Mathematical Model of Step Growth Homopolymerization of Oligomers

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Abstract—An approach to modelling the oligomer composition distribution function in the irreversible step growth homopolymerization process based on a mixture of oligomers of arbitrary composition is developed. The approach is based on consideration of probabilities of processes in the system, proceeding from Flory's principle and obtaining on this basis an infinite system of differential equations linking mole fractions of each oligomer of a finite mixture with the degree of transformation. It is shown that this system has analytical solutions and the Flory distribution is its special case at the initial geometric distribution.

Keywords—step-growth polymerization, oligomers, distribution function, differential equations, numerical solving, style, styling, insert

I. INTRODUCTION

A modern trend in polymer chemistry and technology is the widespread use of reactive oligomers - polymers with a low degree of polymerization containing active end functional groups [1]. The most important characteristic that determines the properties of oligomers is the molecular weight distribution (MWD). In the main method of oligomer synthesis by step growth polymerization, the starting substance is monomer. In this case MWD obeys the geometric Flory distribution [2,3]:

$$N_i = N_0 \cdot (1-x) \cdot x^{i-1} \qquad (1)$$

N_0 is the initial number of monomer molecules, N_i is the number of polymer molecules with the degree of polymerization i, x is the degree of monomer conversion in the step growth polymerization reaction.

The use of low-molecular-weight oligomers in pure form (if such products are available) or in mixtures as starting substances may be promising for the synthesis of oligomers with a different MWD. The optimal way to solve the problem of directed synthesis of oligomers with a given complex of properties may be a combination of mathematical modeling methods and experimental studies based on them.

The traditional approach for theoretical studies of MWD of polymers derived from monomers is the kinetic method combined with the method of derivative functions [4-7]. In the case of oligomers, the use of the derivative function method becomes problematic.

The aim of the present work is to develop an improved probabilistic approach to MWD modeling for polymers and oligomers produced by irreversible stepwise homopolymerization of low molecular weight oligomeric mixtures.

II. MATHEMATICAL MODEL

Irreversible step growth homopolymerization of oligomers of formula X-Ai-H proceeds according to (2):

$$H - A_i - X \; + H - A_j - X \rightarrow H - A_{i+j} - X + HX \qquad (2)$$

A is a monomer fragment that is repeated i times; X, H are the active terminal groups associated with this fragment.

Let at the initial moment of time in the system there are N_i^0 oligomer molecules with the degree of polymerization (DP) i = 1,2,..., M_0 (M_0 is the highest degree of oligomer polymerization in the initial mixture). In each reaction (2) the number of molecules decreases by one, so after m steps the number of molecules of all oligomers will be:

$$N_0^{(m)} = N_0 - i. \qquad (3)$$

Let M_m is the highest DP in the mixture in the system after m process steps, N_i^0, $N_i^{(m)}$ - the number of molecules with $DP = i$ at the initial moment of time and after m process steps; N_0, $N_0^{(m)}$ is the number of molecules of all polymers (oligomers) in the system at the initial moment of time and after m steps of the process, π_i is the fraction of oligomer molecules with the degree of polymerization i in the relation to the total number of molecules N_0 at the initial moment of time.

At the m+1th step, the following events related to $DP = i$ are possible:

- the number of i-oligomer molecules will increase by 1 with probability $p_{+1}^{(m)}$;
- the number of i-oligomer molecules will decrease by 1 with probability $p_{-1}^{(m)}$;
- the number of i-oligomer molecules will decrease by 2 with probability $p_{-2}^{(m)}$;
- the number of i-oligomer molecules will not change with probability $p_0^{(m)}$.

The sum of all probabilities is equal to 1, whence:

$$p_0^{(m)} = 1 - p_{+1}^{(m)} - p_{-1}^{(m)} - p_{-2}^{(m)}. \qquad (4)$$

The average number of molecules with degree of polymerization i at step number m+1 will be:

$$N_i^{m+1} = (N_i^m + 1)\cdot p_{+1}^{(m)} + (N_i^m - 1)\, p_{-1}^{(m)} + (N_i^m - 2)\, p_{-2} + N_i^m\, p_0^{(m)} = N_i^m + p_{+1}^{(m)} - p_{+1}^{(m)} - 2\, p_{-1}^{(m)} \qquad (5)$$

The increment of the number of molecules with degree of polymerization i:

$$\Delta N_i = N_i^{m+1} - N_i^m = p_{+1}^{(m)} - p_{+1}^{(m)} - 2\, p_{-1}^{(m)} \qquad (6)$$

Let us divide both parts of (6) by the minimum possible increment of the number of molecules $\Delta m = 1$. Since the total number of molecules N_0 in the polymer system is always very large, we can assume that $N_0 \rightarrow \infty$ and the ratio of increments can be considered as a derivative of m:

$$\lim_{N_0\to\infty}\left[\frac{\Delta N_i}{(\Delta m=1)}=\frac{\Delta N_i/N_0}{m/N_0}\right]=\frac{d\left(N_i/N_0\right)}{d\left(m/N_0\right)}=$$
$$=\frac{dN_i}{dm}=p_{+1}^{(m)}-p_{-1}^{(m)}-2\cdot p_{-2}^{(m)} \quad (7)$$

Let us express the probabilities through the numbers of molecules with $DP = i$ at step m and make a substitution:

$$x=\frac{m}{N_0};\quad \pi_i=\frac{N_i}{N_0-m} \quad (8)$$

x is the ratio of the number of steps of the step growth polymerization process to the total number of molecules N0, π_i is the mole fraction of oligomer molecules with $DP = i$ in the mixture after m steps. After substitution into (6), in the limit at $M_m\to\infty$ we obtain an infinite system of differential equations of the model:

$$\frac{d\pi_i}{dx}=\frac{1}{1-x}\cdot\left(\sum_{j=1}^{i-1}\pi_i\cdot\pi_{i-j}\ -\ \pi_i\right),\ i=1,2,... \quad (9)$$

Initial conditions are mole fractions of oligomers in the mixture at the initial moment of the process at x=0: $\pi_i(0)=\pi_i^0$ (i=1,2,…).

III. Exploring the Model

The following properties of model (9) were established by methods of mathematical analysis [8]:

1. The system (8) is recurrent, an arbitrary i-th equation (9) contains only unknowns with numbers from 1 to i and does not contain unknowns with higher numbers. Therefore, each partial solution contains initial conditions only for unknowns with numbers not exceeding i.

2. Any equation of the system (9) is integrable in quadrature and can be solved analytically. In this case, any of the roots of the system can be represented as a polynomial whose coefficients are combinations of initial conditions.

3. An infinite sequence of solutions $\pi_i\geq 0$ of the system (9) forms a convergent numerical series with sum equal to 1.

4. If the oligomers have an initial geometric distribution (1), this law is preserved during further interaction. Including, if the initial mixture is a pure monomer, the solution (9) also leads to the distribution (1). This indicates that the geometric distribution (Flory distribution) is a special case of the distribution described by system (9).

IV. Numerical Solution Algorithms

As i increases, the formulas for calculating π_i under arbitrary initial conditions become very cumbersome. Therefore, numerical methods should be used for calculation. In practice, the average degree of polymerization (ADP) is controlled in polymer synthesis:

$$ADP=\sum_{i=1}^{\infty} i\cdot\pi_i \quad (10)$$

Therefore, the formulation of the practical problem: given an initial distribution of oligomers, find the distribution of the final mixture with a given ADP_g value to numerically find π_i (i=1,2,...), we need to find a value $x\in(0;1)$ for which for a given small $\varepsilon > 0$:

$$\left|\sum_{i=1}^{n} i\cdot\pi_i-ADP_g\right|<\varepsilon. \quad (11)$$

It can be assumed that starting from some number $i>n$ the change of π_i can occur according to the law of convergent geometric progression at A>0, 0<b<1:

$$\pi_i=A\cdot b^{i-n-1};\ \log(\pi_i)=\log(A)+(i-n-1)\cdot\log(b) \quad (12)$$

For this case, an equation is derived to estimate π_i for any i:

$$ADP=\sum_{i=1}^{n} i\cdot\pi_i+\left[\frac{A}{1-b}-\sum_{i=1}^{n} i\cdot A\cdot b^{i-1}\right] \quad (13)$$

In (13), the first term is the average degree of polymerization calculated from model (9) with a finite number of equations n, and the second term (in square brackets) is the correction for infinity. The parameters log(A) and log(b) can be calculated from the last 10-15 values of π_i from the logarithmic form of (12) by the least-squares method. Numerical experiments have shown that at sufficiently large n the linear dependence (12) is fulfilled with the coefficient of determination R^2>0.999.

On model systems it is shown that even in unfavorable cases n = 100-1000 is sufficient to obtain a solution that does not change with further growth of n. The capabilities of the proposed method are illustrated by calculation examples. It is shown that the use of mixtures of oligomers as compared to monomers allows to significantly change the Flory MWD

Conclusion

A mathematical model for the distribution function in irreversible step growth homopolymerization of oligomers of arbitrary initial composition has been developed and investigated

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