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ORIGINAL PAPER

Modelling polyurethane synthesis rates on the example of heteropolyaddition of 2,4-toluene diisocyanate (TDI) and 1,4-butanediol (BD)

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Abstract
This paper investigates the effects of increase of reaction mixture viscosity on the kinetics of linear polymer creation in a bulk heteropolyaddition process of 2,4-toluene diisocyanate (TDI) and 1,4-butanediol (BD). The paper presents a method for solving a system of bulk polyaddition of 2,4-toluene diisocyanate and 1,4-butanediol process balance equations, allowing the determination of the process kinetic parameters. Determination of polymerisation reaction kinetic parameters was also made possible by the use of the so-called partial reaction rate constant. Such an approach enabled a significant simplification of the mathematical expressions describing the heteropolyaddition process and provided an opportunity to associate kinetic parameters with the average molar mass of the mixture and, thus, with the viscosity. The method presented herein facilitates an analysis of the linear polymers heteropolyaddition process.

Keywords Kinetics of polymerisations · Reaction rate constant · Linear polymer · Viscosity · Heteropolyaddition · Modelling of polymerisations

List of symbols

E_i	Experimental value (literature), [g/mol]
k_1	Partial reaction rate constant of component 1, [$\mathrm{dm^3/(mol\ s)^{1/2}}$]
k_A, k_B	Partial reaction rate constants of reagents assigned to reagents A and B, respectively, [$\mathrm{dm^3/(mol\ s)^{1/2}}$]
k_AB	Reaction rate constant A + B = AB, [$\mathrm{dm^3/(mol\ s)}$]
k_j	Partial reaction rate constant j of this component, [$\mathrm{dm^3/(mol\ s)^{1/2}}$]
M_0	Molar mass of monomer A or B, [g/mol]
M_n	Polymer number-average molar mass, [g/mol]
O_i	Calculated value, [g/mol]

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t	Time [min]
w_i	Part by weight
Z_i	Correction coefficient of component i
$\beta(\eta)$	Correlation coefficient, $\beta(\eta) \in (0.1)$
γ	Constant coefficient characteristic for a particular polymerisation process

Introduction

Very often during the course of polymerisation processes, the viscosity of the reaction medium changes. When these changes significantly influence the polymerisation process rate, it becomes necessary to take into account these variables in balance equations describing this process. The need to take into account changes in viscosity means that systems of mass balance equations describing the polymerisation process are usually quite complex and often difficult to solve due to the large number of unknown kinetic parameters. In connection with difficulties in determining polymerisation process kinetic parameters, literature often assumes the same value for all constant rates of these reactions ($k = \text{const}$), and the effect of viscosity changes on the numerical values of the k constants is ignored. Used method is appropriate for systems, where viscosity is practically constant.

This paper attempts to take into account increasing viscosity of the reaction medium on the kinetics of the linear polymer creation process occurring during heteropolyaddition process. The increase in average molar mass of the mixture and, thus, the viscosity caused by the course of this process makes the constant reaction rate numerical values decrease and as such may have a significant effect on the results.

Due to the complexity of the mass balance equation system and the necessity to take into account viscosity changes in numerical calculations, this paper uses the concept of partial reaction rate constants, the introduction of which into the balance equations allows a meaningful simplification of the mathematical model describing the polyaddition process being considered here [1]. The influence of viscosity on the polymerisation rate has been taken into account by associating that rate with the number-average molecular mass M_n of the reaction mixture, which provided an opportunity to associate kinetic parameters k with the number-average molar mass M_n. Using the derived mass balance system of equations, which takes into account number-average molar mass changes on the reaction rate constant numerical values, kinetic parameter values for the analysed processes were determined.

The presented method facilitates determination of partial reaction rate constant numerical values and, thus, it assists the progress of polymerisation kinetic parameters definition, which facilitates the system of balance equations to be solved.

The used model

Literature data [1] show that in real systems, very often during the course of polymerisation processes, the viscosity of the reaction medium changes. When the viscosity changes significantly influence the polymerisation process rate, it becomes necessary to take into account these variations in rate equations describing this process. A change in the viscosity of a reaction system, most often exhibiting itself by a change in the numeric kinetic value (which determine rate of reaction), causes a reduction in the reaction rate numerical constants, which should be taken into consideration in numeric calculations. Changes in viscosity, during the course of a polymerisation process, cause a change in the process kinetic parameters, resulting in adding significant complexity to the mass balance equation system. As reaction rate constant values change with the progress of the polymerisation process, it becomes necessary, from the point of view of numeric calculations, to determine the reaction rate values at each step of the said calculations.

This paper uses the mass balance model for the heteropolyaddition process presented in the paper [1]. The model is based on the assumption of a variable reaction rate of the polymerisation process, which results from a change in the numerical values of the kinetic parameters of the process, which is related to the change in the number-average molar mass of the reaction system and the change in the mixture viscosity [2]. Changes in viscosity during the polymerisation process modify the kinetic parameters of the process, making the system of mass balance equations significantly more complex. The values of reaction rate constants vary as the polymerisation process progresses, which means that in numerical calculations they have to be determined at every step of the process. The aforementioned paper assumes that, for a secondary reaction, the rate of which is presented in the form of $r_i = k_{\mathrm{AB}} C_{\mathrm{A}} C_{\mathrm{B}}$, a constant reaction rate is k_{AB}. This value is related to the reaction, not to the reactant. In order to associate the reaction rate with the reactant rather than with the reaction, a partial reaction rate constant was used, which is defined as follows:

$$k_{\mathrm{AB}} = k_{\mathrm{A}} k_{\mathrm{B}}. \tag{1}$$

The paper [1] uses a mass balance model based on the reaction of diphenyl carbonate and diglycidyl ether of bisphenol A in a batch reactor with ideal mixing at 100 °C for 48 h to determine the kinetic parameters of the polymerisation process. As in the cited paper, for calculations, this paper uses the system of mass balance equations for the heteropolyaddition process of an alternating linear polymer in a batch reactor with ideal mixing, working in isothermal conditions defined as follows:

$$\begin{cases}
\frac{\mathrm{d}C_1}{\mathrm{d}t} = -k_1 C_1 \left(S_{\mathrm{A}} + S_{\mathrm{AB}}\right), \\
\frac{\mathrm{d}C_{n+1}}{\mathrm{d}t} = -k_{n+1} C_{n+1} \left(S_{\mathrm{B}} + S_{\mathrm{AB}}\right), \\
\frac{\mathrm{d}C_{2n+1}}{\mathrm{d}t} = k_1 C_1 k_{n+1} C_{n+1} - k_{2n+1} C_{2n+1} \left(S_{\mathrm{A}} + S_{\mathrm{B}} + S_{\mathrm{AB}}\right), \\
\frac{\mathrm{d}C_p}{\mathrm{d}t} = \sum_{i=1}^{p-1} k_i C_i k_{2n+p-i} C_{2n+p-i} - k_p C_p \left(S_{\mathrm{A}} + S_{\mathrm{AB}}\right), \\
\frac{\mathrm{d}C_{n+p}}{\mathrm{d}t} = \sum_{i=1}^{p-1} k_{n+i} C_{n+i} k_{2n+p-i} C_{2n+p-i} - k_{n+p} C_{n+p} \left(S_{\mathrm{B}} + S_{\mathrm{AB}}\right), \\
\frac{\mathrm{d}C_{2n+p}}{\mathrm{d}t} = \sum_{i=1}^{p-1} k_i C_i k_{n+p+1-i} C_{n+p+1-i} + \sum_{i=1}^{\mathrm{floor}\left(\frac{p}{2}\right)} k_{2n+i} C_{2n+i} k_{2n+p-i} C_{2n+p-i} - k_{2n+p} C_{2n+p} \left(S_{\mathrm{A}} + S_{\mathrm{B}} + S_{\mathrm{AB}}\right).
\end{cases} \tag{2}$$

The above system of mass balance was based on the model of aggregation presented in the study [3]. Then, the model presented in the study [4, 5] was modified to obtain the model of mass balance (2). This paper presents research that employs model (2) based on the process of linear polyurethane formation resulting from the heteropolyaddition of toluene-2,4-diisocyanate (TDI) and 1,4-butanediol (BD) in dilute solution [6]. The heteropolyaddition process was based on the reaction of isocyanate with a –OH hydroxyl group compound, in this case with alcohol. The general chemical equation can be represented as [7]:

$$\underset{A}{R_1-NCO}+\underset{B}{R_2-OH}\longrightarrow k_{AB}\ \underset{AB}{R_1{-}NH{-}CO{-}OR_2}.$$

In order to make it easier to associate reactants with the used model (2), toluene-2,4-diisocyanate was marked with symbol A and 1,4-butanediol with symbol *B*. Heteropolyaddition process modelling was performed on the basis of model (2) and laboratory tests carried out in the paper [7]. The authors of this paper focused entirely on the completed research presented in the paper [7]. The heteropolyaddition process was carried out in a batch reactor with ideal mixing at a constant temperature of 86 °C in a solution of chlorobenzene (C_6H_5Cl) and tetrahydrofuran (THF) at a mass ratio of 1:1. The prepared reaction mixture consisted of 30 g of toluene-2,4-diisocyanate (0.172 mol) and 15.5 g of 1,4-butanediol (0.172 mol) dissolved in 409.5 g of chlorobenzene and tetrahydrofuran solution. Due to the 10% concentration of the reactants, the analysed example of the reaction solution should be considered as diluted solution. The heteropolyaddition process was analysed for 300 min during which the authors of [7] took samples at different intervals in order to determine the concentration of free functional groups –NCO using the GPC method. The results of the experimental studies are summarised in Table 1.

The symbols in Table 1 specify, respectively:

- $F1$—fraction 1 is equal to the sum of the concentration of components A and B.
- $F2$—fraction 2 is equal to the concentration of component AB.

Table 1 The mass ratios and number-average molar masses M_n [g/mol] of the selected fractions of the reaction mixture in the heteropolyaddition process in 2,4-TDI (0.172 mol) and 1,4-BD (0.172 mol) in the solution of chlorobenzene and tetrahydrofuran at a temperature of $t_1 = 86$ °C [7]

t [min]	M_n [g/mol]	$F1+F2$	$F3+F4$	$F5+F6$
		Mass proportion		
20	309	0.73	0.252	0.016
40	332	0.574	0.352	0.074
60	356	0.46	0.385	0.155
90	412	0.32	0.354	0.225
120	456	0.252	0.314	0.267
180	537	0.164	0.234	0.269
240	667	0.087	0.157	0.218
300	801	0.067	0.112	0.166

- *F*3—fraction 3 is equal to the sum of the concentration of components A_1B_2 and A_2B_1.
- *F*4—fraction 4 is equal to the concentration of component A_2B_2.
- *F*5—fraction 5 is equal to the sum of the concentration of components A_2B_3 and A_3B_2.
- *F*6—fraction 6 is equal to the concentration of component A_3B_3.

The numerical calculations of the presented heteropolyaddition process were based on model (2), on the basis of which a calculation algorithm was built in the Mathcad Prime 2.0 software that allows for approximation of kinetic parameters of the process and consequently for determining the kinetics of the polyurethane-forming reaction.

The calculations were based on the results of experimental studies in Table 1 and the model of the heteropolyaddition process (2). All calculations were done starting with determining the reaction rate constant $k_{AB}=5\times10^{-4}$ dm^3/(mol s) with the assumption $k_i=\text{const}$.

In the calculations, the correlations describing the partial reaction rate constant k_i and the correction coefficient Z_i presented in [1] were used in an analogous manner. The correlation describing a partial reaction rate constant k_i is presented in the form of:

$$k_i = k_1 \cdot Z_i\left(M_n\right). \tag{3}$$

The correction coefficient Z_i in Eq. (3) is a function of the number-average molecular mass of the reaction mixture. In order to determine the function of $Z_i(M_n)$, the correlation of Z_i correction coefficient was used:

$$Z_i\left(M_n\right) = \gamma_1 \cdot M_n^{-p}, \tag{4}$$

where $\gamma_1 = \gamma \cdot M_0^p$; M_0—molecular mass of monomer A (or B)

Equation (4) defines the correction coefficient, which is a dimensionless number, with two parameters γ_1 and p characteristic for a particular polymerisation process. Due to this fact, the partial reaction rate constant of k_i decreases with the increase in the number-average molar mass of the forming polymer.

Estimation of kinetic parameters (particle reaction rate constants) k_i was performed on the basis of results of experimental research using numerical method of simplex optimisation. The simplex optimisation method minimised the value of the objective function S, determined by the sum of squares of differences in the calculated O_i values and experimental E_i values. The optimum numerical value of this constant was determined by minimising the numerical value of the objective function, defined by the equation:

$$S = \sum_{i=1}^{b} \left(O_i - E_i\right)^2 \rightarrow \min. \tag{5}$$

As a result of the calculations done, parameters $p=0.01$ and $\gamma_1=1$ were obtained from Eq. (4), which then allowed to estimate values of the partial reaction rate constants, as summarised in Table 2.

Table 2 Selected values of the partial reaction rate constant k_i [(dm^3/(mol s))$^{1/2}$] in the heteropolyaddition process in 2,4-TDI (0.172 mol) and 1,4-BD (0.172 mol) in chlorobenzene and tetrahydrofuran solution at temperature $t_1 = 86$ °C are calculated with model (2)

t [min]	k_i [(dm^3/(mol s))$^{1/2}$]
0	0.02020
20	0.02015
40	0.02010
60	0.02006
90	0.02001
120	0.01997
180	0.01991
240	0.01986
300	0.01982

Table 3 Comparison of experimental data and the data calculated with model (2) in the form of mass ratios and number-average molar mass M_n [g/mol] of the selected fractions of the reaction mixture in the heteropolyaddition process in 2,4-TDI (0.172 mol) and 1,4-BD (0.172 mol) in the solution of chlorobenzene and tetrahydrofuran at a temperature of $t_1 = 86$ °C [7]

t [min]	Data from literature [7]				Calculated with model (2)			
	M_n [g/mol]	w_i			M_n [g/mol]	w_i		
		$F1+F2$	$F3+F4$	$F5+F6$		$F1+F2$	$F3+F4$	$F5+F6$
20	309	0.730	0.252	0.016	166	0.818	0.162	0.018
40	332	0.574	0.352	0.074	207	0.590	0.294	0.087
60	356	0.460	0.385	0.155	250	0.430	0.326	0.150
90	412	0.32	0.354	0.225	316	0.284	0.300	0.195
120	456	0.252	0.314	0.267	383	0.200	0.253	0.200
180	537	0.164	0.234	0.269	519	0.114	0.176	0.171
240	667	0.087	0.157	0.218	655	0.074	0.126	0.137
300	801	0.067	0.112	0.166	792	0.052	0.094	0.110
The value of objective function S in accordance with Eq. (5)								
	S_{M_n}	S_{F1+F2}	S_{F3+F4}	S_{F5+F6}	S_{M_n}	S_{F1+F2}	S_{F3+F4}	S_{F5+F6}
S	185,000	0.0480	0.0451	0.0457	62,370	0.0188	0.0274	0.0201
ΣS	–	0.1388			–	0.0623		

Determination of kinetic parameters for two different k_i values, $k_i = \text{const}$ [8] and $k_i = k_1 Z_i$, allowed to determine how the mass ratios of respective polymer fractions change with time, and compare them with the results of experimental research, as shown in the figures below.

The results of model (2) research are summarised in Table 3 and compared with the experimental data.

The points in Figs. 1, 2, 3, 4, 5, 6, 7 and 8 represent the correlations obtained from the literature [7] from experimental research, while the continuous lines represent the correlations calculated using model (2) in two cases:

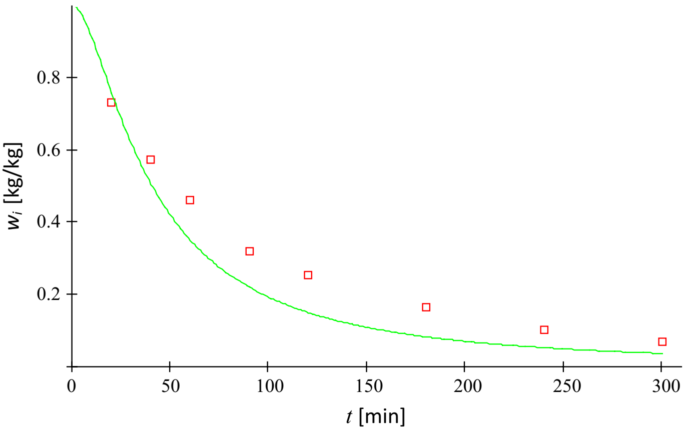

Fig. 1 Change in the mass ratio of polyurethane fraction $F1$ over time, $k_i = \text{const}$; line calculated with model (2), box experimental data [7]

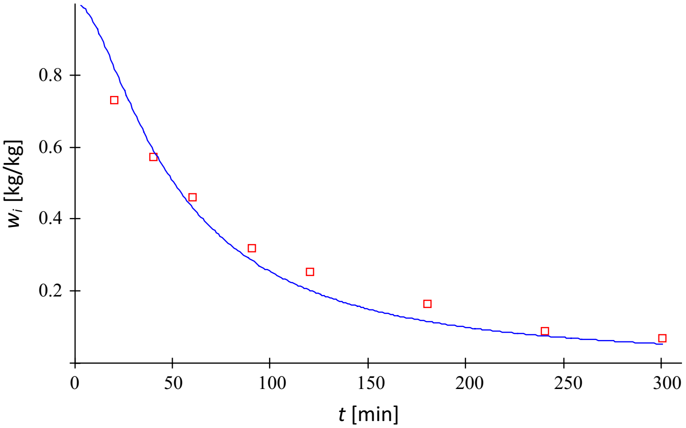

Fig. 2 Change in the mass ratio of polyurethane fraction $F1$ over time, $k_i = k_1Z_i$; line calculated with model (2), box experimental data [7]

- at the same value of reaction rate constant $k_i = \text{const}$
- with a reaction rate constant dependent on the average molecular mass of the polymer $k_i = k_1Z_i$.

On the basis of Figs. 1, 2, 3, 4, 5, 6, 7 and 8 and data in Table 3, it can be concluded that if the increase in viscosity of the reaction mixture is omitted and the same reaction rate is assumed during the whole process of heteropolyaddition of 2,4-TDI with 1,4-BD, the result obtained from the sum of objective function (5) for all analysed fractions $S_{\min} = 0.1388$ is twice higher than when including the

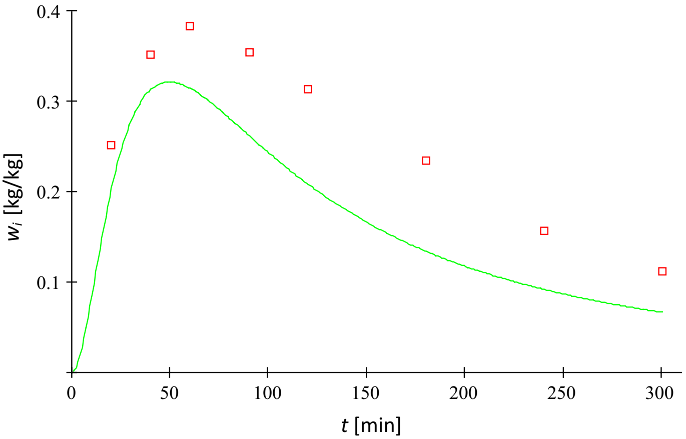

Fig. 3 Change in the mass ratio of polyurethane fraction $F2$ over time, $k_i = \text{const}$; line calculated with model (2), box experimental data [7]

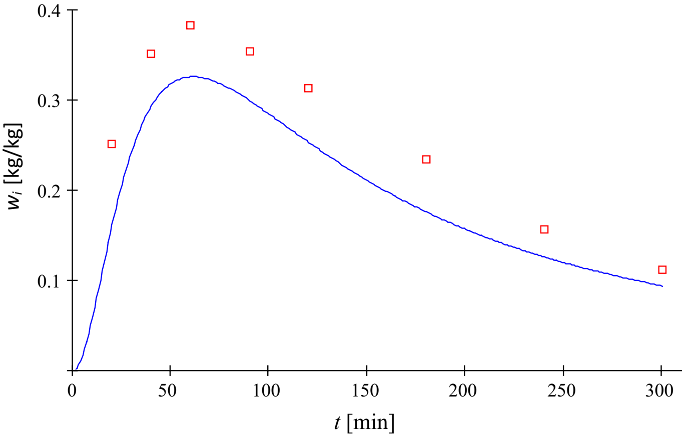

Fig. 4 Change in the mass ratio of polyurethane fraction $F2$ over time, $k_i = k_1 Z_i$; line calculated with model (2), box experimental data [7]

changes in the average molecular mass of the forming polymer (and thus viscosity) $S_{\min} = 0.0623$.

In order to compare the results obtained in Table 3, an additional correlation coefficient $\beta(\eta)$ was introduced, which takes into account the influence of viscosity on the polymerisation process and is expressed in the form of an equation:

$$\beta(\eta) = \frac{S_C - S_\eta}{S_C}. \tag{6}$$

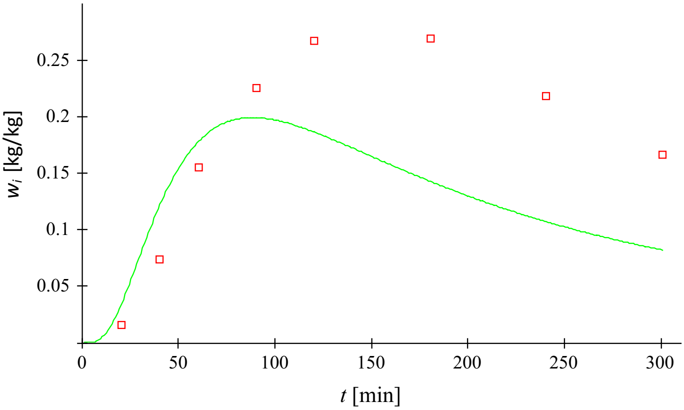

Fig. 5 Change in the mass ratio of polyurethane fraction $F3$ over time, k_i = const; line calculated with model (2), box experimental data [7]

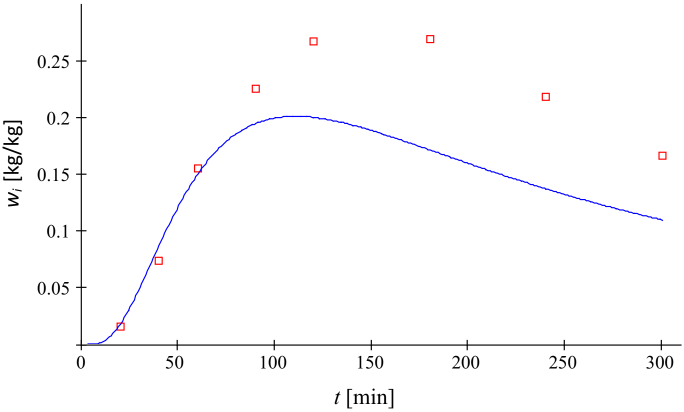

Fig. 6 Change in the mass ratio of polyurethane fraction $F3$ over time, $k_i = k_1 Z_i$; line calculated with model (2), box experimental data [7]

In the above equation, the following symbols were used: S_c—results of calculations without changes in viscosity; S_η—results of calculations with changes in viscosity; and $\beta(\eta)$—numerical value of correlation coefficient included in the range (0,1): $\beta(\eta) \in (0{,}1)$.

Using Eq. (6) and the results compiled in Table 3, a correlation factor $\beta(\eta)$ has been calculated for the theoretical and model (2) values, with the following results:

$$\beta_t(\eta) = \frac{0.1388 - 0.0623}{0.1388} = 0.551. \tag{7}$$

The measure of the influence of viscosity on the polymerisation process in this case is the value of the correlation coefficient $\beta(\eta)$ which increases with the

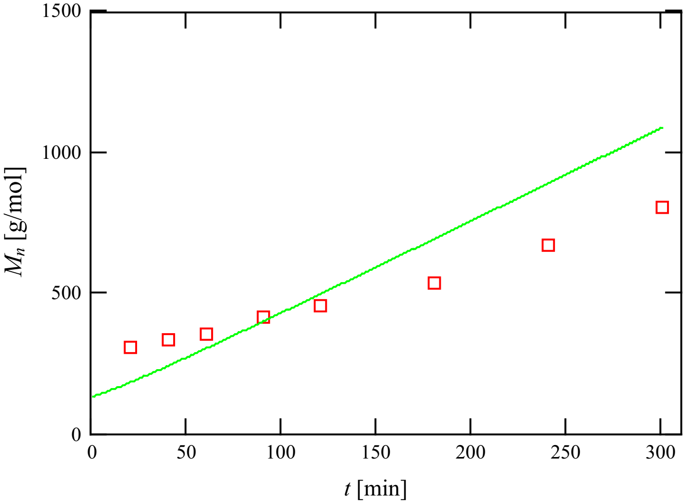

Fig. 7 Correlation of number-average molar mass M_n [g/mol] over time in the heteropolyaddition process in 2,4-TDI (0.172 mol) and 1,4-BD (0.172 mol) in the chlorobenzene and tetrahydrofuran solution at temperature $t_1 = 86$ °C, $k_i = \text{const}$; line calculated with model (2), box experimental data [7]

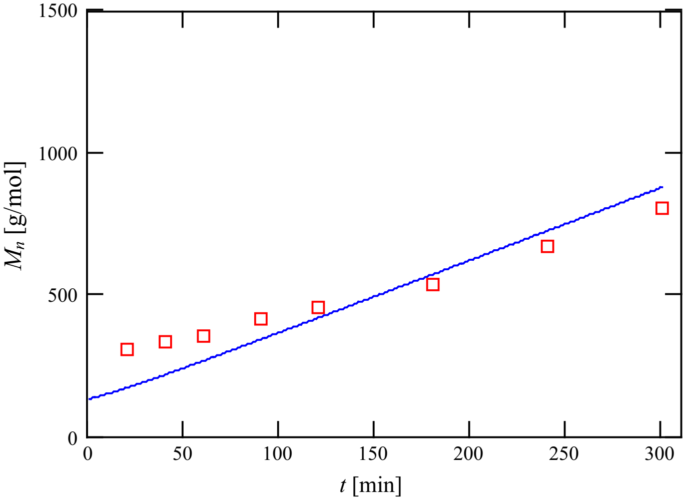

Fig. 8 Correlation of number-average molar mass M_n [g/mol] over time in the heteropolyaddition process in 2,4-TDI (0.172 mol) and 1,4-BD (0.172 mol) in the chlorobenzene and tetrahydrofuran solution at temperature $t_1 = 86$ °C, $k_i = k_1 Z_i$; line calculated with model (2), box experimental data [7]

increase in viscosity influence on the process. The value of this coefficient was $\beta_t(\eta) = 0.551$. The figure below shows the dynamics of changes in the correction coefficient Z_i in relation to the average molar mass.

It is worth noting that this case is an example of a polymerisation in diluted solutions, as evidenced by a small change in the Z_i correction coefficient, varying between 0.9530 and 0.9550.

Conclusions

Comparing the results of polyurethane formation process modelling with the results obtained in the studies [1, 4], it should be emphasised that the proposed method of determining kinetic parameters is rather reserved for cases where the viscosity of the reaction solution has a significant influence on the speed of the polymerisation process. The viscosity influence on the rate of heteropolyaddition process is determined by the correction coefficient Z_i related to the average molar mass of the forming polymer. It should be noted that the Z_i correction coefficient in the analysed process of heteropolyaddition of chloride 1,4-benzene dicarbonate with diglycidyl ether of bisphenol A is in the range of 1.6–0.2 [1], while that in the heteropolyaddition of 2,4-TDI with 1,4-BD is in the range of 0.9530–0.9550 (Fig. 9), which indicates that there is a significant influence of viscosity on the process in the first case. Despite the high dilution of the reaction mixture and slight change in viscosity of the system during the process, it can be observed that the proposed method gives better results in clarifying the process.

This paper deliberately analyses a process in a solution in which the viscosity is not likely to affect the speed of the polymerisation process or its influence is negligible. The aim was to examine how model (2) behaves, assuming a variable value of

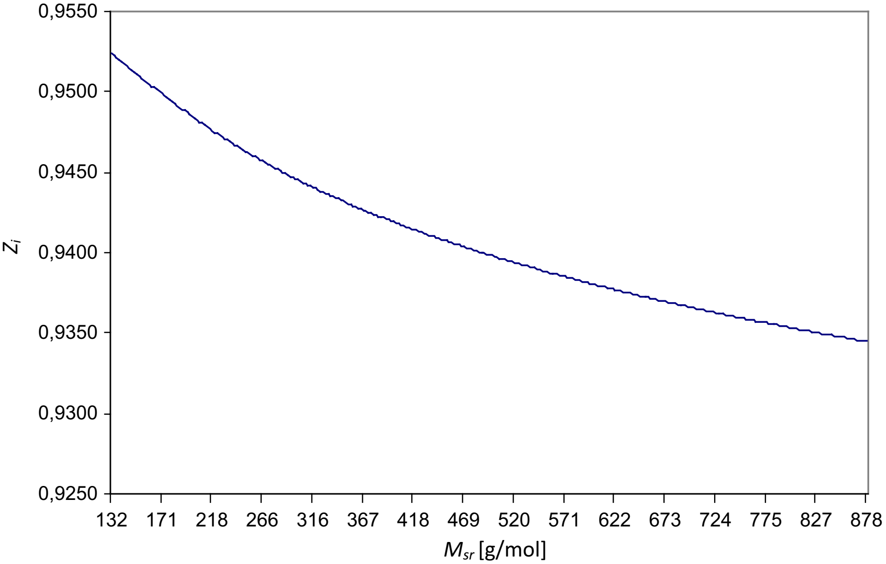

Fig. 9 Change in Z_i correction coefficient in the average molar mass M_{sr} [g/mol] of the forming polyurethane at a temperature of 86 °C calculated with model (2)

kinetic parameters. As we can see, despite slight changes in viscosity of the system resulting from a small increase in average molar mass of polyurethane, the proposed method of kinetic parameters calculation gives a better approximation of the course of polyaddition process of 2,4-TDI with 1,4-BD than the model based on the same kinetic parameters for the whole polymerisation process.

The results obtained show that the applied approach proposed in model (2) is universal, and prove that kinetic parameters change during the heteropolyaddition process.

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