

12. Effect of basalt fibers dispersion on steel fire protection performance of epoxy-based intumescent coatings / Yasir M., Amir N., Ahmad F., Ullah S., Jimenez M. // Progress in Organic Coatings. 2018. Vol. 122. P. 229–238. doi: <https://doi.org/10.1016/j.porgcoat.2018.05.029>
13. Kroezen A. B. J., Wassink J. G., Schipper C. A. C. The flow properties of foam // Journal of the Society of Dyers and Colourists. 2008. Vol. 104, Issue 10. P. 393–400. doi: <https://doi.org/10.1111/j.1478-4408.1988.tb01138.x>
14. Lesov I., Tcholakova S., Denkov N. Factors controlling the formation and stability of foams used as precursors of porous materials // Journal of Colloid and Interface Science. 2014. Vol. 426. P. 9–21. doi: <https://doi.org/10.1016/j.jcis.2014.03.067>
15. Estimation of the Pores Dimensions of Intumescent Coatings for Increase the Fire Resistance of Building Structures / Gravit M., Gumenyuk V., Sychoy M., Nedryshkin O. // Procedia Engineering. 2015. Vol. 117. P. 119–125. doi: <https://doi.org/10.1016/j.proeng.2015.08.132>
16. Kang S., Choi J., Choi S. Mechanism of Heat Transfer through Porous Media of Inorganic Intumescent Coating in Cone Calorimeter Testing // Polymers. 2019. Vol. 11, Issue 2. P. 221. doi: <https://doi.org/10.3390/polym11020221>
17. Ručigaj A., Krajnc M., Šebenik U. Kinetic Study of Thermal Degradation of Polydimethylsiloxane: The Effect of Molecular Weight on Thermal Stability in Inert Atmosphere // Polymer science. 2017. Vol. 03, Issue 02. doi: <https://doi.org/10.4172/2471-9935.100024>
18. Grand A. F., Wilkie C. A. Fire retardancy of polymeric materials: monograph. CRC Press, 2000. 592 p.

На основі механізму перебігу поліконденсації складена схема реакції рівноважної конденсаційної теломеризації, як поліконденсаційного процесу з обривом ланцюга монофункціональним телогеном. Виходячи з цієї схеми складені рівняння матеріального балансу за структурними елементами, що містять нескінченну кількість членів. При виконанні принципу Флорі про однакову реакційну здатність кінцевих груп нескінченної суми являють собою геометричні прогресії з однаковим знаменником. Це дозволяє згорнути модель процесу в замкнуту систему з чотирьох нелінійних алгебраїчних рівнянь.

В результаті досліджень властивостей моделі шляхом математичного аналізу і комп'ютерних експериментів встановлено наступне:

– розподіл продуктів теломеризації представляє суперпозицію геометричних розподілів базових структурних компонентів з одним і тим же знаменником прогресії, але різними величинами вихідних концентрацій. Розподіл Флорі для гомополіконденсації можна розглядати, як окремий випадок цього розподілу;

– система рівнянь моделі може мати до 4 дійсних коренів. При одиничному рішенні системи при випадковому виборі початкового наближення в ~74 % випадків виходить помилковий позитивний корінь. Для перевірки істинності кореня розроблений критерій на основі величини знаменника збіжної геометричної прогресії, запропонована процедура комп'ютерного рішення системи, що дозволяє знайти істинний корінь;

– на моделі виявлені закономірності впливу концентрації реагентів на склад рівноважної суміші при сталості концентрації побічного низькомолекулярного продукту конденсації. Показано, що при прагненні цієї концентрації до нуля склад перестає залежати від значень констант рівноваги.

Розроблена модель дозволяє розраховувати склад рівноважної суміші олігомерів в залежності від співвідношення концентрацій мономерів, телогена і низькомолекулярного продукту конденсації. Це робить її корисною на практиці для попередньої чисельної оцінки складу рівноважних сумішей олігомерів при плануванні синтезів методом конденсаційної теломеризації

Ключові слова: рівноважна конденсаційна теломеризація, нелінійні алгебраїчні рівняння, комп'ютерне моделювання, склад олігомерів

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CONSTRUCTION AND INVESTIGATION OF THE COMPUTER MODEL OF DISTRIBUTION OF THE COMPOSITION OF PRODUCTS FROM EQUILIBRIUM CONDENSATION TELOMERIZATION

S. Kondratov

Doctor of Chemical Sciences, Professor*

Yu. Evtushenko

PhD, Head of Department*

E-mail: julia.evtushenko@ukr.net

Yu. Kravchenko

Department of International Economics

Taras Shevchenko National University of Kyiv

Volodymyrska str., 60, Kyiv, Ukraine, 01033

*Department of Medical and Biological

Physics, Medical Informatics and Biostatistics

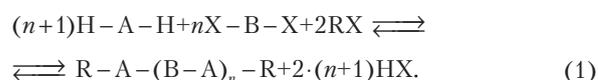
State Establishment

«Lugansk State Medical University»

Budivelnikiv str., 32, Rubizhne, Ukraine, 93012

1. Introduction

Polycondensation is one of the main methods for obtaining polymers. An important kind of polycondensation is the condensation telomerization, which proceeds in accordance with a general pattern:



Condensation telomerization can be regarded as heteropolycondensation with a chain disruption due to the

introduction to the reaction with bifunctional monomers $H-A-H$ and $X-B-X$ a of the monofunctional monomer RX , which is called telogen [1]. In the course of the reaction, a polymer and the low-molecular product HX form. This process is exploited in industry for the synthesis of acrylic oligomers and oligomeric plasticizers [1, 2]. Typically, reactions (1) are reversible. Telomerization processes are carried out under conditions that are close to equilibrium. This is achieved by distilling the low-molecular product HX from the mass (water, lower alcohol, etc.) [1, 2].

Telomerization condensation processes are of interest for new applications. In recent years, they have been used in biology and medicine to obtain so-called «smart» polymers, changing their characteristics with a change in temperature, pH and other properties of external environment. Such polymers were derived by polymerizing the products of telomerization of dimethyl acrylate [ϵ -hydroxycaproate]-co-glycolate] and butyl acrylate [3], short-chain polyethylene glycols and ethylene glycol with esters of acrylic acid [3], ethylene glycol and methyl methacrylate [4, 5]. The methods of synthesis of such «smart» polymers and their application in biomedicine were considered in reviews [6, 7].

Despite the practical importance, theoretical aspects of the condensation telomerization processes have not been sufficiently investigated. That refers to issues related to the distribution of oligomeric products for the types of terminal functional groups and the degree of polymerization, the impact exerted on them by the starting ratio of reagents and the concentration of a low-molecular by-product. It is a relevant task to explore these issues by constructing and examining the properties of mathematical models, so it could be used to obtain polymeric blends with the predefined properties.

2. Literature review and problem statement

Despite the practical importance of equilibrium condensation telomerization, mathematical models of the distribution of products from this process have not been considered in the scientific literature up to now. Equilibrium telomerization is a case of the equilibrium linear polycondensation with a disrupted chain. Therefore, we shall focus on current approaches to modeling the processes of polycondensation in terms of their possible application to constructing a model of condensation telomerization.

Underlying the models of polycondensation products distribution is the theory by P. Flory and W. Carothers, the principal provisions of which are as follows [8–12]:

a) the formation of a polymer occurs statistically. To obtain a polymer with n recurring links, all possible combinations of polymers-predecessors are used, which can interact thereby forming this product;

b) similar terminal functional groups of polymers have the same reactivity that is independent of the length of the polymer chain.

The result is a geometric distribution of polymers based on the degree of polymerization for homopolymers.

Direct application of the Flory-Carothers theory to the more complex process under consideration (1) with the additional participation of telogens turns out to be impossible. The theory should be modified taking into consideration the specificity of process (1). In this case, provisions a) and b) are common and must be used to construct a model of condensation telomerization.

Recently, scientists have intensively studied the role in polycondensation of the processes of forming the macrocyclic products at the expense of competitive intramolecular interaction between different terminal groups. That relates to the observed anomalous increase in the degree of polydispersity (DPD) (a ratio of the weight average polymerization degree to average) above the limit value of 2, following from the Flory-Carothers theory [10, 11]. The formation of macrocycles of different size in the processes of polyesterification has been recently proven for the first time experimentally using the methods of elution liquid chromatography and matrix-activated laser desorption/ionization (MALDI TOF) [9].

Several approaches are currently being developed to account for cyclization in the model of polycondensation. They are based on the introduction of a quantitative characteristic – the cyclization factor β' . This parameter characterizes the share of conversion of terminal groups, which leads to cyclic products. By introducing the assumption on that β' does not depend on the size of the cycle and steric factors, the authors of [8] modified the Flory theory, thereby making it possible to qualitatively explain the existence of $DPD > 2$. Paper [13] assumed that in the process of cyclization a constant value is retained not by the cyclization factor β' , but the cyclization rate constant of the first-order. The equation for polydispersity, derived by the author of [13], turned out to be identical in the form to that described in [8]; it, too, qualitatively explained the existence of $DPD > 2$. However, given the lack of experimental data on the kinetics of cyclization, assumptions about the magnitudes of β' seem to be insufficiently substantiated.

Given the above, there is an issue about a possible role of cyclization processes in the processes of equilibrium condensation telomerization. There are no experimental data on the possibility of such a process. Based on general assumptions, one can assume that its role in telomerization would be negligible. That is associated with the presence of a competitive pathway – a chain disruption by telogen, which prevents the formation of polymers with a high degree of polymerization, susceptible to cyclization.

Some problems that emerge in polycondensation theory should be stated differently for the equilibrium condensation telomerization. Thus, from the standpoint of polycondensation theory, of great interest is the behavior of the system in the neighborhood of the hypothetical singular point, when the complete conversion of monomer has been achieved and a single giant polymer molecule has been formed [10, 11, 14]. It was suggested in [11, 12] that the actual conversion during polycondensation does not reach 100 % with the process terminated at earlier stages. In [14], authors noted that in the Flory theory the limit value $DPD = 2$ is contrary to the fact that at complete transformation of a monomer the only one molecule forms, for which this magnitude must be equal to 1.

In the equilibrium condensation telomerization the formation of a single large molecule is ruled out, to the problem of singularity should be stated differently. It implies the ultimate distribution of products when the low-molecular by-product HX is removed from the reaction zone (equation (1)).

Given the above, there is an issue on the methodology for elaborating the model. In [12], in order to construct a model of equilibrium heteropolycondensation, a systematic approach was used, based on the classification of types of equilibria occurring in the process, by deriving the material balance equations for base components and their convolution

into a system of nonlinear equations. Such an approach seems promising to construct a model of the equilibrium condensation telomerization.

Thus, a model of the equilibrium condensation telomerization process should be constructed based on the theory of the Flory-Carothers model using a systemic approach.

3. The aim and objectives of the study

The aim of this study is to develop a computer model of the equilibrium condensation telomerization products distribution, to explore the features of this model, to examine regularities in telomerization, by employing it, under conditions of controlled concentration of a low-molecular by-product and in the neighborhood of a singular point.

To accomplish the aim, the following tasks have been set:

- to build a mathematical model of telomerization based on the systemic analysis of common regularities in equilibrium polycondensation processes;

- to implement a computer model and examine features in solutions;

- to explore regularities in the distribution of equilibrium telomerization products, by employing the model, under conditions of controlled concentration of a low-molecular by-product, including the neighborhood of a singular point.

We introduce the following notation for equilibrium concentrations:

$$x_1 = [\text{HX}]; \quad x_2 = [\text{RX}]; \quad x_3 = [\text{HAH}]; \quad x_4 = [\text{XBX}].$$

Compare a table of the stepped linearly-independent equilibria of interaction between oligomers ($i = 0, 1, 2, \dots$) and monomers H-A-H, X-B-X and the telogen RX with the formation of new oligomers and the low-molecular product HX (Table 1). Each component in the line differs from the preceding one by the presence of additional group -A-B-. We shall consider the degree of polymerization k in hetero-oligomers to be the largest number of fragments of the initial monomers within its composition. Data in Table 1 are grouped in a series of rows with identical values for degree of polymerization k .

Table 1

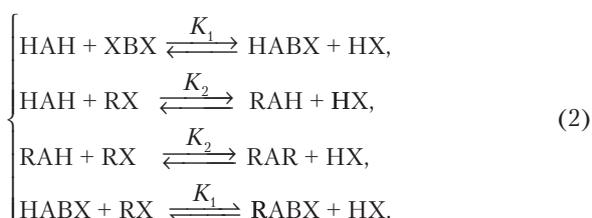
Components of polymer mixture of condensation telomerization

k	Structural elements					
1	HAH x_3	XBX x_4	HABX x_5	RAH x_6	RAR x_7	RABX x_8
2	HABAH x_9	XABAX x_{10}	H(AB) ₂ X x_{11}	RABAH x_{12}	RABAR x_{13}	R(AB) ₂ X x_{14}
3	H(AB) ₂ AH x_{15}	XB(AB) ₂ X x_{16}	H(AB) ₃ X x_{17}	R(AB) ₂ AH x_{18}	R(AB) ₂ AR x_{19}	R(AB) ₃ X x_{20}
...
i	H(AB) _{$i-1$} AH $x_{6(i-1)+3} = x_{6i-3}$	XB(AB) _{$i-1$} X $x_{6(i-1)+4} = x_{6i-2}$	H(AB) _{i} X $x_{6(i-1)+5} = x_{6i-1}$	R(AB) _{$i-1$} AH $x_{6(i-1)+6} = x_{6i}$	R(AB) _{$i-1$} AR $x_{6(i-1)+7} = x_{6i+1}$	R(AB) _{i} X $x_{6(i-1)+8} = x_{6i+2}$
...

4. Distribution model of the equilibrium condensation telomerization products

When constructing a model, we considered the distribution of equilibrium condensation telomerization products from the standpoint of general patterns in the theory of polycondensation processes [1, 2, 8–12]. According to them, the equilibrium condensation telomerization occurs as a system of successive equilibria, resulting in a growth and disruption of the chain. In accordance with the Flory principle [8–12], we believed that the equilibrium constants of growth (K_1) and chain disruption (K_2) did not depend on the length of the polymer chain. Given that the system includes a RX component, capable of not only disrupting the chain of conversions, but also impeding the cyclization, we believed that cyclization could be neglected under these conditions.

When considering the interaction between monomers HAH and XBX and the telogen RX, one can select the following basic linearly-independent reactions:



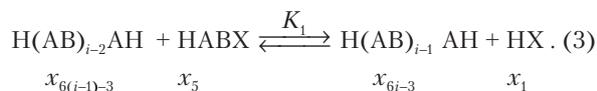
Calculation of equilibrium concentrations of oligomers at $k=1$, based on the schema of equilibria (1), is given in Table 2.

Table 2

Expressions for equilibrium constants of the formation and equilibrium concentrations of oligomers at a polymerization degree $k=1$

Compound	Equilibrium constant	Equilibrium concentration
HABX	$K_1 = \frac{x_5 \cdot x_1}{x_3 \cdot x_4}$	$x_5 = \frac{K_1 \cdot x_3 \cdot x_4}{x_1}$
RAH	$K_2 = \frac{x_6 \cdot x_1}{x_3 \cdot x_2}$	$x_6 = \frac{K_2 \cdot x_3 \cdot x_2}{x_1}$
RAR	$K_2 = \frac{x_7 \cdot x_1}{x_6 \cdot x_2}$	$x_7 = \frac{K_2 \cdot x_6 \cdot x_2}{x_1} = \frac{K_2^2 \cdot x_3 \cdot x_2^2}{x_1^2}$
RABX	$K_2 = \frac{x_8 \cdot x_1}{x_5 \cdot x_2}$	$x_8 = \frac{K_2 \cdot x_5 \cdot x_2}{x_1} = \frac{K_1 \cdot x_3 \cdot x_2 \cdot x_4}{x_1^2}$

Let us analyze Table 1 for columns, starting with the column HAH and the line with a polymerization degree $k=1$. For the cell at the intersection of this column and the arbitrary i -th line that contains H(AB) _{$i-1$} H ($i > 1$), one can write the following formation equation:



Calculate concentration x_{6i-3} and the ratio of concentrations $x_{6i-3}/x_{6(i-1)-3}$:

$$x_{6i-3} = \frac{K_1 \cdot x_{6(i-1)-3} \cdot x_5}{x_1} = \frac{K_1 \cdot x_{6(i-1)-3}}{x_1} \cdot \left(K_1 \cdot \frac{x_2 \cdot x_4}{x_1} \right); \quad (4)$$

$$\frac{x_{6i-3}}{x_{6(i-1)-3}} = \gamma = K_1^2 \cdot \frac{x_3 \cdot x_4}{x_1^2}. \quad (5)$$

Ratio (5) is not dependent on the line number (degree of polymerization). This indicates that concentrations in the column form a geometric progression with denominator:

$$\gamma = K_1^2 \cdot \frac{x_3 \cdot x_4}{x_1^2}. \quad (6)$$

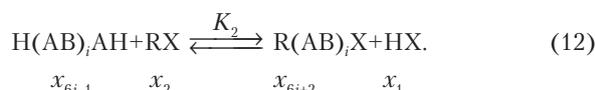
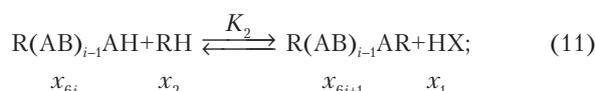
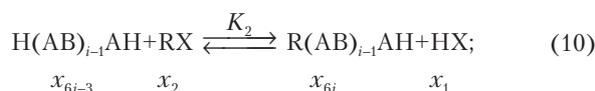
Similar correlations were obtained for the components HAH, XBX, HABX, which are the first terms of progressions:

$$\text{HAH: } \frac{x_{6i-3}}{x_{6(i-1)-3}} = K_1^2 \cdot \frac{x_3 \cdot x_4}{x_1^2} = \gamma; \quad (7)$$

$$\text{XBX: } \frac{x_{6i-2}}{x_{6(i-1)-2}} = K_1^2 \cdot \frac{x_3 \cdot x_4}{x_1^2} = \gamma; \quad (8)$$

$$\text{HABX: } \frac{x_{6i-1}}{x_{6(i-1)-1}} = K_1^2 \cdot \frac{x_3 \cdot x_4}{x_1^2} = \gamma. \quad (9)$$

Below are the equilibria of the formation of compounds $\text{R(AB)}_{i-1}\text{AH}$, $\text{R(AB)}_{i-1}\text{AR}$, $\text{R(AB)}_i\text{X}$ involving the monofunctional telogen RX:



Based on the system of equilibria (10) to (12), we calculated equilibrium concentrations of these compounds for $i = 2, 3, \dots$:

$$x_{6i} = \frac{K_2 \cdot x_{6i-3} \cdot x_2}{x_1} = K_2 \cdot \frac{x_2}{x_1} \cdot x_3 \cdot \gamma^{i-1}; \quad (13)$$

$$x_{6i+1} = \frac{K_2 \cdot x_{6i} \cdot x_2}{x_1} = \left(K_2 \cdot \frac{x_2}{x_1} \right)^2 \cdot x_3 \cdot \gamma^{i-1}; \quad (14)$$

$$x_{6i+2} = \frac{K_2 \cdot x_{6i-1} \cdot x_2}{x_1} = K_2 \cdot K_1 \cdot \frac{x_2 \cdot x_3 \cdot x_4}{x_1^2} \cdot \gamma^{i-1}. \quad (15)$$

Thus, the concentrations of all components in the system are linked to the basic components, given in line 1 in Table 1

by geometric progressions with a single denominator (6). By analogy with the Flory theory [9], we believe that this series converges, that is, $\gamma < 1$. It should be noted that progression denominator coincides in magnitude with that for the model that describes the equilibrium heteropolycondensation [12]. Hence, it follows that in the condensation telomerization, similarly to polycondensation, there is the geometric distribution of the system's components (Flory distribution). For telomerization, geometric progressions are formed based on the equilibrium concentrations of base monomers and telogen, which do not necessarily have to be the same. In this aspect, the distribution of products for equilibrium telomerization differs from the distribution for equilibrium homopolycondensation by the Flory theory, where one observes the concentration of a single monomer.

We shall construct the material balance equations based on fragments A, B, R, X, in the form of a system of equations with an infinite number of terms (respectively, equations (16) to (19)).

$$\sum_{i=1}^{\infty} i \cdot x_{6i-3} + \sum_{i=1}^{\infty} (i-1) \cdot x_{6i-2} + \sum_{i=1}^{\infty} i \cdot x_{6i-1} + \sum_{i=1}^{\infty} i \cdot x_{6i} + \sum_{i=1}^{\infty} i \cdot x_{6i+1} + \sum_{i=1}^{\infty} i \cdot x_{6i+2} = a_0; \quad (16)$$

$$\sum_{i=1}^{\infty} (i-1) \cdot x_{6i-3} + \sum_{i=1}^{\infty} i \cdot x_{6i-2} + \sum_{i=1}^{\infty} i \cdot x_{6i-1} + \sum_{i=1}^{\infty} (i-1) \cdot x_{6i} + \sum_{i=1}^{\infty} (i-1) \cdot x_{6i+1} + \sum_{i=1}^{\infty} i \cdot x_{6i+2} = b_0; \quad (17)$$

$$x_2 + \sum_{i=1}^{\infty} x_{6i} + \sum_{i=1}^{\infty} 2 \cdot x_{6i+1} + \sum_{i=1}^{\infty} x_{6i+2} = r_0; \quad (18)$$

$$2 \cdot \sum_{i=1}^{\infty} x_{6i-2} + \sum_{i=1}^{\infty} x_{6i-1} + \sum_{i=1}^{\infty} x_{6i+2} + x_1 + x_2 = 2 \cdot b_0 + r_0 + [\text{HX}]_0, \quad (19)$$

where a_0 , b_0 , r_0 , $[\text{HX}]_0$ is, respectively, the total concentration in the system of fragments $-A-$, $-B-$, $-R-$ and the component HX. If the process involves the monomers and telogen, these magnitudes are equal to their starting concentrations.

To convolute the infinite sums, we shall use following equalities for the converging geometric progression:

$$\sum_{i=1}^{\infty} \gamma^{i-1} = \frac{1}{1-\gamma}; \quad (20)$$

$$\sum_{i=1}^{\infty} i \cdot \gamma^{i-1} = \sum_{i=1}^{\infty} \frac{d}{d\gamma} [\gamma^i] = \frac{d}{d\gamma} \left[\sum_{i=1}^{\infty} \gamma^i \right] = \frac{d}{d\gamma} \left[\frac{1}{1-\gamma} \right] = \frac{1}{(1-\gamma)^2}; \quad (21)$$

$$\sum_{i=1}^{\infty} (i-1) \cdot \gamma^{i-1} = \gamma + 2\gamma^2 + 3\gamma^3 + \dots + k \cdot \gamma^k + \dots = \gamma \cdot \sum_{i=1}^{\infty} i \cdot \gamma^{i-1} = \frac{\gamma}{(1-\gamma)^2}. \quad (22)$$

Substitute in the system (16) to (19) expressions (20) to (22) and represent by a geometric progression the equilibrium

concentrations of components through the concentrations of monomers, telogen, and HX. As a result, we obtain a system of nonlinear algebraic equations (23) to (26) in order to describe the equilibrium state:

$$\frac{x_3}{(1-\gamma)^2} + \frac{\gamma \cdot x_4}{(1-\gamma)^2} + \frac{K_1 \cdot x_3 \cdot x_4}{x_1 \cdot (1-\gamma)^2} + \frac{K_2 \cdot x_2 \cdot x_3}{x_1 \cdot (1-\gamma)^2} + \left(\frac{K_2 \cdot x_2}{x_1} \right)^2 \cdot \frac{x_3}{(1-\gamma)^2} + K_1 \cdot K_2 \cdot \frac{x_2 \cdot x_3 \cdot x_4}{x_1^2 \cdot (1-\gamma)^2} = a_0; \quad (23)$$

$$\frac{\gamma \cdot x_3}{(1-\gamma)^2} + \frac{x_4}{(1-\gamma)^2} + \frac{K_1 \cdot x_3 \cdot x_4}{x_1 \cdot (1-\gamma)^2} + \frac{K_2 \cdot x_2 \cdot x_3 \cdot \gamma}{x_1 \cdot (1-\gamma)^2} + \left(\frac{K_2 \cdot x_2}{x_1} \right)^2 \cdot \frac{x_3 \cdot \gamma}{(1-\gamma)^2} + K_1 \cdot K_2 \cdot \frac{x_2 \cdot x_3 \cdot x_4}{x_1^2 \cdot (1-\gamma)^2} = b_0; \quad (24)$$

$$x_2 + \frac{K_2 \cdot x_2 \cdot x_3}{x_1 \cdot (1-\gamma)^2} + 2 \cdot \left(\frac{K_2 \cdot x_2}{x_1} \right)^2 \cdot \frac{x_3}{1-\gamma} + \frac{K_1 \cdot K_2 \cdot x_2 \cdot x_3 \cdot x_4}{x_1^2 \cdot (1-\gamma)} = r_0; \quad (25)$$

$$x_1 + \frac{2 \cdot x_4}{1-\gamma} + \frac{K_1 \cdot x_3 \cdot x_4}{x_1 \cdot (1-\gamma)} + \frac{K_1 \cdot K_2 \cdot x_2 \cdot x_3 \cdot x_4}{x_1^2 \cdot (1-\gamma)} = [\text{HX}]_0 + r_0 + 2b_0. \quad (26)$$

In system (23) to (26), magnitude γ is calculated from equation (6).

This system makes it possible to calculate the equilibrium concentrations of HAH, XB, XBX, RX, HX, R, and then, by using ratios (3) to (5), (13) to (15) – the equilibrium concentrations of the remaining products with a predefined degree of polymerization.

5. Numerical study of the model of system (23)–(26)

The system of equations (23) to (26) is non-linear, it is possible to solve it only by numerical methods. This raises the question about the number of roots and their physical sense.

Numerical simulation was performed in the environment of applied mathematics software package Scilab, employing the following algorithm:

- set initial magnitudes: values for the constants of equilibrium K_1 and K_2 , starting concentrations of reactants;
- generate the initial approximations of concentrations of basic reagents HX, RX, HAH, XBX as random magnitudes that are uniformly distributed between 0 and the initial value (for HX – total initial value for the amount of fragment X);
- solve the system of equations of the model numerically and save it;
- based on the derived values, calculate and save the denominator of the progression;
- calculations were repeated 10,000 times.

Upon end of the calculations, we organized the calculated value for roots, analyzed the number of roots and the frequency of their occurrence in the obtained sample.

The result of simulation has revealed the presence of four roots in the system, which appear at a different frequency (Table 3).

Table 3

Roots of the equation system of the model of condensation telomerization at $K_1 = K_2 = 10$. Starting concentration: HAH = XBX = 1, RX = 0.1, HX = 0

No.	x_1	x_2	x_3	x_4	Occurrence frequency	
					Absolute	Relative, %
1	2.399	-2.393	-0.059	-5.3400	5	0.05
2	1.4698	-0.138	0.1172	0.1103	109	1.09
3	1.4788	0.0363	0.0896	0.1168	1977	19.77
4	2.4327	0.900	0.1466	2.7015	7909	79.09

It follows from data in Table 3 that even though all approximations of solutions were positive, certain cases yield roots whose components have negative values and, accordingly, are false: they have no physical sense. They are fairly rare: one per 0.05 %, and the second per 1 % of cases. The remaining 2 roots have only positive components, and there is a question about their physical sense.

In an earlier study [12], in a related modelling task on equilibrium heteropolycondensation, the authors applied, as a criterion of the physical sense of roots, the magnitude of denominator in a geometric progression, which was also described by equation (6). Because the equations of model (23) to (26) were derived under assumption that the geometric progression is converging, that is $\gamma < 1$, the physical sense can acquire only such a solution that makes the magnitude of the denominator smaller than 1. In Table 3, for root No. 3, this magnitude is 0.029, and for root No. 4 it is 6.7. That is, among all roots, only one (No. 3, Table 3) has a physical sense and it is true. Thus, for the case of equilibrium telomerization the value for denominator in progression (6) can also be a validity criterion for the solution.

It should be noted that the existence of two positive roots creates problems in numerical calculations and sets the task on choosing a good initial approximation. As can be seen from Table 3, at a random selection of random approximation out of the permissible domain of its possible values, 81 % of cases yield false roots, and only 19 % of cases produce a true root. Given the lack of information about the «domain of attraction» for the true root, obtaining a true solution in a single calculation at a random selection of initial approximation is unlikely. Therefore, to derive the true root, it is required to perform a series of calculations based on the random selection of initial approximation, as was the case for the algorithm described above. At the same time, to reduce the number of computations, one can perform them until the derived components of the root vector lead to the magnitude $\gamma < 1$ (under conditions of positive values for all components of this vector).

6. Modeling of equilibrium composition of oligomers in the neighborhood of a singular point

In practice, the magnitudes of equilibrium constants K_1 and K_2 are typically small, the order of 1–10. To shift equilibrium towards the products from the system, the process is carried out under conditions of a low content of the low-molecular product HX, controlled by its distillation. As noted in chapter 2, a singular point of the system corresponds to

the limit state at HX content equal to zero. At this point, the denominator of expression (6), which defines the distribution of products, becomes zero. Thus, it is a relevant task to model a composition of the equilibrium mixture at a low content of HX.

The constructed model can be simplified for a given case if one accepts that the content of HX in the system is maintained at a constant level $x_1 = d = \text{const}$. In this case, one can exclude from the system of equations (23) to (26) the last equation, leaving equations (23) to (25).

When modeling using system (23) to (25), we calculated the molecular-mass distribution and apparent number average degree of polymerization \bar{n} :

$$\bar{n} = \frac{N_0}{N}, \quad (27)$$

where $N_0 = N_{\text{HAH}}^0 + N_{\text{XBX}}^0 + N_{\text{RX}}^0$ is the total number of moles of oligomers and telogen introduced to the reaction; N is the total number of moles in the equilibrium mixture.

The magnitude N can be calculated based on the number of basic components with $i=1$ (Table 1) realizing that the number of moles in the compound from each column form a geometric progression with the same denominator. The number of moles RX(x_2) and HX(d) in the resulting equilibrium mixture should be added to the derived sums:

$$N = \frac{x_3 + x_4 + x_5 + x_6 + x_7 + x_8 + x_2 + d}{1 - \gamma}, \quad (28)$$

where, in accordance with the above:

$$x_5 = \frac{K_1 \cdot x_3 \cdot x_4}{d}, \quad x_6 = \frac{K_2 \cdot x_2 \cdot x_3}{d},$$

$$x_7 = \frac{K_2 \cdot x_2 \cdot x_6}{d}, \quad x_8 = \frac{K_2 \cdot x_2 \cdot x_3}{d}.$$

In practice [1] for calculating the average degree of polymerization in the equilibrium condensation polycondensation under conditions of complete transformation of monomers XBX and RX and the total absence of HX in the system the following formula is applied:

$$\bar{n} = \frac{1 + q' + r}{1 + q' - r} = \frac{N_{\text{XBX}}^0 + N_{\text{RX}}^0 + N_{\text{HAH}}^0}{N_{\text{XBX}}^0 + N_{\text{RX}}^0 - N_{\text{HAH}}^0}, \quad (29)$$

where

$$q' = \frac{N_{\text{RX}}^0}{N_{\text{XBX}}^0}; \quad r = \frac{N_{\text{HAH}}^0}{N_{\text{XBX}}^0}.$$

Formula (29) is marginal in essence and does not depend on the equilibrium constants K_1 and K_2 . From this perspective, it is advisable to investigate the asymptotic properties of model (23) to (25) at $d \rightarrow 0$, that is, in the neighborhood of a singular point. To this end, we calculated \bar{n} and the composition of the equilibrium mixture containing HX from 10 to 0.0001 mol per 100 mol XBX at equilibrium constants $K_1 = K_2 = 1, 10, 100$ (Fig. 1).

Fig. 1 shows that at a high content of HX in the system the magnitude \bar{n} heavily depends on the magnitude for equilibrium constants: an increase in them leads to an increase in the average degree of polymerization at fixed values for d .

If this magnitude tends to 0 in the singular point the value of \bar{n} also tends to the limit, which does not depend on the equilibrium constants: curves for different values of K_1 and K_2 converge at one point. This boundary value of \bar{n} , obtained at a very low content of HX ($d = 0.0001$), almost coincides with the magnitude that was calculated from formula (29) (Table 4).

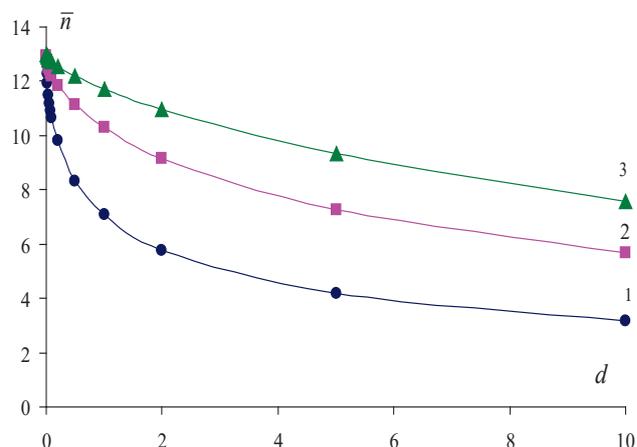


Fig. 1. Dependence of average degree of polymerization on the content of HX in an equilibrium mixture (d , mol/100 mol XBX). Molar ratio

$N_{\text{XBX}}^0 : N_{\text{HAH}}^0 : N_{\text{RX}}^0 = 1 : 1.2 : 0.4$. Equilibrium constants:
1 – $K_1 = K_2 = 1$; 2 – $K_1 = K_2 = 10$; 3 – $K_1 = K_2 = 100$

Table 4

Comparison of magnitude \bar{n} , calculated from formula (29), and according to model (23) to (25), at $d = 0.0001$ depending on ratio $N_{\text{XBX}}^0 : N_{\text{HAH}}^0 : N_{\text{RX}}^0$

$N_{\text{XBX}}^0 : N_{\text{HAH}}^0 : N_{\text{RX}}^0$	1:1.1:0.2	1:1.2:0.4	1:1.3:0.6
\bar{n} according to (29)	23	13	9.66
\bar{n} according to (23)–(25)	22.9	12.9	9.65

The results obtained demonstrate that formula (29) can indeed be regarded as an extreme case of model (23) to (25). At the same time, in the neighborhood of a singular point there is a gradual convergence between the curves of dependence of the average degree of polymerization on the content of HX for different values of equilibrium constants and their intersection at the singular point.

A parameter, defined by the state of equilibrium, is the denominator of geometric progression (6), which depends on the combination of equilibrium concentrations of HAH, XBX and HX. It is of interest to consider the way this parameter changes at the singular point. To this end, we investigated a dependence of the magnitude of progression's denominator on the equilibrium amount of HX. By extrapolating it for 0, we estimated the boundary value of progression's denominator at a singular point (γ_0) and investigated the dependence of this magnitude on equilibrium constants and the equilibrium ratios of reactants. The following patterns were identified:

- magnitude γ_0 does not depend on values for equilibrium constants K_1 and K_2 and the ratio of amounts RH : XBX;
- magnitude γ_0 depends only on the ratio of amounts XBX : HAH and coincides with this ratio (Table 5).

Table 5
Dependence of magnitude γ_0 on the ratio of amounts $\text{XBX:HAH} (b)$

b	0.909	0.833	0.769	0.714	0.667	0.625
γ_0	0.909	0.833	0.769	0.714	0.667	0.625

By calculating the equilibrium amounts of basic compounds in the equilibrium mixture from model (23) to (25), one can estimate the total amounts of compounds of each type depending on equilibrium content of the component HX. One can use the formula for the sum of a geometric progression:

$$x_i^s = \frac{x_i^0}{1-\gamma}, \tag{30}$$

where x_i^0 and x_i^s are, respectively, the equilibrium amount of the i -th base product and all polymers based on it.

It follows from Table 6 that as the equilibrium concentration of HX decreases, the molar quantities of each type of products, except for RAR, reduce sharply. At the same time, there is an increase in the amount of products based on RAR and in the denominator of the geometric progression.

Table 6
Dependence of progression’s denominator (γ) and the total molar amount of compounds of basic types in the equilibrium condensation telomerization on the equilibrium amount of HX (d). Starting amounts: $\text{XBX } 100 \text{ mol, HAH } 110 \text{ mol, RX } 20 \text{ mol, equilibrium constants: } K_1=K_2=10$

d	Basic types						γ
	HAH	XBX	HABX	RAH	RAR	RABX	
10	4.10	3.87	3.52	4.60	5.16	3.95	0.779
1	0.75	0.70	0.68	2.38	7.57	2.15	0.871
0.1	$9.75 \cdot 10^{-2}$	$9.03 \cdot 10^{-2}$	$8.89 \cdot 10^{-2}$	0.939	9.05	0.857	0.899
$1 \cdot 10^{-2}$	$1.06 \cdot 10^{-2}$	$9.71 \cdot 10^{-3}$	$9.66 \cdot 10^{-3}$	0.320	9.68	0.292	0.906
$1 \cdot 10^{-3}$	$1.09 \cdot 10^{-3}$	$9.91 \cdot 10^{-4}$	$9.89 \cdot 10^{-4}$	0.104	9.90	$9.44 \cdot 10^{-2}$	0.908
$1 \cdot 10^{-4}$	$1.10 \cdot 10^{-4}$	$9.98 \cdot 10^{-5}$	$9.98 \cdot 10^{-5}$	$3.31 \cdot 10^{-2}$	9.97	$3.01 \cdot 10^{-2}$	0.909

7. Discussion of results of studying a telomerization model

Within the framework of the set tasks, the systematic approach, proposed earlier in [18] for constructing a model of the linear equilibrium heteropolycondensation, was further advanced for building a model of the equilibrium condensation telomerization. This approach, based on the classification of types of components in the mixture and the equilibria in their formation, has made it possible to build a model in the form of a system of nonlinear algebraic equations. When constructing the model, we have identified the overall pattern, which can be denoted as the generalized Flory distribution: each type of components turns out to be distributed in line with the law of geometric progression with the same denominator. The differences include the first terms of the progression, defined by the concentration of base components that correspond to the respective type. Given this, the classic Flory distribution for homopolycondensation can

be regarded as a special case of the generalized distribution when there is only one type of product.

The special feature of the numerical solution to the model is that it includes, along with the true root, several false roots that have no physical sense. The latter, depending on the random selection of initial approximation from the permissible domain of concentrations, appear much more frequently than the true root. Therefore, to find the true root, a single solution to the system’s equations is not enough. In order to find a true root, we have devised a procedure based on a combination of the Monte-Carlo method for selecting initial approximation with a solution to the system and analysis of the root. A criterion for deriving the true root is a magnitude for the progression’s denominator calculated from equation (6): it must be strictly less than 1.

A numerical computer solution to the system of equations of the model allows the calculation of the equilibrium concentrations of monomers and then the concentrations of all components in the mixture. Thus, the approach considered makes it possible to calculate a complete composition of the equilibrium mixture at any ratio of monomers, telogen, and a low-molecular product in the starting mixture, to determine the mean degree of polymerization, as well as other characteristics.

Of the greatest practical interest is the case of a singular point neighborhood when the low-molecular product HX is removed from the system. When solving a system of equations of the model, one must not formally assign a zero value to the equilibrium amount of this product in the mixture, because in this case the progression’s denominator (6) accepts an invalid value. Therefore, the boundary average degree of polymerization and the progression’s denominator were estimated by extrapolation.

In contrast to existing method [1], the constructed model makes it possible to calculate not only the average degree of polymerization, but also the composition of the equilibrium mixture for types of compounds over a wide range of content of a low-molecular product, up to a singular point. Determining the composition of the equilibrium mixture in the neighborhood of a singular point allows finding the difference between telomerization and polycondensation.

At telomerization, the singular point contains a large number of molecules of the type $\text{R}-(\text{AB})_{i-1}-\text{A}-\text{R}$, distributed in line with the law of geometric progression. At the same time, at polycondensation, a singular point is matched with a single giant molecule.

In terms of practice, the constructed model could prove useful for solving an applied task on the a priori estimate of the composition of a mixture of oligomers when designing the synthesis conditions depending on the ratio of components and values for equilibrium constants.

The drawback of the model is a comparative computational complexity and the necessity for a thorough examination of the solution in order to rule out false roots.

The developed model has limitations. Since the starting point for the model is the Flory principle about independence of the reactivity of terminal groups on the length of a polymer chain, the systems in which this principle does not hold must not be treated with the model. In addition, this model neglects the possibility for cyclization and other equilibrium

processes that could occur in the system. In this case, however, this model can be modified. For example, for the case of cyclization, by assuming that the cyclization equilibrium constant does not depend on the magnitude of a micro cycle, it is possible, by employing the approach described, to introduce for consideration another type of products – macrocycles, and supplement the system with one more balance equation for cyclic products. In this case, by analogy with the above, it can be expected that the concentration of macrocycles under these conditions will also demonstrate a geometric distribution. This indicates the potential for extending the scope of application of the described approach for constructing models of polycondensation processes.

8. Conclusions

1. Based on the understanding of the mechanism of polycondensation processes, we have constructed a mathematical model of the equilibrium condensation telomerization in the form of a system of 4 equations of balance and equilibria with an infinite number of terms. When analyzing this system, we have identified 6 basic structural components of the system. By implementing the Flory principle about independence

of the reactivity of terminal groups of polymers on a chain length, the model can be collapsed into a closed system of 4 nonlinear algebraic equations relative to the concentrations of basic components.

2. Through computer simulation, we have revealed the presence of 4 roots in a system of equations of the model. We have devised criteria for deriving the true value of the root based on the value of a geometric progression and the signs of coefficients, as well as the algorithm for the method to find a solution and to calculate the molecular-mass distribution based on it.

3. It was established in modeling that in the neighborhood of a singular point the limit value for the denominator of geometric progression, characterizing the distribution of compounds based on their type, does not depend on the magnitudes for the equilibrium constants of growth and a chain disruption and the concentration of telogen and is numerically equal to the ratio of amounts of bifunctional monomers, introduced to the reaction. We have identified a dependence of the composition of the equilibrium mixture of oligomers on its content of a low-molecular product of polycondensation.

4. The model constructed could prove useful for the a priori assessment of the composition of a mixture of oligomers when planning synthesis conditions.

References

1. Akrilovye oligomery i materialy na ih osnove: monografiya / Berlin A. A., Korolev G. V., Kefeli T. Ya., Sivergin Yu. M. Moscow: Himiya, 1983. 232 p.
2. Barshteyn R. S., Kirillovich V. I., Nosovskiy Yu. E. Plastifikatory dlya polimerov: monografiya. Moscow: Himiya, 1982. 200 p.
3. Vancoillie G., Frank D., Hoogenboom R. Thermoresponsive poly (oligo ethylene glycol acrylates) // *Progress in Polymer Science*. 2014. Vol. 39, Issue 6. P. 1074–1095. doi: <https://doi.org/10.1016/j.progpolymsci.2014.02.005>
4. Hu Z., Cai T., Chi C. Thermoresponsive oligo (ethylene glycol)-methacrylate- based polymers and microgels // *Soft Matter*. 2010. Vol. 6, Issue 10. P. 2115. doi: <https://doi.org/10.1039/b921150k>
5. Lutz J.-F. Polymerization of oligo (ethylene glycol) (meth) acrylates: Toward new generations of smart biocompatible materials // *Journal of Polymer Science Part A: Polymer Chemistry*. 2008. Vol. 46, Issue 11. P. 3459–3470. doi: <https://doi.org/10.1002/pola.22706>
6. Stimuli-responsive polymers and their applications in drug delivery / Bawa P., Pillay V., Choonara Y. E., du Toit L. C. // *Biomedical Materials*. 2009. Vol. 4, Issue 2. P. 022001. doi: <https://doi.org/10.1088/1748-6041/4/2/022001>
7. Stimuli-responsive polymers and their applications / Wei M., Gao Y., Li X., Serpe M. J. // *Polymer Chemistry*. 2017. Vol. 8, Issue 1. P. 127–143. doi: <https://doi.org/10.1039/c6py01585a>
8. Wutz C., Kricheldorf H. R. Molecular Weight Distribution of Linear Chains in Step-Growth Polymerization Under the Influence of Cyclization Reactions // *Macromolecular Theory and Simulations*. 2012. Vol. 21, Issue 4. P. 266–271. doi: <https://doi.org/10.1002/mats.201100084>
9. Kricheldorf H. R., Weidner S. M., Scheliga F. Cyclization and Dispersity of Polyesters // *Macromolecular Symposia*. 2017. Vol. 375, Issue 1. P. 1600169. doi: <https://doi.org/10.1002/masy.201600169>
10. Mizerovskii L. N., Padokhin, V. A. Molecular-weight distribution of linear polycondensation polymers. Flory theory // *Fibre Chemistry*. 2013. Vol. 44, Issue 6. P. 337–355. doi: <https://doi.org/10.1007/s10692-013-9458-4>
11. Mizerovskii L. N. Flory theory applied to polycondensation polymers with a finite number of fractions // *Fibre Chemistry*. 2013. Vol. 45, Issue 1. P. 9–16. doi: <https://doi.org/10.1007/s10692-013-9472-6>
12. Kondratov S. A., Oleynik V. V. Ob osobennostyah uravneniy zakona deystvuyushchih mass dlya ravnovesnoy polikondensacii // *Voprosy himii i himicheskoy tekhnologii*. 2012. Issue 1. P. 51–58.
13. Szymanski R. The Molar Mass Distribution of Polymers in Step-Growth Polymerization is Influenced by Cyclization Reactions. The Simplified Case of Irreversible Reactions with Cyclizations is Independent of the Ring Size // *Macromolecular Theory and Simulations*. 2013. Vol. 22, Issue 6. P. 335–343. doi: <https://doi.org/10.1002/mats.201300102>
14. Kéki S., Zsuga M., Kuki Á. Theoretical Size Distribution in Linear Step-Growth Polymerization for a Small Number of Reacting Species // *The Journal of Physical Chemistry B*. 2013. Vol. 117, Issue 15. P. 4151–4155. doi: <https://doi.org/10.1021/jp401238m>