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Calculation of the Kinetic Parameters of the Modification Reaction of Polyisobutylene With Acrylonitrile

Abstract

In the article, the results of the research on the calculation of the mathematical model and parameters of the copolymer production process by modifying polyisobutylene with acrylonitrile polar monomer at a temperature of 20-60^{0}C in the presence of $AlCl_3$ catalyst have been reflected. Using this, the results of the study of the effect of polyisobutylene with acrylonitrile on the reaction conditions have been given, the kinetic equations of those reactions have been calculated, the values of the parameters, the analysis of the researches in the field of mathematical modeling of the process were reflected. This method allows us to reduce the number of experiments, resources and time, and also to obtain an arbitrary ratio of acrylonitrile to polyisobutylene that satisfies us within the limits of experimental parameters. The functional dependence between those parameters has been drawn up by analyzing the regularities of the ratio of the solidities of [AN] and [PIB] in the copolymer on temperature, reaction time, and the solidities of PIB, AN and the catalyst ($AlCl_3$) in the initial solution. The kinetic parameters of the PIB modification reaction with AN have been calculated on the basis of the developed kinetic model and experimental materials. The rate constants of the reactions corresponding to the temperatures of 20, 40, 60^{0}C for 1.8% (mass)

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catalyst amount are 0.7699; 0.8322 and 0.89 s^{-1} have been obtained. The rate constants corresponding to those temperatures and 0.92% amount of catalyst were 0.2976, 0.3288, 0.3581s^{-1}. The effect of the amount of catalyst on the activation energy has also been studied; E=3000 C/mol. (AlCl3=1.8%) (mass) and E=3750 C/mol. (AlCl3=0.92%).

Keywords: *Polyisobutylene, acrylonitrile, polar polymer, $AlCl_3$ catalyst, copolymer, temperature*

Introduction

In general, there is no clear boundary between empirical and kinetic modeling methods. The study of the kinetic mechanism in detail can be more or less in-depth depending on the conditions imposed. In one case, the set low speeds will have a significant effect on the operation, and in the other case, they may have little effect on the progress of the synthesis. In addition, the detailed kinetic explanation of the process, some parts of the elementary stages can be replaced by gross rates. Gross-kinetic can fully characterize the process along with a good structure explanation and can be considered useful for process intensification and optimization. An example of this is the mathematical explanation of the thermally excited radical polymerization process of styrene in bulk. However, the given explanation can be obtained on the basis of an accurate study of the chemistry and physics of the process. Therefore, there is an imprecise boundary between empirical and fundamental explanations of the process, and it is determined not by the form of the problem, but in the first case by a formal mathematical method, and in the second case by physical and chemical studies of the process (Agakishiyeva, Aliyeva, 2007; Kondaurov, 2005).

Research

Methods of calculating chemical reactors in cases where the reaction mechanism and kinetic constants are known, have been given in the literature. However, during the fundamental research of chemical processes, it is usually necessary to solve opposite problems. In cases where it is possible to experimentally measure the concentration of substances, it is possible to restore the kinetic constants if the mechanism of the reaction is known. This issue is complicated because in this case it is also necessary to solve the straight issue (Azizov, Alosmanov, Akberov, 2004).

The reverse problem of restoring the kinetic mechanism is simple. This is the issue

It becomes simpler if several more hypothetical mechanisms are taken and one of them is selected. The problem is solved by calculating all the options and finding the option that pays the experimental indicators more accurately. If the number of experiments is not enough, it is important to add additional experiments (Berengarten, Bondareva, Kutepov, 2007).

If the rate constants of only a few elementary stages are unknown, then the problem is devoted to finding those constants. Let's assume that the following are given: Kinetic mechanism (perhaps the values of several constants are also given); Process conditions (temperature, pressure, etc.); Time dependence of the concentration of some substances (or kinetic curves).

For polymer problems, some properties of molecular distributions must also be known. Let us denote them by $A_{ig}(t)$ $i=1,....,n$. The objective function $f(k_1,...k_m)$ is taken. Here $k_1,\ldots,k_m$ are unknown constants. The following function should be minimized.

$$F(k \quad k \quad) = \sum_{i=1}^{n} \sum_{\gamma=1}^{m} \left[A \ (t \ ) - A \ (t \ )\right]^2$$
$$1....,\ m \qquad iP \quad \gamma \qquad ig \quad \gamma$$

where $t_1, \ldots, t_m$ - the times when the densities of Aig are measured; $A_{ir}(t)$ - kinetic curves calculated for the case where the constants $k_1,\ldots, k_m$ are given..

Mathematical methods for minimizing multiple unknown functions are divided into two groups: gradient and Monte Carlo random search methods (General course of processes and apparatuses of chemical technology, 2002; Savelyanov, 2007). During the development and optimization of new technological processes of polymer synthesis, the analysis of the kinetic model of the process is the basis for calculating the operating mode of the reactor. The kinetic model describes the speed of the reaction and the structure of the formed polymer in time and space. Changes in time and space occur due to the influence of temperature, pressure, concentration of reagents and other factors.

One of the most difficult points in this field is the development of a kinetic model. The model should adequately describe the experimental data over a wide range of conditions.

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Until recent years, the kinetic method of analysis has been used as a laboratory method to determine the chemical mechanism of a reaction, which, depending on the problem, usually separated any stage of the reaction. The choice of experimental conditions has been also determined by the problem at hand. Usually, the kinetic region of the reaction process was considered in the periodic regime of the synthesis in concentrated solutions (Bilalov, Huseynov, Abbasova, 2002; Hajiahmedzadeh, 2017).

The analysis of industrial processes by the kinetic method and their research began in the last decades. At the present stage, the high quality of the product, the demand for the creation of units with great power, the development of computing techniques and the development of the methods of analysis of the structure of products have been the stimulus for the solution of the mentioned issues. The rate of the reaction, the average molecular masses and the ratio of the first cycles of the distribution according to the molecular masses are considered as the object of the calculation of the kinetic schemes of the polymerization processes. In general, other parameters of the molecular structure can be taken into account, for example, composition, compositional inhomogeneity for copolymers, etc (Smirnov, Volzhinsky, 1977; Yusubov, 2015).

A joint consideration of the values of the parameters of the reaction rate, the convection of monomers and the structure of the polymer allows to solve the problem of choosing the optimal configuration of the reactor and the optimal mode of synthesis. It is convenient to divide the parameters that determine the progress of the process into two groups: discrete parameters and continuously variable parameters. Discrete parameters determine the phase state of the reagents, the mechanism of the reaction (including the method of adjusting the molecular weight and the type of initiator). Continuously variable parameters determine the concentration of reagents, temperature, pressure, linear velocity of the flow, linear dimensions and volume of the reactor.

A common approach to optimization is to select the second set of parameters while keeping the first set of parameters fixed. The limits of the second group are generally determined by the thermodynamics of the process for the limit values of density, temperature, pressure, possibility of additional reactions and technical considerations. But even in this case, it is not possible to select and cover all values of the parameters. Three methods of approaching the solution of the mentioned problem are shown: 1. Solving the problem by "Random search", that is, by the method of arbitrary combination of the first and second group parameters. The construction of that combination is based on the experience and intuition of the researcher; 2. Selection of values of parameters determined with the help of various efficiency criteria and changed in a certain field; 3. Special mathematical methods of searching for the extremum (for example, dynamic programming method, variation method, Box-Williams method, etc.) are the first approach in the technology up to now.

Technologists are more inclined to the "black box" approach to optimization. In this case, the internal relations of the object are not studied, but the changes in the output caused by the change of the input parameters are fixed. Obtaining the results accordingly allows you to get the most general picture of the mathematical model (in the form of a matrix of polymers). Such a regression model differs from a kinetic model in that it does not clearly provide information about the physical and chemical mechanism of the process. Such a model is effective in automatic process control or modeling processes that require a lot of difficult calculations in a theoretical approach (Ablonin, 2001; Kahramanov, Kasumova, Osipchik, 2017).

It should be noted here that regression models lag behind kinetic models in terms of accuracy when extrapolating results beyond the range of parameters.

Experimental part: During the modeling and optimal design of the polymerization process, the kinetic model is preferred because the extrapolation of the results is an important issue considering all the parameters.

Concrete issues in the field of optimization of polymerization processes can be conventionally divided into two groups: 1) development of new technological processes; 2) improvement of industrial facilities.

The difference here is that the restrictions imposed on the first and second groups are different. In the second case, it is more difficult to solve the problem, because a lot of capital investment is allocated to their reconstruction, and in addition, various technical issues arise.

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PIB modification reaction with acrylonitrile at temperature 5–60^{0}C, catalyst ($AlCl_3$) concentrations 0.92 ÷ 1.8%(mass), reaction time 0.0833 ÷ 1.5 hours, initial $[AN]_0$ in initial solution 4 ÷ 32% (mass) concentrations and the initial concentration of $[PIB]_0$ in the initial solution was 6.12% (wt.) (Jantas, Draczynski, Herezynska, Stawski, 2012; Salimova, Shahpelangova, 2009).

The main goal of the research described in this section is to develop a kinetic model of the reaction of modification of PIB with acrylonitrile, and to calculate kinetic parameters based on it and using experimental data.

Some of the experimental materials of the kinetic studies of the reaction of PIB modification with acrylonitrile are given in Tables 1 and 2.

$AlCl_3$ has been used as a catalyst and hexane as a solvent for all versions of the reaction.

For the calculation of kinetic parameters, the reactions have been carried out at temperatures of 20, 40, 60^{0}C. Kinetic parameters have been determined to be recorded at the initial fixed time 5 minutes after the start of the reaction. The equilibrium time of the reaction was 90 minutes (Mirzai, Ibragimov, Gashimov, Yusubov, 2008; Naibova, 2014).

For each temperature, the reaction product copolymer was analyzed 5, 10, 20, 30 and 90 minutes after the start of the reaction. Experimental data obtained under the same conditions for all three temperatures have been used, that is, the same initial amount of AN and PIB, the reaction product analysis times, the same amount of catalyst and solvent have been taken.

In order to clarify the influence of the amount of catalyst on kinetic parameters, calculations have been made in two variants: 1) the amount of catalyst is 1.8% (by mass) of the initial mixture (tab.1); 2) the amount of the catalyst is 0.92% (by mass) of the initial mixture. The amount of solvent corresponding to them is determined. The rest of the conditions remain unchanged and are taken the same.

As can be seen from Table 1, the largest destruction percentage of PIB is 11.5% (mol) relative to its initial value (calculations are obtained from the ratio $[AN]c/[PIB]_0 \cdot 100\%$ (mol)). This indicator has a temperature of 60 ^{0}C and a reaction time of 1.5 hours. 0.576 g (1.8%) of the catalyst has been obtained. In this case, acrylonitrile is used up to 2.1% of its initial amount.

Table 1.

Kinetic parameters of PIB modification reaction with acrylonitrile: catalyst – amount of $AlCl_3$ 0.576g (up to 1.8% of the mass of the mixture), amount of solvent hexane 24.932 (77.91%); $[AN]_0$ = 0.14g/g; $[PIB]_0$=0.062 g/g; the amount of mixture in the reactor is 32g.

Temperature, ^{0}C	Time, hour	$[AN]_c$, q/q	*k*, hour^{-1}
20	0	0	–
– " –	0.0833	0.0005344	0.7706
– " –	0.1667	0.001078	0.7448
– " –	0.333	0.002191	0.7747
– " –	0.5	0.003344	0.7895
– ″ –	1.5	0.003937	0.3197
40	0	0	–
– " –	0.0833	0.0005812	0.7855
– " –	0.1667	0.001178	0.8158
– " –	0.333	0.002400	0.8542
– " –	0.5	0.003656	0.8734
– ″ –	1.5	0.004344	0.3473
60	0	0	–
– " –	0.0833	0.0006094	0.8607
– " –	0.1667	0.001228	0.8790
– " –	0.333	0.002503	0.8909
– " –	0.5	0.003825	0.9294
– ″ –	1.5	0.004537	0.3707

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It can be seen from Table 2 that by reducing the amount of catalyst from 0.576 g (1.8%) to 0.295 g (0.92%), PIB is destroyed up to 7.34% (mol). In this case, the consumption of AN is only 1.35% (other parameters do not change) (Smirnov, Volzhinsky, 1977).

Let's make a kinetic model of PIB modification reaction with acrylonitrile. Consider that the density of acrylonitrile in the reaction system at time t=0 was $[AN]_0$ g/g, and the density of polyisobutylene was $[PIB]_0$ g/g.

Acrylonitrile in the amount of [AN]c g/g and polyisobutylene in the amount of [PIB]c g/g react during the time t. In this case, unreacted acrylonitrile remains in the system in the amount of $[AN]_0$ - [AN]c and polyisobutylene $[PIB]_0$ - [PIB]c. Then the rate of PIB modification reaction with acrylonitrile can be expressed by the following equation (Beskov, 2005):

Table 2.

Kinetic indicators of the reaction of PIB modification with acrylonitrile: the amount of catalyst - AlCl3 is 0.295 g (1.8% of the mixture), the amount of solvent - hexane is 25.241 (78.88%); $[AN]_0$ = 0.41g/g; $[PIB]_0$=0.062 g/g; the amount of mixture in the reactor is only 32g.

Temperature, ^{0}C	Time, hour	$[AN]_c$, q/q	*k,* hour^{-1}
20	0	0	–
– " –	0.0833	0.0002062	0.3021
– " –	0.1667	0.0004156	0.3027
– " –	0.333	0.0008344	0.2983
– " –	0.5	0.001259	0.2873
– ″ –	1.5	0.001884	0.1478
40	0	0	–
– " –	0.0833	0.0002312	0.3520
– " –	0.1667	0.0004625	0.2976
– " –	0.333	0.0009344	0.3336
– " –	0.5	0.001412	0.3322
– ″ –	1.5	0.002131	0.1696
60	0	0	–
– " –	0.0833	0.0002469	0.4018
– " –	0.1667	0.0004937	0.3351
– " –	0.333	0.0009937	0.3437
– " –	0.5	0.001503	0.3518
– ″ –	1.5	0.002309	0.1829

$$-\frac{d([AN]_0-[AN]_c)}{dt}=k([AN]_0-[AN]_c)([PIB]_0-[PIB]_c) \quad (1)$$

It is obvious that the equation (2) can be written as follows:

$$\frac{d[AN]_c}{dt}=k([AN]_0-[AN]_c)([PIB]_0-[AN]_c) \quad (2)$$

Here $[AN]_0$, g/g – the initial amount of AN in the reaction mixture; $[PIP]_0$, g/g – amount of PIP in the initial mixture; k, hour-1 – rate constant of PIB modification reaction; [AN]c, w/w – the amount of AN in the resulting copolymer; [PIP]c, w/w – the amount of PIP in the copolymer (Timofeev, Serafimov, Timoshenko, 2010).

Taking into account the initial conditions, the integral of (3) gives the following expression:

$$k=\frac{1}{t}\cdot\frac{1}{[AN]_0-[PIB]_0}\ln\frac{[PIB]_0([AN]_0-[AN]_c)}{[AN]_0([PIB]_0-[AN]_c)} \quad (3)$$

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Indicators for calculating k have been taken from tables 1. and 2.

The values of k for each fixed reaction time and temperatures of 20, 40, 60^{0}C are given in tables 1. and 2.

Let's determine the activation energy E and the exponential front stress A based on the Arrhenius equation – $\bar{k}$ =Aexp[-E/(RT)] using the indicators of obtained for three temperatures. It is obvious that

$$\ln \bar{k} = \ln A - \frac{1}{RT} \cdot E$$

According to the conditions of the reaction that we are looking at, the parameters of the Arrhenius equation are as follows: $\bar{k}$, hour^{-1}; A, hour^{-1}, E,C/mol; R, C·mol^{-1}·K^{-1}; T,K.

If we replace the values of and universal gas constant R= 8.3143 C·mol^{-1}·K^{-1} in the Arrhenius equation by performing calculations by the least squares method from tables 1. and 2. 3. we get the indicators in the table.

As can be seen from table 3, activity energy does not receive a large price. This shows that the reaction of modification of PIB with acrylonitrile takes place easily in the temperature range of 20-60^{0}C and under the conditions of the catalytic process (Yusubov, 2015). Thus, based on the research, we come to the conclusion that the values of the kinetic parameters of the reaction of modification of PIB with acrylonitrile are suitable for the course of the process.

Table 3.

Results of calculation of activation energy and exponential forward stresses.

T, K	$\bar{k}$, saat^{-1}	$\ln \bar{k}$	*R*,C mol^{-1} K^{-1}	$\frac{1}{RT}$, C^1·mol^{-1}	*A,* saat^{-1}	*E*, C/mol
$AlCl_3$ =1.8 %						
293	0.7699	– 0.2615	8.3143	$4.105 \cdot 10^{-4}$	2.63	3000
313	0.8322	–0.1837	8.3143	$3.843 \cdot 10^{-4}$	2.63	3000
333	0.89	$\bar{0.1165}$	8.3143	$3.612 \cdot 10^{-4}$	2.63	3000
$AlCl_3$ =0.92 %						
293	0.2976	–1.212	8. 3143	$4.105 \cdot 10^{-4}$	1.3935	3760
313	0.3288	–1.112	8.3143	$3.843 \cdot 10^{-4}$	1.3935	3760
333	0.3581	–1.027	8.3143	$3.612 \cdot 10^{-4}$	1.3935	3760

Activity energy values – E= 3000 C/mol ($AlCl_3$=1.8% (mass)) and E= 3760 C/mol ($AlCl_3$=0.92% (mass)) is satisfactory.

Conclusion

The average value of k for the temperature of 20^{0}C has been calculated $\bar{k}_{20}$=0.7699 h $^{-1}$. In this case, the k found for the equilibrium state of the reaction after 1.5 hours has not been taken into account, because during this period k, which reflects the rate of the reaction, drops sharply. At a temperature of 20^{0}C, the deviation (difference) of the values of the rate constants obtained for different times from their average value is on average ±3%.

Average values of k for temperatures of 40^0 and 60^{0}C are: $\bar{k}_{40}$=0.8322 h^{-1}, $\bar{k}_{60}$=0.89 h^{-1}. The average error of the deviation of the rate constants from the mean value was ±3 and ±4% for temperatures of 40^0 and 60^{0}C , respectively. As can be seen from table 1, as the temperature increases, the value of the rate constant of the reaction increases, which is a legitimate case.

Using the indicators of table 2, the rate constant of the reaction was determined for the case of 0.92% penetration of the catalyst (that is, 2 times less than in table 1). Here, the average value of the rate

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constant of the reaction of modification of PIB with AN is =0.2976 according to the temperatures of 20, 40, 60^0 C; $\bar{k}_{20} = 0.2976$; $\bar{k}_{40} = 0.3288$; $\bar{k}_{60} = 0.3581$ h^{-1} has been obtained.

The deviation of the values of speed constants obtained for different times from the average value is on average ±2÷3%. We accept this as normal, because this value is within the margin of error of experiments.

At different catalyst prices and other factors being held constant, comparison of the average values of the obtained rate constants leads to the conclusion that the amount of the catalyst has a significant effect on the reaction rate. For example, increasing the amount of the catalyst from 0.92% to 1.8% of the mixture increases the reaction rate by 2.5 at temperatures of 20, 40 and 60^0C, respectively; 2.53; causes an increase of 2.49 times

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