

EMPIRICAL MODELS FOR VISCOSITY VARIATION IN BULK FREE RADICAL POLYMERIZATION

The validity of the Lyons–Tobolsky equation for bulk polymerization systems was verified by comparing simulation results to experimental data for different reaction conditions (temperature and initiator concentration). In this model, formerly applied for solution polymerization, the viscosity of the reaction mass was used instead of solvent viscosity. For example, the chemically initiated free radical polymerization of methyl methacrylate was considered to be achieved in a batch bulk process. In the Lyons–Tobolsky equation, the viscosity was calculated using the values of the conversion and molecular weight resulting from the kinetic model simulation. Consequently, a general discussion about the concordance between the simulation and experiment was useful, especially to emphasize the causes that generate modeling errors. It is more convenient to estimate the viscosity independently of conversion and molecular weight and, in this way, without solving the kinetic model. Empirical relations which correlate viscosity with time were elaborated using experimental viscosity data. Two kinds of models were proposed: a) two fifth order polynomials corresponding to the conversion domains before and after the gel effect; b) a model that fits the experimental data well in the whole conversion domain. Generally, these empirical models provide good simulation results and they can be easily handled.

One of the most important features of a polymerization is the large increase of viscosity as the reaction progresses, especially in homogeneous systems such as bulk and solution polymerization.

The reaction kinetics, as well as the heat, mass and momentum balances of the polymerization reactor, are significantly affected by the viscosity changes. Increased viscosity results in a decreased heat transfer coefficient and increased power consumption of the stirrer and, consequently, a poorer cooling capacity of the reactor. Thus, difficulties in reactor control and stability may arise. The viscosity of the reaction mass also influences the molecular diffusion and mass transfer coefficients. The mixing time required to reach the desired homogeneity increases and the degrees of macromixing and micromixing are reduced.

From the kinetic point of view, the change in viscosity makes the initiation, propagation and especially termination reactions become diffusion controlled. Three diffusion-controlled processes can take place in a free radical polymerization along with ordinary chemical reactions: the gel, glass and cage effects which are related to the termination, propagation and initiation reactions, respectively. These processes strongly affect the polymerization rate, influencing the molecular properties of the polymer.

Therefore, the two important sources of problems encountered in a free radical polymerization are the increase of viscosity and the heat released in a highly exothermic reaction.

The viscosity prediction might be of significant help for the on-line optimal control of polymerization

reactors. Moritz [1] reviewed the work on viscosity in polymerization processes, while Lyons and Tobolsky [2] proposed a simple model for viscosity.

In this paper, the viscosity of the reaction mass for the free radical polymerization of methyl methacrylate was estimated as function of time with the Lyons–Tobolsky equation in order to determine if this equation is satisfactory. Furthermore, some other empirical equations were proposed to describe the dependence of the bulk viscosity on time over the entire concentration range.

MODELS OF REACTION KINETICS AND OF GEL AND GLASS EFFECTS

The chemically initiated free radical polymerization of methyl methacrylate (MMA) was considered to be achieved in a batch bulk process. The reaction steps taken into account were: initiation by azobisisobutyronitrile (AIBN) decomposition, propagation, chain transfer to monomer and termination by disproportionation. The mass balance equations for monomer conversion (x), initiator concentration (l), and moments of radicals (λ_k) and dead polymer (μ_k) ($k=0,1,2$) providing the distribution of the chain length represented the kinetic model of the polymerization process.

$$\frac{dl}{dt} = -k_d l - l \varepsilon \frac{1-x}{1+\varepsilon x} \lambda_0 (k_p + k_{tm}) \quad (1)$$

$$\frac{dx}{dt} = (k_p + k_{tm}) (1-x) \lambda_0 \quad (2)$$

$$\frac{d\lambda_0}{dt} = 2fk_d l - k_t \lambda_0^2 - \lambda_0^2 \varepsilon \frac{1-x}{1+\varepsilon x} (k_p + k_{tm}) \quad (3)$$

$$\begin{aligned} \frac{d\lambda_1}{dt} = & 2fk_d l + k_p M_0 \frac{1-x}{1+\varepsilon x} \lambda_0 - k_t \lambda_0 \lambda_1 - \\ & - \lambda_0 \lambda_1 \varepsilon \frac{1-x}{1+\varepsilon x} (k_p + k_{tm}) - k_{tm} M_0 \frac{1-x}{1+\varepsilon x} (\lambda_1 - \lambda_0) \quad (4) \end{aligned}$$

$$\frac{d\lambda_2}{dt} = 2fk_dI + k_p M_0 \frac{1-x}{1+\varepsilon X} (2\lambda_1 + \lambda_0) - k_t \lambda_0 \lambda_2 - \lambda_2 \lambda_0 \varepsilon \frac{1-x}{1+\varepsilon X} (k_p + k_{tm}) - k_{tm} M_0 \frac{1-x}{1+\varepsilon X} (\lambda_2 - \lambda_0) \quad (5)$$

$$\frac{d\mu_0}{dt} = k_i \lambda_0^2 - \mu_0 \lambda_0 \varepsilon \frac{1-x}{1+\varepsilon X} (k_p + k_{tm}) + k_{tm} M_0 \frac{1-x}{1+\varepsilon X} \lambda_0 \quad (6)$$

$$\frac{d\mu_1}{dt} = k_i \lambda_0 \lambda_1 - \mu_1 \lambda_0 \varepsilon \frac{1-x}{1+\varepsilon X} (k_p + k_{tm}) + k_{tm} M_0 \frac{1-x}{1+\varepsilon X} \lambda_1 \quad (7)$$

$$\frac{d\mu_2}{dt} = k_i \lambda_0 \lambda_2 - \mu_2 \lambda_0 \varepsilon \frac{1-x}{1+\varepsilon X} (k_p + k_{tm}) + k_{tm} M_0 \frac{1-x}{1+\varepsilon X} \lambda_2 \quad (8)$$

The moments λ_k and μ_k were defined as follows:

$$\lambda_k = \sum_{n=1}^{\infty} n^k P_n^* \quad (9)$$

$$\mu_k = \sum_{n=1}^{\infty} n^k D_n \quad (10)$$

where P_n^* and D_n are the growing and the dead polymer with n monomer units.

It was assumed that no monomer was consumed in the initiation process and that the quasi-steady state approximation for the initiator fragment balance was valid. The notations used in equations (1) – (8) represent: ε – a parameter accounting for the variation in volume that accompanies polymerization; f – initiator efficiency; M_0 – monomer concentration at time $t = 0$; k_d , k_p , k_{tm} , k_t – rate constants for initiator decomposition, propagation, chain transfer to monomer and termination, respectively.

In order to describe the decrease of the termination (k_t) and propagation (k_p) rate constants during polymerization, Chiu et al. [3] proposed models that consider diffusional constraints as an integral part of these reactions even from the beginning of the process:

$$\frac{1}{k_t} = \frac{1}{k_{t0}} + \theta_t \frac{\lambda_0}{\exp\left[\frac{2.303(1-x)}{A+B(1-x)}\right]} \quad (11)$$

$$\frac{1}{k_p} = \frac{1}{k_{p0}} + \theta_p \frac{\lambda_0}{\exp\left[\frac{2.303(1-x)}{A+B(1-x)}\right]} \quad (12)$$

$$\theta_t = \frac{\theta_t^0}{I_0} \exp\left(\frac{E_{\theta_t}}{RT}\right) \quad (13)$$

$$\theta_p = \frac{\theta_p^0}{I_0} \exp\left(\frac{E_{\theta_p}}{RT}\right) \quad (14)$$

$$A = C_1 - C_2 (T - T_{gp})^2 \quad (15)$$

In equations (11)–(15), k_{t0} , k_{p0} are the rate constants of termination and propagation in the absence of gel and glass effects; θ_t , θ_p – the characteristic migration times; θ_t^0 , θ_p^0 – the pre-exponential factors for θ_t and θ_p ; E_{θ_t} , E_{θ_p} – the activation energies for θ_t and θ_p ; T – the temperature; T_{gp} – the glass transition temperature

of the polymer; B , C_1 , C_2 – constants; R – the universal gas constant.

A similar decrease as that of the propagation rate constant was proposed for the rate constant of chain transfer to monomer [4] because both reactions involve the same diffusion mechanism, the monomer molecules migrating toward the growing macroradicals:

$$k_{tm} = k_{tm0} \frac{k_p}{k_{p0}} \quad (16)$$

where k_{tm0} is the rate constant of chain transfer to monomer in the absence of the glass effect.

RESULTS AND DISCUSSION

Validation of the kinetic model

Many simulations were performed at different temperatures and initial concentrations of the initiator using a Matlab program, based on special functions for solving stiff differential equations. The numerical values and computing equations of some parameters are presented in Table 1 [4,5] where the following notations were used: k_d^0 , k_{p0}^0 , k_{t0}^0 , k_{tm0}^0 are the frequency factors for the rate constants; E_d , E_p , E_t , E_{tm} – the activation energies; \bar{M}_n , \bar{M}_w – the number – and weight average – molecular weights.

The kinetic model (1)–(8), (11)–(16) was validated for different reaction conditions ($T = 50, 70, 90^\circ\text{C}$ and $I_0 = 15.48, 20.18, 25.8, 100 \text{ mol/m}^3$), using experimental data from the literature [5]. Two examples are presented in Figures 1 and 2 for monomer conversion and molecular weights.

A sudden increase of monomer conversion, as well as of molecular weight indicates an autoacceleration phenomenon. The transition from "normal" kinetics to autoaccelerated kinetics due to the

Table 1. The parameters used in MMA polymerization

$k_d^0 = 1.053 \times 10^{15} \text{ s}^{-1}$ (for initiation with AIBN); $k_{p0}^0 = 4.917 \times 10^2 \text{ m}^3/(\text{mol s})$;
$k_{t0}^0 = 9.8 \times 10^4 \text{ m}^3/(\text{mol s})$; $k_{tm0}^0 = 4.66 \times 10^6 \text{ m}^3/(\text{mol s})$; $E_d = 1.2845 \times 10^5 \text{ J/mol}$;
$E_p = 1.822 \times 10^4 \text{ J/mol}$; $E_t = 2.937 \times 10^3 \text{ J/mol}$; $E_{tm} = 7.428 \times 10^4 \text{ J/mol}$;
$f = 0.58$ (AIBN); $\varepsilon = -(0.1946 + 0.16 \times 10^{-3} \times T [^\circ\text{C}])$; $C_1 = 0.15998$; $C_2 = 7.812 \times 10^{-6}$;
$B = 0.03$; $T_{gp} = 387 \text{ K}$; $\theta_p^0 = 3.99822 \times 10^{-12} \text{ s}$; $E_{qp} = 1.02451 \times 10^5 \text{ J/mol}$;
$\theta_t^0 = 2.8883 \times 10^8 \text{ (mol s)/m}^3$; $E_{\theta_t} = 1.48924 \times 10^5 \text{ J/mol}$;
$k_d = k_d^0 \exp[-E_d/(RT)]$; $k_{p0} = k_{p0}^0 \exp[-E_p/(RT)]$; $k_{t0} = k_{t0}^0 \exp[-E_t/(RT)]$;
$k_{tm0} = k_{tm0}^0 \exp[-E_{tm}/(RT)]$; $\bar{M}_n = \frac{\lambda_1 + \mu_1}{\lambda_0 + \mu_0}$; $\bar{M}_w = \frac{\lambda_2 + \mu_2}{\lambda_1 + \mu_1}$

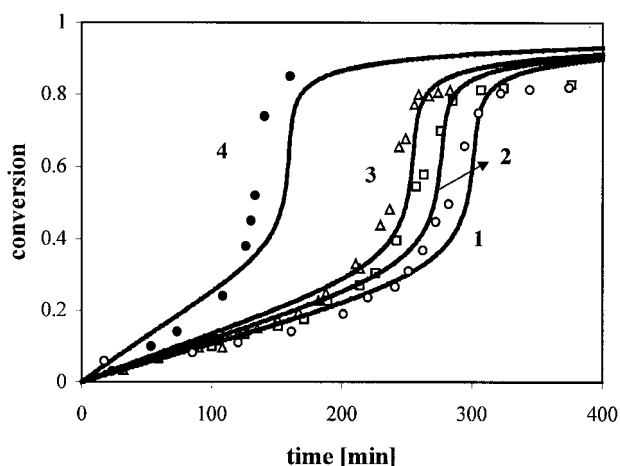


Figure 1. The dependence of monomer conversion on polymerization time at 50°C and different initiator concentrations, obtained by simulation (1 – 15.48 mol/m³, 2 – 20.18 mol/m³, 3 – 25.8 mol/m³, 4 – 100 mol/m³) and experimental (○ – 15.48 mol/m³; □ – 20.18 mol/m³; △ – 25.8 mol/m³; ● – 100 mol/m³).

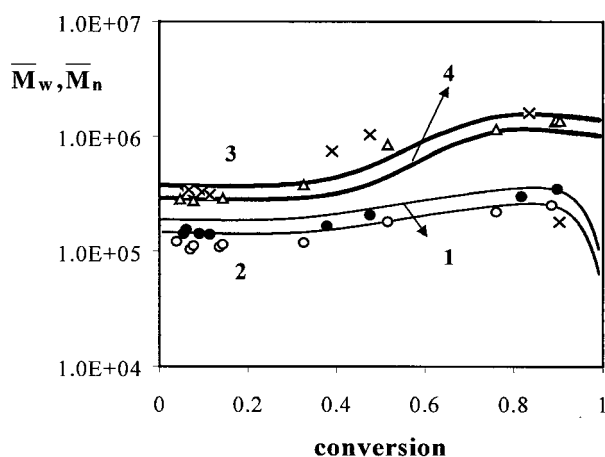


Figure 2. The dependence of molecular weights \bar{M}_w and \bar{M}_n on monomer conversion at 70°C and different initiator concentrations, obtained by simulation (1 – \bar{M}_n at 15.48 mol/m³, 2 – \bar{M}_n at 25.8 mol/m³, 3 – \bar{M}_w at 15.48 mol/m³, 4 – \bar{M}_w at 25.8 mol/m³) and experimental (● – \bar{M}_n at 15.48 mol/m³; × – \bar{M}_w at 15.48 mol/m³; ○ – \bar{M}_n at 25.8 mol/m³; △ – \bar{M}_w at 25.8 mol/m³).

gel effect is more pronounced for higher molecular weights. Higher values of molecular weights are obtained at low temperatures, denoting a higher viscosity of the medium and slow diffusion of the radicals. Also, high values of the temperature and initiator concentration result in shorter reaction times.

Both the monomer conversion and number average molecular weight (\bar{M}_n) fit the experimental data well, whereas the experimental weight average molecular weights (\bar{M}_w) show some differences from the modeling results. The scattering of the experimental data for \bar{M}_w might have two reasons: experimental errors and the fact that the cage effect was not included in the model. This phenomenon affects the molecular weight curves, especially in the last part of the process where

the molecular weight decreases since the model does not account for the lowering of initiator efficiency (cage effect) at high conversions. One should consider that, at the end of the process, the diffusion of both the monomer and free radicals decreases, diminishing the possibilities of chain growth and decreasing the formation of new macroradicals.

However, one can conclude that the kinetic model (1)–(8), (11)–(16) adequately describes the system behavior, so it can be used to model the viscosity variation of the reaction mass in the free radical polymerization of methyl methacrylate.

MODELING OF VISCOSITY VARIATION WITH THE LYONS – TOBOLSKY EQUATION

Knowledge of the increase in viscosity with monomer conversion is very important when operating a polymerization reactor. One empirical approach to calculate the dependence of the viscosity on polymer concentration, intrinsic viscosity and temperature was proposed by Lyons and Tobolsky [2]:

$$\eta = \eta_{\text{sol}} \left[1 + c_{\text{polym}} [\eta] \exp \left(\frac{k_H [\eta] c_{\text{polym}}}{1 - b c_{\text{polym}}} \right) \right] \quad (17)$$

where η represents the viscosity of the reaction mass; η_{sol} – the viscosity of pure solvent; c_{polym} – the polymer concentration; $[\eta]$ – the intrinsic viscosity of the polymer system; k_H – the Huggins constant; b – a temperature dependent parameter.

The polymer concentration is usually substituted by the monomer conversion:

$$c_{\text{polym}} = \frac{x M_0 M_m}{(1 + \epsilon x)} 10^{-3} \quad (18)$$

where M_m is the molecular weight of the monomer and M_0 the initial monomer concentration. While the concentration dependence of the viscosity is explicitly expressed by the Lyons – Tobolsky equation, the molecular weight, temperature and solvent dependencies are contained within the parameters $[\eta]$, k_H , b and η_{sol} . The intrinsic viscosity $[\eta]$ obeys the Mark – Houwink equation [6] which relates it to the weight-average molecular weight, \bar{M}_w , as:

$$[\eta] = K \cdot \bar{M}_w^a \quad (19)$$

where "a" and "K" are constants depending on the polymerization system.

The Lyons–Tobolsky equation was first designed and applied to polymer solutions. Here, it was adapted for bulk polymerization, so η_{sol} is considered to be the viscosity of the reaction medium (MMA).

The model of viscosity variation, (17) – (19), based on the Lyons–Tobolsky equation, was added to the kinetic model (1) – (8), (11) – (16). The numerical values used in the simulations are listed in Table 2 [5].

Table 2. The parameters used in modeling the viscosity of MMA polymerization with the Lyons–Tobolsky equation

$K = 6.75 \times 10^3 \text{ ml/g}; a = 0.72;$
$\eta_{\text{sol}} = 5.32 \times 10^{-4} \text{ Pa}\cdot\text{s (at } 50^\circ\text{C)};$
$\eta_{\text{sol}} = 4.66 \times 10^{-4} \text{ Pa}\cdot\text{s (at } 70^\circ\text{C)};$
$\eta_{\text{sol}} = 4.00 \times 10^{-4} \text{ Pa}\cdot\text{s (at } 90^\circ\text{C)}.$

Table 3. Adjusted values of parameters b and k_H

Reaction conditions		b (ml/g)	k_H
T ($^\circ\text{C}$)	l_0 (mol/m ³)		
50	15.48	-3.50	0.200
50	20.18	-3.80	0.200
50	25.80	-3.80	0.200
70	15.48	-3.25	0.400
70	25.80	-3.25	0.400
90	15.48	-3.00	1.000
90	25.80	-3.00	1.000

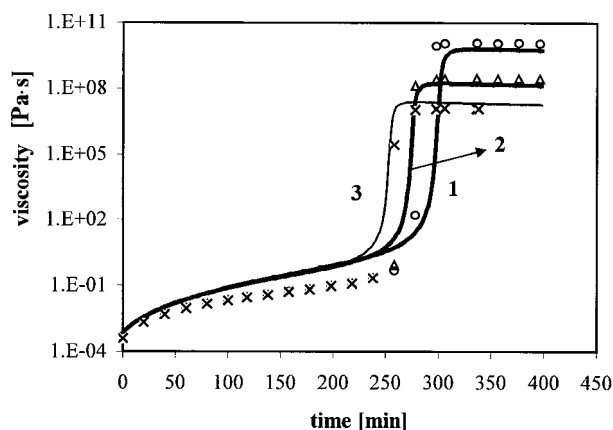


Figure 3. The dependence in time of viscosity on polymerization time at 50°C and different initiator concentrations, obtained by simulation (1 – 15.48 mol/m^3 , 2 – 20.18 mol/m^3 , 3 – 25.8 mol/m^3) and experimental (o – 15.48 mol/m^3 ; Δ – 20.18 mol/m^3 ; x – 25.8 mol/m^3).

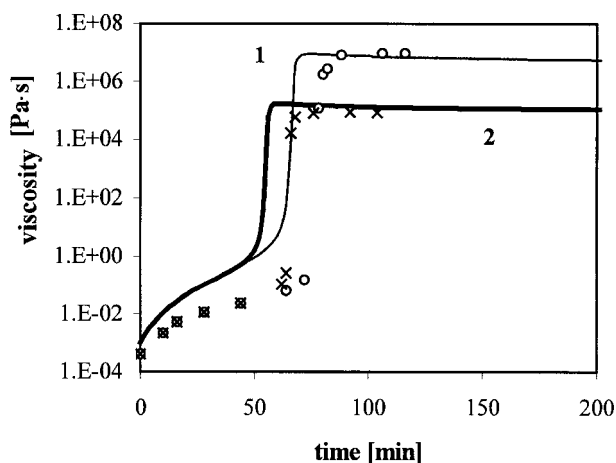


Figure 4. The dependence of viscosity on polymerization time at 70°C and different initiator concentrations, obtained by simulation (1 – 15.48 mol/m^3 , 2 – 25.8 mol/m^3) and experimental (o – 15.48 mol/m^3 ; x – 25.8 mol/m^3).

The Huggins constant (k_H) and parameter "b" in equation (17), upon which the viscosity is very sensitive, were obtained by fitting experimental data [7] for different reaction conditions (temperature and initiator concentration). The best values are given in Table 3.

Figures 3 and 4 contain some examples for viscosity variation as a function of time under the following operating conditions: $T = 50$ and 70°C and $l_0 = 15.48, 20.18, 25.8 \text{ mol/m}^3$. The diagrams were plotted in a logarithmic scale.

A very sharp increase in viscosity is associated with the gel effect and it is stronger at low temperatures. So, it is recommended to carry out the reaction at high temperatures.

The agreement between the simulated values of the viscosity and the experimental data is satisfactory. At all three temperatures ($50, 70, 90^\circ\text{C}$), a deviation of the experimental data from the calculated curves is observed, especially in the first part of the reaction (before the gel effect). This domain cannot be adjusted with parameters b and k_H because it depends on the constants of the gel and glass effect models.

On the other hand, the agreement between the simulation and the experiments for monomer conversion (Figure 1) is very good before the gel effect, as well as in the entire reaction domain. Better values for viscosity might be obtained by changing the $\theta_t^0, \theta_p^0, E_{\text{th}}, E_{\text{tp}}, C_1$ or C_2 values in the Chiu model.

It must be emphasized that the errors in weight average molecular weight (previously pointed out) do not cause differences between the calculated and experimental viscosities because these errors appear during the gel effect and after this phenomenon. The modeling of the viscosity was properly performed in this domain by the adjusting b and k_H values. It was less satisfactory before the gel effect, where modification of the parameters in the diffusion control reaction models is suggested.

Therefore, two working procedures can be used: a) modeling the conversion, molecular weight and viscosity using the same values of the constants (this paper is an example), with a satisfactory, but not very good agreement between simulation and experiment; b) modeling with different values of the parameters, the agreement of the curve fit being good. This last solution, involving different constants in the gel and glass effect models can also be applied to improve the simulation data for the weight-average molecular weight.

We can conclude that the alternative a), illustrated in this paper, is preferable. That means that it is more convenient to use a single set of constants from the point of view of working procedure, as well as the obtained results.

The Lyons–Tobolsky equation was designed and used for solution polymerization processes. Here we have proved its ability to determine the reaction mass viscosity in poly(methyl methacrylate) synthesis and so

its applicability to bulk polymerizations. For each studied system and reaction conditions, the adjustment of parameters b and k_H is necessary. These constants significantly influence the viscosity, especially in the domain of the maximum values (at the end of the reaction). Low k_H values result in a decrease of the maximum viscosity, while low b values result in an increase of the maximum viscosity. A possible approximation might be the correlation of these constants with temperature and polymerization system, neglecting the initiator concentration, the influence of which is small.

The model described and used in this paper provides important information about the conversion, molecular weight, polydispersity index and viscosity in MMA polymerization. Therefore, one might predict by simulation some parameters which characterize the evolution of the synthesis process and of the product quality at different times and reaction conditions.

The Lyons–Tobolsky equation may be quite useful for predicting the viscosity over the entire concentration range when experimental data are limited.

MODELING OF VISCOSITY VARIATION WITH POLYNOMIAL EXPRESSIONS

The actual value of the viscosity provides information about the stage of the reaction compared to the onset of the gel effect a significant increase of the viscosity occurs at this moment. Because the viscosity can be measured on-line more easily than monomer conversion, it may be considered one of the control variables (like temperature). At a certain value of the viscosity (before the gel effect), the prepolymerization stage might be considered to be finished. On other hand, from viscosity measurements, the molecular weight of the polymer can also be obtained.

In order to calculate the viscosity with the Lyons–Tobolsky equation, one must know the monomer conversion and molecular weight. But, it is more convenient to estimate the viscosity independently by conversion and molecular weight which are obtained from the kinetic model. Using experimental data (viscosity vs. time for different reaction conditions) [7], empirical relations correlating the viscosity with time were developed. Each set of experimental data was modeled with a fifth order polynomial in a logarithmic scale. The splitting of the data was determined by the sudden increase of viscosity, so one polynomial was used to fit the experimental data before the gel effect (equation 20) and another after this phenomenon (equation 21):

$$\log(\eta) = a_0 + a_1 \cdot t + a_2 \cdot t^2 + a_3 \cdot t^3 + a_4 \cdot t^4 + a_5 \cdot t^5 \quad (20)$$

$$\log(\eta) = b_0 + b_1 \cdot t + b_2 \cdot t^2 + b_3 \cdot t^3 + b_4 \cdot t^4 + b_5 \cdot t^5 \quad (21)$$

where t represents time.

To obtain good agreement between the simulated and experimental results, 8 to 10 decimals are necessary for the constants in models (20) and (21). The special software used for curve fitting (*CurveExpert*) provided the values of the numerical coefficients with different significant digits. If some of them are dropped, the approximation accuracy will suffer. The numerical values of this coefficients are given in Table 4 where *corr* shows the agreement between simulation and the experiment. A value approaching 1 shows good agreement between simulation and experiment.

Two examples are given in Figures 5 and 6 where the dotted line separates the modeled domains.

The "critical" time corresponds to the critical conversion, which can be calculated as shown in Figure 7 where $T = 50^\circ\text{C}$ and $l_0 = 15.48 \text{ mol/m}^3$. For these reaction conditions, $x_{\text{crit}} = 0.33$ and $t_{\text{crit}} = 264 \text{ min}$.

Table 4. The coefficients in equations (20) and (21)

	50°C 15.48 mol/m ³	50°C 20.18 mol/m ³	50°C 25.8 mol/m ³	70°C 15.48 mol/m ³	70°C 25.8 mol/m ³	90°C 15.48 mol/m ³	90°C 25.8 mol/m ³
a_0	-3.383181157005	-3.3905	-3.38529812	-3.396131445110	-3.4453299916	-3.39469495	-3.397612657685
a_1	0.044282212011	0.046829	0.0449962611	0.1036181874250	0.4637211248	0.23470932	0.7322848730964
a_2	-0.553918954x10 ⁻³	-0.65049x10 ⁻³	-0.580720266x10 ⁻³	-0.295062455395x10 ⁻²	-0.0611325168	-0.921624x10 ⁻²	-0.251930733329
a_3	0.4113580063x10 ⁻⁵	0.53548x10 ⁻⁵	0.445718242x10 ⁻⁵	0.52970453565x10 ⁻⁴	0.3083425x10 ⁻²	-0.37646x10 ⁻³	0.0388238496385
a_4	-0.15181364x10 ⁻⁷	-0.21613x10 ⁻⁷	-0.16970004x10 ⁻⁷	-0.529343219x10 ⁻⁶	-0.625994x10 ⁻⁴	0.4015x10 ⁻⁴	-0.25274900289x10 ⁻²
a_5	0.22005x10 ⁻¹⁰	0.33559x10 ⁻¹⁰	0.252421481x10 ⁻¹⁰	0.2488661x10 ⁻⁸	0.434x10 ⁻⁶	-0.71x10 ⁻⁶	0.57086075234x10 ⁻⁴
corr	0.999	0.995	0.999	0.999	0.913	1	0.885
b_0	-10053.40038997	-347.75	-19986.5559184	45093.06619077	-8.025844619	24886.69297759	121039.453521
b_1	131.62684775362	4.6233	324.6639437957	-2554.31936644	0.4222103682	-4598.49595188	-26687.154064
b_2	-0.683939234751	-0.023835	-2.10597380545	57.29784640577	-0.45496032x10 ⁻²	336.8494246854	2330.94494250
b_3	0.17650871291x10 ⁻²	0.61020x10 ⁻⁴	0.68209810907x10 ⁻²	-0.63628775333	0.162352x10 ⁻⁴	-12.2290703870	-100.71766079
b_4	-0.2262984313x10 ⁻⁵	-0.77588x10 ⁻⁷	-0.110307625x10 ⁻⁴	0.003498786218	0	0.220080653621	2.15040634
b_5	0.1153313x10 ⁻⁸	0.39204x10 ⁻¹⁰	0.7125428x10 ⁻⁸	-0.00000762300	0	0.15707618815x10 ⁻²	-0.01812347
corr	0.983	0.994	0.999	0.896	0.999	0.929	0.990

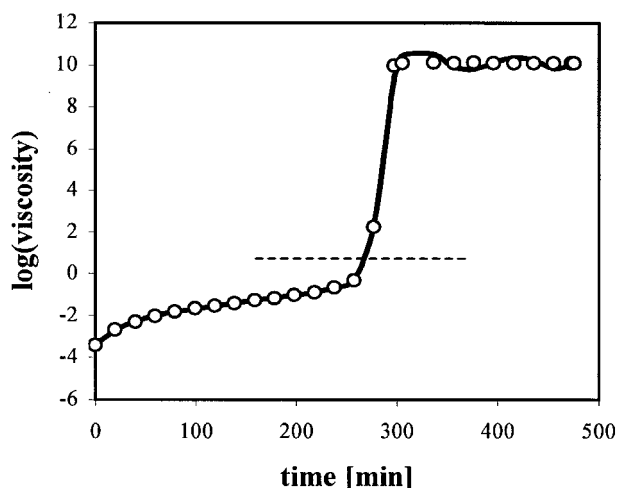


Figure 5. The dependence of viscosity on polymerization time obtained by simulation with polynomial models (solid line) and experimental values (o) at $T = 50^{\circ}\text{C}$ and $I_0 = 15.48 \text{ mol/m}^3$.

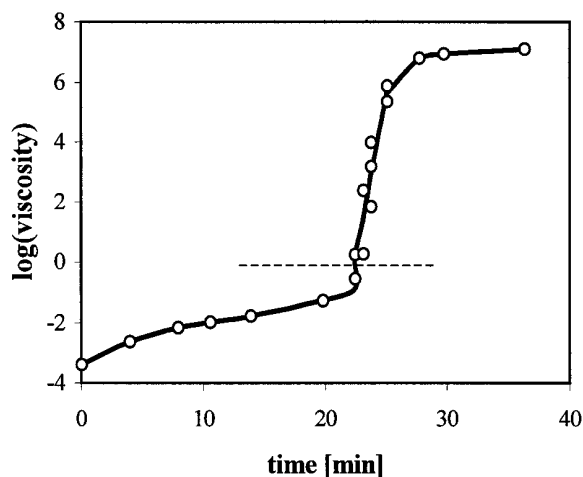


Figure 6. The dependence of viscosity on polymerization time obtained by simulation with polynomial models (solid line) and experimental values (o) at $T = 90^{\circ}\text{C}$ and $I_0 = 15.48 \text{ mol/m}^3$.

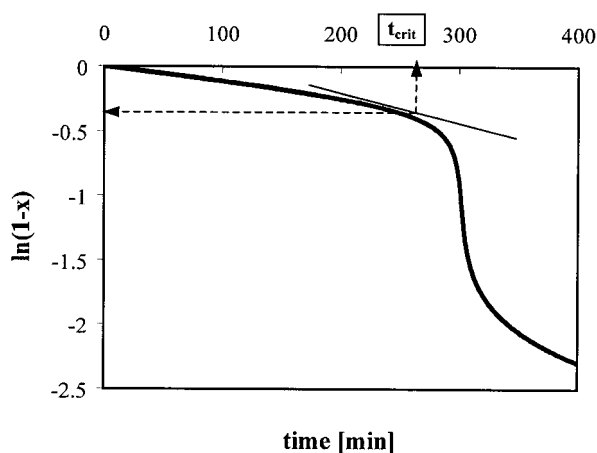


Figure 7. Calculation of the critical conversion for $T = 50^{\circ}\text{C}$ and $I_0 = 15.48 \text{ mol/m}^3$ in MMA free radical polymerization.

Table 5. Errors of the polynomial models

T ($^{\circ}\text{C}$)	I_0 (mol/m^3)	Errors
50	15.48	0.03728
50	20.18	0.002861
50	25.80	0.002544
70	15.48	0.1429
70	25.80	0.2843
90	15.48	0.1220
90	25.80	0.1084

A global comparison between the experimental data and the results of the polynomial models is adequate by considering the error function:

$$E = \frac{1}{N_{\text{exp}}} \sqrt{\sum_{i=1}^{N_{\text{exp}}} (p_{i,\text{exp}} - p_{i,c})^2} \quad (22)$$

where $p = \log(\eta)$, N_{exp} is the number of the experiments and the subscripts "exp" and "c" denote experimental and calculated values, respectively.

Some values are given in Table 5. The small errors prove the validity of the polynomial equations. However, the large number of decimals and the fact that different coefficients are used for two conversion domains represent the drawbacks of the models, making their handling difficult.

THE WILLIAMSON MODEL

The available experimental data [7] were processed in accordance with the Williamson model [8]. Equation (23) represents an adaptation derived from the extended Williamson model used in the rheology of non-Newtonian fluids:

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + \left(\frac{t}{t_{\text{inf}}}\right)^c} \quad (23)$$

For viscosity modeling, the parameters of the models are considered as follows: η_0 is the minimum value of the viscosity; η_{∞} – the maximum value of the viscosity; t_{inf} – the abscissa of the inflexion point on the curve $\eta = f(t)$; c – an empirical constant.

This work contains the first use of such an equation to calculate the mass reaction viscosity for bulk polymerization systems.

Figure 8 shows the possibility of obtaining t_{inf} , while parameter "c" results from the curve fitting procedure. For $T = 50^{\circ}\text{C}$ and $I_0 = 15.48 \text{ mol/m}^3$, $t_{\text{inf}} = 300 \text{ min}$ (Figure 8).

Figures 9 and 10 depict the approximation of viscosity experimental data with the Williamson model for two sets of reaction conditions. Good results were also obtained for other temperatures and initiator concentrations.

The constant values in the Williamson model for different reaction conditions are given in Table 6.

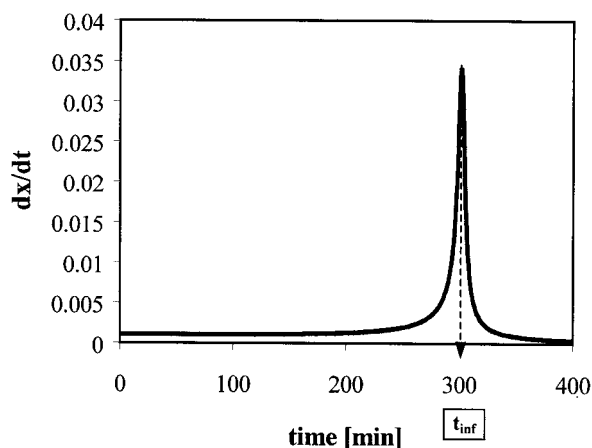


Figure 8. Calculation of the time corresponding to the inflexion point of conversion vs. time for $T = 50^{\circ}\text{C}$ and $I_0 = 15.48 \text{ mol/m}^3$.

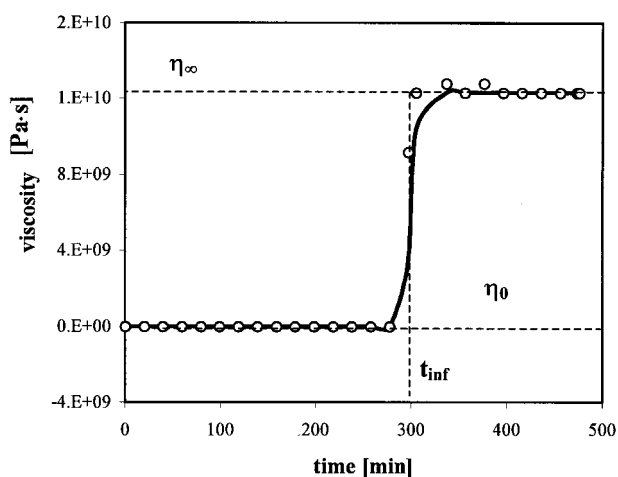


Figure 9. The dependence of viscosity on polymerization time obtained by simulation with the Williamson model (solid line) and experimental values (o) at $T = 50^{\circ}\text{C}$ and $I_0 = 15.48 \text{ mol/m}^3$.

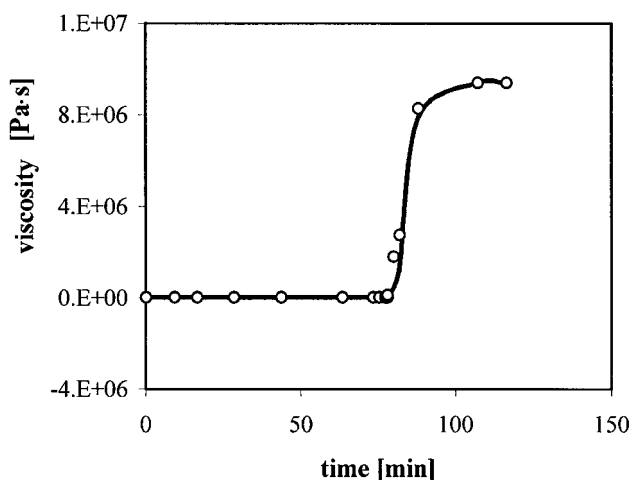


Figure 10. The dependence of viscosity on polymerization time obtained by simulation with the Williamson model (solid line) and experimental values (o) at $T = 70^{\circ}\text{C}$ and $I_0 = 15.48 \text{ mol/m}^3$.

Table 6. Parameters of the Williamson model

Reaction conditions		$\eta_0 \times 10^4$	η_{∞}	t_{inf}	C
T ($^{\circ}\text{C}$)	I_0 (mol/m^3)				
50	15.48	4.03	1.23×10^{10}	300	100
50	20.18	4.03	2.53×10^7	277	100
50	25.80	4.03	1.21×10^8	262	30
70	15.48	4.03	8.63×10^4	70	50
70	25.80	4.03	9.38×10^6	85	50
90	15.48	4.03	1.26×10^7	28	20
90	25.80	4.03	9.39×10^4	23	30

It may be concluded that the Williamson model provides good results for viscosity modeling. Also, it is continuous in the whole conversion domain, easy to use and its empirical parameters can be determined without difficulty by successive trials.

The prediction of viscosity is important when operating a polymerization reactor. Unlike other parameters (conversion, molecular weight) which need more complex and inapplicable on-line methods, the viscosity is easy to measure. Continuous monitoring of the viscosity during polymerization allows control of the reaction and determines the moment of passing from prepolymerization to final polymerization. In this way, the gel effect is kept under control (even avoided) assuring the desired properties of the final product.

CONCLUSIONS

The kinetic model proposed for chemically initiated bulk MMA polymerization provides conversions and molecular weights in good agreement with experimental data. While conversions and number-average molecular weights obtained in the simulation fit the experimental \bar{M}_w data well, the weight average molecular weights were modeled approximately. The scattering of the experimental \bar{M}_w data compared to the simulation results mainly originates from experimental errors. In addition, the decrease in \bar{M}_w at the end of the reaction is related to a decrease in the initiator efficiency; the cage effect was not included in the kinetic model. Moreover, the model was considered adequate to be used in the prediction of the dependence of viscosity on polymerization time.

This approach demonstrates that the Lyons-Tobolsky equation, initially used to solution polymerizations, can be applied with good results for bulk polymerization systems. To improve the agreement between experiment and simulation, the adjustment of empirical parameters in the viscosity and gel effect models was proposed. The drawback of the Lyons-Tobolsky model is related to the need to use conversion and molecular weight for estimation of the viscosity.

The dependence viscosity vs. time was modeled using two fifth-order polynomials corresponding to the conversion domains before and after the gel effect. The advantage of this model was that the viscosity – one of

the reaction's control variables – was correlated only with time. The disadvantages of the polynomial models originated from the large number of decimals of the coefficients and the separate modeling of the viscosity in two conversion domains.

The Williamson model allowed quite simple estimation of the dependence of viscosity on time in the whole conversion domain. Also, the model was not sensitive to the number of decimals of its coefficients. Note that was the first use of this model to obtain the viscosity in a bulk polymerization system.

The modeling efforts of this paper focused on the use of viscosity as the main variable for the optimal control or inferential state estimation of MMA free radical polymerization.

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IZVOD

EMPIRIJSKI MODEL ZA IZRAČUNAVANJE PROMENE VISKOZNOSTI KOD RADIKALNE POLIMERIZACIJE U MASI

(Naučni rad)

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Primenljivost jednačine Lajons–Tobolski (L–T) za slučajevne polimerizacije u masi je verifikovana poređenjem podataka koji su izračunati na osnovu ove jednačine sa eksperimentalno određenim. Ova poređenja su ispitana za različite reakcione uslove (temperatura i koncentracija inicijatora). U ovom modelu, koji je prvo iskorišćen za slučaj polimerizacije u rastvoru, koristi se podatak o viskozitetu reakcione smeše umesto viskoziteta rastvarača kada se radi o polimerizaciji u rastvoru. Tako je, hemijski inicirana radikalna polimerizacija metil metakrilata razmatrana kao primer fazne polimerizacije u masi. U jednačini L–T viskozitet je izračunavan na osnovu podataka o konverziji i molskoj masi koje je moguće simulirati kinetičkim modelom.

Ovim radom se, između ostalog, ukazuje na podudarnost simulacije i eksperimentalnih podataka što ima odgovarajuće koristi kod analize uzročnika odgovarajućih grešaka koje se dobijaju pri simulaciji odnosno korišćenju modela. Mnogo je praktičnije da se utvrdi zavisnost viskoznosti od molske mase i stepena konverzije i na taj način da se ne ulazi u rešavanje kinetičkog modela. Na osnovu eksperimentalno određenih podataka o viskoznosti, razvijene su empirijske relacije za proračun viskoznosti reakcione smeše sa vremenom. Dva vrste modela su predložene: a) dva polinoma petog stepena kojima se može definisati konverzije pre i posle pojave gel–efekta i b) model kojim se dobro predskazuju (fituju) eksperimentalne vrednosti u celokupnom opsegu konverzije. Generalno, prednosti izvedenih empirijskih modela su jednostavnost i mogućnost dobre simulacije procesa polimerizacije u masi.

Ključne reči: Radikali • Polimerizacija • Poli(metil metakrilat) • Polimerizacija u masi • Modelovanje viskoznosti •

Key words: Free radical polymerization • Poly(methyl methacrylate) • Modeling of viscosity •