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Peculiarities of establishment of steady-state frontal polymerization of vinyl monomers

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ABSTRACT

Frontal radical polymerization of vinyl monomers in non-stationary mode is investigated theoretically. It is shown that the formation and the time of establishment of steady-state polymerization heat autowaves considerably depend on the initial temperature, T_i. When T_i is less than the adiabatic heating temperature (T_a), the excess heat and relatively high conversion foster front formation before the non-stationary one. Whereas, for $T_i > T_a$, steady-state frontal polymerization regime is established, when the heat flow from the outer source is considerably less than the heat evolving due to the chemical reaction.

1. Introduction

Many theoretical and experimental works are available in literature [1–25] concerning the influence of various factors on the frontal polymerization, for example, high (up to 5 kbar) [1] and low (dozens of bars) [3–5,7,13] pressures; the type of polymerization [1,3–5,7–10]; nature of monomer [1,4,7,9] and initiator [1,12]; heat regimes [3,6,7,13,16–25] on the travelling velocity of the front [1,3–5,9,12–14]; conversion level [5,6,12,14], molecular-mass characteristics [10,15] and steadiness [7,10,13,16,19] of frontal regimes are studied.

An important issue of the formation of frontal polymerization regime is the initiation of heat autowaves, the following propagation of non-stationary front until the establishment of a steady state.

It is known that frontal polymerization is initiated in the reaction media by the local impact of heat from an outer source. A widespread method is the direct application of the heated surface to the butt end of reaction mixture.

There are no data available in literature on the investigation of the initiation of polymerization heat waves, on its formation and the establishment of a steady-state regime. The aim of this work is to investigate theoretically the peculiarities of the formation of steady-state regimes during radical polymerization of vinyl monomers.

2. Problem statement

Let us consider radical polymerization, which includes the following steps: initiation by the decomposition of the initiator, its growth and bimolecular termination of the chains via recombination mechanism.

Equations describing temperature (T), initiator (I), monomer (M) and macroradical (R) concentration changes during propagation of one-dimensional front of radical polymerization could be written in the following way:

$$c\rho \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} - Q \frac{\partial M}{\partial t} \tag{1}$$

$$-\frac{\partial I}{\partial t} = f \cdot K_i \cdot I \tag{2}$$

$$-\frac{\partial M}{\partial t} = K_p \cdot R \cdot M \tag{3}$$

$$\frac{\partial R}{\partial t} = f \cdot K_i \cdot I - K_t \cdot R^2 \tag{4}$$

where c, ρ, λ are the heat capacity, density and heat conductance coefficient, respectively; f is the initiation efficiency the value of which is assumed to be unit for convenience; $K_i = K_{i0} \times \exp(-E_i/R_gT)$, $K_p = K_{p0} \times \exp(-E_p/R_gT)$, $K_t = K_{t0} \times \exp(-E_t/R_gT)$ are the temperature dependences of the rates of initiation, growth and bimolecular termination; E_i, E_p and E_t are pre-exponential factors and activation energies of the rate constants of initiation, growth and bimolecular termination, R_g is the absolute gas constant.

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The initial and boundary conditions are

$$t=0,\quad T=T_0,\quad I=I_0,\quad M=M_0,\quad R=0\quad \text{for any } x>0;$$
$$x=0,\quad T=T_i\quad \text{for any } t>0,\quad \left.\frac{\partial T}{\partial x}\right|_{x\to+\infty}=0. \tag{5}$$

Numerical solution of the system of differential Eqs. (1)–(4), with conditions (5) was carried out by the FTCS (Forward-Time Central-Space) a finite difference method.

During simulation basic kinetic and other parameters were taken for methyl methacrylate, and these parameters were varied for some vinyl monomers [26,27]. As the initiators we used parameters for benzoyl peroxide and 2,2′-azobis-isobutyronitrile (AIBN).

$$K_p = K_{p0}\times \exp\left(-\frac{E_p}{R_gT}\right) = 5.35\times 10^5 \times e^{-19,740/R_gT}\,\mathrm{l\,mol^{-1}\,s^{-1}},$$

$$K_{p0} = 5\times 10^5 \text{ to } 5\times 10^6\,\mathrm{l\,mol^{-1}\,s^{-1}},\quad E_p = 18.9\text{–}25.2\,\mathrm{kJ\,mol^{-1}},$$

$$K_t = K_{t0}\times \exp\left(-\frac{E_t}{R_gT}\right) = 4.0\times 10^7 \times e^{-1680/R_gT}\,\mathrm{l\,mol^{-1}\,s^{-1}},$$

$$K_{t0} = 2.5\times 10^7 \text{ to } 1.4\times 10^8\,\mathrm{l\,mol^{-1}\,s^{-1}},\quad E_t = 0\text{–}6.3\,\mathrm{kJ\,mol^{-1}},$$

$$\mathrm{BP}: K_i = 1.18\times 10^{14}\times e^{126,000/R_gT}\,\mathrm{s^{-1}},$$
$$\mathrm{AIBN}: K_i = 1.0\times 10^{15}\times e^{128,940/R_gT}\,\mathrm{s^{-1}},$$

$\rho = 0.94\,\mathrm{g\,cm^{-3}}$, $c = 1.89\,\mathrm{J\,g^{-1}\,K^{-1}}$, $Q_{pol} = 54.6\,\mathrm{kJ\,mol^{-1}}$, $\lambda = 3.6\times 10^{-2}\,\mathrm{cal\,min^{-1}\,K^{-1}\,cm^{-1}}$.

Thus, it is presumed that constant temperature is assigned on the surface $T(x=0)=T_i$ and $T_i > T_0$, while in the $0 < x < +\infty$ half-space the reaction media is present. Under the impact of high temperature the close to surface layers of the monomer and initiator mixture are activated. These layers are heated, the initiator decomposes and exothermic polymerization starts. Part of the evolved heat is transmitted to neighboring layers where, again polymerization begins under the impact of heating and thus heat autowaves are formed.

3. Analysis of the numerical results

It is known that initiation of frontal regimes by the outer heat source is carried out differently at different T_i values [28,29]. Hence, the initiation temperature, following considerations of [30], could be characterized by the dimensionless parameter, $\sigma = (T_i - T_0)/(T_M - T_0)$, where T_M is the maximal temperature in the steady-state adiabatic wave.

Obviously, for the initiation of polymerization frontal regimes it is required that $\sigma > 0$, and σ could be both lesser and larger than unity. If $\sigma < 1$ then, as it is accepted in the combustion theory, the regime is called "induction ignition", while if $\sigma > 1$ then the process is called "combustion regime".

Let us consider the peculiarities of the formation of non-stationary frontal regimes during induction period (t_{in}) corresponding to the period starting from $t=0$ up to the establishment of the steady-state regime for $\sigma > 1$, $\sigma < 1$, and $\sigma \approx 1$. In Fig. 1, an example of the formation of steady-state frontal regime is presented when $\sigma < 1$. Here, non-stationary (curves 1–5) and steady-state (curves 6–8) temperature (Fig. 1a) and monomer concentration (Fig. 1b) profiles are presented. As it follows from Fig. 1a and b initiation stage of polymerization front has induction character. The time when steady-state autowaves are formed at $\sigma < 1$ depends on the temperature of outer heat source and the rate of polymerization heat evolution. The characteristic trend of the curves in Fig. 1 is that the conversion (Fig. 1b) is considerably higher on the non-steady-state curve segment than on the established steady-state regime where the conversion is ca. 0.45. This is explicable by the fact that relatively high values of autowave maximal temperature lead to the quick "burn-out" of initiator on the section of steady-state regime, reduces the lifespan of macroradicals, and, hence, reduces the conversion level.

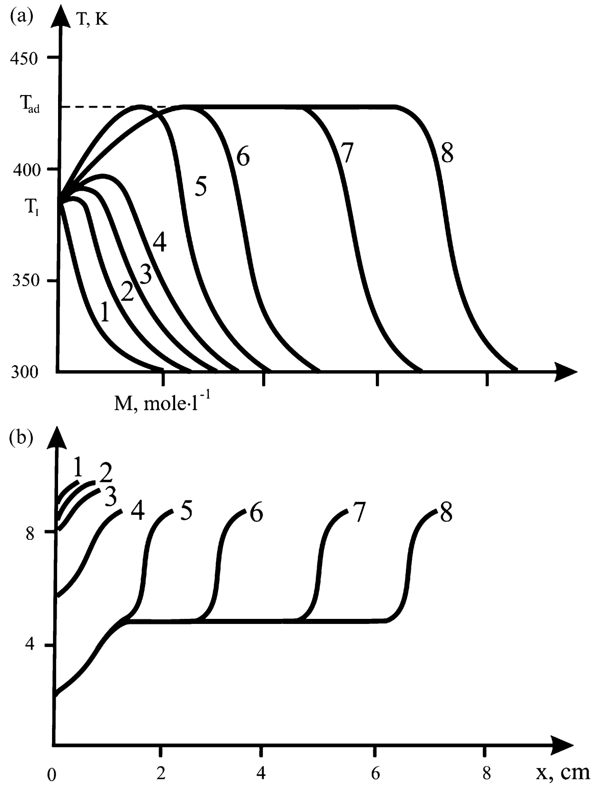

Fig. 1. Spatio-temporal distribution of temperature (a) and concentration of monomer (b), t in min; 1(1); 3(2); 13(3); 27(4); 40(5); 50(6); 56(7); 61(8); $T_0 = 300$ K, $I_0 = 10^{-2}$ mol l^{-1}, $M_0 = 9$ mol l^{-1}.

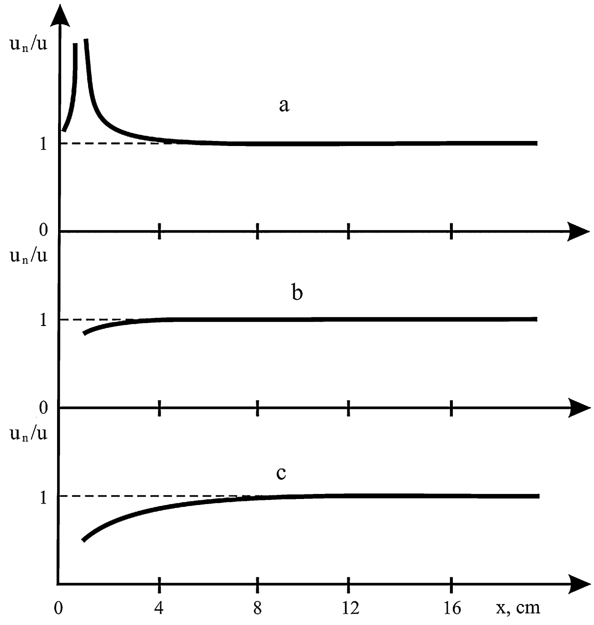

Fig. 2. Change of non-stationary front rate (u_n) vs. the stationary one, for (a) $\sigma = 0.6$; (b) $\sigma \approx 1$; (c) $\sigma = 1.6$.

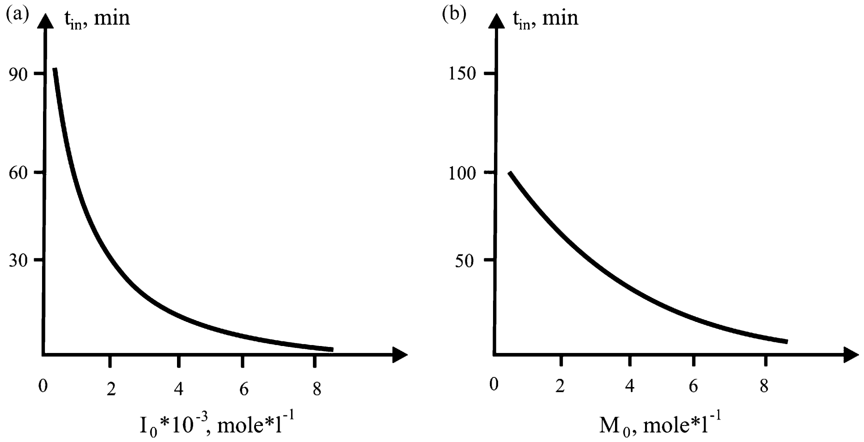

Fig. 3. t_{in} vs. the initiator (a) and monomer (b) initial concentrations. $\sigma = 0.6$.

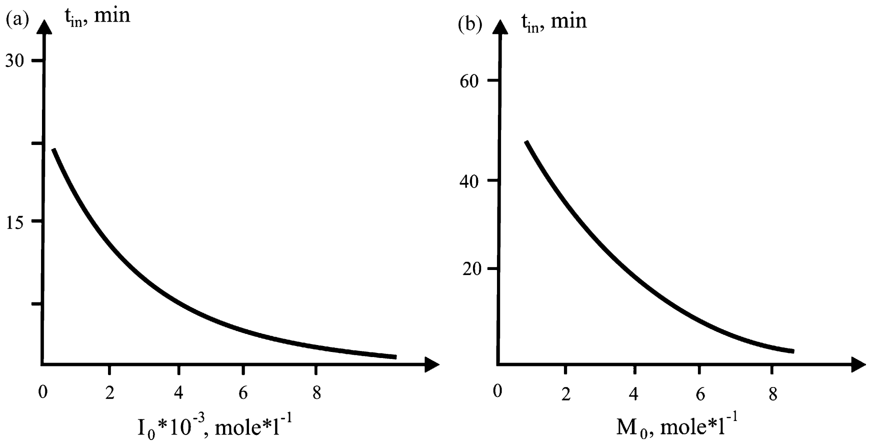

Fig. 4. t_{in} vs. the initiator (a) and monomer (b) initial concentrations in the presence of gel-effect. $\sigma = 0.6$.

Both the excess heat present before the front (Fig. 1a) as well as relatively high conversion levels foster the formation and propagation of the non-stationary heat autowaves when $\sigma < 1$. The very factors explain the non-monotonous dependence of the ratio of non-established front velocity (u_n) to that of steady-state one (u) on x presented in Fig. 2a.

In Figs. 3 and 4 the data on the influence of the initiator (Fig. 3a, 4a) and monomer (Fig. 3b, 4b) initial concentrations on the induction period in the absence (Fig. 3) and presence (Fig. 4) of gel-effect are presented.

The influence of gel-effect on the frontal radical polymerization was considered by the following relation:

$$K_t^g = K_t \cdot \exp[-a(\alpha - \alpha_g)] \tag{6}$$

obtained in [27,31]. In expression (6) K_t^g and K_t are rate constants of the bimolecular chain termination reaction in the presence and absence of gel-effect, respectively; a is the parameter of gel-effect and α_g is the of conversion level when gel-effect starts.

From Figs. 3 and 4 it follows that gel-effect has no impact on the character of relation, however, it considerably reduces the induction period. Actually, from Fig. 5 it follows that t_{in} is ca. 1.6 min at $\alpha_g = 0.1$, while it increases up to 6 min at $\alpha_g = 0.5$.

The induction period is added up from two constituents[1]: the time of steady-state front formation (t_1) and the time of propagation of non-stationary heat autowaves (t_2) up to the establishment of steadiness, i.e. $t_{in} = t_1 + t_2$ [28,29]. Numerical calculations showed that the relation between t_1 and t_2 is determined by the approximate expression deduced in [28,29].

$$t_2 = 2 \cdot \sqrt{t_1 \cdot t_0} \tag{7}$$

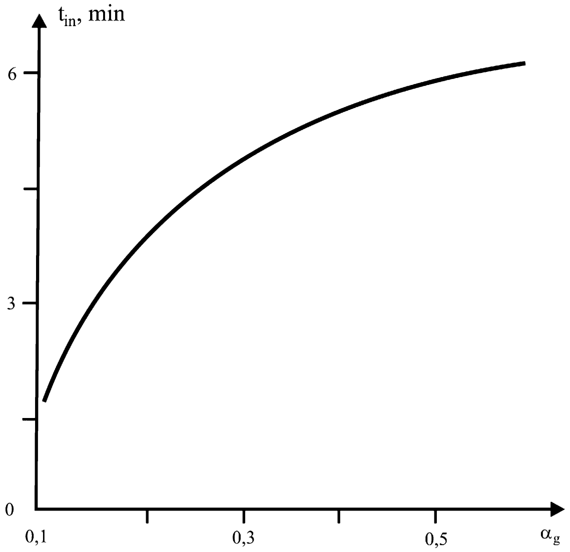

Fig. 5. Influence of α_g on t_{in}. $\sigma = 0.6$.

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[1] It is to be noted that such kind of division is provisional as t_{in} vs. x relationship has asymptotic character.

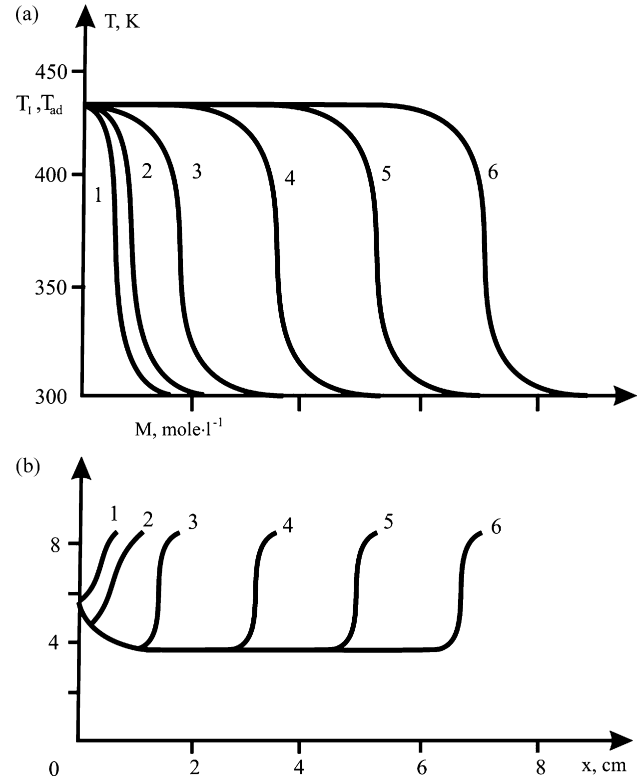

Fig. 6. Spatio-temporal distribution of temperature (a) and monomer concentration (b) at $T_0 = 300$ K, $\sigma \approx 1$, $I_0 = 10^{-2}$ mol l^{-1}, $M_0 = 9$ mol l^{-1}. t, min: 0.5(1); 1(2); 7(3); 15(4); 21(5); 26(6).

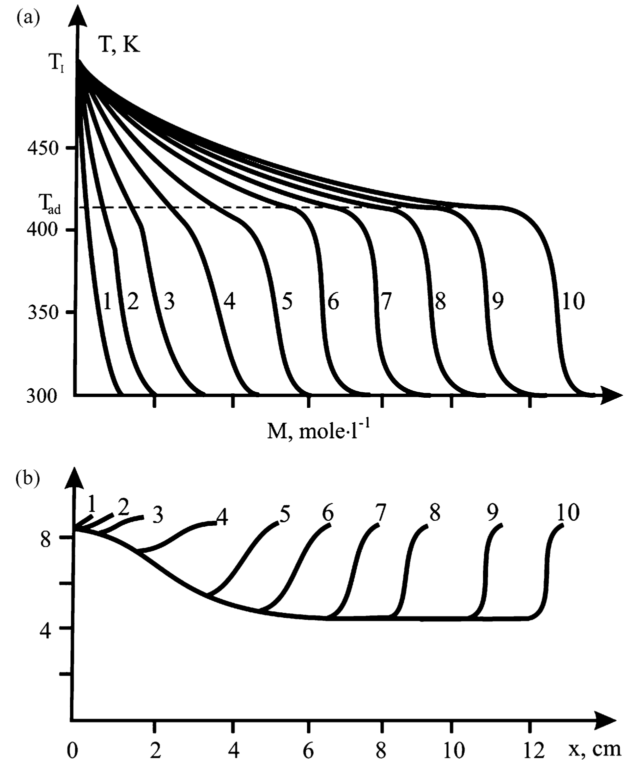

Fig. 7. Spatial-temporal distribution of temperature (a) and monomer concentration (b) at $T_0 = 330$ K, $\sigma \approx 1$, $I_0 = 10^{-2}$ mol l^{-1}, $M_0 = 9$ mol l^{-1}. t, min: 2(1);6(2); 7(3); 21(4); 36(5); 48(6); 58(6); 64(7); 72(8); 78(9); 84(10).

where $t_0 = \lambda\rho/cu^2$ is the characteristic time of propagation of stationary front over the heated layer. Component t_1 could be estimated from [29].

When σ is increased up to 1, as a rule, $t_1 > t_2 > t_0$ inequality holds. It is interesting to note, that for the frontal radical polymerization of vinyl monomers t_2 remains practically unchanged. Reduction of the total induction time takes place due to the shortening of t_1. In this case, the practical independence of t_2 from σ relates to the decomposition of initiator and its burning-out during σ increase.

Eq. (7) is not suitable for the evaluation of t_1 and t_2 at $\sigma > 0.95$, while t_1 is equal to t_2 at $0.97 \le \sigma < 1.20$. These regimes are characterized by the minimal induction period. Concentration and temperature profiles of the monomer at $\sigma \approx 1.0$ are presented in Fig. 6. As it follows from Fig. 6a and b, steady-state conditions are established faster for $\sigma = 1.0$ than when $\sigma = 0.6$ (Fig. 1). The dependence of u_i/u from x for $\sigma \approx 1.0$ is presented in Fig. 2b.

When outer heat source temperature (T_i) is considerably higher than the temperature of the steady-state radical polymerization front ($\sigma = 1.6$), the initiation regime significantly differs from the ignition processes. Here due to high initiation temperatures (Fig. 7a) an instant burn-out of initiator takes place. This steeply increases the quadratic termination of radicals, and hence, produces insignificant conversion levels (Fig. 7b).

As it follows from Fig. 7 only at a definite distance from the heat source, where temperature is significantly lower, a significant heat evolution due to the chemical reaction is observed, which leads to the formation of steady-state regimes. In this case, a steady-state frontal polymerization regime is established when at a distance where the heat flow from the external source of heat is considerably less than the heat evolved during the chemical reaction. For the calculation of t_2 in [29] the following approximate formula is proposed ($\sigma > 1$):

$$\left(\frac{t_2}{t_0}\right)^{1/2} \cdot \exp\left(\frac{t_2}{t_0}\right) = \frac{10}{\sqrt{\pi}} \cdot \sigma \qquad (8)$$

Numerical calculations carried out varying the value of σ ($\sigma > 1$), show that Eq. (8) for the frontal radical polymerization processes of vinyl monomers will be ruled out.

The unsuitability of expression (8) for the determination of t_2 can be explained by the fact that in combustion processes just after the ignition by $\sigma > 1$ the frontal regime of the process is established immediately [29]. This is different from frontal radical polymerization processes.

The dependence of u_i/u from x for $\sigma > 1$ is presented in Fig. 2c, where also considerable difference from that of ignition processes is observed [28,29]. As it follows from Fig. 2, there is no abrupt transition between the heat regimes for $\sigma > 1$ and $\sigma < 1$.

Numerical calculations carried out at various σ values show that the minimal induction period corresponds to $0.97 \le \sigma \le 1.2$ (Fig. 8).

This result asserts that the frontal polymerization steady-state regime is easier to establish with the help of an external heat source when the temperature is close to adiabatic heating.

In conclusion it has to be added that sometimes, dying oscillation (i) heat waves; (ii) conversion levels; and (iii) front rates do precede to steady-state frontal radical polymerization regimes [19] (Fig. 9).

The reason of short-term loss of stability in the form of dying oscillations is explicable by the redundant enthalpy before (ahead of) the front zone.

4. Comparison of theoretical results with experimental data

To verify theoretical results series of experiments have been carried out studying the time of establishment of the frontal polymerization steady-state regimes using Co-

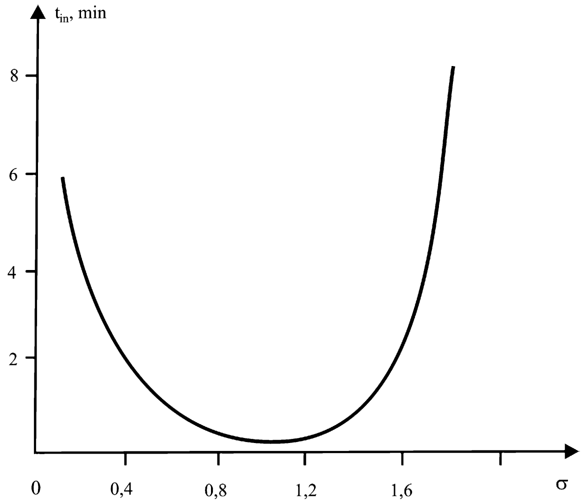

Fig. 8. Influence of σ on t_{in}. $I_0 = 10^{-2}$ mol l^{-1}, $M_0 = 9$ mol l^{-1}.

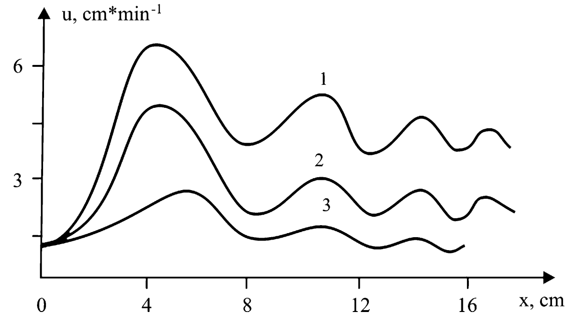

Fig. 9. Dying oscillation of front rate: $T_0 = 300$ K, $\sigma = 0.33$ and α_g: 0.15(1); 0.2(2); 0.3(3).

containing metallocomplex monomers with acryl amide (general formula—AAM·Co(NO_2)$_3$·2H_2O). The experimental technique of Co-containing metallocomplex monomer's frontal polymerization is described in detail in [16]. Frontal polymerization was carried out with different temperatures of initiation. Experimental results on the establishment of steady state of frontal polymerization velocity depending on the initiation temperature are presented in Fig. 10.

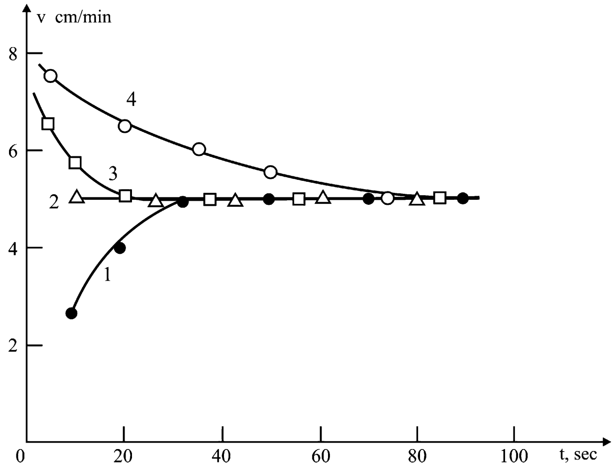

Fig. 10. Dependence of the propagating front velocity on the initiation temperature for the polymerization of Co-containing metallocomplex monomers. T_i °C: 120(1); 220(2); 270(3); 320(4).

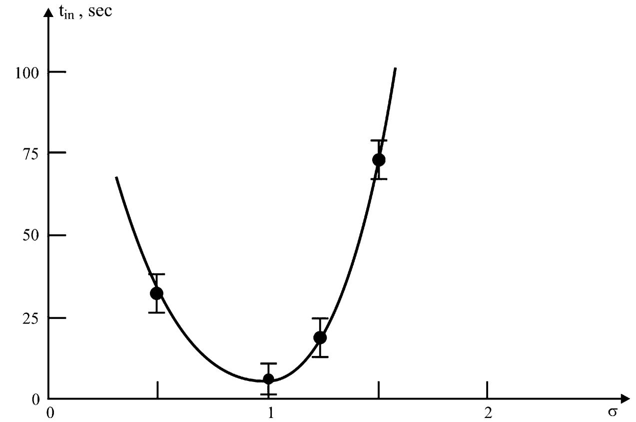

Fig. 11. The dependence of the induction period on the initiation temperature.

It should be mentioned that the maximal heating temperature for the Co-containing metallocomplex monomer is approximately 220 °C [16]. As it can be seen from curve 1 in Fig. 10 at low initiation temperatures ($T_i = 120$ °C) the velocity of non-steady front increases up to its steady value of ~5 cm min^{-1}. At the same time the non-steady time interval corresponds to ~30 s.

When initiating the front of polymerization by the temperature equal to the temperature of maximal heating ($T_i = 220$ °C), the steady value of the front velocity is established rather quickly (curve 2, Fig. 10).

For the frontal polymerization initiated by the temperature higher than the temperature of maximal heating ($T_i = 270$ and 320 °C), the time of steady-state establishment sufficiently depends on the initiation temperature (Fig. 10, curves 3 and 4). For example, at $T_i = 270$ °C t_{in} is about 20 s, whereas at $T_i = 320$ °C the time of the steady-state establishment is approximately 80 s.

Experimental results presented in Fig. 10 indirectly justify the theoretical data presented in Figs. 1, 6 and 7.

For the direct confirmation of theoretical results, from data in Fig. 10 the dependence of time of steady-state establishment on the initiation temperature can be plotted. Fig. 11 illustrates the obtained results.

As it can be seen from Fig. 11, the minimal value of the induction period in accordance with the obtained theoretical results is at initiation temperature interval of 170–250 °C. When increasing or decreasing the initiation temperature of the reaction front, the induction period increases.

Thus, experimental results obtained for frontal polymerization of Co-containing metallocomplex monomers (Fig. 11) completely confirm theoretical results presented in Section 2.

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