

HETEROGENEIDADE CINÉTICA DE PRODUTOS POLIMÉRICOS OBTIDOS NA PRESENÇA DE SISTEMAS CATALÍTICOS MICROHETEROGÊNEOS BASEADOS EM CROMATOGRAMAS DE GEL

KINETIC HETEROGENEITY OF POLYMER PRODUCTS OBTAINED IN THE PRESENCE OF MICROHETEROGENIC CATALYTIC SYSTEMS BASED ON GEL CHROMATOGRAMS

АНАЛИЗ КИНЕТИЧЕСКОЙ НЕОДНОРОДНОСТИ ПОЛИМЕРНЫХ ПРОДУКТОВ, ПОЛУЧАЕМЫХ В ПРИСУТСТВИИ МИКРОГЕТЕРОГЕННЫХ КАТАЛИТИЧЕСКИХ СИСТЕМ, НА ОСНОВЕ ГЕЛЬ-ХРОМАТОГРАММ

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Received 17 March 2021; received in revised form 25 May 2021; accepted 22 June 2021

RESUMO

Introdução: o produto polimérico obtido na presença de sistemas catalíticos microheterogêneos é caracterizado por uma distribuição de peso molecular bastante razoável (MWD), resultante de centros ativos cineticamente não equivalentes (ACs) no sistema que inicia o processo de polimerização. A natureza e a composição dos ACs são determinadas definindo e resolvendo um problema inverso na formação de MWD. Este problema é agudo porque revelar a natureza da heterogeneidade cinética explica as mudanças nos parâmetros moleculares e de consumo do produto para diferentes composições de catalisador e modos de propagação em polimerizações. **Objetivo:** o presente estudo teve como objetivo desenvolver métodos e algoritmos de interpretação de cromatogramas em gel para analisar a heterogeneidade cinética de um produto polimérico obtido industrialmente em sistemas catalíticos microheterogêneos. **Métodos:** o método de solução parte do pressuposto de que o MWD formado é uma superposição de distribuições inerentes a cada tipo de ACs. Como o problema na formulação final se refere às equações integrais de Fredholm do primeiro tipo, o método de regularização de A. N. Tikhonov é usado para sua solução numérica, com o problema original sendo preliminarmente discretizado. Esta metodologia e os algoritmos de software desenvolvidos foram usados para determinar a heterogeneidade cinética de sistemas catalíticos contendo titânio e neodímio. **Resultados e discussão:** a análise MWD revelou dois tipos de ACs com um peso molecular médio de $A_{Ti} - \ln M = 11.3$ e $B_{Ti} - \ln M = 13.2$ no catalisador de titânio, e três tipos de $A_{Nd} - \ln M = 11.1$, $B_{Nd} - \ln M = 12.7$ e $C_{Nd} - \ln M = 14$ para o catalisador de neodímio, respectivamente. **Conclusões:** experimentos computacionais repetidos sob diferentes condições de polimerização e requisitos para a preparação de um sistema catalítico permitem revelar uma relação com a heterogeneidade resultante de ACs. Ele nos permite definir e resolver problemas de controle das características moleculares do produto polimérico resultante.

Palavras-chave: poliisopreno, problema inverso, distribuição de peso molecular, titânio, neodímio.

ABSTRACT

Background: the polymer product obtained in the presence of microheterogeneous catalytic systems is characterized by fairly molecular weight distribution (MWD), resulted from kinetically nonequivalent active centers (ACs) in the system that initiate the polymerization process. The nature and composition of ACs are determined by setting and solving an inverse problem on the formation of MWD. This problem is acute because revealing the nature of the kinetic heterogeneity explains changes in the molecular and consumer parameters of the product for different catalyst compositions and propagation modes in polymerizations. **Aim:** This study aimed to develop methods and algorithms for interpreting gel chromatograms to analyze the kinetic heterogeneity of a polymer product obtained industrially in microheterogeneous catalytic systems. **Methods:** the solution method is based on the

assumption that the formed MWD is a superposition of distributions inherent in each type of ACs. Since the problem in the final formulation refers to the Fredholm integral equations of the first kind, the regularization method of A. N. Tikhonov is used for its numerical solution, with the original problem being preliminary discretized. This methodology and the developed software algorithms were used to determine the kinetic heterogeneity of titanium- and neodymium-containing catalytic systems. **Results and discussion:** The MWD analysis revealed two types of ACs with an average molecular weight of $A_{Ti}-\ln M = 11.3$ and $B_{Ti}-\ln M = 13.2$ in the titanium catalyst and three types of ACs $A_{Nd}-\ln M = 11.1$, $B_{Nd}-\ln M = 12.7$ and $C_{Nd}-\ln M = 14$ for the neodymium catalyst, respectively. **Conclusions:** repeated computational experiments under different polymerization conditions and requirements for the preparation of a catalytic system make it possible to reveal a relationship with the resulting heterogeneity of ACs. It allows us to set and solve problems of controlling the molecular characteristics of the resulting polymer product.

Keywords: *polyisoprene, inverse problem, molecular weight distribution, titanium, neodymium.*

АННОТАЦИЯ

Предпосылки: полимерный продукт, получаемый в присутствии микрогетерогенных каталитических систем, характеризуется достаточно широким молекулярно-массовым распределением, в основе формирования которого лежит наличие в системе кинетически неэквивалентных активных центров, инициирующих процесс полимеризации. Определение характера и состава активных центров проводится путем постановки и решения обратной задачи формирования молекулярно-массового распределения. Такая задача является актуальной поскольку определение характера кинетической неоднородности позволяет ответить на вопросы изменения молекулярных и потребительских параметров продукта для различного состава каталитического комплекса и режима ведения процесса. **Цель:** разработка методов и алгоритмов интерпретации гель-хроматограмм для анализа кинетической неоднородности полимерного продукта, получаемого промышленным способом в присутствии микрогетерогенных каталитических систем. **Методы:** в основе метода решения лежит предположение о том, что формируемое молекулярно-массовое распределение является суперпозицией распределений, присущих каждому типу активных центров. Поскольку задача в конечной постановке относится к интегральным уравнениям Фредгольма 1 рода, то для ее численного решения используется метод регуляризации А.Н. Тихонова, с предварительной дискретизацией исходной задачи. Данная методология и разработанные алгоритмы были использованы для определения кинетической неоднородности титан- и неодимсодержащих каталитических систем. **Результаты и обсуждение:** описанная методология и разработанные алгоритмы в программном исполнении были применены для определения кинетической неоднородности титансодержащих и неодимсодержащих каталитических систем. Проведенный анализ молекулярно-массового распределения для титанового катализатора выявил наличие двух типов активных центров с характерной средней молекулярной массой $A_{Ti} - \ln M = 11.3$ и $B_{Ti} - \ln M = 13.2$, для неодимового катализатора соответственно трех типов активных центров $A_{Nd} - \ln M = 11.1$, $B_{Nd} - \ln M = 12.7$ и $C_{Nd} - \ln M = 14$. **Выводы:** многократное проведение вычислительных экспериментов при различных условиях полимеризации и правилах приготовления каталитического комплекса позволяет установить взаимосвязь с получаемой неоднородностью активных центров, что позволяет ставить и решать перспективные задачи управления молекулярными характеристиками получаемого полимерного продукта.

Ключевые слова: *полиизопрен, обратная задача, молекулярно-массовое распределение, титан, неодим.*

1. INTRODUCTION:

Over the past decades, Ziegler-Natt catalysts have been actively used to produce stereoregular polydienes (Monakov *et al.*, 1988; Sabirov *et al.*, 1989; Skuratov *et al.*, 1992; Jie Liu *et al.*, 2018). Industrial production of polydienes is

based on d-element (Ti, Co, V) (Uetsuki and Fujiwara, 1976; Wu and Li, 2011) and f-element catalysts (Rakhimov *et al.*, 1997; Ryo Tanaka *et al.*, 2016). The latter composites include the lanthanides. In particular, titanium-based catalytic systems can produce up to 96% of cis-1,4 polyisoprene (Marina *et al.*, 1983). Lanthanide

catalysts allow obtaining dienes with more cis units (up to 98%) (Monakov and Tolstikov, 1990). Modern industrial production is focused on getting a product with specified consumer properties, which is determined by the molecular characteristics of the resulting product. Experimental estimation of molecular parameters is based on gel chromatographic analysis of the resulting product (Belenkii and Vilenchik, 1983) and molecular weight distribution (MWD) (Rudin, 1969).

The estimation of the MWD at the initial stage of modeling allows the study of the kinetic heterogeneity of the resulting product (Usmanov *et al.*, 2004; Monakov *et al.*, 2005). Microheterogeneous Ziegler-Natta catalysts during the polymerization process entail several kinetically nonequivalent active centers (ACs) that produce macromolecules of a certain molecular weight. Subsequent polycentricity broadens the MWD of the product that cannot be described by any of the known model functions corresponding to certain kinetic mechanisms. The broad MWD leads to a deterioration in the molecular and consumer properties of the end polymer product. A successful approach for regulating the number of ACs is to change their dispersed structure by changing the chemical composition of the reaction mixture (Zakharov *et al.*, 2015) and applying hydrodynamic effects in turbulent flows (Zakharov *et al.*, 2013).

To produce a turbulent effect at the stage of the catalyst preparation, a small-sized tubular turbulent device of the diffuser-confusor design is installed that modifies the dispersion of the initial microheterogeneous catalyst components. The induced hydrodynamic effect results in lower catalyst consumption as well as a change in polydispersity nature. The mathematical interpretation of the gel chromatograms reveals the dynamics of the ACs (Bigaeva *et al.*, 2015; Garifullin *et al.*, 2004) that initiate polymerization. Information about the number and proportion of ACs gives a clear picture of polymerization kinetics. It enables to conduct an empirical study and set future-proof objectives to control polymer product formation on an industrial scale. In this regard, an urgent challenge is a methodology for analyzing the obtained MWDs to identify the number and composition of ACs and implement them in the form of programs solved with the known calculation methods and algorithms.

This study aimed to develop methods and algorithms for interpreting gel chromatograms to analyze the kinetic heterogeneity of a polymer product obtained industrially in

microheterogeneous catalytic systems.

2. MATERIALS AND METHODS:

The study of the kinetic heterogeneity of polymer products is based on the solution of an inverse MWD problem (Usmanov *et al.*, 2004). The method is based on the assumption that the resulting MWD of the product can be represented as a superposition of distributions formed by each active center separately. The presence of kinetically nonequivalent ACs in the system leads to broadened MWD. The given problem is solved using model functions (Usmanov *et al.*, 2005; Usmanov *et al.*, 2003) typical for a certain kinetic mechanism. In particular, Ziegler-Natta catalysts are characterized by the monomolecular decay of ACs. In this regard, the Flory distribution represents a model function that determines the dynamics of each AC. The superposition of these distributions explains the broad nature of the resultant MWD.

Experimental studies conducted in industrial conditions determined the molecular weight distribution of the end isoprene polymerization product in titanium and neodymium catalytic systems.

In particular, to produce isoprene rubber in a $TiCl_4$ /TIBA (triisobutylaluminum) catalytic system, a suspension of the titanium catalytic complex was obtained at $-10^\circ C$ by decanting toluene solutions $TiCl_4$ (catalyst) with $Al(i-C_4H_9)_3$ (co-catalyst), p-electron-donating diphenyloxide (DFO) and electron-donating piperylene. DFO and piperylene increase the chain propagation rate and the AC concentration, respectively. The ratio of the supplied reagents was as follows: $TiCl_4/Al(i-C_4H_9)_3/piperylene/DFO = 1/1/0.2/0.15$ mol. The process was carried out continuously at an initial temperature of $-5^\circ C$ in a cascade of perfectly mixed reactors with a volume of $16.6 m^3$ and a length of 2 or 3 reactors, depending on the requirement of the final product conversion. The reagent flowrate was 19 t/h at 15 wt % of an isoprene concentration in isopentane. The consumption of the titanium catalyst was 1 mol per 980 mol of isoprene. The polymerization was terminated, and the polymerizate was washed with demineralized water when the final product conversion reached 70-75%.

Polymer samples were taken at the delivery end of the terminal reactor. They were analysed by Waters-2000 using gel-penetrating chromatography, a method for separating a mixture of substances with different molecular weights by filtering through so-called cellular gels.

Gel filtration was necessary to determine the polymer fractions with a certain molecular weight and build a pattern of the molecular weight distribution. Figure 1 shows the MWD of the final polyisoprene based on the $TiCl_4/Al(i - C_4H_9)_3$ piperylene/DFO catalytic system.

Similarly, the molecular characteristics of the isoprene polymerization product in the neodymium catalytic complex was studied. It was produced from a hydrate $NdCl_3 \cdot 0.6H_2O$ (hereinafter $NdCl_3$) with isopropyl alcohol in a liquid paraffin medium at 25 °C to get a 9 % suspension weight. The initial molecular ratio of reagents $NdCl_3 / IPA = 1/3$. The catalytic complex of the composition $NdCl_3 \cdot nИПC/Al(i - C_4H_9)_3/piperylene = 1/13/2.6$ mol was prepared in toluene. Polymerization was carried out in isopentane with isoprene concentrations of 16.6 wt%. The catalyst rate was 1 mol (according to $NdCl_3$) per 24.97 thousand mol of isoprene. The ratio of the supplied reagents was as follows: $NdCl_3/Al(i - C_4H_9)_3/piperylene = 1/12/2$. The process was carried out in a continuous manner in a cascade of perfectly mixed reactors with a volume of 16.6 m³. The reagent flowrate was 19 t/h at 15 wt % of an isoprene concentration in isopentane. The molecular weight was regulated by supplied diisobutylaluminium hydride in the volume of 0.04 kg per 1 ton of monomer. The process was terminated when the conversion rate of the final product reached 72-75%.

A gel chromatographic analysis to build the molecular weight distribution of the final polyisoprene based on the $NdCl_3/Al(i - C_4H_9)_3/piperylene$ catalytic system was conducted in the same way.

Based on the fact that every AC is characterized by a certain value of the statistical parameter λ underlying the Flory distribution, the experimental curve of the MWD $q_{exp}(M)$ can be described by Equation 1.

$$q_{exp}(M) = \int_0^{\infty} \varphi(\lambda)K(\lambda, M)d\lambda, \quad (\text{Eq.1})$$

where $K(\lambda, M) = \lambda^2 M \exp(-\lambda M)$ is the function that reflects the polymerization mechanism (Flory distribution), $\varphi(\lambda)$ is the distribution function of the ACs.

Since the gel chromatography determines the MWD of the product in coordinates binding q_w with $\ln M$, it is advisable to use new variables $x = \ln M$ and $s = \ln \lambda$. Equation 1 will take the form of Equation 2.

$$q_{exp}(M) = \int_{-\infty}^{+\infty} \psi(s)e^{2(s+x)-\exp(s+x)} ds. \quad (\text{Eq.2})$$

The equation $\exp[2(s+x) - \exp(s+x)]$

under the integral sign is a function $K(\lambda, M)$ in new coordinates (s, x) .

Then the inverse MWD problem is reduced to finding a subintegral function $\psi(s)$. Its analysis identifies the patterns in distributing polymerization centres of different types in the catalytic system. The problem of finding a function $\psi(s)$ in the Equation 2 refers to the Fredholm integral equations of the first kind (Polyanin and Manzhurov, 2003), i.e., it is ill-posed. The correct solution to the inverse problem accepts the Tikhonov regularization method (Tikhonov and Arsenin, 1986; Tikhonov *et al.*, 1990), involving a composite function and minimizing the following functional (3):

$$M_{\alpha}[\varphi] = \int_c^d \left[\int_a^b \varphi(s)K(s, x)ds - q_{exp}(x) \right]^2 dx + \alpha \int_a^b \left[\varphi^2 + \left(\frac{d\varphi}{ds} \right)^2 \right] ds \rightarrow \min, \quad (\text{Eq.3})$$

where α is the regularization parameter, finding its value is a separate task.

Since it is impossible to find an analytical solution to the problem (Equation 3), the equation will be preliminary discretized. The given function will be approximated (Tikhonov *et al.*, 1983; Verlan and Sizikov, 1986). To do this, there will be added a uniform $[a, b]$ grid $[c, d]$ with points $\{s_j\}: j = 1, \dots, n$ and n on intervals $\{x_i\}: i = 1, \dots, m$ and m points, respectively. Grid step $h_s = (b - a)/(n - 1)$ and $h_x = (d - c)/(m - 1)$. As a result of discrete transformations and replacement of the integral expression by the trapezoid formula, Equation 3 is reduced to a system of linear algebraic equations:

$$W_{\alpha}Z = WZ + \alpha CZ = V, \quad (\text{Eq.4})$$

where vector $V_j = \sum_{i=1}^m \beta K(s_j, x_i) q_i h_x$, $W_{jk} = \sum_{i=1}^m \beta K(s_j, x_i) \beta(j) K(s_i, x_k) q_i h_x$, $\beta(x) = 0.5$, if $x = 1, n$, otherwise $\beta(x) = 1$. The square matrix C has a dependence on the size of the grid step:

$$C = \begin{bmatrix} 1 + \frac{1}{h_s^2} & -\frac{1}{h_s^2} & \dots & 0 \\ -\frac{1}{h_s^2} & 1 + \frac{2}{h_s^2} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & 1 + \frac{1}{h_s^2} \end{bmatrix}$$

The solution of the inverse problem of MWD given in Equation 4 is reduced to finding a vector Z whose values form a discrete function $\psi(s)$. The classical approach to such problems is reduced to the use of numerical methods for solving systems of linear equations. Since the matrix W_{α} is symmetric, and the dimension depends on the number of partition points of the original segment, it is optimal to use exact solution methods, for

example, the square root method. However, these methods do not always meet the nonnegativity requirement Z of the vector. In this case, it is more convenient to write the original problem (equation 4) in the form of a linear programming problem with nonnegativity requirements of the vector elements V and apply the appropriate numerical methods for solving it (the simplex method, the method of internal points).

In particular, the original problem for the simplex method can be represented as Equation 5:

$$\begin{aligned} |WZ + \alpha CZ - V| &\rightarrow \min, & (\text{Eq.5}) \\ Z &\geq 0, & i = \overline{1, n}. \end{aligned}$$

The regularization parameter in the numerical solution is of great interest α . Its choice determines the correctness and accuracy in solving the inverse problem of the MWD. The regularization parameter α is selected based on the minimum conditions of the residual Equation 6:

$$\beta(\alpha) = \|\varphi(s)K(s, x) - q_{exp}(x)\|^2 = \delta^2. \quad (\text{Eq.6})$$

To make a correct choice of the value α , the multiple solutions of the problem (4) are carried out in the interval $[0;1]$ with a step not exceeding the value of the permissible accuracy. Then, based on the minimum condition of the functional, the value α and $\varphi(s)$ are fixed. When the described method is solved utilizing a computer, such iteration does not cause difficulties.

3. RESULTS AND DISCUSSION:

3.1. Results

This research uses the described approach to study kinetic heterogeneity on the example of polyisoprene obtained in titanium-based catalytic systems.

Since the developed methodology requires a discrete representation of the MWD, a graph of the polymer product's MWD (Fig.1) with a step of 0.1 included a grid and values that formed a curve $q_{эксп}(x)$. These values determine the vector components $q_{exp}(x)$ necessary to solve the problem (3) in a discrete form. After fixing 30 points, the inverse MWD problem in the formulation (4) was solved. The Flory distribution was used as the core of the original $K(s, x)$ integral equation 4. To find a vector forming a discrete view Z , an algorithm, and a software $\varphi(s)$ implementation of the internal point method were used (Zorkaltsev and Mokryi, 2018). The solution of the inverse problem and the function $\varphi(s)$ of active center distribution are shown in Figure 2.

Each maximum on the curve $\varphi(s)$ (Figure 2) corresponds to a specific type of polymerization centers that form a polymer fraction with an average molecular weight of $\ln M$. The value of the average molecular weight is determined based on the value corresponding to the next peak of the curve. The conducted MWD analysis proves that the system has at least two types of ACs: $A_{Ti-\ln M} = 11.3$ and $B_{Ti-\ln M} = 13.2$. Besides, the curve determines the position of the maxima, i.e., the average molecular weight formed on this type of ACs. However, detailed characteristics of the AC behavior can be obtained by evaluating the contribution of each centre to the overall polymerization process. To do this, the function $\varphi(s)$ was divided into elementary functions of the Gauss distribution according to the Equation 7

$$\varphi(s) = \sum_{k=1}^n p_k \frac{1}{\sigma_k \sqrt{2\pi}} \exp\left(-\frac{(s_i - s_k)^2}{2\sigma_k^2}\right), \quad (\text{Eq.7})$$

where n is the number of ACs in the system, s_k is the position of the maxima, σ_k is the width of the Gauss distribution, p_k is the proportion of each AC in the catalytic system, and $p_1 + p_2 + \dots + p_k = 1$. Since the figure depicts the presence of two types of active centers, then $n=2$.

In the studied case, the maxima in Figure 2 overlap each other. The effect of each type of active centre can be evaluated roughly. Since the original problem was presented in a discrete form, there was another problem created to find parameters $p_1, p_2, \sigma_1, \sigma_2$ corresponding to the first and second types of the active centre:

$$\begin{aligned} \sum_{i=1}^m \left[\varphi(s_i) - p_1 \frac{1}{\sigma_1 \sqrt{2\pi}} \exp\left(-\frac{(s_i - s_1)^2}{2\sigma_1^2}\right) - \right. \\ \left. p_2 \frac{1}{\sigma_2 \sqrt{2\pi}} \exp\left(-\frac{(s_i - s_2)^2}{2\sigma_2^2}\right) \right] \rightarrow \min, \quad (\text{Eq.8}) \end{aligned}$$

where m is the number of segment division points. The algorithm for problem-solving in a statement (8) is reduced to selecting a value for system parameters $p_1, p_2, \sigma_1, \sigma_2$ when at each step of the initial discrete partition the deviation of the sum of Gaussian distributions from the complex function $\varphi(s)$ will be minimal

The optimization problem (8) for parameter identification $p_1, p_2, \sigma_1, \sigma_2$ was solved by the configuration method (Hooke-Jeeves) (Panteleev and Letova, 2015). Since $p_1 + p_2 = 1$, the value p_2 is used instead $1 - p_1$ in the expression (8). Then problem (8) is the problem of finding three parameters of the system. As the initial condition of the problem (5), the parameters $\sigma_1 = 0.5, \sigma_2 = 0.5, p_1 = 0.1, p_2 = 0.9$ are used. The initial conditions for p_1, p_2 were proposed based on the quadrature error estimate of the curve in Figure 2. In particular, the authors used the trapezoid

method.

The minimization problem (8) solution provided the values $\sigma_1 = 0.44$, $\sigma_2 = 0.65$, $p_1 = 0.15$, $p_2 = 0.85$. Then the proportion of A_{Ti} centres is 0.15, the proportion of B_{Ti} centres is 0.85. To find the deviation of the resulting calculated curve, which is the sum of the Gaussian distributions from the original curve $\varphi(s)$, an absolute difference was recorded at each point of the discrete partition. Figure 3 displays a graphical representation of the resulting distributions. The mean-square deviation of the Gauss distribution from the calculated curve $\varphi(s)$ reached 5.4%.

In practice, the number of AC types usually reaches four. The small number of AC types in the very study is explained by the multi-component chemical composition of the reaction mixture (Zakharov *et al.*, 2015) and the hydrodynamic effect in turbulent flows (Nasyrov *et al.*, 2016).

To get isoprene on the catalytic system $NdCl_3/Al(i-C_4H_9)_3$ /piperylene, the inverse MWD problem is solved. To solve the inverse problem and determine the number and composition of ACs, the same methodology was used in the titanium catalyst. As a method of solving the problem in the form (4), internal points were used. The number of partition points to represent the original problem in discrete form was set to 30. The solution of the problem for the function $\varphi(s)$ is shown in Figure 4.

The result of the inverse MWD problem solution gives grounds for stipulating that there are three AC types in the system $A_{Nd-InM} = 11.1$, $B_{Nd-InM} = 12.7$, and $C_{Nd-InM} = 14$. To find additional parameters of the system, the AC distribution function was expanded in Gauss distributions by minimizing the functional of the following form (Equation 9):

$$\sum_{i=1}^m \left[\varphi(s_i) - \sum_{j=1}^3 p_j \frac{1}{\sigma_j \sqrt{2\pi}} e^{-\frac{(s_i-s_j)^2}{2\sigma_j^2}} \right] \rightarrow \min. \text{(Eq.9)}$$

Since the number of types of ACs has increased to 3, the task of identifying the system parameters is reduced to identifying 6 parameters, the initial approximation of the parameters p_1 , p_2 and p_3 is of great importance. They were found by estimating the areas under each peak using the trapezoid method

The minimization problem solution provided the values $\sigma_1 = 0.15$, $\sigma_2 = 0.26$, $\sigma_3 = 0.26$, $p_1 = 0.12$, $p_2 = 0.48$, $p_3 = 0.4$. Thus, the proportion of A_{Nd} centers is 0.12, the proportion of B_{Nd} centers equals 0.48, and the share of C_{Nd} centers is 0.4.

3.2. Discussion

The research results of titanium catalyst heterogeneity depict two AC types: $A_{Ti-InM} = 11.3$ and $B_{Ti-InM} = 13.2$. The proportion of active centers forming fractions with the lowest molecular weight is small and does not exceed 15%. An additional impact on the catalytic complex can lead to a further reduction in the proportion of A_{Ti} -type centers and make the system monocentric (Zakharov *et al.*, 2013).

Studies of a neodymium catalyst system show that there are at least three types of active centers: $A_{Nd-InM} = 11.1$, $B_{Nd-InM} = 12.7$, and $C_{Nd-InM} = 14$. The proportion of active centers with a typical low molecular weight does not exceed 12%, with the B_{Nd} and C_{Nd} AC types being very close in molecular weight.

4. CONCLUSIONS:

The solution of the inverse MWD problems provides a clear picture of the AC dynamics that initiate the polymerization process. The developed methods and algorithms based on the regularizing operator of A.N. Tikhonov have been successfully applied to analyze the nature of polycentricity of titanium-and neodymium-based catalytic systems. As a result, industrial polymer samples are characterized in terms of their nature and the AC composition.

Repeated computational experiments under different polymerization conditions and catalytic complex preparation reveal a relationship with the resulting heterogeneity of the active centers. In the future, it can be used to control the polymerization process with modeling tools.

The MWD width is often estimated using the polydispersity value, expressed as the ratio of the average mass and the average calculated molecular mass. However, polymer products have the same width but a completely different number and the ratio of ACs. Accurate data on the nature and composition of the ACs lays the basis for modeling the polymerization kinetics and answering the questions on developing polymer product's consumer and molecular properties during empirical studies.

In addition, the control of the kinetic polymerization product heterogeneity remains an urgent target of industrial production in the search for better catalyst system modification and preparation modes. This explains the need for continuous gel chromatographic analysis of the product at different stages of its preparation and analysis of the MWD being built up.

5. ACKNOWLEDGMENTS:

The study was carried out within the framework of the state assignment of the Ministry of Science and Higher Education of the Russian Federation (scientific topic code FZU-2020-0027).

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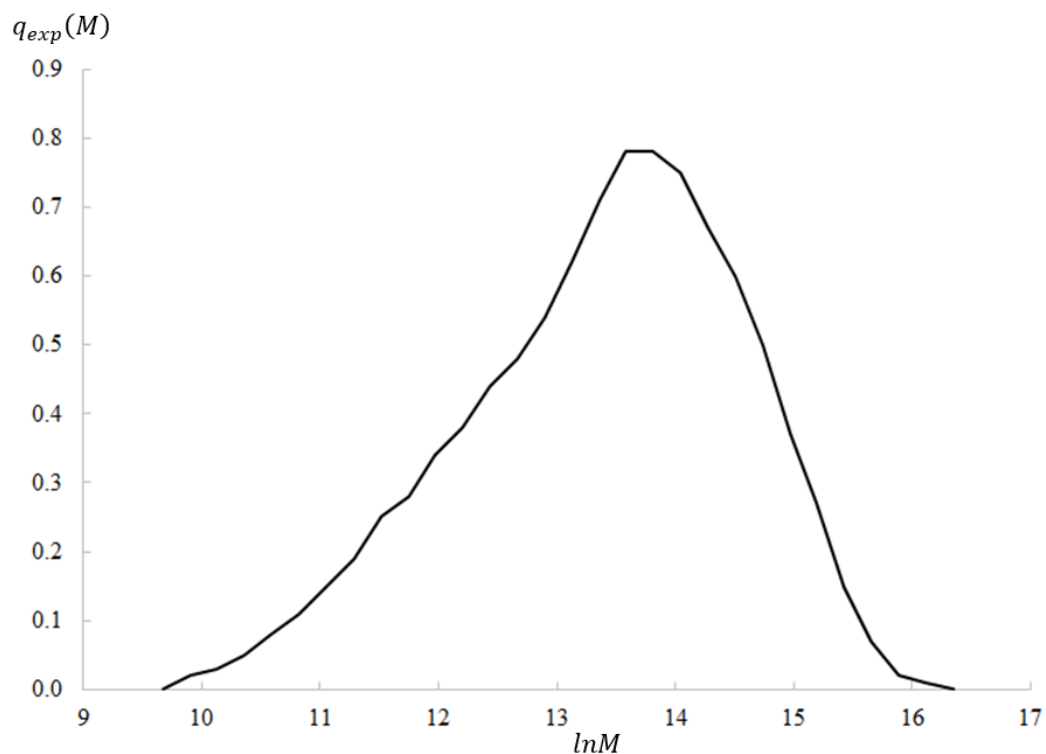


Figure 1. The MWD of the isoprene polymerization product on the catalytic system $TiCl_4/Al(i - C_4H_9)_3$ /piperylene/DFO. Source: the author

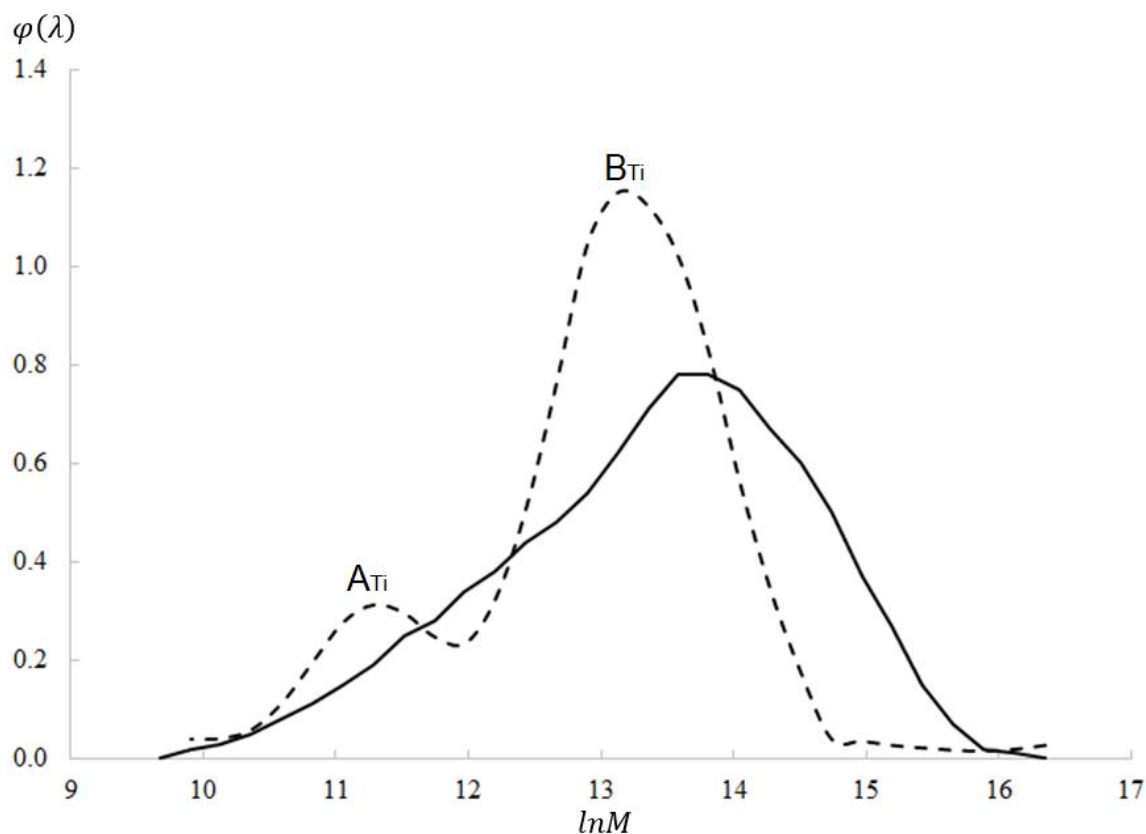


Figure 2. The solution results of the inverse MWD problem for isoprene on a catalytic system $TiCl_4/Al(i - C_4H_9)_3$ /piperylene/DFO (a continuous line presents the initial distribution of the product, a dotted line shows the AC distribution). Source: the author

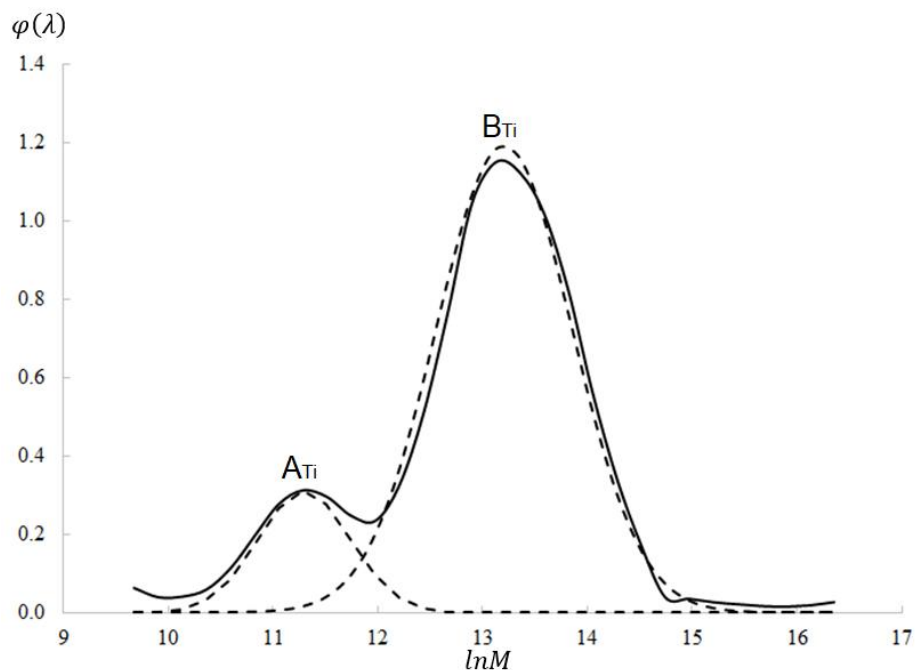


Figure 3. Expansion of the AC distribution function into the Gauss distribution (a continuous line is a calculated function $\varphi(s)$, a dotted line stands for the Gauss distribution for each AC).
Source: the author

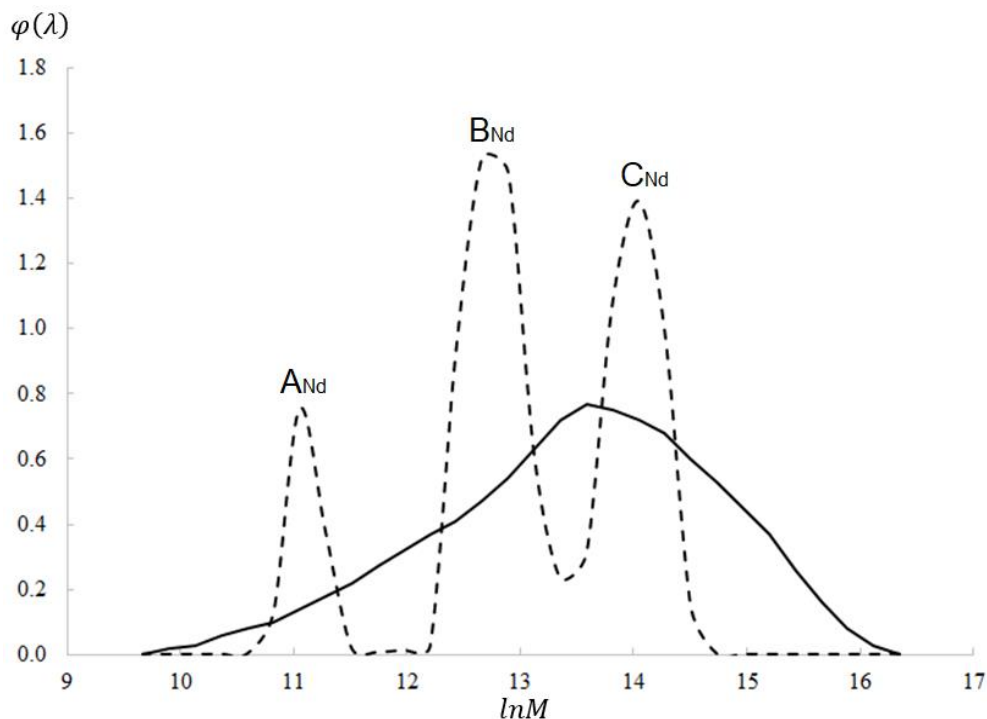


Figure 4. The results of the inverse isoprene MWD problem solution for a catalytic system $NdCl_3/Al(i-C_4H_9)_3/piperylene$ (a continuous line presents the initial distribution of the product, a dotted line shows the AC distribution). Source: the author