MATHEMATICAL MODELLING OF THE REACTION OF CONDENSATION TELOMERIZATION AND THE INVESTIGATION OF THE MODEL

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Abstract: A mathematical model of the distribution of mixture components in the equilibrium condensation telomerization is developed depending on the ratio of the amounts of monomers and telogen, as well as the number of HX as regulating parameters, the computer implementation of the model is carried out, and its study is carried out by numerical simulation. The model is based on the well-known schematic diagram of the flow of the condensation telomerization process under the assumption of equal reactivity of the same functional groups (Flory principle). Based on the analysis of the flow pattern of the process, 6 structural elements are identified, reproducible at each stage associated with an increase in the degree of polymerization based on 4 basic components. It is proved that the equilibrium concentrations of these elements, depending on the polymerization degree, depend on the equilibrium concentration of products with a degree of polymerization 1 and are described by infinite geometric progression with the same denominator. According to the physical content of the task, this progression must be convergent. Equations of material balance of components are contained in the form of a system with 4 equations containing infinite sums. It is possible to minimize these sums using the properties of geometric progressions and to obtain a closed system with 4 nonlinear equations for the equilibrium concentrations of the base components.
The Monte Carlo method is used to study the features of the numerical solution of the system of equations of the model. It is found that with a random choice of initial approximations of solutions from an admissible region, the system contains 4 roots, of which 2 contain positive and negative components and are false, and 2 have completely positive components. A valid criterion for finding a real root has a physical meaning based on the calculation of the denominator of a geometric progression. The possibilities of practical use of the model are discussed.

Keywords: condensation telomerization, geometric progression, system of nonlinear equations, numerical simulation of solutions, Monte Carlo method.

1. Introduction

Condensation telomerization occurring by equation (1) is one of the important reactions in the synthesis of polymers [1]

$$\begin{aligned}&(n+1)H-A-H+nX-\\&-B-X+2RX\rightleftarrows\\&\rightleftarrows R-A-(B-A)_n-\\&-R+2(n+1)HX,\end{aligned}\qquad(1)$$

where H–A–H, X–B–X – monomer molecules with terminal groups H and X; RX – monofunctional compound (chain shaker, telogen) with terminal group X, usually an ester of acrylic and methacrylic acid; HX – easy boiling condensation product.

As a result of reaction (1), a mixture of telomers (in particular, oligoester acrylates) is formed, which are used to obtain acrylic polymers having valuable properties. These polymers are widely used in medicine, in particular in dentistry, in the manufacture of fiberglass, varnishes and paints [1].

Process (1) should be considered as an equilibrium polycondensation with an open circuit. Despite the fact that the theory of polycondensation processes is well developed [2–7], mathematical models of equilibrium condensation telomerization processes are still lacking. Development of such models is an urgent task, since its presence will allow a more focused approach to the selection of optimal conditions for the synthesis of compounds with a given composition (polymerization degree).

The aim of research is development of a mathematical model of the distribution of the components of mixtures in the equilibrium condensation telomerization depending on the ratio of the number of monomers and telogen, as well as the number of HX, as regulating parameters, computer implementation of the model and its study by numerical simulation.

2. Methods

To build a mathematical model, the theoretical approach described in [8] for the processes of equilibrium heteropolycondensation is used. It is based on the conclusion of an infinite system of equations of material balance and equilibrium, based on the general mechanism of the process, their folding into a system of a finite number of equations and its solution. Computer simulation is performed using the original author's computer programs in the environment of the Scilab package of applied mathematics.

3. Results

Creation of model equations. When simulating, under the assumption, the Flory principle of equal reactivity of identical groups in polymer systems is used, regardless of the length of the polymer chain. This means that the equilibrium constants for processes of the same type can be considered identical. It is believed that polymers are present in the equilibrium state according to the polymerization degree from 1 to ∞ [3, 8]. Equation (1) only roughly conveys the composition of the products, because condensation telomerization, as a polycondensation process, proceeds statistically [3, 7]. If to consider the interaction of only monomer substances, it is possible to distinguish the following basic linearly independent reactions:

$$\begin{aligned}&HAH+XBX\overset{K_1}{\leftrightarrow}HABX+HX,\\&HAH+RX\overset{K_2}{\leftrightarrow}RAH+HX,\\&RAH+RX\overset{K_2}{\leftrightarrow}RAR+HX,\\&HABX+RX\overset{K_2}{\leftrightarrow}RABX+HX.\end{aligned}\qquad(2)$$

In (2) the equilibrium constants K_1 and K_2 are associated, respectively, with the processes of growth and chain termination. Let's compile a table of stepwise linearly independent reactions in which oligomers interact with the monomers HAH and XBX and RX to form the by-product HX (**Table 1**). In this table, each component in a row differs from the previous one in the presence of an additional grouping AB–.

Considering the elementary reactions of formation of the corresponding oligomers in columns, it is proved that the equilibrium concentrations of the compounds located in each column form geometric progression with the same denominator γ:

$$x_{6(i-1)+k}=x_k\cdot\gamma^{i-1},\qquad(3)$$

$$\gamma=K_1^2\cdot\frac{x_3\cdot x_4}{x_1^2},$$

where K_1 – equilibrium constant (system 2, equation 1); x_1, x_3, x_4 – equilibrium concentrations HX, HAH, XBX, mol/kg; i – polymerization degree; k=3, 4, …, 8.

Table 1

The components of the polymer mixture and the designation of their concentrations (mol/kg)

No. of row	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}	$H(AB)_2X$ x_{11}	RABAH x_{12}	RABAR x_{13}	$R(AB)_2X$ x_{14}
3	$R(AB)_2AH$ x_{15}	$XB(AB)_2X$ x_{16}	$H(AB)_3X$ x_{17}	$R(AB)_2AH$ x_{18}	$R(AB)_2AR$ x_{19}	$R(AB)_3X$ x_{20}
…	…	…	…	…	…	…
i	$R(AB)_{i-1}AH$ $x_{6(i=1-)3}+-x_{6i-3}$	$XB(AB)_{i-1}X$ $x_{6(i=1-)4}+-x_{6i-2}$	$H(AB)_iX$ $x_{6(i-1)+5}=x_{6i-1}$	$R(AB)_{i-1}AH$ $x_{6(i-1)+6}=x_{6i}$	$R(AB)_{i-1}AR$ $x_{6(i=1-)7}+-x_{6i+1}$	$R(AB)_iX$ $x_{6(i-1)+8}=x_{6i+2}$
…	…	…	…	…	…	…

Based on the presence of polymers with and from 1 to ∞ in the system, a system of 4 material balance equations (in fragments A, B, R, X) is obtained containing sums of an infinite number of members. Due to the presence of a connection between the components in the form of a geometric progression (3), which, according to the content of the problem, must be convergent, infinite sums are folded and a closed system of equations of model (4)–(7) is obtained:

$$\frac{x_3}{(1-\gamma)^2}+x_4\frac{\gamma}{(1-\gamma)^2}+\frac{K_1\cdot x_3\cdot x_4}{x_1}\cdot\frac{1}{(1-\gamma)^2}+$$
$$+\frac{K_1\cdot x_2\cdot x_3}{x_1}\cdot\frac{1}{(1-\gamma)^2}+\left(\frac{K_2\cdot x_2}{x_1}\right)^2\cdot x_3\cdot\frac{1}{(1-\gamma)^2}+$$
$$+K_1\cdot K_2\cdot\frac{x_2\cdot x_3\cdot x_4}{x_1^2}\cdot\frac{1}{(1-\gamma)^2}=a_0; \quad (4)$$

$$x_3\frac{\gamma}{(1-\gamma)^2}+\frac{x_4}{(1-\gamma)^2}+\frac{K_1\cdot x_3\cdot x_4}{x_1}\cdot\frac{1}{(1-\gamma)^2}+$$
$$+\frac{K_2\cdot x_2\cdot x_3}{x_1}\cdot\frac{\gamma}{(1-\gamma)^2}+\left(\frac{K_2\cdot x_2}{x_1}\right)^2\cdot x_3\cdot\frac{\gamma}{(1-\gamma)^2}+$$
$$+K_1\cdot K_2\cdot\frac{x_2\cdot x_3\cdot x_4}{x_1^2}\cdot\frac{1}{(1-\gamma)^2}=b_0; \quad (5)$$

$$x_2+\frac{K_2\cdot x_2\cdot x_3}{x_1}\cdot\frac{1}{(1-\gamma)^2}+2\left(\frac{K_2\cdot x_2}{x_1}\right)^2\cdot x_3\cdot\frac{1}{1-\gamma}+$$
$$+K_1\cdot K_2\cdot\frac{x_2\cdot x_3\cdot x_4}{x_1^2}\cdot\frac{1}{1-\gamma}=r_0; \quad (6)$$

$$x_1+\frac{2x_4}{1-\gamma}+\frac{K_1\cdot x_3\cdot x_4}{x_1}\cdot\frac{1}{1-\gamma}+$$
$$+K_1\cdot K_2\cdot\frac{x_2\cdot x_3\cdot x_4}{x_1^2}\cdot\frac{1}{1-\gamma}=[HX]_0+r_0+2b_0. \quad (7)$$

In system (4)–(7) a_0, b_0, r_0, $[HX]_0$, respectively, the initial concentrations of the monomers of the HAH, XBX, telogen RX and the by-product of the easily boiling product HX, mol/kg As a result of solving the system (4)–(7), the equilibrium concentrations of the products is obtained in line 1 of the **Table 1**. Further, using equation (3), it is possible to calculate the equilibrium concentrations of any component of the mixture, based on the corresponding product in line 1. Thus, it is possible to completely model the distribution of products and calculate the moments of this distribution used in the physics and chemistry of polymers [4].

The roots of the model equations. Since the system of equations of the condensation telomerization model is nonlinear, its solution is possible only by numerical methods. This raises the question of the number of roots and their physical meaning, as well as the choice of the initial approximation for solving the system.

To establish the number of roots, a Monte Carlo numerical simulation is used, according to the following algorithm:

a) set the initial values: the values of the equilibrium constants K_1 and K_2, the initial concentrations of the reactants;

b) generate approximations of equilibrium concentrations of base reagents HX, RX, HAH, XBX as random variables uniformly distributed between 0 and the initial value (for HX – the total initial value X);

c) numerically solve the system of equations of the model (4)–(7);

d) for each outcome, the denominator of the progression is calculated (3);

e) the calculations are repeated 10,000 times, in order of the roots in ascending order, the number of roots and their content in the sample are analyzed. The results are shown in **Table 2.**

4. Discussion of results

As follows from the **Table 2,** despite the fact that the initial approximations of solutions are positive, in some cases, the roots are obtained, the components of which have negative values, that is, those that have no physical meaning.

Table 2

The roots of the system of equations of the condensation telomerization model at $K_1=K_2=10$. Initial concentrations: HAH=XBX=1, RX=0.1, HX=0 kmol/kg

No.	x_1	x_2	x_3	x_4	Detection rate	
					Absolute	Relative, %
1	2,399	–2,393	–0,059	–5,34	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

They are quite rare: one – in 0.05 %, and the second – in 1 % of cases. The other 2 roots are positive. In this regard, the question arises, which of the roots has a physical meaning. Since the system (4)–(7) is obtained under the condition that $0<\gamma<1$, at which the progression coincides, the criterion for the root that has a physical meaning should be the simultaneous fulfillment of the following conditions:

1) All concentrations of HX, RX, HAH, XBX should be positive.

2) The size denominator of the progression

$$\gamma = K_1^2 \cdot \frac{x_3 \cdot x_4}{x_1^2};$$

must be less than 1.

If at least one of these conditions is not met, the resulting root is erroneous and has no physical meaning. In (**Table 2**), the root number 3 gives the value $\gamma = 0{,}029$, that is, is real, and the root number 4 is equal $\gamma = 6{,}7$, that is, it is erroneous. Let's note a characteristic detail: if one chooses an initial approximation in the permissible range of concentration values randomly, then the real root can be obtained in a single test only with a probability of 0.19, making false roots more likely (**Table 2**). Therefore, in practice, to obtain a real root, it is necessary to use the proposed approach: the communication of the solution of the system with a random choice of the initial approximation by the Monte Carlo method with subsequent analysis of the obtained roots. At the same time, the number of random tests should be large enough.

The developed model can be useful for chemistry and polymer technology, since it allows to simulate the distribution of all components of the equilibrium mixture, including in conditions of low concentrations of low-boiling component, which is implemented in practice when this component is distilled from the mixture to shift the equilibrium position towards the products.

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