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MECHANISMS OF CATALYTIC REACTIONS

Kinetic Heterogeneity of the Active Sites of Titanium-Containing Catalytic Systems in the Stereospecific Polymerization of Isoprene

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Abstract—The kinetic heterogeneity of the active sites of titanium-containing catalytic systems in the stereospecific polymerization of isoprene was studied based on solving inverse problems for the molecular-weight distribution of polyisoprene with the use of the Tikhonov regularization method. It was found that from two to four types of active sites can occur depending on the nature of the organoaluminum compound used in the catalytic system. The rate constants of elementary steps of the polymerization process for particular types of active sites were obtained for the first time by solving inverse kinetic problems.

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INTRODUCTION

Titanium catalytic systems are widely used in the commercial synthesis of both polyolefins and polydienes. Stereoregular 1,4-*cis*-polyisoprene, which is commercially manufactured in the presence of $TiCl_4$–$Al(i\text{-}C_4H_9)_3$, is a large-scale product in synthetic rubber industry; it ranks second among elastomers in terms of industrial consumption. Therefore, the processes of diene polymerization on titanium-containing catalytic systems are well understood [1–5]. However, a number of aspects remain unclear or questionable. The problem of multicenter catalytic systems belongs to these aspects.

The occurrence of several types of active sites on the surface of heterogeneous catalysts has been repeatedly reported. However, studies in this area have been primarily concerned with the polymerization of olefins (e.g., see [6–12]). The occurrence of various types of active sites does not manifest itself in an explicit form in the polymerization of dienes, when the polymerization system occurs in many cases in an ultramicroheterogeneous or, occasionally, homogeneous state. However, there is indirect evidence for multicenter catalytic systems: the compositional and microstructural heterogeneity of copolymers, a polymodal molecular-weight distribution (MWD), etc.

A method based on solving inverse problems of MWD was developed at the Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, in order to evaluate the kinetic heterogeneity of the active sites of catalytic systems in a stereospecific polymerization process [13, 14]. The kinetic heterogeneity of lanthanide- and vanadium-containing catalytic systems in the polymerization of dienes (butadiene, isoprene, and piperylene) was studied with the use of this method [15]. There is no data of this kind available for catalytic systems containing titanium and organoaluminum compounds (OACs) ($TiCl_4$–OAC).

The aim of this work was to study the kinetic heterogeneity of the active sites of the $TiCl_4$–OAC titanium-containing catalytic systems in the stereospecific polymerization of isoprene and the effect of the nature of the OAC on the kinetic heterogeneity of the active sites and on the molecular characteristics of polyisoprene.

EXPERIMENTAL

The polymerization of isoprene was performed in toluene at 25 ± 1°C in the absence of impurities, moisture, and air from the reaction vessels. The monomer concentration (C_m) was varied from 0.1 to 2.5 mol/l, whereas the catalyst concentration (C_{Ti}) was varied from 1.0×10^{-3} to 10.0×10^{-3} mol/l. The following OACs were used: $Al(i\text{-}C_4H_9)_3$, $AlH(i\text{-}C_4H_9)_2$, $AlCl(i\text{-}C_4H_9)_2$, and $Al(C_2H_5)_3$. The catalytic complex was prepared by mixing the solutions of $TiCl_4$ and OACs in toluene at the following Al/Ti ratios corresponding to maximum activities of the catalytic systems: 1.1, 1.2, and 4.0 for the systems with $Al(i\text{-}C_4H_9)_3$, $Al(C_2H_5)_3$ or $AlH(i\text{-}C_4H_9)_2$, and $AlCl(i\text{-}C_4H_9)_2$, respectively.

The molecular weights (M_w and M_n) and MWDs of polyisoprene were determined on a Waters GPC 2000 gel-permeation chromatograph at 30°C with toluene as an eluant. The system of three columns packed with Styragel was calibrated using narrow-MWD polystyrene standards ($M_w/M_n \le 1.2$) based on the Benoit universal calibration curve and an equation that relates the

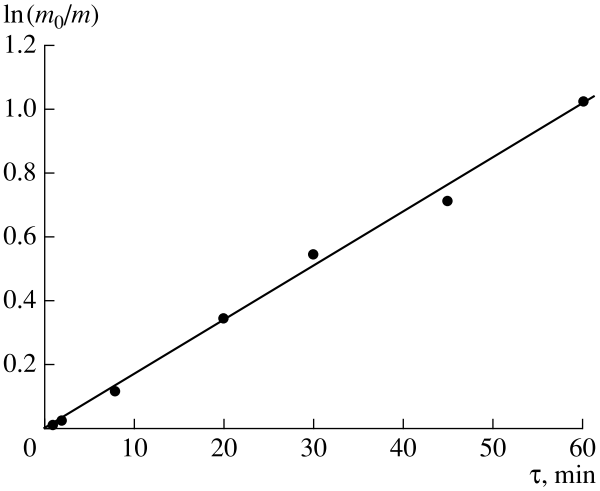

Fig. 1. Dependence of $\log(m/m_0)$ on polymerization time (m and m_0 are the current and initial concentrations of the monomer, mol/l).

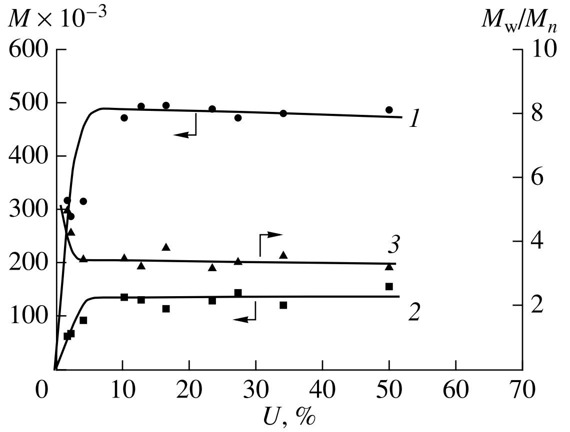

Fig. 2. Dependence of the (*1*) M_w, (*2*) M_n, and (*3*) M_w/M_n of polyisoprene on monomer conversion (U). Catalytic system: $TiCl_4$–$Al(i\text{-}C_4H_9)_3$. Isopentane, C_m = 1.5 mol/l; C_{Ti} = 1 × 10^{-3} mol/l; Al/Ti = 1.1; T_p = 25°C.

molecular weight of 1,4-*cis*-polyisoprene with characteristic viscosity [16]. The MWD curves were corrected for instrumental broadening in accordance with a published procedure [17].

The kinetic heterogeneity of the catalytic system was evaluated by solving an inverse problem for the formation of MWD with the use of the Tikhonov regularization method [13, 14, 18, 19].

RESULTS AND DISCUSSION

In the majority of cases, the polymerization of isoprene on the $TiCl_4$–OAC catalytic system occurred at a high initial rate and an induction period was not observed. The $\log(m/m_0)$–τ (where m and m_0 are the current and initial monomer concentrations, respectively, and τ is the polymerization time) linear relationship held true to high degrees of monomer conversion; this is indicative of the retention of a constant total concentration of active sites in the course of polymerization (Fig. 1).

In the test concentration ranges of polymerization system components, the reaction exhibited first order with respect to the monomer and catalyst.

Figure 2 shows the resulting conversion dependence of the molecular characteristics (M_w, M_n, and M_w/M_n) of polyisoprene in the case of the use of the $TiCl_4$–$Al(i\text{-}C_4H_9)_3$ catalytic system. As can be seen in Fig. 2, the values of M_w and M_n increased and the polydispersity decreased approximately to a 10% conversion of the monomer. A further increase in the conversion of isoprene did not cause detectable changes in the molecular characteristics. This character of the dependence of the molecular weights and polydispersity of a polydiene on the conversion of a monomer is typical of Ziegler catalytic systems and related to the occurrence of chain termination reactions and monomer consumption in the course of polymerization. In this case, the polydispersity is high; that is, the polymer exhibits a sufficiently broad MWD, although the shape of polyisoprene MWD curves is unimodal (Fig. 3).

We believe that the reason for the broad MWD of polyisoprene is the occurrence of several types of active sites that have different kinetic parameters of processes with the participation of these active sites. In this case, each particular type of active sites forms a polymer

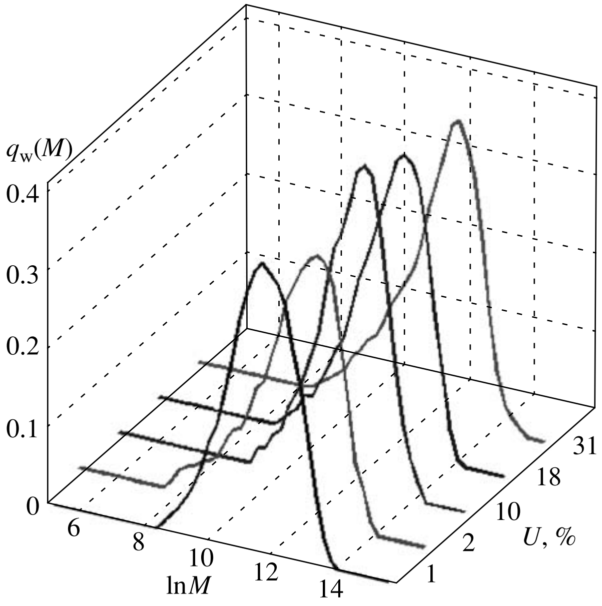

Fig. 3. MWD curves for polyisoprene prepared on the $TiCl_4$–$Al(i\text{-}C_4H_9)_3$ catalytic system at various monomer conversions.

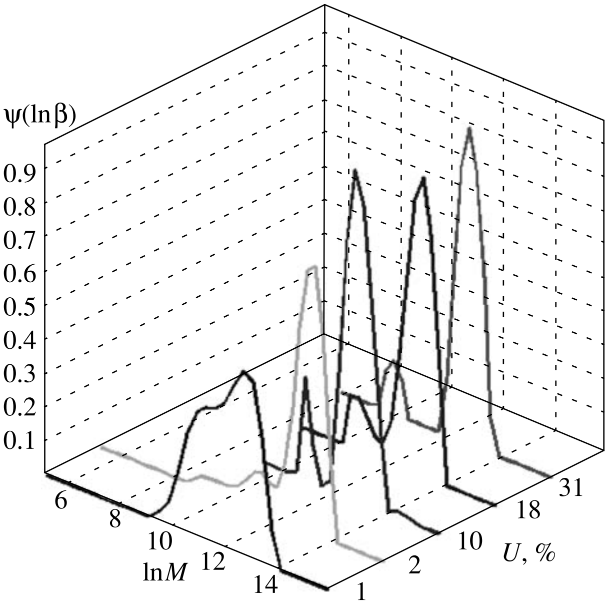

Fig. 4. Kinetic heterogeneity distribution of active sites in the $TiCl_4$–$Al(i\text{-}C_4H_9)_3$ catalytic system at various isoprene conversions. The conditions are specified in Fig. 1.

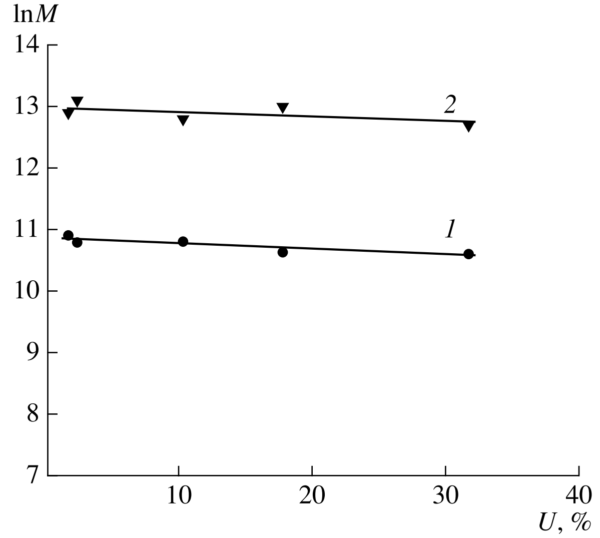

Fig. 5. Dependence of the positions of maximums in the Gaussian functions of the kinetic heterogeneity distribution curves of the $TiCl_4$–$Al(i\text{-}C_4H_9)_3$ catalytic system on isoprene conversion.

fraction whose MWD is described by the most probable Flory distribution [20]

$$q_w(M) = \beta\exp(-\beta M) \qquad (1)$$

(the quantity β characterizes the probability of chain termination processes, and $q_w(M)$ is the molecular-weight distribution function). At the rate of polymer chain growth V_g and the overall rate of chain termination V_t, $\beta = 1/m_m \times V_t/V_g$ (m_m is the molecular weight of the monomer).

The total MWD is a superposition of distributions obtained at individual types of active sites.

Based on the experimentally found MWD curves, we calculated kinetic heterogeneity distribution curves in the $\Psi(\ln\beta)$–$\ln M$ coordinates, where $\psi(\ln\beta) = \varphi(\beta)\beta^2$ (ψ is the kinetic heterogeneity distribution function of active sites), by solving inverse problems of MWD using the Tikhonov regularization method and the program developed.

The calculated kinetic heterogeneity distributions of active sites were bimodal (Fig. 4), and two maximums were clearly defined. Because each point in the kinetic heterogeneity distribution curve corresponded to the fraction of active sites with a given probability of chain termination processes, the occurrence of a bimodal distribution suggested the kinetic heterogeneity of the catalytic system. In this case, the kinetic heterogeneity manifested itself starting with low conversions of the monomer. Previously, in the study of lanthanide and vanadium catalysts, the manifestations of kinetic heterogeneity were also observed starting with low monomer conversions (1–3%) [13–15]. Consequently, it is believed that various types of active sites initially appeared in a catalytic system and this is a common property of ion-coordination catalytic systems.

We assumed that each maximum in the distribution curves corresponded to at least one type of active sites. Consequently, the test catalytic system contained two types of active sites. It is interesting that two types of active sites were also revealed in the polymerization of ethylene on this catalytic system [21].

Because deviations from the maximum were of a statistical character, the $\psi(\ln\beta)$–$\ln M$ curves were subdivided into individual Gaussian functions [13, 14]. The positions of maximums in each particular Gaussian function remained practically unchanged in the course of the polymerization process (Fig. 5). This was related to the fact that either particular type of active sites was characterized by certain relative rate constants of chain termination reactions (k_t^j/k_g^j, where k_t^j and k_g^j are the reaction rate constants of chain termination and growth, respectively, for particular types of active sites).

The areas restricted by Gaussian curves (S_i) correspond to the polymer fraction obtained at a given type of active sites or the monomer fraction reacted at the given type of active sites. Consequently, S_i is adequate to the kinetic activity exhibited by the given type of active sites. Figure 6 shows separately the conversion dependence of the kinetic activity of each particular type of active sites in the $TiCl_4$–$Al(i\text{-}C_4H_9)_3$ catalytic systems. It can be seen that the kinetic activity of sites that form the lower molecular weight fraction in the course of polymerization decreased; correspondingly, the activity of sites responsible for the formation of a higher molecular weight polymer increased. Changes

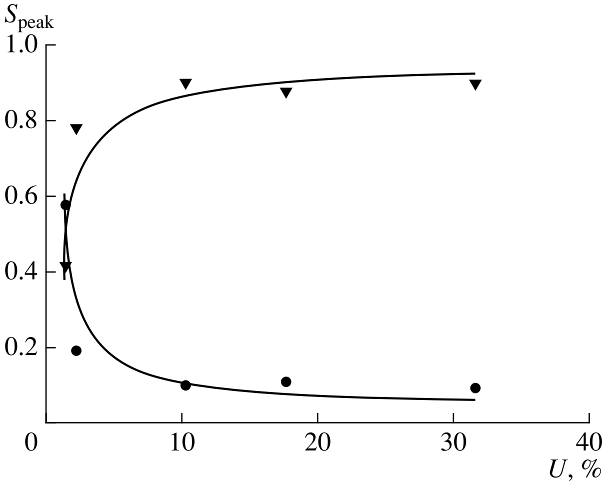

Fig. 6. Changes in the kinetic activity of various types of polymerization sites in the $TiCl_4$–$Al(i\text{-}C_4H_9)_3$ catalytic system as functions of isoprene conversion.

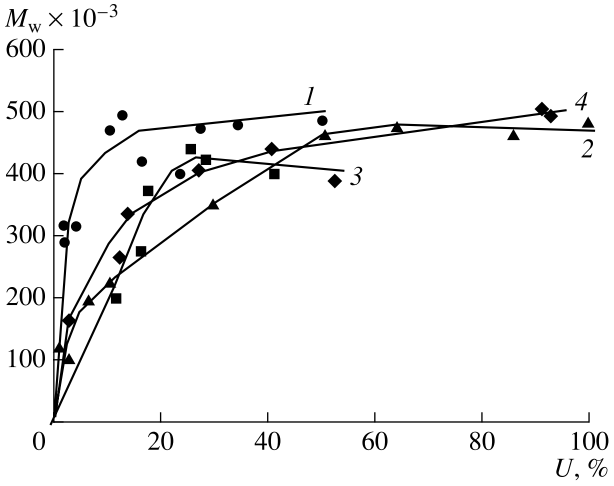

Fig. 7. Dependence of the M_w of polyisoprene on isoprene conversion in the course of polymerization on the $TiCl_4$–OAC catalytic systems: (*1*) $Al(i\text{-}C_4H_9)_3$, (*2*) $Al(C_2H_5)_3$, (*3*) $AlH(i\text{-}C_4H_9)_2$, and (*4*) $AlCl(i\text{-}C_4H_9)_2$. Polymerization conditions: T_p = 25°C; (*1*) isopentane or (*2–4*) toluene; C_{Ti} = (*1*) 1 $\times 10^{-3}$ or (*2–4*) 0.01 mol/l; C_m = (*1*) 1.5 or (*2–4*) 2.0 mol/l; Al/Ti = (*1*) 1.1, (*2*, *3*) 1.2, or (*4*) 4.0.

in the kinetic activity of individual types of active sites were related to changes in their concentrations in the course of polymerization. In this case, the total concentration of active sites remained constant. Therefore, it is likely that changes in the concentrations of particular types of active sites resulted from a mutual transition, that is, a transition of a type of active sites to the other type in the course of polymerization.

Figure 7 shows the conversion dependence of the M_w of polyisoprene prepared with the use of the $TiCl_4$–OAC catalytic systems. It can be seen that the shapes of these curves were similar for all of the test systems. The values of M_w increased with monomer conversion; then, after 10–40% conversion was reached, the molecular weights remained almost unchanged. Polymer samples synthesized on the catalytic system with triisobutylaluminum exhibited somewhat higher values of M_w, whereas macromolecules with practically equal molecular weights were formed on the other catalytic systems at higher degrees of monomer conversion.

The polydispersity decreased in the course of polymerization; this decrease was especially noticeable in the system with $Al(C_2H_5)_3$.

The MWD curves of polyisoprene prepared on the test catalytic systems were differently shaped depending on the nature of the OAC used in the catalytic system. Thus, on the systems with $AlH(i\text{-}C_4H_9)_3$ and $Al(C_2H_5)_3$, samples were prepared whose MWD curves had a bimodal shape. The use of diisobutylaluminum chloride in the catalytic complex resulted in the production of polyisoprene with a unimodal but broad MWD (M_w/M_n = 3–5).

The kinetic heterogeneity distributions were polymodal regardless of the shape of MWD curves. Two maximums corresponding to two types of active sites for the systems with $AlH(i\text{-}C_4H_9)_3$ and $AlCl(i\text{-}C_4H_9)_3$ or four types of active sites in the polymerization of isoprene on the catalytic system with $Al(C_2H_5)_3$ can be recognized (Fig. 8).

Thus, the nature of the OAC in the titanium catalytic systems can affect the number of formed types of active sites.

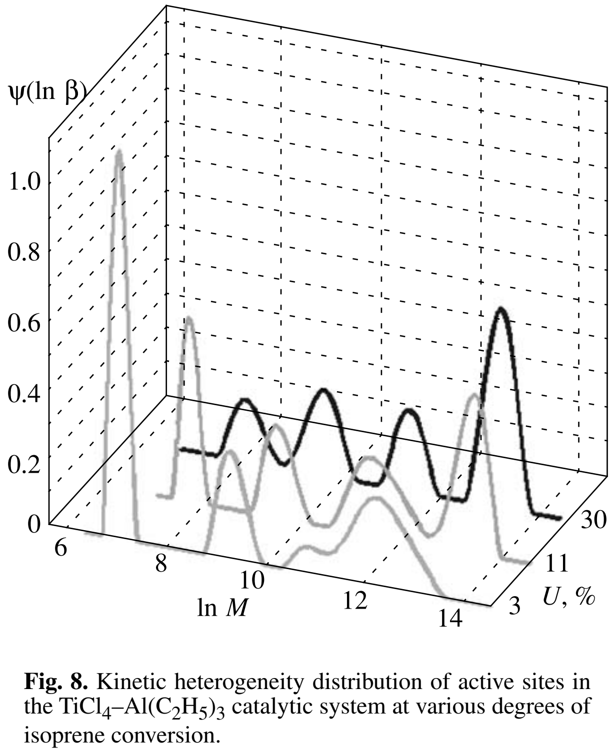

Fig. 8. Kinetic heterogeneity distribution of active sites in the $TiCl_4$–$Al(C_2H_5)_3$ catalytic system at various degrees of isoprene conversion.

Reaction rate constants (l mol^{-1} min^{-1}) of chain growth (k_g) and chain transfer to the monomer (k_t^m) and OAC (k_t^{Al}) and the concentrations (mol/l) of individual types of active sites (C_a) in the $TiCl_4$–OAC catalytic systems for isoprene polymerization

Parameter		$AlCl(i\text{-}C_4H_9)_2$	$AlH(i\text{-}C_4H_9)_2$	$Al(C_2H_5)_3$
k_g	k_{g1}	57.5	32.6	8.6
	k_{g2}	419.1	955.0	31.1
	k_{g3}	–	–	287.5
	k_{g4}	–	–	2268
	Σk_{gj}	357	335.2	19.2
$k_t^m \times 10^2$	k_1^m	1.5	0.06	0.1
	k_2^m	1.7	4.8	1.1
	k_3^m	–	–	7.8
	k_4^m	–	–	7.2
	$\Sigma k_0^{m_i} \times 10^2$	1.6	1.6	7.2
k_t^{Al}	k_1^{Al}	1.05	0.03	4.7
	k_2^{Al}	0.4	2.0	0.5
	k_3^{Al}	–	–	1.8
	k_4^{Al}	–	–	5.9
	Σk_j^{Al}	0.5	3.5	3.7
$C_a \times 10^5$	C_{a1}	1.2	17.9	92.9
	C_{a2}	5.9	8.7	17.9
	C_{a3}	–	–	7.9
	C_{a4}	–	–	0.7
	ΣC_{aj}	7.1	26.6	119.4

Note: Polymerization conditions: toluene; 25°C; $C_m = 1.0$ mol/l; $C_{Ti} = 5 \times 10^{-3}$ mol/l.

We constructed kinetic models that allowed us to solve separately inverse problems for each particular type of active sites. We were the first to find the rate constants of elementary steps of the process of isoprene polymerization for individual types of active sites by solving an inverse kinetic problem; this inverse kinetic problem consists in a search for minimums of adherence functions of the values of M_n and monomer conversion obtained experimentally and by calculations.

Unlike single-site models [22], inverse problems for multicenter kinetic models are intricate since the number of sought constants is several times greater. The simultaneous search for all kinetic constants, firstly, disturbs the stability of solution and, secondly, leads to the inefficient use of computer time. Therefore, kinetic models were constructed that allow inverse problems to be solved separately for each type of active sites.

Because the error in the determination of monomer conversion (U) does not exceed 1%, these values were initially compared. Knowing the functional dependence of the total monomer conversion on polymerization time

$$U(t) = 1 - e^{-\sum_{j=1}^{n}(k_{gj}C_{aj})t} \quad (2)$$

(here, j is the active site type number, $j = 1, 2, \ldots, n$; C_{aj} is the concentration of active sites of the jth type) and optimizing the functional

$$Z = \sum_{i=1}^{n}[U_{expt}(t_i) - U_{calcd}(t_i)]^2, \quad (3)$$

we can unambiguously determine the value of $\sum_{j=1}^{n}(k_{gj}C_{aj})$. In this case, the functional dependence of monomer conversion on each type of active sites is of the form

$$U_j(t) = \frac{k_{gj}C_{aj}}{\sum_{j=1}^{n}(k_{gj}C_{aj})}U(t). \quad (4)$$

Thus, the first stage in solving an inverse kinetic problem consisted in the determination of the products $k_{gj}C_{aj}$ for each type of active sites, which were considered fixed.

At the next stage, the experimentally obtained values of M_n were compared with their calculated analogs. For this purpose, the minimum of the following function was found:

$$S = \sum_{i=1}^{n}[M_{n,\,expt j}(t_i) - M_{n,\,calcd j}(t_i)]^2. \quad (5)$$

Because the explicit functions for M_n were not determined for the reason of the complexity of the set of differential equations that describe the process, the comparison was performed by repeatedly solving a direct problem; in this case, the minimizing vector of constants $\mathbf{R}_j(K)$ was found using the Hook–Jeeves method [23].

Thus, as a result of solving an inverse kinetic problem for a multicenter model, we found the vector of constants $\mathbf{R}(K)$, whose elements were the kinetic rate constants of elementary reactions and the concentrations of all types of active sites. The table summarizes the kinetic parameters obtained in this manner. Summarizing the parameters for individual types of active sites

$$\sum k_{gj} = \frac{k_{g1}C_{a1} + k_{g2}C_{a2} + k_{g3}C_{a3} + k_{g4}C_{a4}}{\sum C_{aj}},$$

$$\sum k_j^{\mathrm{m}} = \frac{k_1^{\mathrm{m}} C_{\mathrm{a}1} + k_2^{\mathrm{m}} C_{\mathrm{a}2} + k_3^{\mathrm{m}} C_{\mathrm{a}3} + k_4^{\mathrm{m}} C_{\mathrm{a}4}}{\sum C_{\mathrm{a}j}},$$

$$\sum k_j^{\mathrm{Al}} = \frac{k_1^{\mathrm{Al}} C_{\mathrm{a}1} + k_2^{\mathrm{Al}} C_{\mathrm{a}2} + k_3^{\mathrm{Al}} C_{\mathrm{a}3} + k_4^{\mathrm{Al}} C_{\mathrm{a}4}}{\sum C_{\mathrm{a}j}}, \qquad (6)$$

$$\sum C_{\mathrm{a}j} = C_{\mathrm{a}1} + C_{\mathrm{a}2} + C_{\mathrm{a}3} + C_{\mathrm{a}4},$$

we obtained the overall rate constants of chain growth and transfer reactions and the concentrations of active sites, which were consistent with the overall constants obtained by a commonly used procedure from the kinetic dependence of the number-average degree of polymerization. It can be seen that the active sites of type nos. 3 and 4 exhibited the highest values of k_g regardless of the nature of OACs. However, the concentration of these sites was much lower than that of sites that form lower molecular weight fractions (nos. 1 and 2).

It can be seen that the nature of OACs in the catalytic complexes affected not only the reaction rate constants of chain transfer to the OAC; the reaction rate constants of chain transfer to the monomer and chain growth were different. For the $TiCl_4$–$Al(C_2H_5)_3$ catalytic system, the overall value of k_g was lower than the values of k_g in isoprene polymerization on the systems with $AlCl(i\text{-}C_4H_9)_2$ and $AlH(i\text{-}C_4H_9)_2$ by a factor of ~20. The kinetic parameters for individual types of active sites were also different from each other. The nature of the OAC in titanium catalytic systems affects both the overall kinetic parameters and the kinetic parameters of individual types of active sites.

Thus, we found the occurrence of two to four types of active sites in the ion-coordination titanium catalytic systems for isoprene polymerization. The nature of the OAC and the conditions of polymerization affect the character of changes in molecular characteristics, the shapes of MWD curves and the kinetic heterogeneity distributions of active sites in the titanium catalytic systems, the number of active site types, and the kinetic activity of these active sites in the course of polymerization. The above additionally supports the hypothesis that OACs affect not only the stage of formation of active sites but also the stage of their operation; that is, the OAC can be a constituent of some types of active sites.

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