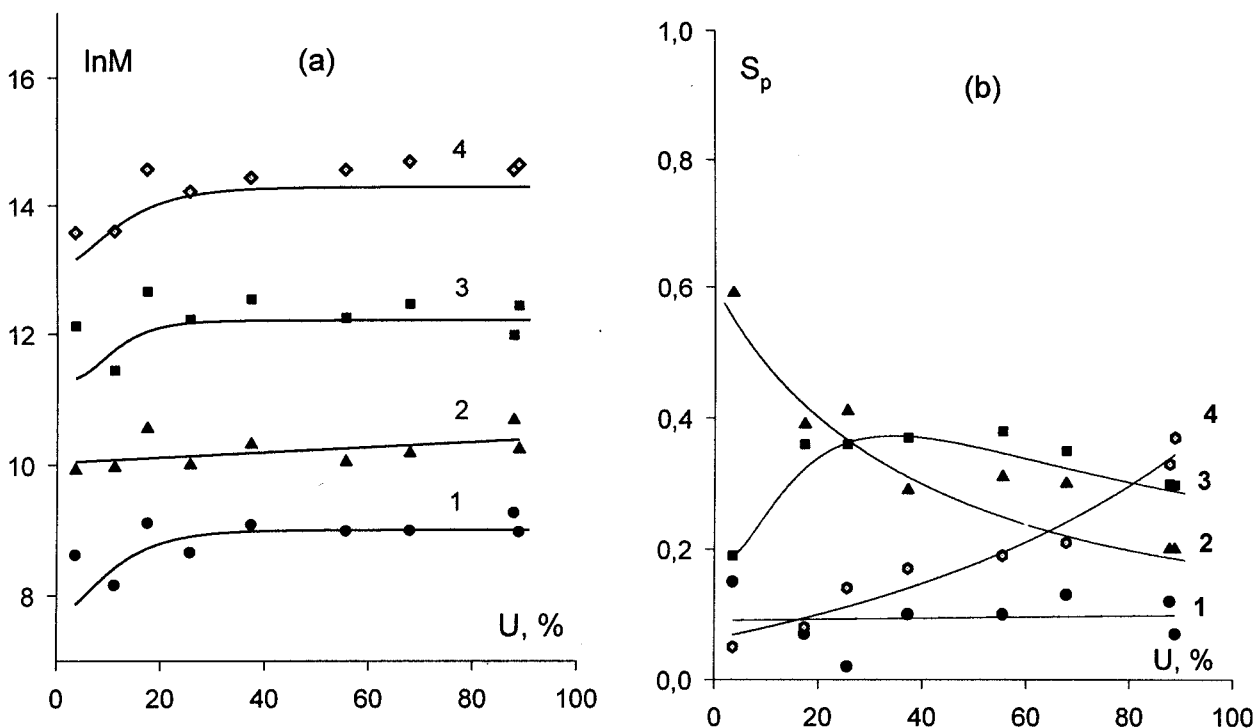
Figure 11 Positions of (a) maximums and (b) kinetic activity of butadiene polymerization centers versus monomer conversion. $NdCl_3\dot{s}3L–Al(i-C_4H_9)_3$ catalytic system.

acterized by very low activity, which is slightly increased in the course of polymerization.

A reduction in activity was obtained for the second active-center type, growth with saturation for the third, and a constant activity increase throughout polymerization for the fourth type. Some disconnection of data can be explained by the static nature of the polymerization process. It is really difficult to prepare two polymer products with equal molecular masses and consequently with identical MWDs in two different experiments. In their turn, even insignificant deviations in MWD form lead to essential changes in the distributions of kinetic activity. However, the tendency of the activity changes of various centers can be estimated. Curves of the kinetic activity change of $NdCl_3\dot{s}3L–OAC$ catalytic systems are separately grouped for every type of active center type in Figure 13. This permits the establishment of the tendency of kinetic heterogeneity change of catalytic systems containing different organoaluminum compounds. It is obvious that with the use of $Al(i-C_4H_9)_3$, $Al(C_6H_{13})_3$, and $Al(C_8H_{17})_3$ as organoaluminum compounds, kinetic activity of all four center types was different in intensity but was equally changed with monomer conversion. Active centers generating the lowest molecular fractions increased their activity in the course of polymerization. The activity of this center was decreased for the catalytic system using $Al(C_2H_5)_3$. The activity of centers corresponding to the second and third maximums decreased for all catalytic systems

used. There was constant growth for the fourth type of active center, independently of use in the catalytic system organoaluminum compound. The low intensity values of the second and the third peaks for $NdCl_3\dot{s}3L–Al(C_2H_5)_3$ catalytic system also must be noted.

The kinetic activity change of the four active-center types of the investigated catalytic systems at various ratios of Al/Nd is depicted in Figure 14. It is obvious that the course of kinetic activity dependence on the Al/Nd ratio practically coincides with the use of $Al(i-C_4H_9)_3$, $Al(C_6H_{13})_3$, and $Al(C_8H_{17})_3$, as in the conversion curves. There are increases of activity for the first and the second peaks, and activity decrease for the third, with the fourth peak showing growth of OAC content in the catalytic system. In contrast to the other investigated catalysts, for the catalytic system $NdCl_3\dot{s}3L–Al(C_2H_5)_3$ the first maximum had high activity values, which were slightly reduced with the increase of the Al/Nd ratio. The change in the fourth peak intensity also differed from the rest of the catalytic systems. With $Al(C_2H_5)_3$ content growth its intensity increased.

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

The influence of the butadiene polymerization temperature on the distributions of kinetic activity of the investigated catalytic systems was also studied (Fig.
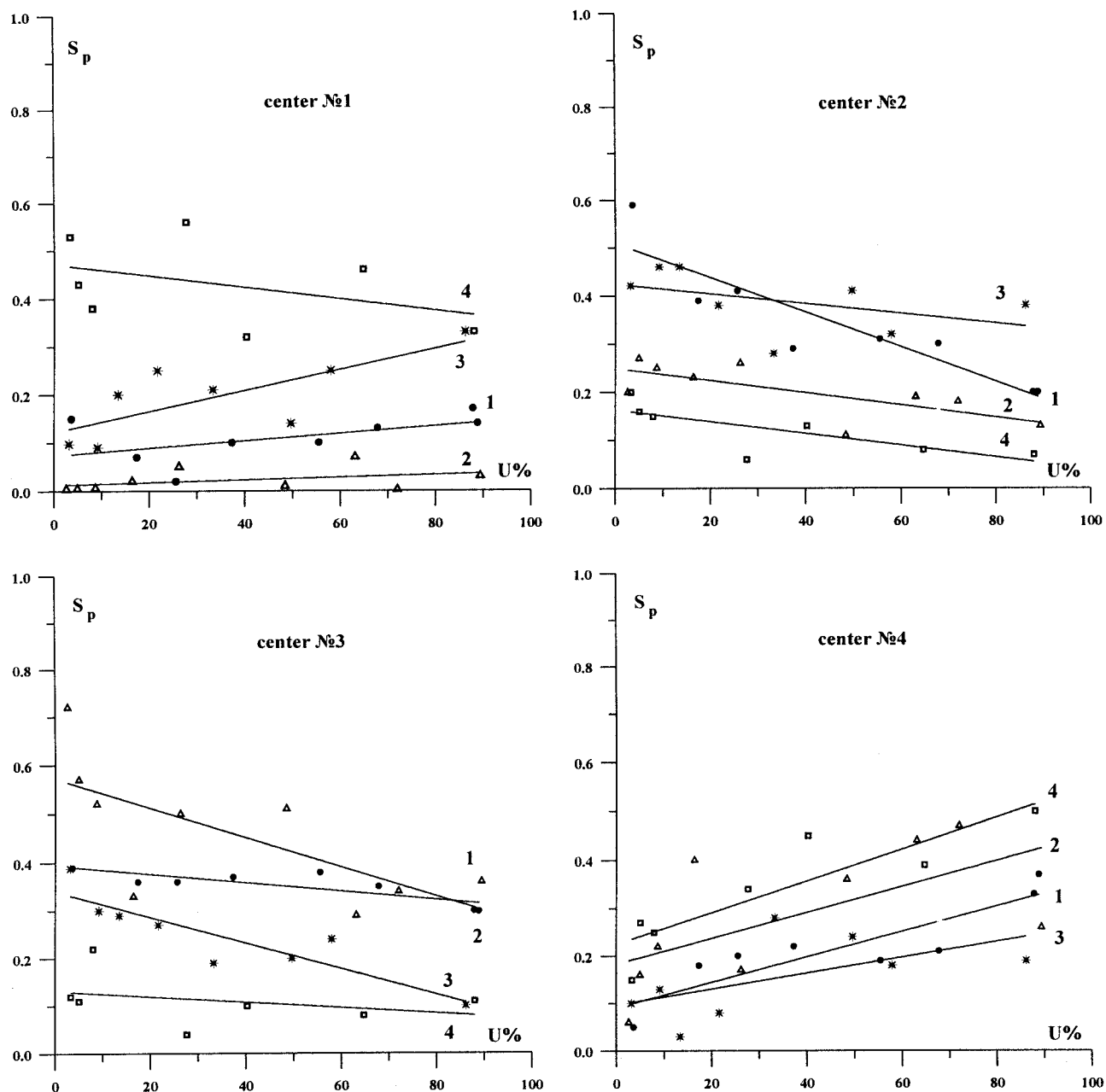
Figure 12 The plots of kinetic activity of four types of butadiene polymerization active centers versus monomer conversion. $NdCl_3$s3L–OAC catalytic system [1—$Al(i$-$C_4H_9)_3$, 2—$Al(C_6H_{13})_3$, 3—$Al(C_8H_{17})_3$, 4—$Al(C_2H_5)_3$]. Polymerization conditions are given in Figure 1.

16). It is obvious that with a temperature increase, the intensity of the second and third peaks, which had been producing low molecular polymer, grew. In contrast, the centers responsible for generating high molecular fractions (peaks 3 and 4) decreased their activity. Obviously, the active centers forming high molecular fractions were less thermostable than the active centers on which the low molecular polymer was formed. As for conversion dependence, the kinetic activity of centers corresponding to peaks 2 and 3 was very low when using $Al(C_2H_5)_3$ as the organoaluminum component.

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

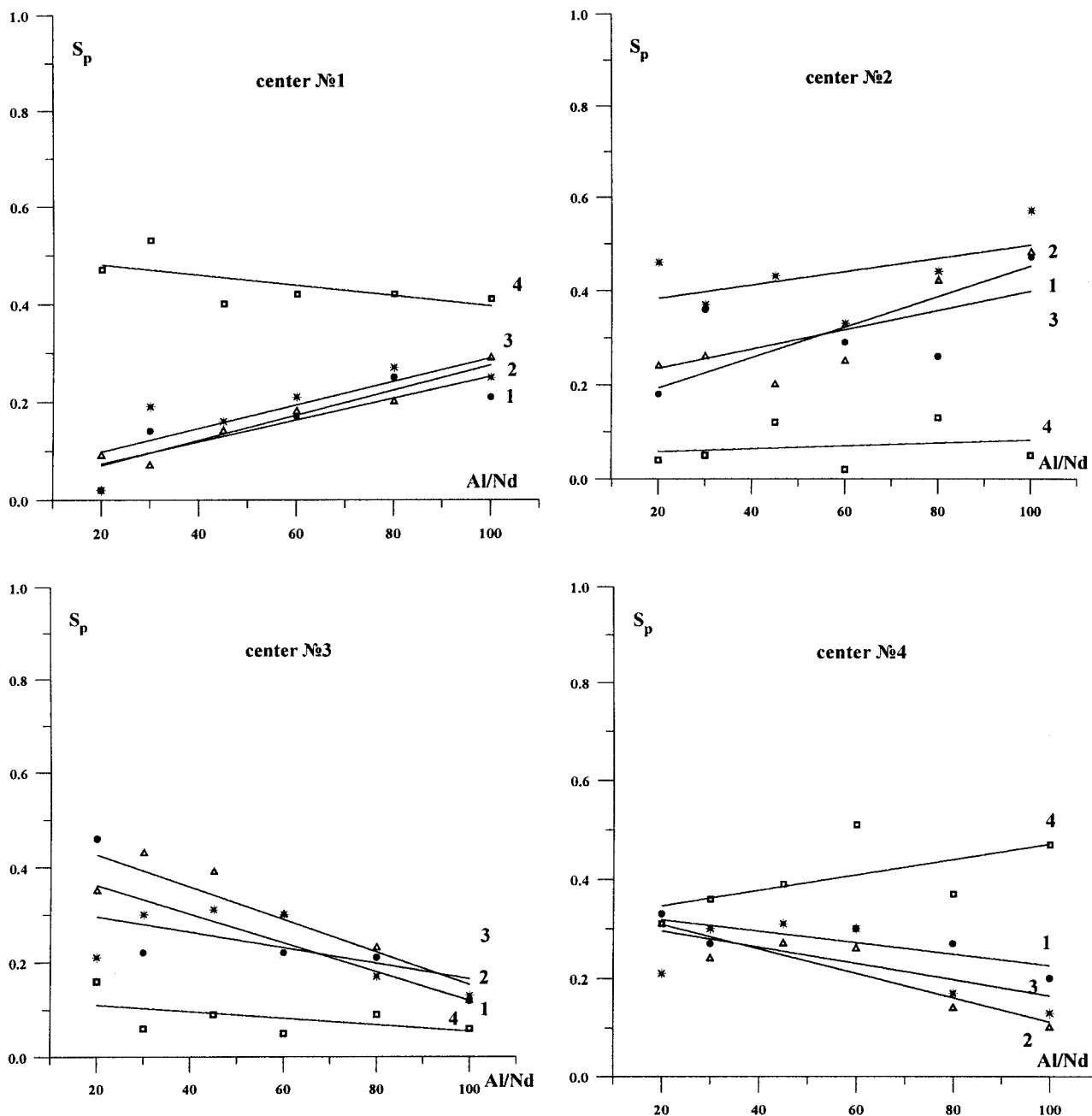$$S_i = \frac{Q_{oi}}{Q_o} \tag{5}$$

Suppose

Figure 13 Kinetic activity change of butadiene polymerization centers at various ratios of Al/Nd. $NdCl_3\dot{s}3L$–OAC catalytic system [1—$Al(i\text{-}C_4H_9)_3$, 2—$Al(C_6H_{13})_3$, 3—$Al(C_8H_{17})_3$, 4—$Al(C_2H_5)_3$].

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

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

Then the magnitude

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

is the number of "dead" chains formed on the ith center by transfer reactions to monomer and OAC at conversion moment x, where k_{mi} and k_{Ali} are the rate constants for the reactions of the chain transfer to the monomer and OAC, respectively; 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 ith center is

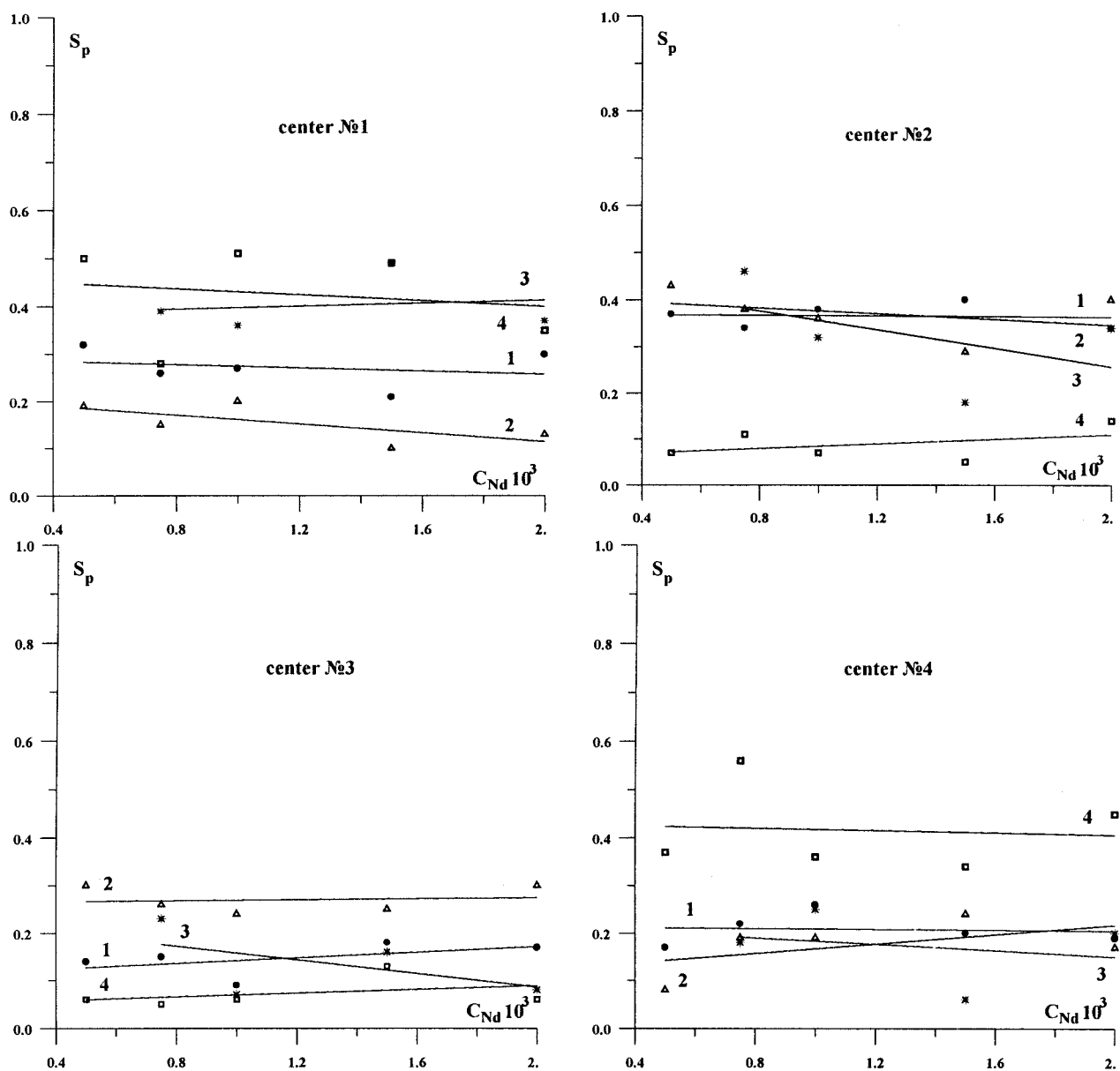$$Q_{oi} = C_{ai} + \frac{k_{mi}C_m + k_{Ali}C_{Al}}{k_{pi}C_m} \cdot \frac{C_{m0}C_{ai}}{\sum C_{ai}} x \qquad (8)$$

Figure 14 Kinetic activity change of butadiene polymerization centers at various catalyst concentrations. NdCl₃·3L–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)$_3$].

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:

$$Q_0 = \frac{C_{m0}}{P_n} x \qquad (9)$$

With regard to eqs. (8) and (9) after noncomplicated transformations, eq. (5) may be represented as

$$\frac{S_i C_{m0} x}{P_n} = C_{ai}\left[1 + \frac{C_{m0} k_{mi}}{k_{pi} \Sigma C_{ai}} x + \frac{C_{Al} k_{Ali} C_{m0}}{C_m k_{pi} \Sigma C_{ai}} x \right] \qquad (10)$$

Then let's assume:

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

The position of the maximum curve of distribution of kinetic activity characterizes the degree of polymerization, P_{ni}, of the polymer fractions formed on the corresponding active centers. The degree of polymerization, in turn, is determined as a ratio of the monomer quantity, μ, reacted on ith center and the number of chains, Q_{0i}, formed on it.

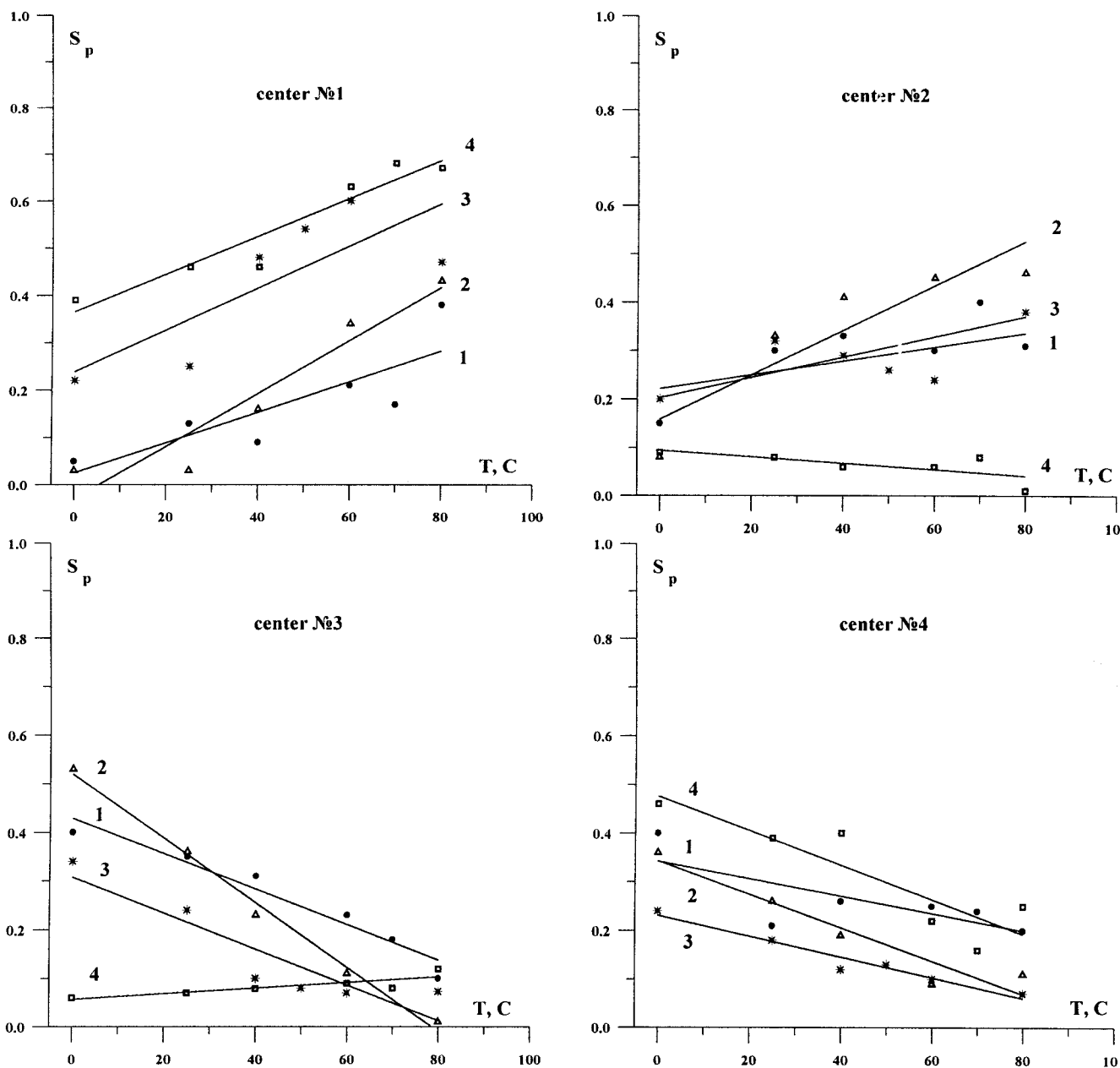Using eq. (6), the following is obtained:

Figure 15 Kinetic activity change of butadiene polymerization centers at various polymerization temperatures. $NdCl_3\acute{s}3L$–OAC catalytic system [1—$Al(i-C_4H_9)_3$, 2—$Al(C_6H_{13})_3$, 3—$Al(C_8H_{17})_3$, 4—$Al(C_2H_5)_3$].

$$P_{ni} = \frac{C_{m0}C_{ai}}{Q_{0i}\,\Sigma\,C_{ai}}\,x \qquad (11)$$

Taking into account that conversion is determined as

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

for the initial polymerization moment, at $\tau \rightarrow 0$, it can be assume that

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

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

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

As it follows from eq. (13), the angle of dependences of P_{ni} on τ at $\tau \rightarrow 0$ is a constant magnitude for all active centers and characterizes this catalytic system. Thus, the positions of the maximums shifting, as shown in Figure 10, at the initial moment of polymerization is a natural phenomenon, and this effect
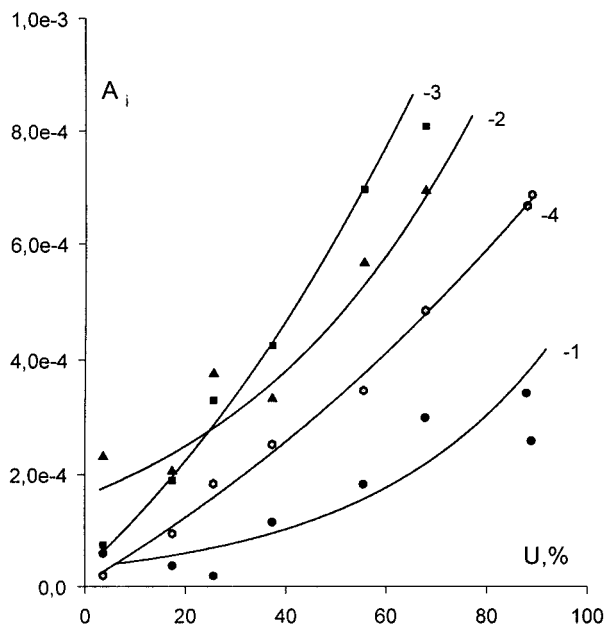
Figure 16 The plot of A_i versus monomer conversion under butadiene polymerization on $NdCl_3 \cdot 3L–Al(i-C_4H_9)_3$ catalytic system.

should be observed in all cases in a more detailed study of the polymerization process at low conversions.

The following expression for analysis P_{ni} by substituting eq. (8) in eq. (11) can be obtained:

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

Equations (10) and (14) permit a clearer analysis of the change in kinetic activity of the catalytic systems. The dependences of magnitude A_i on monomer conversion x are depicted in Figure 15. Extrapolation of these curves to zero conversion, according to eqs. (10) and (14), makes it possible to determine C_{ai}, the concentration of every active center separately, and also the total concentration of the polymerization centers, ΣC_{ai}.

The various concentrations of different active-center types under butadiene polymerization of the investigated catalytic systems are shown in Table I. ΣC_{ai} is the total concentration of all the types of active centers;

the values $\langle C_a \rangle$ are also the total concentration of the active centers, but they were obtained by analysis of polymerization process kinetics using the equation

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

It is obvious that results of both calculation methods are in good agreement, confirming that adequacy of the model used.

CONCLUSION

Thus, heterogeneity of the investigated catalytic systems has been shown by the existence of four types of active centers. They were formed at the beginning of the polymerization process and produced macromolecules of lengths that were definite for each type of active center. The kinetic activity of the polymerization centers depended on the concentration and nature of the OAC and on the polymerization temperature. For the catalytic systems with $Al(i-C_4H_9)_3$, $Al(C_6H_{13})_3$, and $Al(C_8H_{17})_3$ the kinetic activity of polymerization centers changed equally versus the polymerization conditions and the change in monomer conversion. Perhaps this is a consequence of the identical structure of different active centers types of these catalytic systems.

The difference in the distributions of kinetic activity and the behavior of active centers of the catalytic system with $Al(C_2H_5)_3$ and the similarity of the behavior of the systems with $Al(i-C_4H_9)_3$, $Al(C_6H_{13})_3$, and $Al(C_8H_{17})_3$ can be explained by the difference in degree of association of free OAC molecules in the polymerization system. It is known that organoaluminum compounds with direct carbon chains are dimeric. The inclination to association is greatly increased with the decrease in carbon radical length. Thus, the dimer molecules of $Al(C_2H_5)_3$ were stable even in a vaporous state and dissociated only at temperature greater than 100°C. In solution $Al(C_2H_5)_3$ took a monomer shape only with dilutions of greater than 0.1% concentration. Probably, the greater inclination to association of $Al(C_2H_5)_3$ molecules [in comparison with $Al(C_6H_{13})_3$, $Al(C_8H_{17})_3$, and $Al(i-C_4H_9)_3$ ($Al(i-C_4H_9)_3$ is incapable of association because it has the ramified structure of a carbon radical] leads to the

TABLE I
Neodymium Catalytic System Active Center Concentrations under Butadiene Polymerization

| Catalytic system | $C_{ai} \cdot 10^5$ (mol/L) | | | | $\Sigma C_{ai} \cdot 10^5$ (mol/L) | $\langle C_a \rangle \cdot 10^5$ (mol/L) |
	C_{a1}	C_{a2}	C_{a3}	C_{a4}		
$NdCl_3 \cdot 3L–Al(i-C_4H_9)_3$	3.9	21.7	7.5	5.7	38.8	40.1
$NdCl_3 \cdot 3L–Al(C_6H_{13})_3$	0.05	0.9	1.5	0.8	3.3	3.0
$NdCl_3 \cdot 3L–Al(C_8H_{17})_3$	2.39	6.2	6.9	28.7	65.6	65.0
$NdCl_3 \cdot 3L–Al(C_2H_5)_3$	6.8	3.9	3.0	6.8	20.5	25.0

obtained differences in distributions of the polymerization centers.

In this article a method of analysis of the curves' maximums of distribution of kinetic activity and the change of kinetic activity of every type of active center was proposed. It permits the calculation of the concentration values of every type of active center separately.

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