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EFFECT OF VISCOSITY CHANGES OF REACTION MIXTURE ON THE KINETICS OF FORMATION OF LINEAR LIVING POLYMER

WPLYW WZROSTU LEPKOŚCI ŚRODOWISKA REAKCYJNEGO NA KINETYKĘ PROCESU POWSTAWANIA POLIMERU LINIOWEGO W POLIMERYZACJI ŻYJĄCEJ

Abstract: In the studies presented herein an attempt to include the impact of the increase in viscosity of the reaction mixture on the kinetics of living polymers formation was carried out and this effect should be included in the numerical calculations. The presented method of solving the equations system of mass balance allows a determination of values of the kinetic parameters of polymerization by introducing a correction factor and a partial reaction rate constant. This move enabled a simplification of the mathematical expressions describing the polymerization process and a possibility of connecting the kinetic parameters with the average molar mass of the system and thus – with the viscosity of the reaction mixture. The presented method enables studies on the polymerization processes in cases, when the rate of reaction does not depend on the viscosity increase or rate of reaction depends on the viscosity increase and on the average molecular mass.

Keywords: kinetics of polymerization, reaction rate constant, linear polymer, viscosity, living polymerization

Introduction

Mathematical modelling is a method of studying polymerization processes that is much cheaper than experimental studies. Therefore, mathematical models are often used both for analysis of the polymerization processes and in the design of chemical equipment. The bases of such a modelling are mass and heat balances. However, in the polymerization processes the heat balance is very often neglected because of the practically constant process temperature. So the mass balances of each component of the mixture have been derived to describe the polymerization process. The process of living polymerization has been taken into account in this paper.

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Results

The mathematical model presented in work allows a determination of the values of the kinetics parameters of polymerization reactions. We have assumed that only irreversible reactions of the $A + B \rightarrow C$ type [1, 2], rate was described by the second order kinetic equation of the form:

$$r_i = k_{AB} \cdot C_A \cdot C_B \quad (1)$$

have been taken into account in this paper.

We are interested in polymerization reactions in which the reaction rate depends on viscosity of the reaction mixture, *ie* increase of viscosity causes decrease of the reaction mixture [3, 4].

Mathematical models describing the polymerization processes are usually very complex because of a great number of unknown kinetic parameters. The most popular method of describing the polymerization processes bases on the assumption that the values of all reaction rate constants are identical [5–9]. This assumption makes possible to reduce the very complex set of balance equations to a rather simple form. Another simplification of the most frequent occurrence in the literature depends on the assumption that viscosity of the reaction mixture does not have any effect on the reaction rates.

Another way of solving the set of balance equations describing the polymerization process has been presented in this paper. We have got the significant simplification of the mathematical model by introducing in place of reaction rate constant k_{AB} the product of two partial reaction rate constants k_A and k_B [10–12]:

$$k_{AB} = k_A \cdot k_B \quad (2)$$

where k_A and k_B refer to the components A and B , respectively.

Although from a formal point of view the expressions k_{AB} and $k_A \cdot k_B$ means the same, the latter one has the form that is much more convenient for numerical calculations because it helps to present equation (1) in the form [13]:

$$r_{ij} = k_i \cdot k_j \cdot C_i \cdot C_j \quad (3)$$

Let us consider the living polymerization process carried out in the batch type reactor. Assuming that all monomers B (activated monomers A^*) have been created at the same time only the *propagation step* (PS) of the *living polymerization process* (LPP) have to be analysed. When the propagation step starts only monomer B and monomer A (inactive) are present in the reaction mixture, so the first reaction of the propagation step is of the form:



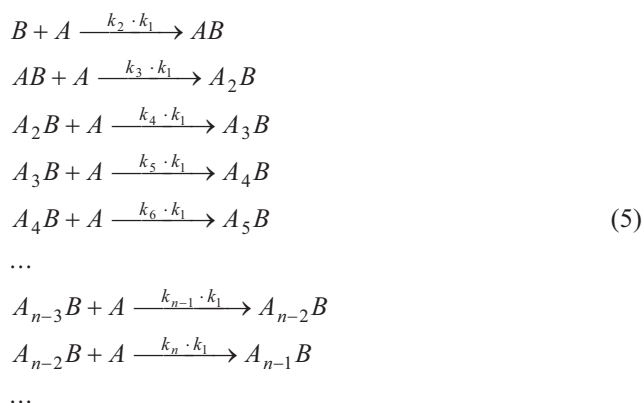
The method of designating all the components of the reaction mixture with the corresponding partial reaction rate constants is presented in Table 1.

Table 1

Components of reaction mixture with the corresponding partial reaction rate constants numbers of monomers in polymer chains

Components of reaction mixture	Partial reaction rate constants	Numbers of monomers
$[A] = C_1$	k_1	1
$[B] = C_2$	k_2	1
$[AB] = C_3$	k_3	2
$[A_2B] = C_4$	k_4	3
$[A_3B] = C_5$	k_5	4
...
$[A_iB] = C_{i+2}$	k_{i+2}	$i + 1$
...

According to Table 1 the living polymerization process has been described by the following system of the stoichiometric equations:



where: k_j – partial reaction rate constant of component j .

Using the equation (5) and remembering about earlier assumptions we have established the rate of reaction for all components of the process in the following form:

$$\frac{d[B]}{dt} \equiv \frac{dC_2}{dt} = -k_1 C_1 k_2 C_2 \tag{6}$$

$$\frac{dC_1}{dt} = -k_1 C_1 \sum_{i=2}^n k_i C_i \tag{7}$$

$$\frac{dC_3}{dt} = -k_1 C_1 (k_2 C_2 - k_3 C_3) \quad (8)$$

$$\frac{dC_4}{dt} = -k_1 C_1 (k_3 C_3 - k_4 C_4) \quad (9)$$

...

$$\frac{dC_{n-1}}{dt} = -k_1 C_1 (k_{n-2} C_{n-2} - k_{n-1} C_{n-1}) \quad (10)$$

...

And the general equation for m -component was described using the following expression:

$$\frac{dC_m}{dt} = -k_1 C_1 (k_{m-1} C_{m-1} - k_m C_m) \quad \text{for } 2 < m \quad (11)$$

Using the formulas (5–10) for particular odd fractions, the general mathematical models of analyzed polymerizations process for odd fractions has been introduced:

$$\begin{cases} \frac{dC_1}{dt} = -k_1 C_1 \sum_{i=2}^n k_i C_i \\ \frac{dC_2}{dt} = k_1 C_1 k_2 C_2 \\ \frac{dC_m}{dt} = k_2 C_2 (k_{m-1} C_{m-1} - k_m C_m) \end{cases} \quad (m = 3, 4, \dots, n) \quad (12)$$

Bearing in mind the dependencies describing viscosity changes with the progress of polymerization, expressing viscosity as a function of the average molar mass M_n of the reaction mixture, we included an impact of viscosity increase on the rate of polymerization by introducing a correction factor Z_i .

This factor allows expressing a partial reaction rate constant as a function of the average molar mass of the reaction mixture:

$$k_i = k_1 \cdot Z_i(M_n) \quad (13)$$

Correction factor Z_i is a function of the average molar mass of the reaction mixture M_n . To determine $Z_i(M_n)$ function we used the simplest form of correction factor Z_i :

$$Z_i(M_n) = \gamma \cdot \left(\frac{M_n}{M_0} \right)^{-p} \quad (14)$$

where: p – a parameter,
 γ – a constant factor characterized for the polymerization process;
 M_0 – the molar mass of the monomer.

The range of the linear increase of viscosity as a function of number average molecular weight, has been described by the following equation [1]:

$$\eta = \text{const} \cdot M_n \quad (15)$$

Equations (13), (14) and (15) allow expression of viscosity as a function of kinetic parameters k_i :

$$\eta = \text{const} \cdot M_0 \left(\frac{k_1 \cdot \gamma}{k_i} \right)^{\frac{1}{p}} \quad (16)$$

and then:

$$k_i = \text{const} \cdot k_1 \gamma \left(\frac{\eta}{M_0} \right)^{-p} \quad (17)$$

The above equation makes it possible for both simplification of the mathematical expressions describing the polymerization process and connecting the kinetic parameters k_i with the average molar mass of the system M_n , and thus – with the viscosity of the reaction mixture. Estimation of kinetic parameters k_i based on experimental results given in the literature and depended on minimization the objective function of the form:

$$S = \sum_{i=1}^b (O_i - E_i)^2 \rightarrow \min \quad (18)$$

where b is a number of empirical data, E_i is the empirical value, O_i is the calculated value.

We have done numerical calculations for living polymerization of 2-phenyl-2-oxazoline including increase of viscosity followed by the increase of the average molar mass in each calculation step.

The ring-opening polymerization of 2-oxazolines in acetonitrile was investigated under pressure conditions with conventional heating. The investigated polymerizations were performed at 120 °C and 140 °C in acetonitrile under 1.5 MPa external nitrogen pressure with methyl tosylate as initiator as depicted in Fig. 1. When all monomer is consumed, a second monomer can be added to synthesize block copolymers or a

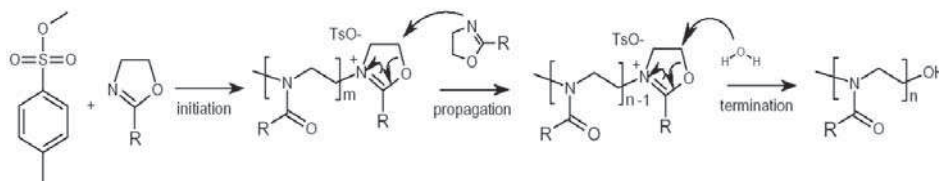


Fig. 1. Reaction mechanism for the cationic ring-opening polymerization of 2-oxazolines utilizing methyl tosylate as initiator

nucleophile can be added to introduce a functional end-group (Fig. 1 depicts the addition of water as terminating agent).

Two reactors were filled with 2-phenyl-2-oxazoline (1.1 g, 7.5 mmol) and 1.4 cm³ of a methyl tosylate as initiator stock solution (0.091 M; 0.41 g methyl tosylate in 19 g acetonitrile), resulting in 2.5 cm³ reaction mixtures with 3 M 2-phenyl-2-oxazoline (45 w%) and a monomer to initiator ratio of 60. After applying a pressure of 15 bar to the reactors, the polymerization mixtures were heated to 120 °C or 140 °C for a predefined time. Subsequently, the reactors were cooled to 60 °C, the pressure was released and the polymerizations were finished with water (100 cm³). This procedure

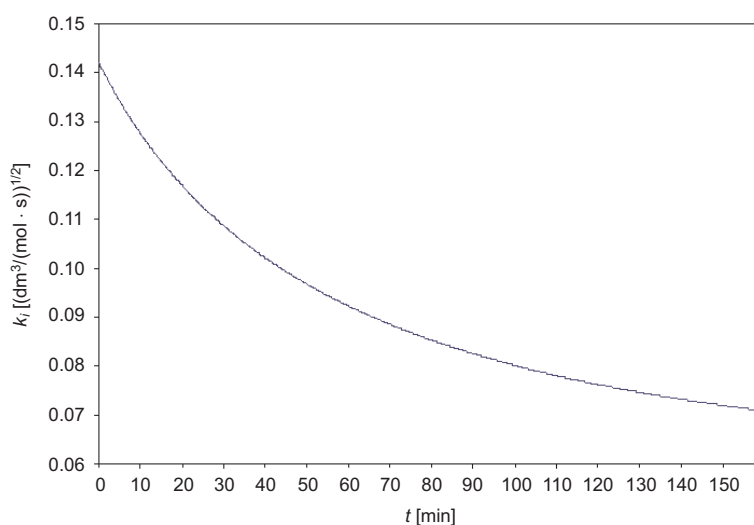


Fig. 2. Dependence of the reaction rate constants k_i [(dm³/(mol · s))^{1/2}] in time t [min] during living polymerization process of 2-phenyl-2-oxazoline at 120 °C calculated according model (12)

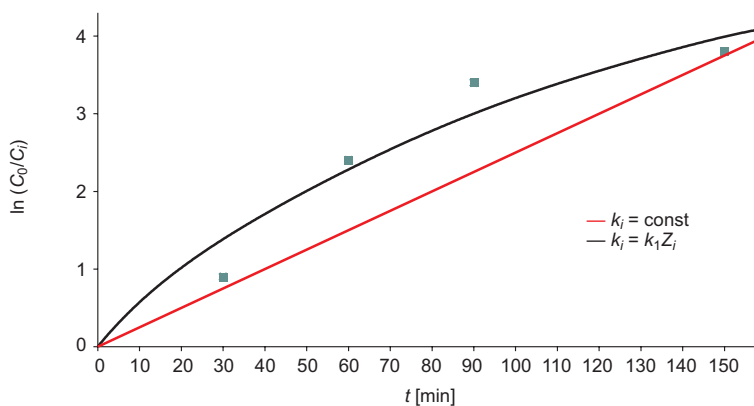


Fig. 3. Dependence of the $\ln(C_0/C_i)$ in time t [min] during living polymerization process of 2-phenyl-2-oxazoline at 120 °C: (—) theoretical line, when $k = \text{const}$; (—) calculations using model (12), when $k_i = k_1 Z_i$; (■) experimental data [14]

was repeated for four different reaction times (120 °C: 15, 25, 95 and 155 min; 140 °C: 15, 25, 35 and 50 min) after which all mixtures were characterized by ¹H NMR and GPC. As a consequence, the first quenched polymerization mixtures were heated three additional times to 120 °C before analysis [14].

On the basis of the experimental results available in [14] and own calculations, we have determined the values of both kinetic parameters (Fig. 2) and dependence $\ln(C_0/C_i)$ at 120 °C, which is shown in Fig. 3.

Estimation of kinetic parameters k_i and equation (17) allowed for the calculation of the objective function S , which is presented in Table 2 and Table 3.

Table 2

Comparison of the calculated values of $\ln(C_0/C_i)$ with those obtained from experimental data

t [min]	Polymerization of 2-oxazoline at 120 °C $\ln(C_0/C_i)$	
	Literature data $k_i = \text{const}$	The calculated values according model (12) $k_i = k_1 Z_i$
30	0.90	1.377
55	2.25	2.146
87	3.35	2.898
155	3.90	4.092
	$S_c = 1.912$	$S_\eta = 0.480$

Table 3

Comparison of the calculated values of $\ln(C_0/C_i)$ with those obtained from experimental data

t [min]	Polymerization of 2-oxazoline at 140 °C $\ln(C_0/C_i)$	
	Literature data $k_i = \text{const}$	The calculated values according model (12) $k_i = k_1 Z_i$
15	1.8	2.223
25	3.8	3.078
35	4.1	3.752
50	4.3	4.596
	$S_c = 2.956$	$S_\eta = 0.909$

On the next step we have determined the values of both kinetic parameters (Fig. 4) and dependence $\ln(C_0/C_i)$ in time during living polymerization process of 2-phenyl-2-oxazoline at 140 °C, which is shown in Fig. 5.

Estimation of kinetic parameters k_i and equation (17) allowed for the calculation of the correlating factor, which is presented in Table 4.

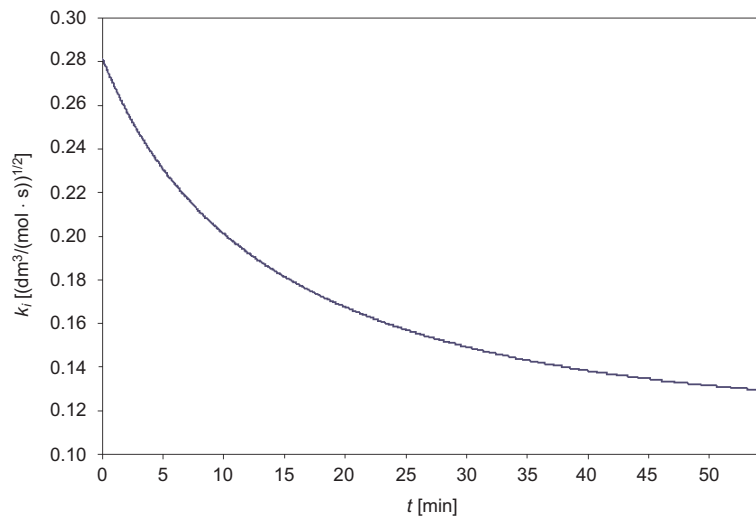


Fig. 4. Dependence of the reaction rate constants k_i $[(\text{dm}^3/(\text{mol} \cdot \text{s}))^{1/2}]$ in time t [min] during living polymerization process of 2-phenyl-2-oxazoline at 140 °C calculated according model (12)

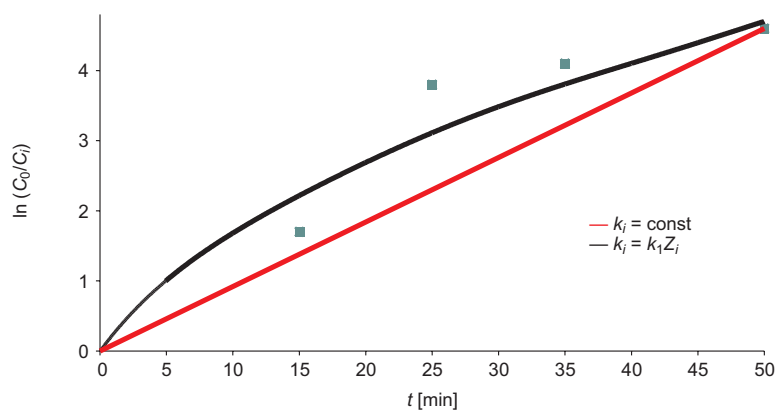


Fig. 5. Values of the $\ln(C_0/C_i)$ in time t [min] during living polymerization process of 2-phenyl-2-oxazoline at 140 °C: (—) theoretical line, when $k = \text{const}$; (—) calculations using model (12), when $k_i = k_1 Z_i$; (■) experimental data [14]

Table 4

Value of the objective function (18) and of the correlating factor $\beta(\eta)$

Investigated process	S_c ($k = \text{const}$)	S_η ($k_i = k_1 Z_i$)	$\beta(\eta)$
Polymerizations of 2-phenyl-2-oxazoline in 120 °C	1.912	0.480	0.749
Polymerizations of 2-phenyl-2-oxazoline in 140 °C	2.956	0.909	0.692

where $\beta(\eta)$ correlating factor, $\beta(\eta) \in (0,1)$, described by the equation:

$$\beta(\eta) = \frac{S_c - S_\eta}{S_c} \quad (19)$$

where: $\beta(\eta)$ – correlating factor, $\beta(\eta) \in (0,1)$,

S_c – minimum value of the objective function (18) when $\eta = \text{const}$,

S_η – minimum value of the objective function (18) when $\eta \neq \text{const}$.

This shifts are respectively equal to 10 min for the propagation step at temperature 120 °C and 7 min for the propagation step at temperature 140 °C. The results are shown

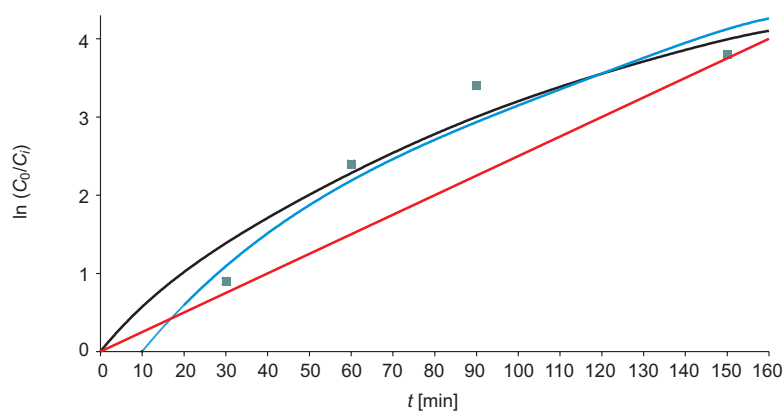


Fig. 6. Dependence of the $\ln(C_0/C_i)$ in time t [min] during living polymerization process of 2-phenyl-2-oxazoline at 120 °C: (–) theoretical line, when $k = \text{const}$; (–) calculations using model (12), when $k_i = k_i Z_i$, $t_0 = 0$ min; (–) calculations using model (11), when $k_i = k_i Z_i$, $t_0 = 10$ min; (■) experimental data [14]

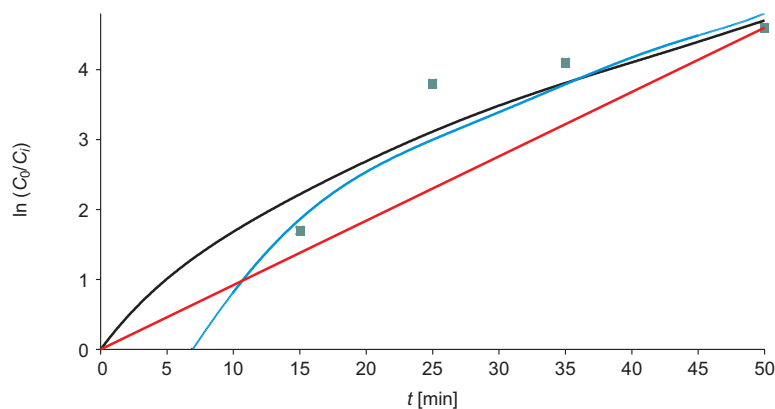


Fig. 7. Dependence of the $\ln(C_0/C_i)$ in time t [min] during living polymerization process of 2-phenyl-2-oxazoline at 140 °C: (–) theoretical line, when $k = \text{const}$; (–) calculations using model (12), when $k_i = k_i Z_i$, $t_0 = 0$ min; (–) calculations using model (11), when $k_i = k_i Z_i$, $t_0 = 7$ min; (■) experimental data [14]

in Fig. 6 and 7 and the Table 5. The delay of the start of the propagation step may be caused by the imperfection of mixing of the reaction mixture.

Table 5

Value of equation (18) and correlating factor β

Investigated process	S_c when $k = \text{const}$	S_η (when $k_i = k_1 Z_i$)	$\beta(\eta)$
Polymerizations of 2-phenyl-2oxazoline at temperature 120 °C	1.912	0.480	0.749
Polymerizations of 2-phenyl-2oxazoline at temperature 120 °C – shift in time $t_0 = 10$ min	1.912	0.409	0.786
Polymerizations of 2-phenyl-2oxazoline at temperature 140 °C	2.956	0.909	0.692
Polymerizations of 2-phenyl-2oxazoline at temperature 140 °C – shift in time $t_0 = 7$ min	2.956	0.768	0.740

Summary

The method of solving the set of mass balance equations describing the propagation step of the living polymerization process has been presented in this paper.

Two cases have been taken into account:

- the reaction rate does not depend on viscosity changes of the reaction mixture,
- the reaction rate depends on viscosity changes and decreases with increasing viscosity of the reaction mixture

In this paper we have the significant simplification of the mathematical model of living polymerization process by introducing in place of the reaction rate constant k_{ij} the product of two partial reaction rate constants presented in form (2). Using partial reaction rate constants, the number of mass balance equations have been reduced to the number of components in the reaction mixture.

The introduction of partial reaction rate constant also makes it relatively easy to connect kinetics parameters k_i with average molar mass of polymer M_n and consequently with viscosity of reaction mixture η .

On the basis of the experimental results and own calculations, we have determined the values of kinetics parameters of living polymerization process and the influence of viscosity changes on rate of living polymerization process reaction by setting the correction factor Z_i described by the equation (14). In order to find the minimum value of the objective function (18) the simplex optimisation method has been used. As the result, the correlating factor $\beta(\eta)$ was calculated. Correlating factor $\beta(\eta)$ allowed to define experimental values of the degree of representation.

Each experimental case described theoretically in this paper is nearer to the reality when changes in viscosity have been taken into account.

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WPLYW WZROSTU LEPKOŚCI ŚRODOWISKA REAKCYJNEGO NA KINETYKĘ PROCESU POWSTAWANIA POLIMERU LINIOWEGO W POLIMERYZACJI ŻYJĄCEJ

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Streszczenie: Praca prezentuje wpływ wzrostu lepkości mieszaniny reakcyjnej na kinetykę tworzenia polimeru liniowego w procesie polimeryzacji żyjącej 2-fenylo-2-oksazoliny. Efekt wzrostu lepkości mieszaniny reakcyjnej wskutek procesu polimeryzacji uwzględniono w obliczeniach numerycznych. W pracy przedstawiono metodę rozwiązywania układu równań bilansu masy procesu polimeryzacji żyjącej 2-fenylo-2-oksazoliny, pozwalającą na wyznaczenie parametrów kinetycznych procesu polimeryzacji. Możliwość wyznaczenia parametrów kinetycznych reakcji polimeryzacji osiągnięto przez wprowadzenie tzw. cząstkowej stałej szybkości reakcji. Wprowadzenie cząstkowej stałej szybkości reakcji pozwoliło na znaczne uproszczenie wyrażenia matematycznych opisujących proces polimeryzacji oraz dało możliwość powiązania parametrów kinetycznych ze średnią masą molową mieszaniny, a przez to z lepkością układu reakcyjnego. Przedstawiona metoda pozwala analizować proces polimeryzacji żyjącej polimerów liniowych, nie tylko gdy zmienia się lepkość mieszaniny reakcyjnej, ale również gdy lepkość jest stała lub gdy parametry kinetyczne nie zależą od lepkości, a zależą od mas molekularnych poszczególnych reagentów.

Słowa kluczowe: kinetyka polimeryzacji, stała szybkości reakcji, polimer liniowy, lepkość, polimeryzacja żyjąca