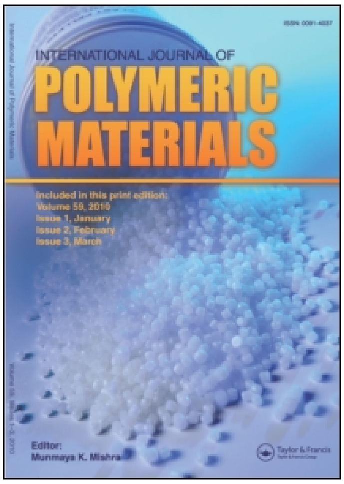

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Determination of a Cumulative Distribution Function of Kinetic Activity of Lanthanide Ion-coordination Catalytic Systems Used for Diene Polymerization

N. N. Sigaeva[a]; T. S. Usmanov[a]; V. P. Budtov[a]; S. I. Spivak[a]; Yu. B. Monakov
[a] The Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, Russia, Ufa, Prospekt Oktyabrya

To cite this Article Sigaeva, N. N. , Usmanov, T. S. , Budtov, V. P. , Spivak, S. I. and Monakov, Yu. B.(2001) 'Determination of a Cumulative Distribution Function of Kinetic Activity of Lanthanide Ion-coordination Catalytic Systems Used for Diene Polymerization', International Journal of Polymeric Materials, 49: 4, 475 — 489

To link to this Article: DOI: 10.1080/00914030108035879

URL: http://dx.doi.org/10.1080/00914030108035879

Intern. J. Polymeric Mater., 2001, Vol. 49, pp. 475–489
Reprints available directly from the publisher
Photocopying permitted by license only

Determination of a Cumulative Distribution Function of Kinetic Activity of Lanthanide Ion-coordination Catalytic Systems Used for Diene Polymerization*

N. N. SIGAEVA, T. S. USMANOV, V. P. BUDTOV,
S. I. SPIVAK and Yu. B. MONAKOV†

The Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, Russia, 450054, Ufa, Prospekt Oktyabrya, 71

(Received 1 December 1999; In final form 16 December 1999)

From the experimentally obtained of curves 1,4-*cis*-polybutadiene molecular weight-distribution the cumulative distribution functions on kinetic activity of polymerization centers of $NdCl_3 3L\text{-}Al(i\text{-}C_4H_9)_3$ catalytic system are obtained by the Tikhonov regularization procedure. At least four types of active sites distinguished by kinetic activity are detected. The influence of polymerization condition and concentration of the components of the polymerization system on a modification of their activity is shown.

Keywords: Lanthanide catalytic systems; Active sites; Distribution on kinetic activity; Regularization method

INTRODUCTION

The lanthanide catalytic systems allow to obtain stereoregular polydienes with a high content (up to 98%) of 1,4-*cis*-units and the

---

* This work was supported by Russian Foundation of Fundamental Investigations (RFFI) No. 99-03-33437.

† Corresponding author. Tel.: (3472)35-60-96.

total absence of an insoluble gel fraction and low molecular oligomers [1–3]. However, at the same time, the polymers obtained on them are characterized by broad molecular weight distribution (MWD), large in a comparison with those theoretically predicted [4]. It is possible to assume that the process of diene polymerization in the presence of lanthanide catalysts proceeds on centers with different kinetic parameters.

It is well known that various types of active sites coexist on the surface of heterogeneous catalytic systems [5–11]. The broadened molecular weight distribution [5–8], the presence of polymer fractions with different stereoregularity [9, 10], and the broad distribution of copolymer composition [11] are believed to be the result of active sites multiplicity. However, in spite of the fact that the non-uniformity of ion-coordination catalysts was considered repeatedly, it is still very difficult to determine the actual distribution of active sites, namely, the number, kinetic parameters, stereospecificity for each active center type.

It is usual for scientist to point out only the presence of various active centers, but there are a few reports where the distribution was obtained [12–16]. Moreover, by distribution they mean different, in a physical sense, cumulative distribution functions. So in [12] was calculated the distribution of active sites over activation energy of Ti—C bond thermal destruction obtained from mass-spectrometric study of temperature programmed desorption products from the catalyst surface of olefin gas-phase polymerization. In [13] the distribution of active sites is a superposition of 3–5 Schulz-Flory most probable distribution peaks of different positions and intensities; in [15] the distribution was obtained by fractionating the polymer according to molecular weight and determining the number of active centers in each fraction.

However, all these works are still an indirect way to study the active center distribution, which needs to be confirmed by more direct results. In this connection it should be noted that in [16] the kinetic activity distributions were obtained with no assumptions made on the polymerization mechanism.

In this article we report results of active center distribution obtained in more direct way for diene polymerization, namely, by the Tikhonov regularization method.

EXPERIMENTAL

The butadiene polymerization was carried out in the presence of the catalytic system $NdCl_3 \cdot 3L-Al(i\text{-}C_4H_9)_3$, where L-tributilphosphate.

The complexes were prepared according to the technique described in [17]. A complex formed by an *in-situ* procedure, *i.e.*, the solutions of $Al(i\text{-}C_4H_9)_3$ and $NdCl_3 \cdot 3L$, were added sequentially into a toluene monomer solution at 25°C.

The molecular weight distribution (MWD) of 1,4-*cis*-olybutadiene was estimated by gel permeating chromatography (chloroform, 1 ml/min, 25°C). Four "Waters" columns packed with 10^6 Å, 10^5 Å, 10^4 Å and 10^3 Å μ-styragel were used. The system of columns was calibrated under the standards with narrow MWD ($M_w/M_n \leq 1,2$) using the universal relationship of Benoit [18] and equation connecting the molecular weight of polydiene with it's characteristic viscosity [19].

Theory and Method of Computation

Extremely broad molecular weight distributions are common in Ziegler polymerization. In a general view the breadth of polymers MWD can be represented by [20]:

$$Q = PSX \tag{1}$$

where Q-polydispersibility of polymer, is magnitude equal to the ratio of a weight-average molecular weight to a number-average molecular weight; P is measure of importance of diffusion; S is a function of site activity distribution; and X is function of particle size distribution.

Diffusion, as a rate controlling mechanism, adds new dimensions to the complexity of polymerizations in which dispersed-phase catalysts produce insoluble polymer. The accumulation of polymer on the catalyst may "block up" to varying degrees different sites from the penetrating monomer. As result of this a very broad molecular weight distribution may be produced. A particle size distribution will also effect a broadening of molecular weight distribution but only for diffusion-controlled polymerization.

The other way in which the broad molecular weight distributions may be generated is by catalyst which has a distribution of site activities. Thus, some sites may produce short chains and other sites may produce longer chains, and as a result the collection of chains has a broad molecular weight distribution and a large Q value.

The lanthanide catalytic systems, in contrast to classical Zigler catalysts, are homogeneous, therefore it is possible to assume that the diffusion restrictions are insignificant and to neglect functions P and X in Eq. (1). In other words, it is the case, when the breadth of molecular weight distribution will depend only on the non-uniformity of active sites.

When the polymerization proceeds by coordination mechanism with chemical reactions constants and reagents concentration kept invariable, the differential weight distribution of "dead chains" is described by the most probable distribution (Flory distribution):

$$q_w(M) = M\beta^2 \exp(-\beta M) \tag{2}$$

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

In the case of the catalyst with active sites differing in chain transfer probability, the polymer MWD is defined as:

$$q_w(M) = \int_0^\infty \varphi(\beta) M^2 \exp(-\beta M) d\beta \tag{3}$$

where $\varphi(\beta)$ – required cumulative kinetic activity distribution function of a catalytic system.

The complexity of calculating $\varphi(\beta)$ from the Eq. (3) is in the fact that it has to do with the class of ill-posed problems.

If in experiments $q_w(M)$ can be determined to a high degree of precision, then the solution for $\varphi(\beta)$ can be obtained with a high degree of confidence regardless of the method used (Fourier transform or other). In reality this condition can't be fulfilled and as a result the uncertainties in experimental data are easily transformed into oscillations in $\varphi(\beta)$. This problem is more severe when the level of experimental errors δ is large. It is also more pronounced at the ends of molecular weight distribution curve where the $q_w(M)$ function is even less precisely known.

To overcome these difficulties we used the Tikhonov regularization method [21–25], permitting to avoid the emerging undesirable "oscillation" in a sought solution.

Changing to new variables $x = \ln M$, $s = \ln \beta$; $U_\delta(x) = q_w(M)$, Eq. (3) can be presented as an integral equation of the Fredholm of the first sort:

$$Az \equiv \int_{-\infty}^{\infty} K(x,s)Z(s)ds = U_\delta(x), \tag{4}$$

where $K(x,s) = \exp[s + x - \exp(x + s)]$ – kernel of an integral equation (4), and $Z(s) = \varphi(e^s)\, e^{2s}$.

With the use of the Tikhonov's regularization method such solution as $Z_\alpha\,(s)$ is determined, which minimizes the functional $M_\alpha(Z)$:

$$M_\alpha(Z) = \int_a^b [Az - U_\delta(x)]^2 dx + \alpha\Omega[Z] \tag{5}$$

($\alpha > 0$ is the regularization parameter). The first part of $M_\alpha(Z)$ is a discrepancy which shows how well the vector satisfies the equation $A_h z = U_\delta$. The second part estimates the deviations of solution from zero (the so-called "stabilizer" of Tikhonov's functional). We were limited to considering the stabilizer of the first order:

$$\Omega(Z) = \int_a^b \left[Z^2 + \left(\frac{\partial Z}{\partial s}\right)^2\right] ds. \tag{6}$$

It was been proved [21], that the minimum of the Tikhonov's functional $M_\alpha(Z)$ is achieved on function $Z_\alpha(s)$. In a method of a regularization of the first order, from conditions of the functional $M_\alpha(Z)$ minimum, the Euler equation follows:

$$\alpha[Z(x) - Z(x)] + \int_a^b B(x,s)Z(s)ds = V(x), \tag{7}$$

$$B(x,s) = \int_a^b K(t,x)K(t,s)dt; \tag{8}$$

$$V(x) = \int_a^b K(t,x)U_\delta(t)dt. \tag{9}$$

As a result, instead of Eq. (4) we need to solve an integral equation of the second sort, Eq. (7). The solution of Eq. (7) with an optimum choice of the parameter α is steady since the addend $\alpha Z(x)$ shifts the whole spectrum of eigenvalues of an integrated spectrum: $\int_a^b K(x,s) Z(s)ds$ on magnitude α.

The definition of a parameter α is the most important step in the regularization method. Herein generalized-discrepancy principle was used to choose the regularization parameter. In this mode the errors δ of the input data were used as additional information:

$$\gamma(\alpha) = \|A_h Z - U_\delta\|^2 - (\delta + h\Omega(Z))^2$$

where h is an error of an operator A in Eq. (4). This function, called the generalized discrepancy, was introduced and investigated in [22, 23].

It was assumed in our model that each active site produces fractions that can be described by the Flory distribution, Eq. (3). We proceeded from these reasons and selected the kernel of an integral Eq. (3). There are no theoretical premises to consider that the kernel is not defined precisely. Therefore we can assume $h = 0$ to simplify the discrepancy expression.

It was shown in [24], that the equation $\gamma(\alpha) = 0$ is continuous, increases monotonically and has a unique root. Therefore the well-known bisection method was used to solve the equation with one variable function.

Thus, it is necessary, that the following two conditions be fulfilled simultaneously to search a solution for Eq. (4) with approximately given right member $U_\delta(x)$: (a) the solution $Z_\alpha(s)$ should be such that the norm of a discrepancy may not exceed an error of experimental data, *i.e.*,

$$\int_c^d \left[\int_a^b K(x,s)Z(s)ds - U_\delta(x)\right]^2 dx \le \delta^2; \tag{10}$$

and (b) it is necessary to minimize Tikhonov's functional on Z_α(s):

$$M_\alpha[Z] = \int_c^d \left[\int_a^b K(x,s)Z(s)ds - U_\delta(x)\right]^2 dx + \alpha \int_a^b \left[Z^2(s) + \left(\frac{dz}{ds}\right)^2\right] ds \tag{11}$$

In the calculations, the errors of input data were taken to be 5%. The computations were carried out using a Turbo Pascal program.

The molecular weight distribution functions of polymer obtained from gel permeation chromatography experiment were used as input data. The function $Z(s)$ under the integral in Eq. (4) is very sensitive to inaccuracies of the initial information, and even an insignificant variation in the slope of $U_\delta(x)$ will bring about a considerably large variation in the slope of $Z(s)$. Therefore, much attention was given to the procedure of instrumental spreading correction of chromatograms. The technique described in [26] was used.

RESULTS

We calculated the cumulative distribution function of kinetic activity of polymerization centers of $NdCl_3 \cdot L - Al(i\text{-}C_4H_9)_3$ catalytic system from the 1,4-*cis*-polybutadiene MWD curves obtained in experiment [1].

Since β is a magnitude inverse to molecular weight, it is convenient to represent the solution of Eq. (3) as a table of values or graph of $\varphi(\beta)$ functions in coordinates $\Psi(\ln\beta) - \ln M$, where $\Psi(\ln\beta) = \beta\varphi(\beta)$. Such representation clearly demonstrates the influence of a kinetic heterogeneity of a catalytic system on polymer MW, since the area under a curve $\Psi(\ln\beta)$, limited by abscissas $\ln(M_1)$ and $\ln(M_2)$, corresponds to the fraction of chains obtained with a given mechanism on a given type of active site.

In Figure 1 the distribution curves of kinetic activity of a catalytic system for various values of butadiene conversion are represented. It is obvious, that even in an initial moment of polymerization with a low degree of conversion (about 3%), the represented curves are multimodal. It testifies to a primary heterogeneity of the catalytic system. Each maximum on a curve of distribution corresponds, at least, to one type of active centers with a given probability of a chain termination. The redistribution of relative intensities of various maximums takes place with increasing conversion. The number of maximas adequately types the active centers, which in the butadiene polymerization process increases from three up to four.

Assuming that the deviations of active centers from a position of a maximum occur under the statistical law, the obtained curves were

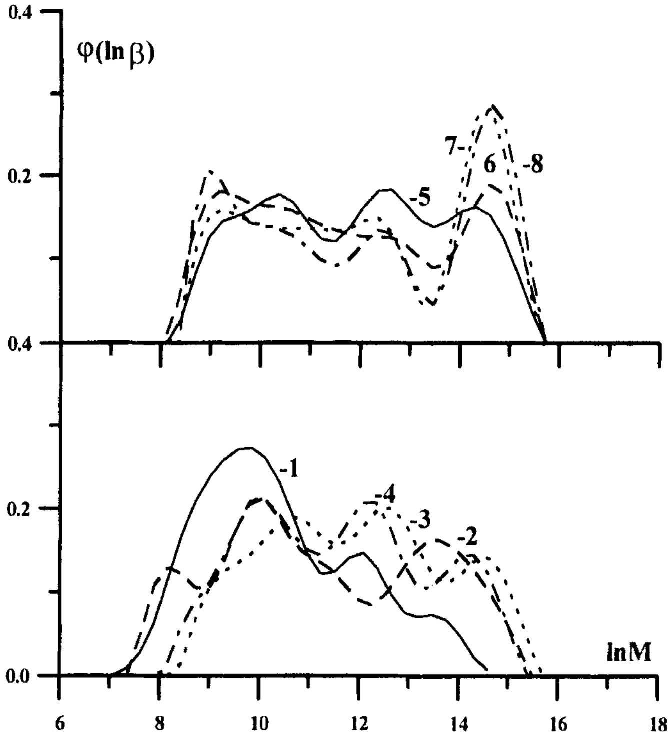

FIGURE 1 Distributions on activity of a catalytic system $NdCl_3 \cdot 3L - Al(i\text{-}C_4H_9)_3$ with butadiene polymerization from conversion a monomer U (%): 1-3.61, 2-11.1, 3-17.4, 4-25.6, 5-37.3, 6-67.8, 7-87.9, 8-88.8. Toluene, 25°C, $C_{Nd} = 1 \cdot 10^{-3}$ mol/L, $C_M = 1{,}5$ mol/L, Al/Nd = 30.

broken to separate Gauss functions. It has enabled us to estimate the relative contribution of each type of active centers separately, and to trace their modifications, *i.e.*, has allowed not only to qualitatively specify the presence of kinetic heterogeneity in a catalytic system, but also to estimate it quantitatively.

With the partition of distribution curve to separate peaks the position of maxima (Fig. 2), as it turned out, remains practically constant during the whole process of polymerization. Only for the fourth peak in an initial moment the displacement in a log of large molecular weights is observed. Thus each active center synthesizes macromolecules of defined length.

Modifications of the kinetic activity of polymerization centers from reaction time are represented on Figure 3. It is shown, that the

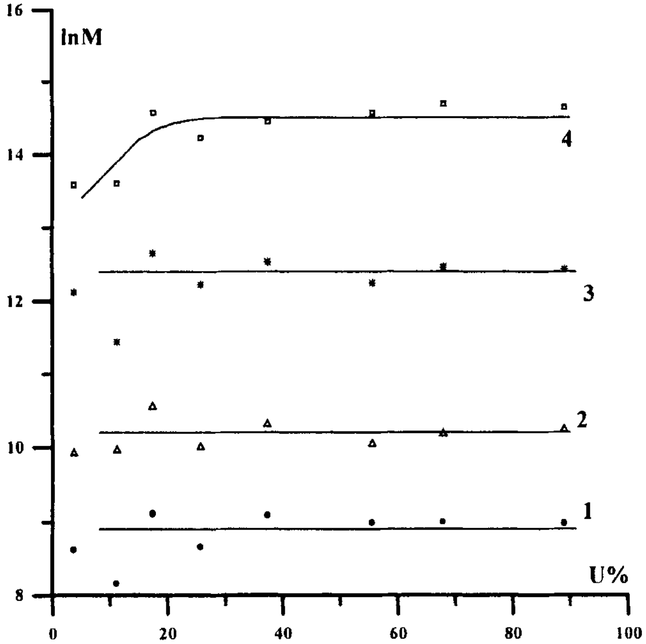

FIGURE 2 Dependence of maximum positions of distribution on kinetic activity curve with various monomer conversions. Conditions in Figure 1.

activity of centers, which corresponds to a maximum on the curve of the distribution generating a polymeric fraction with the lowest molecular weight, practically does not change during the whole process of polymerization. The activity decreases of centers correspond to a maximum number two, producing macromolecules with molecular weight 10^5. The intensity of the third type center grows in the beginning, and then practically do not vary; and for the fourth type of active centers, a constant growth of activity is observed.

The influence of polymerization temperature (Figs. 4, 5) on the distribution of kinetic activity of centers of a catalytic system $NdCl_3 \cdot L - Al(i\text{-}C_4H_9)_3$ was investigated. With the temperature increase of butadiene polymerization the intensity increased of peak 1 and 2, forming polymer with low molecular weight. On the contrary, centers responsible for generation of high molecular weight fractions (peaks 3 and 4), reduce the activity. It is obvious, that the active centers responsible for generation of high molecular weight fractions, has

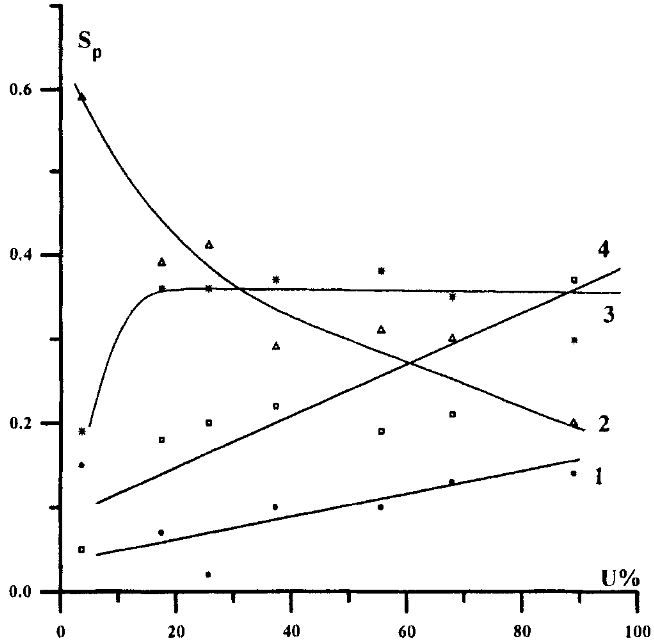

FIGURE 3 A modification of kinetic activity of butadiene polymerization centers with various monomer conversions. Conditions in Figure 1.

lower stability at high temperatures, than active centers generating low molecular weight fractions.

As can be seen from the data presented in Figure 6, the modification of Nd concentration in the catalytic systems practically does not modify the kinetic activity of polymerization centers. In fact, the concentration of the catalyst influences the total number of active sites in a polymerization system, without essentially changing of relations between existing types of active centers.

The modifications of kinetic activity of active sites with various ratios of Al/Nd are shown in Figures 7, 8, where for the first and the second peak an increase in activity, and for the third and the fourth peak a decrease is observed of activity with increase in the content of organoaluminium compound in a polymerization system.

The reason for such non-uniformity of lanthanide catalytic systems is due, first of all, to the nature of the catalyst. All results of theoretical research indicate the complexity of structure of the lanthanide systems.

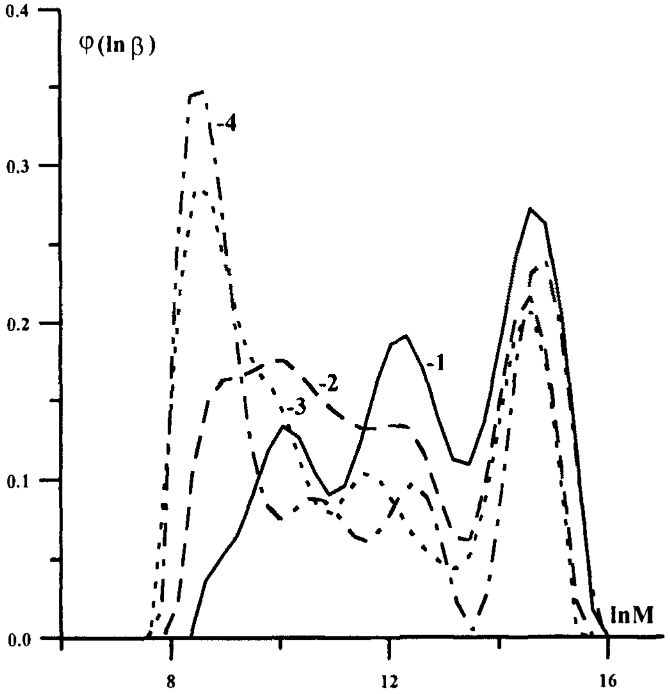

FIGURE 4 Distributions on activity of a catalytic system $NdCl_3 \cdot 3L - Al(i\text{-}C_4H_9)_3$ with butadiene polymerization. Temperature of polymerization t°C: 1-0, 2-40, 3-60, 4-80. Conditions in Figure 1.

They (as well as active sites of traditional Ziegler-Natta catalysts) are part of complicated associations, consisting of halide derivatives of transition metal connected to other components of a polymerization system. It is known, that 4-f-elements have high coordination number – from 8 up to 12 [27]. The molecules of solvent, monomer, and organoaluminium compound, together forming the catalytic complex, can use free coordination places. Besides, we can not deny the possibility of the repositioning of the ligands during the polymerization process. The possibility of such interactions is proved by changes in the levels of kinetic constants with variations of the polymerization conditions, the nature of components of a catalytic system, and the catalyst preparation procedure [1].

In view of the above, and the fact that the *cis*-stereospecificity of catalysts is retained during the whole polymerization period [28], the

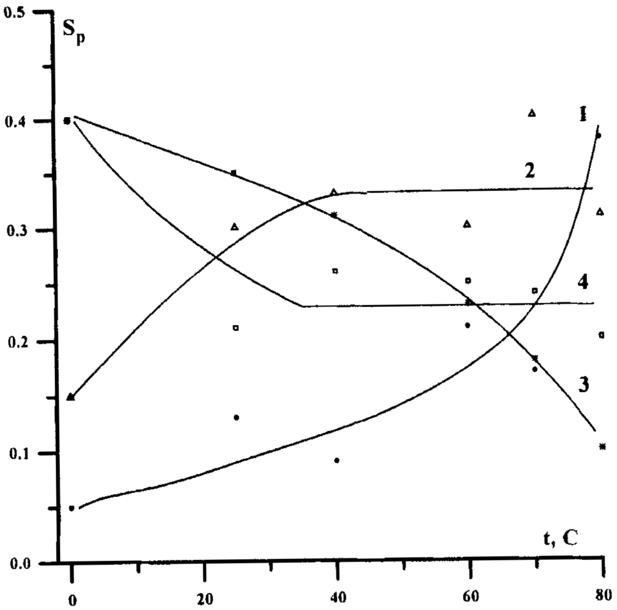

FIGURE 5 A modification of kinetic activity of butadiene polymerization centers with various polymerization temperatures. Conditions in Figure 1.

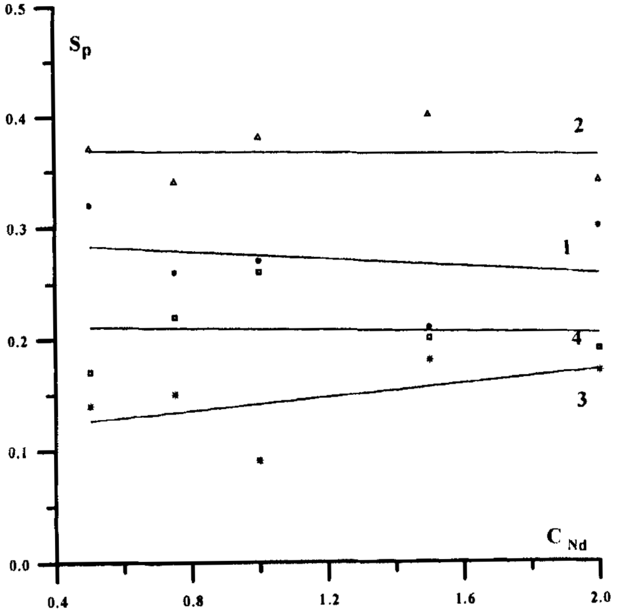

FIGURE 6 A modification of kinetic activity of butadiene polymerization centers with various catalyst concentrations. Conditions in Figure 1.

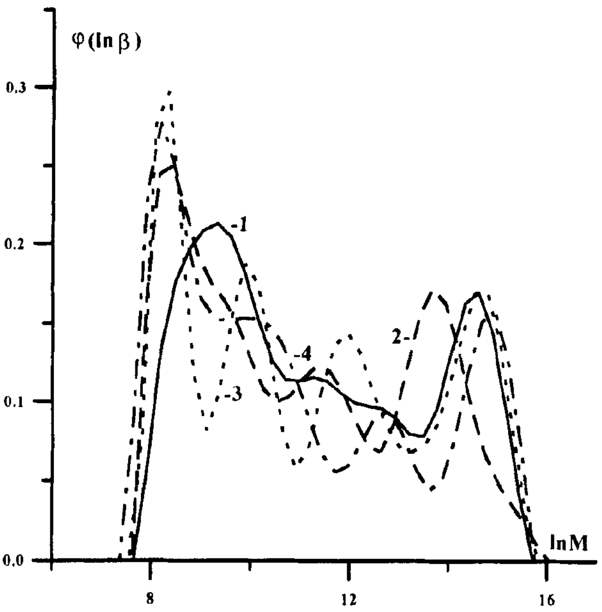

FIGURE 7 Distributions on activity of a catalytic system $NdCl_3 \cdot 3L - Al(i\text{-}C_4H_9)_3$ with butadiene polymerization from concentration $Al(i\text{-}C_4H_9)_3$ (mol/L): 1-1,5.10-2, 2-4,5.10-2, 3-9.10-2, 4-12.10-2. Conditions in Figure 1.

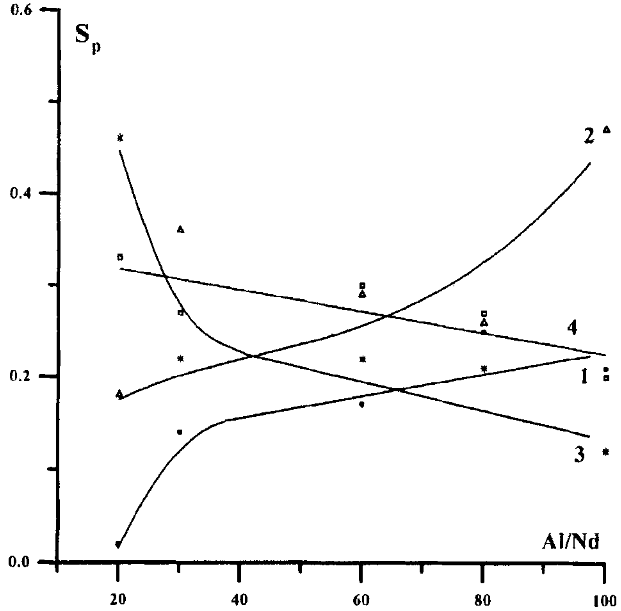

FIGURE 8 A modification of kinetic activity of butadiene polymerization centers with various relations Al/Nd. Conditions in Figure 1.

structure of the active centers of lanthanide catalytic systems can be represented as follows:

$$(\text{anti} - \text{P} - \text{C}_4\text{H}_6)\text{LnCl}_k\text{R}_{3-k} \cdot z\text{AlCl}_n\text{R}_{3-n},$$

(where P – butadiene polymeric chain, R – radical of a organoaluminium compound), and with various relations $k{:}n{:}z$ active sites can be prepared distinguished by differing constants of growth and chain transfer.

CONCLUSIONS

The multimodal aspect of an obtained curve testifies to an essential heterogeneity of kinetic performances of a catalytic system and to dependance of this heterogeneity on the polymerization conditions. For the catalytic system $NdCl_3{\cdot}3L-Al(i\text{-}C_4H_9)_3$ in the butadiene polymerization process, at least four active centers distinguished on kinetic activity are detected. The influence is shown of temperature, concentration of monomer, organoaluminium compound and catalyst on a modification of their activity.

Thus, the offered technique for the analysis of a kinetic heterogeneity of a catalytic system allows to proceed from qualitative reasoning to strictly quantitative relations, capable of possibly revealing correlations between the structure of a polymerization system and properties of the obtained polymers.

Acknowledgements

We are grateful to the Russian Foundation of Fundamental Investigations (grant No. 99-03-33437) for support of this work. We are also thank our coworker professor Z. M. Sabirov.

References

[1] Kozlov, V. G., Sigaeva, N. N., Nefedjev, K. V., Savel'eva, I. G., Marina, N. G. and Monakov, Yu. B. (1994). *J. Polym. Sci., Polym. Chem.*, **32**, 1237.

[2] Kozlov, V. G., Marina, N. G., Savel'eva, I. G., Monakov, Yu. B. and Tolstikov, G. A. (1988). *Inor. Chim. Acta.*, **154**, 239.

[3] Monakov, Yu. B., Marina, N. G., Khairullina, R. M., Kozlova, O. I. and Tolstikov, G. A. (1988). *Inor. Chim. Acta.*, **142**, 161.

[4] Frenkel, S. Ya., *Vvedenie v statisticheskuyu teoriyu polimerizatsii*. Moskow, Nauka, 1965, 267 p.

[5] Clarc, A. and Bailey, G. C. (1963). *J. Catal.*, **2**, 230.

[6] Keii, T. (1990). *Stud. Surf. Sci. Catalysts.*, **56**, 1.

[7] Keii, T., Doi, Y., Suzuki, E., Tamura, M., Murata, M. and Soga, K. (1984). *Macromol. Chem.*, **185**, 1537.

[8] Khairullina, R. M., Marina, N. G., Kozlova, O. I., Duvakina, N. V., Sigaeva, N. N. and Kozlov, V. G. (1991). *Vysokomol. Soed.*, **33**, 463.

[9] Monakov, Yu. B., Sabirov, Z. M. and Marina, N. G. (1996). *Vysokomol. Soed.*, **38**, 407.

[10] Locatelli, P., Sacchi, M. C., Tritto, I. and Zannoni, G. (1988). *Macromol. Chem. Rapid Commun.*, **9**, 575.

[11] Kissin, Y. V. (1974). *Adv. Plym. Sci.*, **15**, 71.

[12] Novokshonova, L. A., Kovaleva, N. Yu., Gavrilov, Yu. A., Krasheninnikov, V. G., Leipunskii, I. O., Zhigach, A. N., Larichev, M. N, and Chebunin, M. N. (1997). *Polym. Bull.*, **39**, 59.

[13] Fan, Z.-Q., Feng, L.-X. and Yang, S.-L. (1992). *Chem. J. Chinese Univ.*, **13**, 137.

[14] Zakharov, V. A., Bukatov, G. D. and Yermakov, Y. I. (1983). *Adv. Polym. Sci.*, **51**, 61.

[15] Fan, Z.-Q., Feng, L.-X. and Yang, S.-L. (1996). *J. Polym. Sci., Polym. Chem.*, **34**, 3329.

[16] Budtov, V. P., Zotikov, E. G., Ponomareva, E. L. and Gandelsman, M. I. (1985). *Vysokomol. Soed.*, **27**, 1910.

[17] Murinov, Yu. I., Monakov, Yu. B., Shamaeva, Z. G., Marina, N. G., Kolosnitsyn, V. S., Nikitin, Yu. E. and Rafikov, S. R. (1977). *Izv. Akad. Nauk SSSR Seriya himich.*, **12**, 2790.

[18] Benoit, H., Crubisic, L. and Rempp, P. A. (1967). *J. Polym. Sci. B.*, **5**, 753.

[19] Berg, A. A., Kozlov, V. G., Budtov, V. P., Monakov, Yu. B. and Rafikov, S. R. (1980). *Vysokomol. Soed.*, **22**, 543.

[20] Schmeal, W. R. and Street, J. R. (1972). *J. Polym. Sci., Polym. Phys. Ed.*, **10**, 2173.

[21] Tikhonov, A. N., Goncharsky, A. V., Stepanov, V. V. and Yagola, A. G., "*Numerical Methods for the Solution of Ill-Posed Problems*", Kluwer, Dordrecht, 1995, ISBN 0-7923-3593-X.

[22] Goncharsky, A. V., Leonov, A. S. and Yagola, A. G. (1972). *Dokl. Akad. Nauk SSSR*, **203**, 1238.

[23] Yagola, A. G. (1980). *USSR Comput. Math. Math. Phys.*, **20**, 586.

[24] Tikhonov, A. N., Leonov, A. S. and Yagola, A. G., "*Nonlinear Ill-posed Problems*". Chapman & Hall, 1998, ISBN 0-412-78660-5.

[25] Kochikov, I. V., Kuramshina, G. M. and Yagola, A. G. (1998). *Surv. Math. Ind.*, **8**, 63.

[26] Kislov, E. N., Zotikov, E. G., Podosenova, N. G., Ponomareva, E. L. and Budtov, V. P. (1978). *Vysokomol. Soed.*, p. 1910.

[27] Panyushkin, V. T., Afanas'ev, V. A. and Garnovskii, A. D. (1977). *Uspehi Khimii*, **46**, 2106.

[28] Sabirov, Z. M. and Monakov, Yu. B. (1994). *Chem. Reviews.*, **18**, 1.