

# Quasi-stationary concentration principle for auto-wave processes

S.P. Davtyan\*, H.H. Zakaryan, A.O. Tonoyan

*State Engineering University of Armenia, Yerevan, Armenia*

Received 22 March 2007; received in revised form 12 June 2007; accepted 16 June 2007

Available online 21 June 2007

---

## Abstract

Quasi-Stationary Concentration (QSC) principle was used to study radical polymerization of vinyl monomers during reaction traveling front. Based on the experimental results and numerical calculation of one-dimensional front it was shown that the reaction zone could be both narrow and wide. Full and quasi-stationary problems were solved for different sets of kinetic and thermo-physical parameters typical for vinyl monomers' radical polymerization. Polymerization proceeds practically at a constant temperature for narrow-reaction-zone case as was shown by comparing the dimensionless values of heat-wave velocities and the final temperatures. Hence, criterial conditions obtained for isothermal polymerization permit to use QSC principle accurately.

© 2007 Elsevier Ltd. All rights reserved.

**Keywords:** Frontal radical polymerization; Quasi-stationary concentration's principle; Criterial conditions

---

Numerous experimental [1–13] and theoretical [14–25] works concerning frontal radical polymerization of vinyl monomers are quoted in literature. However, it should be specially pointed out that the applicability of Quasi-Stationary Concentration (QSC) principle has not been studied fully. This is because, in the theory of frontal radical polymerization as well as for the combustion and Self-Propagating High-Temperature Synthesis (SHS) processes (besides the QSC principle) Frank-Kamenecki method of the reaction zone narrowness [26] is often used. At the same time, the net polymerization reaction order exceeds one and the effective activation energies are relatively low (40–80 kJ mol<sup>−1</sup>) while the reaction zone is not necessarily narrow for frontal radical polymerization. However, for most of combustion and SHS processes the reaction zone is narrow. Consequently, for frontal polymerization, the temperature range, in which the bulk of monomer-to-polymer conversion holds, depends on a number of kinetic factors: on the reaction order (vs. monomer and initiator), on the activation energy of the rate constants of chain initiation and growth. Hence, for frontal polymerization processes, either the narrowness of the reaction

zone is in place and, actually, polymer is formed at constant temperature (close to the temperature of limit heating), or it forms at a different temperatures. Expectantly, accuracy of quasi-stationary approximation is determined either by narrow or wide reaction zones. Therefore, it is necessary to examine temperature and conversion profiles quantitatively as before studying the applicability of QSC principle for frontal radical polymerization of vinyl monomers.

## 1. Conversion and temperature profile analysis

The equations describing temperature<sup>1</sup> (*T*), initiator (*I*), monomer (*M*) as well as macro-radicals' (*R*) concentrations change during propagation of one-dimensional front of the polymerization waves, could be described in the following manner:

$$c\rho\frac{\partial T}{\partial t} = \lambda\frac{\partial^2 T}{\partial x^2} - Q\frac{\partial M}{\partial t}, \quad (1)$$

---

\* Corresponding author.

E-mail address: [davtyans@seua.am](mailto:davtyans@seua.am) (S.P. Davtyan).

---

<sup>1</sup> It is assumed that the thermo-physical characteristics do not depend on the temperature and conversion level.

$$-\frac{\partial I}{\partial t} = fK_i I, \quad (2)$$

$$-\frac{\partial M}{\partial t} = K_p R M, \quad (3)$$

$$\frac{\partial R}{\partial t} = fK_i I - K_t R^2, \quad (4)$$

where  $c$ ,  $\rho$ , and  $\lambda$  denote thermal capacity, density and heat conductivity coefficient,  $Q$  is the thermal effect of the reaction,  $f$  is the effectiveness of initialization, the value of which is henceforth taken as equal to 1 for simplicity,  $x$  is the reaction coordinate, and  $K_i = K_{i0} \exp(-E_i/R_g T)$ ,  $K_p = K_{p0} \exp(-E_p/R_g T)$ ,  $K_t = K_{t0} \exp(-E_t/R_g T)$  are the temperature dependences of the rate constants of chains initiation, growth and bimolecular chain rupture.  $K_{i0}$ ,  $K_{p0}$ ,  $K_{t0}$ , and  $E_i$ ,  $E_p$ ,  $E_t$  are the preexponential factors and the activation energies of the above-mentioned rate constants correspondingly,  $R_g$  – universal gas constant. Initially, it is assumed that:

$$t = 0, T(x > 0) = T_0, I = I_0, M = M_0, R = 0, \\ T(x = 0) = T_1, \left. \frac{dT}{dx} \right|_{x=+\infty} = 0. \quad (5)$$

$T_0$  is the initial temperature,  $T_1$  is the applied outer temperature for the initiation of thermal wave,  $I_0$  and  $M_0$  are the initial concentrations of initiator and monomer.

The system of differential Eqs. (1)–(4) with conditions (5) was solved numerically. We have used kinetic and thermo-physical parameters, typical of the radical polymerization processes of vinyl monomers [2,15,16,27–29].

Fig. 1 presents temperature profiles and conversion rate change in the direction of the polymerization front. Apparently, heating of the layers close to the reactor inlet part is due to an outer heat source ( $T_1 = 380$  K), which leads to polymerization in these layers.

As the polymerization proceeds, the evolved heat transmits to adjacent layers where polymerization is initiated. Henceforward, outer heat source practically play no role in sustaining the reaction within 2–3 cm from reactor inlet. Actually, from this point on steady-state condition is established and propagation of the polymerization front proceeds due to exothermicity of the polymerization reaction. Conversion, maximum heating temperature and traveling velocity of the front remain unchanged throughout the reactor length at steady-state condition. During steady-state frontal polymerization, the conversion is determined by the “burnout” of the initiator [2]. Comparison of the curves 1 and 2 (Fig. 2) shows that the width<sup>2</sup> of the reaction zone ( $\Delta x_M$ ) is much smaller than the temperature change gap ( $\Delta x_T$  is determined for the steady-state frontal polymerization). Actually, the bulk of monomer reacts close to limiting heating

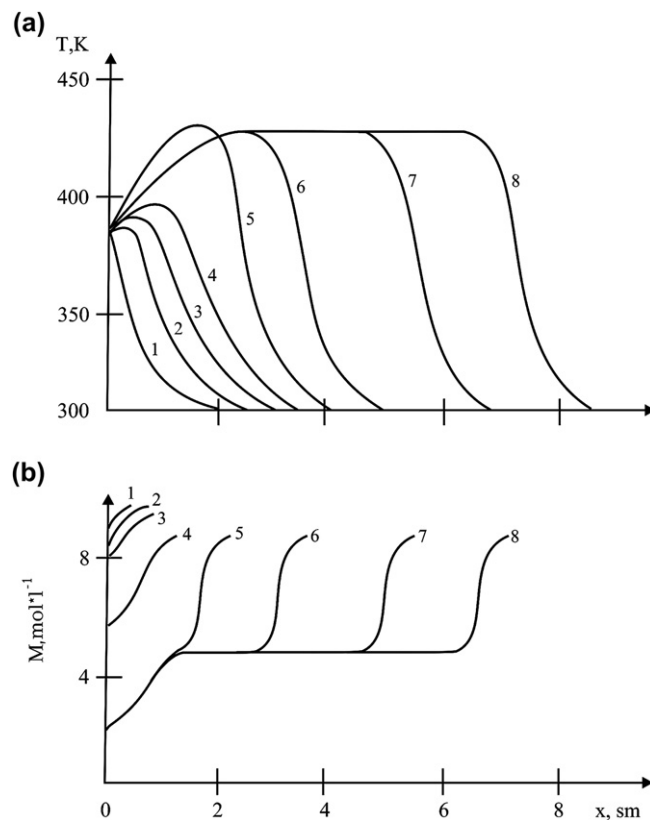


Fig. 1. The profiles of temperature change (a) and monomer concentration (b) in the direction of the reaction front,  $t$ , s: 200(1), 800(2), 1600(3), 2400(4), 3000(5), 3600(6),  $I_0 = 10^{-2} \text{ mol l}^{-1}$ ,  $M_0 = 10 \text{ mol l}^{-1}$ .

temperatures of reaction mixture. In this case, the reaction zone is narrow and polymerization proceeds close to maximum heating temperature.

The system of Eqs. (1)–(4) was numerically calculated to study the influence of various kinetic parameters on the width

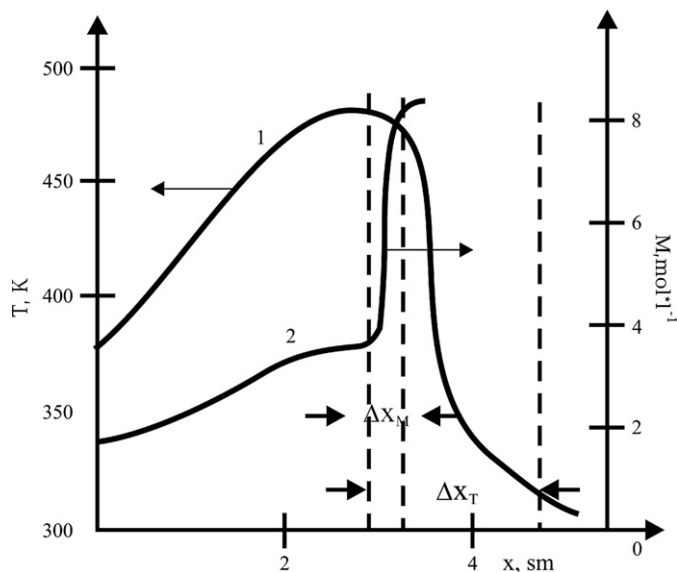


Fig. 2. The profiles of temperature change (1) and monomer concentration (2) on the stationary section of the polymerization wave. The dotted lines show the width of the monomer conversion zone ( $\Delta x_M$ ) and temperature change ( $\Delta x_T$ ).

<sup>2</sup> For the reaction zone span and temperature change span it is customary to calculate/consider the corresponding intervals by the front coordinate ( $x$ ), where the main conversion of the monomer ( $\Delta x_M$ ) takes place and the temperature is changed from maximum value to the initial one ( $\Delta x_T$ ).

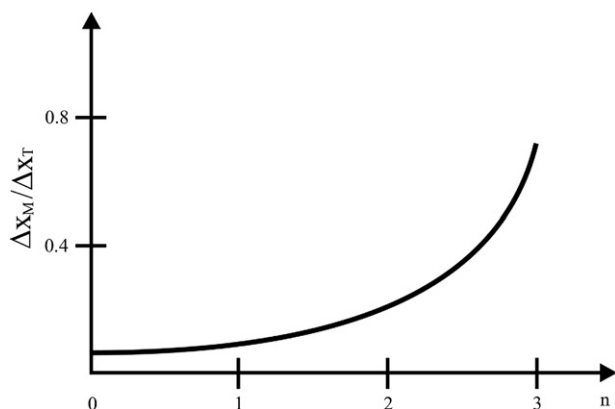


Fig. 3. Dependence of  $X_M/X_T$  on the formal reaction order by monomer.

of reaction zone by varying the reaction rate constants, their activation energy, monomer and initiator concentrations, as well as the reaction order with respect to monomer and initiator. Numerical calculation results show that the reaction zone virtually remains narrow during monomer and initiator concentrations and rate constants change between reasonable limits. As it was observed, the reaction zone widens when polymerization effective activation energy decreases or when reaction order with regard to monomer or initiator increases. As an example, in Fig. 3,  $\Delta x_M/\Delta x_T$  ratio dependence on formal reaction order ( $n$ ) with regard to monomer is shown.

It could be seen that the reaction zone is narrow when  $n$  equals 0 or 1. For  $n > 1$ , the reaction zone widens and polymerization proceeds at different temperatures. As a wide reaction zone illustration, in Fig. 4, the profiles of the conversion (curve 2) and temperature (curve 1) change are depicted. It is apparent from Fig. 4 that  $\Delta x_M$  and  $\Delta x_T$  are commensurable quantities.

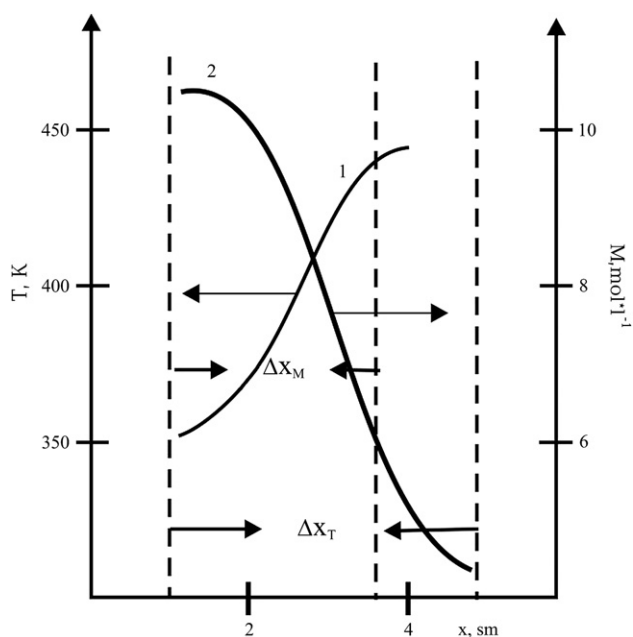


Fig. 4. Temperature (1) and monomer concentration profiles (2) with the formal reaction order by monomer equal to 3.

## 2. Applicability and the criterial conditions of QSC principle during isothermal polymerization

QSC principle applicability for isothermal radical polymerization of vinyl monomers presumes [30] that the rate of macro-radicals' concentration change is lower than the polymerization rate, i.e.  $|dR/dt| < |dM/dt|$ . Hence, we could assume  $dR/dt = 0$ , as:

$$\frac{dR}{dt} = K_i I - K_t R^2. \quad (6)$$

Then for the quasi-steady concentration of macro-radicals we have:

$$R_{QSC} = \left( \frac{K_i I}{K_t} \right)^{1/2}. \quad (7)$$

At constant rate of initiation ( $K_i I = \text{constant}$ ) the solution of Eq. (6) is as follows:

$$R(t) = \left( \frac{K_i I}{K_t} \right)^{1/2} \cdot \text{th} \left[ (K_i I K_t)^{1/2} \cdot t \right]. \quad (8)$$

From Eqs. (7) and (8) it follows:

$$\frac{R(t)}{R_{QSC}} = \text{th} \left[ (K_i I K_t)^{1/2} \cdot t \right]. \quad (9)$$

Analysis of Eq. (9) shows that QSC principle works if average life span of growing polymer chains ( $t_{ch} \approx 1/(K_i I K_t)^{1/2}$ ) is much shorter than the typical polymerization time ( $t_p \approx 1/K_p R_{QSC} = (1/K_p) \cdot (K_t/K_i I)^{1/2}$ ), i.e. if  $t_{ch} < t_p$ , and  $R(t)/R_{QSC} = 1$ . From  $t_{ch} < t_p$  it follows that:

$$A_1 = \frac{K_t}{K_p} \gg 1, \quad (10)$$

which is a must for applying QSC principle. Here, if the polymerization initiation rate changes, it is additionally required that the average life span of the growing macromolecules will be much shorter than complete consumption of the initiator ( $t_i$ ). Since  $t_i \sim 1/K_i$ , from condition  $t_i > t_{ch}$  we get:

$$A_2 = \left( \frac{I \cdot K_t}{K_i} \right)^{1/2} \gg 1. \quad (11)$$

Thus, QSC principle for the isothermal radical polymerization of vinyl monomers works for simultaneous compliance of the inequality conditions (10) and (11). Let us consider the QSC principle for frontal radical polymerization processes.

## 3. Small parameter and physical criteria of applicability of QSC principle

For the established steady-state frontal polymerization regime, Eqs. (1)–(4) system with conditions (5) can be substituted by a system of dimensionless variables, i.e. temperature ( $\theta$ ), conversion ( $\alpha$ ), concentration of macro-radicals ( $r$ ) and initiator ( $i$ ) as follows:

$$\frac{d\theta}{d\xi} = u \frac{[\gamma(\theta - \theta_0) - \alpha]}{\gamma}, \quad (11)$$

$$\frac{d\alpha}{d\theta} = \frac{\omega \Gamma \varphi_0(\theta)(1 - \alpha)r}{\Omega(\theta, \alpha)}, \quad (12)$$

$$\frac{dr}{d\theta} = \omega \frac{b\eta\varphi_1(\theta)(1 - i) - B\varphi_2(\theta)r^2}{\Omega(\theta, \alpha)}, \quad (13)$$

$$\frac{di}{d\theta} = \omega\eta \frac{\varphi_1(\theta)(1 - i)}{\Omega(\theta, \alpha)}, \quad (14)$$

$$\begin{aligned} \omega &= \frac{\gamma^2}{u^2}, \quad \Omega(\theta, \alpha) = \gamma(\theta - \theta_0) - \alpha, \\ \theta &= \theta_0; \quad \alpha = r = i = 0, \\ \theta &= \theta_k; \quad \alpha = \alpha_k; \quad r = 0; \quad i = 0, \end{aligned} \quad (15)$$

$$\theta_k = \theta_0 + \frac{\alpha_k}{\gamma},$$

$$\varphi_j(\theta) = \begin{cases} 0 & \text{with: } \theta_0 \leq \theta \leq \theta_0 + \delta \\ \exp\left(\frac{S_j\theta}{1+\beta\theta}\right) = [\varphi(\theta)]^{S_j} & \text{with } \theta > \theta_0 + \delta; \quad j = 0, 1, 2. \end{cases} \quad (16)$$

Following notations are used in Eqs. (11)–(16):

$$\begin{aligned} \theta &= \frac{E_{\text{ef}}}{R_g T_*} (T - T_*), \quad \theta_0 = \frac{E_{\text{ef}}}{R_g T_*} (T_0 - T_*), \quad \tau = \frac{t}{t_*}, \\ \xi &= \frac{x}{x_*}, \quad x_*^2 = \frac{\lambda t_*}{c\rho}, \end{aligned}$$

$$t_* = \frac{\gamma}{K_{\text{ef}} \exp(-E_{\text{ef}}/R_g T_*) \cdot M_0^{1/2}}, \quad \gamma = \frac{c\rho \cdot \beta T_*}{QM_0},$$

$$\beta = \frac{R_g T_*}{E_{\text{ef}}}, \quad \alpha = \frac{M_0 - M}{M_0},$$

$$i = \frac{I_0 - I}{I_0}, \quad r = \frac{R}{M_0}, \quad b = \frac{I_0}{M_0}, \quad B = K_{i0} \cdot \exp\left[\frac{E_{\text{ef}} - E_i}{R_g T_*}\right] \cdot \frac{M_0^{1/2}}{K_{\text{ef}}},$$

$$\begin{aligned} \Gamma &= K_{p0} \cdot \exp\left[\frac{E_{\text{ef}} - E_p}{R_g T_*}\right] \cdot \frac{M_0^{1/2}}{K_{\text{ef}}}, \quad \eta = \frac{B}{\Gamma^2} \\ &= \frac{K_{i0}}{K_{\text{ef}} \cdot M_0^{1/2}} \cdot \exp\left[\frac{E_{\text{ef}} - E_i}{R_g T_*}\right], \end{aligned} \quad (17)$$

$$S_0 = \frac{E_p}{E_{\text{ef}}}, \quad S_1 = \frac{E_i}{E_{\text{ef}}}, \quad S_2 = \frac{E_t}{E_{\text{ef}}}, \quad \xi = \xi_0 + u \cdot \tau.$$

In Eqs. (11)–(17),  $\theta_k = \theta(+\infty)$  and  $\alpha_k = \alpha(+\infty)$  are the finite values of dimensionless temperature and conversion;  $\theta_0$  is the

initial temperature;  $T_*$ ,  $t_*$ , and  $x_*$  are some scaling variables of temperature, time, and coordinate;  $u$  is the velocity of the front;  $\delta$  is the piecewise heat generation source<sup>3</sup>;  $K_{\text{ef}}$  and  $E_{\text{ef}}$  are the effective polymerization rate constant and activation energy,  $\varphi_j(\theta)$  ( $j = 0, 1, 2$ ) are continuous functions of  $\theta$  and  $S_1 > 1$ ,  $S_1 > S_2$ .

In the given problem  $\theta_k$  and  $\alpha_k$  are unknown values that must be determined along with the traveling velocity of the front  $u$ . This is what makes this problem somewhat different from the conventionally studied ones.

Let's recall Eqs. (11)–(16) problem as complete, and QSC principle reduces the problem to quasi-stationary one, i.e.:

$$\frac{d\alpha}{d\theta} = \frac{\omega b^{1/2} \varphi_0(\theta)(1 - \alpha)(1 - i)^{1/2}}{\Omega(\theta, \alpha)}, \quad (12a)$$

$$r = \frac{1}{\Gamma} [b\varphi_1(\theta)(1 - i)/\varphi_2(\theta)]^{1/2}, \quad (13a)$$

$$\frac{di}{d\theta} = \omega\eta \frac{\varphi_1(\theta)(1 - i)}{\Omega(\theta, \alpha)}, \quad (14a)$$

$$\begin{aligned} \theta &= \theta_0; \quad \alpha = i = 0, \\ \theta &= \theta_k; \quad \alpha = \alpha_k; \quad i = 1. \end{aligned} \quad (15a)$$

The comparison of the set of Eqs. (12)–(15) and Eqs. (12a)–(15a) shows that the quasi-stationary system Eqs. (12a)–(15a) can be obtained from the full system Eqs. (12)–(15) as an asymptotics with regard to small parameter ( $\varepsilon$ ), which is a multiplier to the derivative in Eq. (13). The set with a small parameter could be obtained if, for example,  $\Gamma$  and  $B$  are presented in the form of  $\Gamma = \bar{\Gamma}/\varepsilon$  and  $B = \bar{B}/\varepsilon^2$ , where  $\varepsilon < 1$ ; and the magnitudes of  $\Gamma$  and  $B$  are of the order of one. Introducing the variable  $v = r/\varepsilon$  instead of the set of Eqs. (12), (13), and (15), we will get:

$$\frac{d\alpha}{d\theta} = \omega \frac{\bar{\Gamma} \varphi_0(\theta)(1 - \alpha)v}{\Omega(\theta, \alpha)}, \quad (18)$$

$$\varepsilon \frac{dv}{d\theta} = \frac{\omega b\eta\varphi_1(\theta)(1 - i) - \bar{B}\varphi_2(\theta)v^2}{\Omega(\theta, \alpha)}, \quad (19)$$

$$\theta = \theta_0; \quad \alpha = v = i = 0. \quad (20)$$

As it was already mentioned, Eqs. (10) and (11) conditions serve as criteria of applicability of QSC principle in isothermal regime, where the rate constants  $K_t$ ,  $K_p$ , and  $K_i$  are determined at isothermal temperature. During non-isothermal conditions,  $A_1$  and  $A_2$  are temperature dependant functions and could change considerably. From Eq. (17) it follows that

$$\Gamma = \frac{A_2(T_*)}{b^{1/2}}; \quad B = \frac{A_1(T_*)A_2(T_*)}{b^{1/2}}; \quad \eta = \frac{B}{\Gamma^2};$$

During frontal polymerization, as  $T_*$ , it is relevant to take temperature which corresponds to maximum of heat evolution function, i.e. a temperature value when  $A_1$  and  $A_2$  usually are close to minimal. Therefore, if conditions (10) and (11) are met, then the

<sup>3</sup> The procedure of cropping the heat generation function is connected with the fact that the heat generation speed close to the initial temperature of the environment  $T_0$  must be equal to 0. Otherwise, the thermal conductivity equation has no stationary solution.

QSC method could give satisfactory approximation since  $\Gamma = \bar{T}/\varepsilon$ ,  $B = \bar{B}/\varepsilon^2$ ,  $\varepsilon < 1$  throughout the whole temperature range during polymerization.

#### 4. The results of numerical calculation and the analysis of

Full and a quasi-stationary tasks were solved for different sets of kinetic and thermo-physical parameters typical for vinyl monomers' radical polymerization. Traveling velocities (dimensionless value) of the front ( $u$ ) and final temperatures ( $\theta_k$ ) have been compared. The discrepancy between the QSC and full tasks is  $\Delta u = 0.02\%$  and  $\Delta\theta = 0.063\%$ , if the reaction zone is sustained narrow, where  $\Delta u = u - u_0/u_0 \cdot 100\%$ ;  $\Delta\theta = \theta_k - \theta_{k0}/\theta_{k0} \cdot 100\%$ . Here  $u$ ,  $u_0$ , and  $\theta_k$ ,  $\theta_{k0}$  are the velocities and final temperatures for the full and quasi-stationary problems, respectively. It was assumed that  $\varepsilon \sim 10^{-6}$  in dimensionless set of equations. Further, the parameters were changed in such a way that  $\varepsilon$  took  $10^{-4}$ ,  $10^{-2}$  and 1 values. The  $\Delta u$  and  $\Delta\theta$  correspondingly equaled to 1.8% and 1.8%, 8% and 22%, 20% and 97%.

The dependences of  $\Delta u$  and  $\Delta\theta$  on a number of kinetic parameters are shown in Figs. 5 and 6. From Fig. 5 (curves 1, 2) it follows that  $\Delta u$  increases insignificantly with the growth of  $I_0/M_0$  ratio, whereas  $\Delta\theta$  decreases. However,  $\Delta u$  and  $\Delta\theta$  depend on  $I_0/M_0$  slightly to the extent that quasi-stationary approximation deviation is 1% in the examined  $I_0/M_0$  change range.

Numerical calculations on the influence of activation energy of initiator decomposition constants, growth and bimolecular rapture of the chains at  $\Delta u$  and  $\Delta\theta$  values have been performed. Analysis of the obtained results show that quasi-stationary approximation gives good accuracy if  $E_i \geq (138-147)$  kJ mol $^{-1}$ , irrespective of  $E_p$  and  $E_t$ . However, if  $E_i < 138$  kJ mol $^{-1}$ , then approximation accuracy decreases at  $E_{ef} \leq 75$  kJ mol $^{-1}$ . For instance, Fig. 6 presents the influence of  $S_1$  on  $\Delta u$  and  $\Delta\theta$  at  $E_i = 126$  kJ mol $^{-1}$ . It could be seen that for  $S_1 \leq 1.5-1.6$ , then  $\Delta u$  and  $\Delta\theta$  slightly depend on  $S_1$ , whereas  $\Delta u$  and  $\Delta\theta$  increase considerably at  $S_1 > 1.6$ .

Actually, the reaction zone is narrow when the solutions of the full and quasi-stationary problems coincide with sufficient

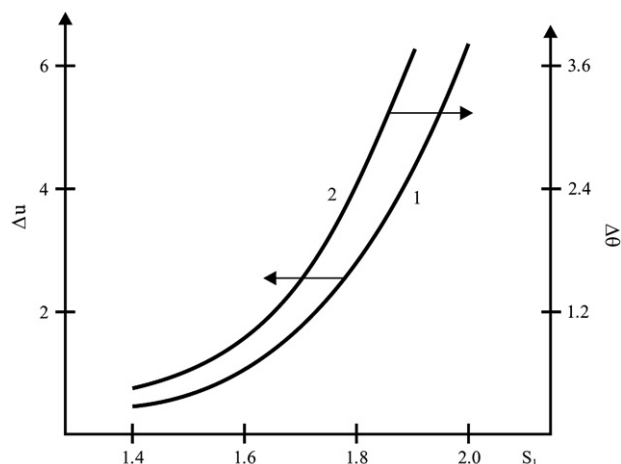


Fig. 6. Influence of parameter  $S_1$  on (1) and (2).

accuracy. Under these conditions, the polymerization proceeds close to maximum heating temperature, i.e. monomer consumption obeys to isothermal conditions.

Analysis of temperature and conversion profiles shows that beginning with  $E_{ef} \leq 75$  kJ mol $^{-1}$ , widening of the reaction zone is observed, which increases the relative deviations  $\Delta u$  and  $\Delta\theta$  (Fig. 6).

Apart from kinetic Eqs. (1)–(4), the kinetic model of polymerization was studied numerically. Here, reaction order with regard to  $M$  was formally increased in Eq. (3) i.e.  $-dM/dt = K_p R M^n$ , where  $n = 2, 3$ . Options for  $n = 2, 3$  with the same kinetic and thermo-physical parameters as in the case of Eqs. (12)–(15) were also considered. Actually,  $\varepsilon$  increases with the increase of  $n$  in the non-dimensional system of Eqs. (12)–(15), which directly have influences on  $\Delta u$  and  $\Delta\theta$  (Fig. 7). The analysis of temperature and conversion profiles shows also that augmentation of relative deviations ( $\Delta u$  and  $\Delta\theta$ ) is accompanied by the widening of the temperature span where monomer is consumed.

Thus, numerical calculation of vinyl monomers' frontal radical polymerization and the analysis of the obtained results permit to conclude that for narrow-reaction zones the QSC principle could be applied with high accuracy meeting

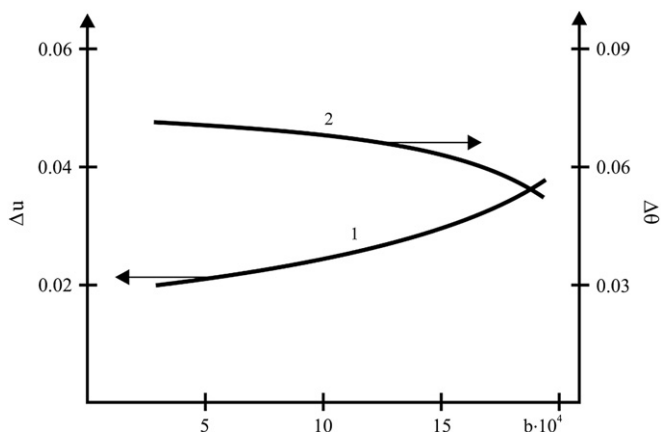


Fig. 5. Dependence of (1) and (2) on parameter  $b$ .

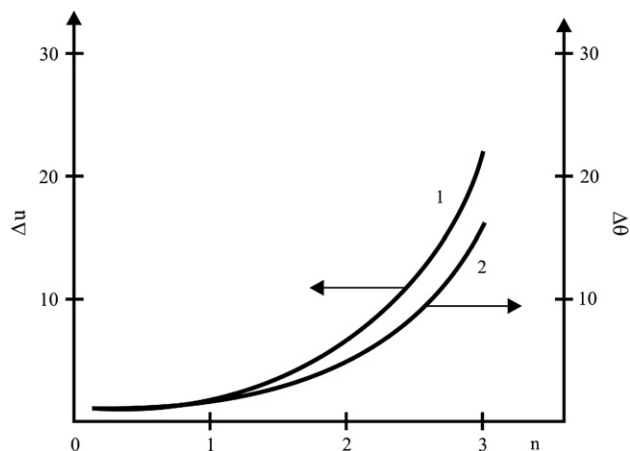


Fig. 7. Dependence of (1) and (2) on the formal reaction order by monomer.



conditions (10) and (11). For wide reaction zones, (10) and (11) inequalities worsen which affects the accuracy of quasi-stationary approximation. In such cases, it is necessary to carry out additional investigations concerning the applicability of QSC principle, which is the purpose of our subsequent studies.

## Acknowledgement

The work is supported by NFSAT-CRDF, MES RA (Grant BRAU -01-05).

## References

- [1] Chechilo NM, Enikolopyan NS. Dokl Akad Nauk SSSR 1974;214:113 [in Russian].
- [2] Davtyan SP, Jirkov VP, Volfson SA. Usp Khim 1984;53(2):251 [in Russian].
- [3] Pojman JA, Fortenberry DI, Ilyashenko VM. Int J Self-Propag High-Temp Synth 1997;6:355.
- [4] Davtyan SP, Tonoyan AO, Radugina AA, Davtyan DS, Abrosimov AF, Savchenko VI. Polym Sci 1999;41(2):138.
- [5] Chekanov YA, Pojman JA. J Appl Polym Sci 2000;78:2398.
- [6] Davtyan SP, Bagdasaryan AE, Tonoyan AO, Karapetyan ZA, Davtyan SP. Polym Sci 2000;42:1197.
- [7] Davtyan SP, Hambartsumyan AF, Davtyan DS, Tonoyan AO, Hayrapetyan S, Bagyan SH, et al. Eur Polym J 2002;38:2423.
- [8] Pujari NS, Vishwakarma AR, Kelkar MK, Ponrathnam S. e-Polymers 2004;49:1.
- [9] Chen S, Sui J, Chen L. Colloid Polym Sci 2005;283:932.
- [10] Qingzhi Y, Xintai S, Changchun G. Prog Chem 2005;17:1081.
- [11] Chen S, Sui J, Chen L, Pojman JA. J Polym Sci Part A Polym Chem 2005;43:1670.
- [12] Nason C, Roper T, Hoyle C, Pojman JA. Macromolecules 2005;38:5506.
- [13] Yan-yan C, Jian-wen Y, Zhao-hua Z, Yong-lie Ch. Chin Polym Bull 2006;8:44.
- [14] Khanukaev BB, Kojushner MA, Enikolopyan NS. Dokl Akad Nauk SSSR 1974;214:625 [in Russian].
- [15] Aleksanyan GG, Harutiunyan KhA, Bodneva VL, Davtyan SP. Vysokomolekulyarnye Soedineniya 1975;17A:913 [in Russian].
- [16] Davtyan SP, Surkov NF, Rozenberg BA, Enikolopyan NS. Dokl Akad Nauk SSSR 1977;232:379 [in Russian].
- [17] Bostanjian SA, Shulikovskaya MV, Davtyan SP. Teoreticheskie Osnovi Khimicheskoy Tekhnologii 1989;23:340 [in Russian].
- [18] Megrabova IN, Volpert ViA, Volpert ViA, Davtyan SP. Fizika Gorenia i Vzriva 1990;4:45 [in Russian].
- [19] Volpert Vit, Volpert VI, Ilyashenko V, Pojman J. Chem Sci 1998;53:1655.
- [20] Spade CA, Volpert VA. Chem Eng Sci 2000;55:624.
- [21] Spade CA, Volpert VA. Macromol Theory Simul 2000;9:26.
- [22] Bessonov N, Pojman JA, Volpert VA. Matapli (Journal of Société de Mathématiques Appliquées & Industrielles) 2004;75:51.
- [23] Devadoss DE, Pojman JA, Volpert VA. Chem Eng Sci 2006;61:1257.
- [24] Davtyan DS, Pirumyan PH, Bagyan SH, Zakaryan HH, Tonoyan AH, Mair Tomas, et al. Chem J Armenia 2006;59(4):22.
- [25] Davtyan DS, Pirumyan PH, Bagyan SH, Zakaryan HH, Tonoyan AH, Mair Tomas, et al. Chem J Armenia 2007;60(1):12.
- [26] Frank-Kamenecki DA. Diffusion and heat transfer in chemical kinetics. Moscow: Nauka; 1967.
- [27] Tonoyan AO, Leykin SP, Davtyan SP, Rozenberg BA, Enikolopyan NS. Vysokomolekulyarnye Soedineniya 1974;16A:1847 [in Russian].
- [28] Davtyan S. Non-isothermal methods of synthesis of polymers, I: theory and practice of adiabatic polymerization processes. Yerevan: Asogik; 2004 [in Russian].
- [29] Tonoyan AO, Harutiunyan KhA, Davtyan SP, Rozenberg BA, Enikolopyan NS. Vysokomolekulyarnye Soedineniya 1974;16A:768 [in Russian].
- [30] Bamford CH, Barb WG, Jenkins AD, Onyon PF. The kinetics of vinyl polymerization by radical mechanisms. London: Butterworths Scientific Publications; 1958.