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# On principal approximations in theory of frontal radical polymerization of vinyl monomers

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**Abstract. The principal approximations used in the theory of frontal polymerization of vinyl monomers are considered and quantitative estimates of their applicability are given. It is shown that stationary state is met with rather high accuracy under frontal radical polymerization conditions. The effect of the polymer – monomer equilibrium on the limiting temperature of the thermal polymerization autowaves and on the degree of conversion is considered. The temperature and conversion profiles for narrow and broad reaction zones are analyzed and the results of studies on the derivation and use of criterial conditions for the principle of quasi-stationary concentrations in theory of frontal radical polymerization are discussed. The bibliography includes 78 references.**

## I. Introduction

Local heating of reactive media by an external heat source causes the development of an exothermic reaction. Heat released during the process is transferred by the heat conduction mechanism to neighbouring layers where the reaction begins, and thus a thermal wave is formed, which spontaneously propagates through the reaction medium.

Typical examples of thermal waves of chemical nature are provided by the flame propagation in gases,[1–4] self-propagating high-temperature synthesis,[5–12] glow waves in solid nitrogen,[13] heterogeneous catalytic reactions on smooth surfaces[14] and frontal polymerization.[15–35]

The theory of thermal waves studies the character of wave propagation, the extent to which it can be treated stationary, the dependence of the stationary velocity and the wave structure on various macrokinetic factors, methods of wave initiation, stability, the oscillatory and spinning regimes, as well as the existence and uniqueness of thermal chemical waves. In addition to the characteristics mentioned above, investigations of the dependence of the degree of conversion, the molecular mass and the molecular mass distribution of the polymer formed on various kinetic, macrokinetic and thermal physical parameters are of great practical importance for frontal polymerization.

It should be noted that, compared to traditional methods of fabrication of polymeric materials and various composites based on them, frontal polymerization offers a number of significant advantages. In particular, this technique makes it possible to obtain polymeric materials with novel[36–44] and improved[45–52] properties, to synthesize polymeric nanocomposites[53, 54] with uniform distribution of nanoadditives in the polymer matrix and to design[55] new energy-saving, high-performance and environmentally safe production facilities.

Comprehensive experimental and theoretical research on flame propagation in gases began long before the studies of related phenomena in condensed media. Meanwhile, an analogy between these processes makes it possible to apply the approximations and advances in well-developed theory of flame propagation in gases to condensed media and, in particular, to frontal polymerization. However, it should be noted that in this case the principal approximations used in the studies of various problems concerning the propagation of a reaction front in gases and in condensed media require additional substantiation. In this respect, one should analyze the concepts of the accuracy of establishment of the steady state and the correctness of the use of the notion 'narrow reaction zone' in the case of frontal radical polymerization. Significant problems in theory of frontal poly-

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merization also include the approximation based on the use of the principle of quasi-stationary concentrations and the effect of the polymer–monomer equilibrium on the dynamics of the reaction front propagation.

## II. On the steady state of frontal polymerization

The meaning of the most important dimensionless parameters [$\beta = R_g T_k/E$, $\Gamma = R_g T_k T_0/E(T_k - T_0)$, for literal notations, see text after Eqns (1) and (2)] for the thermal wave front propagation in gases and condensed media and for the frontal polymerization are quite similar, whereas the thermal effects, activation energies of reactions and, therefore, the adiabatic heating temperature and the thermal wave propagation velocities in the case of combustion and polymerization differ significantly. For instance, the adiabatic heating temperatures of polymerizable media are in the range from about 100 to 250 °C (*cf.* nearly 1000–3000 °C for combustion), while the combustion wave propagates more than tenfold faster than the polymerization front. Taking account of these data and following the main concepts,[1,6] we will consider the physical prerequisites to the existence of stationary combustion and frontal polymerization waves.

The problem of stationary, normal flame propagation in gases was first studied by Zeldovich and Frank-Kamenetskii.[1] The propagation of a thermal wave from a chemical reaction is described by the one-dimensional heat conduction and diffusion equations. In this case, the stationary character of the problem ($x = x' + ut$, $u$ is the normal flame propagation velocity, $x$, $x'$ are coordinates and $t$ is time) makes it possible to consider the heat conduction and diffusion equations as ordinary rather than partial differential equations:

$$c\rho u\frac{dT}{dx} = \lambda\frac{d^2T}{dx^2} + QV, \tag{1}$$

$$u\frac{da}{dx} = D\frac{d^2a}{dx^2} - V, \tag{2}$$

where $c$ is the heat capacity, $\rho$ is the density, $\lambda$ is the heat conductivity coefficient, $D$ is the diffusion coefficient, $Q$ is the thermal effect of the reaction per unit mass, $V$ is the rate of conversion [for a monomolecular reaction, $V = k_0 \exp(-E/R_g T)a$, $k_0$ is the pre-exponent, $E$ is the activation energy and $R_g$ is the universal gas constant] and $a$ is the concentration of the reactant.

The boundary conditions for Eqns (1) and (2) have the form:

$$\begin{aligned} &x = -\infty,\ T = T_0,\ a = 1; \\ &x = +\infty,\ \frac{dT}{dx} = 0,\ T = T_k = T_0 + \frac{Q}{c\rho},\ a = 0, \end{aligned} \tag{3}$$

where $T_0$ and $T_k$ are the initial and final temperature, respectively. The heat flow and the flow of matter at the boundaries $x = \pm\infty$ are equal to zero.

Reduction of the system of equations to only two equations in the case of complex kinetics of the chemical reaction is based on the assumption that the reaction is completely characterized by the corresponding kinetics equation,[1] which includes only one starting reactant. Other components of the reaction system including possible intermediates are characterized by nearly equal diffusion coefficients. These assumptions mean that all rate-limiting intermediates are in the quasi-equilibrium state.

A significant aspect of theory of flame propagation in gases is similarity between the temperature and concentration fields in a thermal wave;[1] it follows that the total enthalpy of the gas mixture in the reaction zone is a constant. The similarity between the temperature and concentration fields allows one to relate the concentration to temperature and to suppose that the rate of heat release depends only on temperature. Thus, to solve the problem is to solve only one equation (the heat conduction equation or the diffusion equation). Indeed, having made some transformations[1] in Eqns (1)–(3), assumed that the quantities $\chi$ ($\chi = \lambda/c\rho$) and $D$ have close values ($\chi \approx D$) for gases and denoted $H = cT + Qa$, the solution to the transformed equation can be represented as follows:

$$c(T - T_0) = Q(1 - a) \text{ or at } a = 0\ T_k = T_0 + \frac{Q}{c}, \tag{4}$$

which just points to the similarity between the temperature and concentration fields in the thermal wave. Expression (4) allows one to express the concentration ($a$) through temperature and thus reduce the system of two equations (1) and (2) to one equation:

$$u\frac{dT}{dx} = \chi\frac{d^2T}{dx^2} + V(T), \tag{5}$$

$$x = -\infty,\ T = T_0;\ x = +\infty,\ T = T_k,$$

$$\text{where } V(T) = k_0 \exp\left(-\frac{E}{R_g T}\right)(T_k - T).$$

The solvability of Eqn (5) for an arbitrary case of the rate heat release $V(T)$ was studied.[3] It was shown that Eqn (5) has no solution at $V(T_0) \neq 0$. At $V(T_0) = 0$ and $V'(T) > 0$, there is an infinite number of solutions. At $V(T_0) = 0$ and $V'(T) \leqslant 0$, there is a unique solution to Eqn (5). Owing to high activation energies, many chemical reactions correspond to the last-mentioned case. However, it should be noted that the reaction can occur, although very slowly, for all real reaction systems at temperatures close to $T_0$, *i.e.*, $V(T_0) > 0$. Therefore, at $V(T_0) > 0$ the heat conduction equation has no stationary solution; therefore, one should understand the physical prerequisites responsible for the lack of steady-state thermal regimes of combustion and frontal polymerization. The case in point is that at a non-zero rate reaction in the starting reaction medium the degree of conversion at the forefront of the combustion zone continuously increases (the more distant the reacting layer of the starting reactant from the combustion zone the higher the degree of conversion). This leads to the situation where the velocity of the combustion wave becomes time dependent and, consequently, there should be no stationary thermal regimes of the combustion wave propagation. However, the authors of Ref. 6 pointed that '... it would be incorrect to conclude that a stationary regime is physically impossible. The lack of solution to the stationary problem at $V(T_0) > 0$ means that the notion of stationary regime of propagation of a combustion wave is approximate'. Therefore, one should determine the extent of accuracy of stationary regimes for the reaction front propagation in gases and condensed media and for frontal polymerization. A possible criterion for the accuracy of stationary regimes of

propagation of heat chemical waves is the ratio of the rate of the chemical reaction at the adiabatic heating temperature ($T_k$) to the reaction rate at the initial temperature ($T_0$).[2] Clearly, the larger this ratio the higher the accuracy of stationary wave regimes. Using the activation energy, initial temperature and adiabatic heating temperature typical of combustion ($E \approx 120$ kJ mol$^{-1}$, $T_0 = 300$ K, $T_k = 2000$ K), this ratio was estimated [2] at

$$\frac{\exp(-E/R_g T_k)}{\exp(-E/R_g T_0)} \approx e^{42.5} \approx 4 \times 10^{18};$$

this value remains virtually unchanged when varying $E$, $T_0$, $T_k$ within the limits corresponding to combustion. Based on the estimate,[2] one can suggest that the notion of stationary propagation of combustion wave holds with 'exponential' [6] accuracy.

Now we will assess the accuracy of the notion of stationary regimes for frontal polymerization. To this end, we will compare the activation energies of the key stages of radical polymerization of vinyl monomers:

$$\text{initiator decomposition: I} \xrightarrow{k_i} 2\,\text{R}, \tag{6}$$

$$\text{chain propagation: R} + \text{M} \xrightarrow{k_p} \text{R}, \tag{7}$$

$$\text{bimolecular chain termination: R} + \text{R} \xrightarrow{k_t} \text{P}, \tag{8}$$

where I is initiator; M is monomer; R and P are the reactive ('living') and pendant ('dead') macromolecules; $k_i = k_{i0}\exp(-E_i/R_gT)$, $k_p = k_{p0}\exp(-E_p/R_gT)$, $k_t = k_{t0}\exp(-E_t/R_gT)$ are the temperature dependences of the rate constants for initiator decomposition, chain propagation and bimolecular chain termination, respectively; $k_{i0}$, $k_{p0}$, $k_{t0}$ are the corresponding pre-exponents; and $E_i$, $E_p$, $E_t$ are the activation energies of the corresponding reactions.

The characteristic values of activation energy of particular stages for monomers and initiators of different nature are as follows: $E_i \approx 100-150$ kJ mol$^{-1}$, $E_p \approx 15-40$ kJ mol$^{-1}$, $E_t \approx 2-20$ kJ mol$^{-1}$; the thermal effect of polymerization varies from 20 to 100 kJ mol$^{-1}$.

From these data it follows that if the polymerizing medium contains free radicals, polymerization will proceed at a rather high rate even at temperatures close to room temperature ($T_0 \approx 300$ K). This is substantiated by the data on the initiation of radical polymerization of vinyl monomers under the action of peroxide–amine complex systems.[56–62] Therefore, unlike combustion, the accuracy of the notion of stationary frontal regimes should be compared using the rates of initiator decomposition at the temperatures $T_k$ and $T_0$ rather than the polymerization rates and using the thermal effect of polymerization to determine $T_k$. The ratio of the initiation rates for the maximum activation energies of initiator decomposition and, correspondingly, the thermal effects of polymerization gives a value of $4.5 \times 10^{11} - 4 \times 10^{13}$. Prior to comparing this result with the published value [2] we will assume that at the temperature $T_k$ the initiator is consumed after 1 min rather than 1 ms; this is more realistic for frontal polymerization. Then, using a front propagation velocity of 3 cm min$^{-1}$, which is typical of frontal polymerization, we get that at the temperature $T_0$, the initiator is completely consumed after the front travels a distance of $1.2 \times 10^7$ km from the reactor (*cf.* $1.6 \times 10^9$ km for combustion [2]). Therefore, for many polymerizable media the notion of stationary propagation of polymerization waves holds with high accuracy.

For the minimum activation energy of initiator decomposition and the thermal effect of polymerization the ratio of the initiation rates is in the range from $4 \times 10^4$ to $6 \times 10^6$. Strictly speaking, stationary regimes of frontal radical polymerization are impossible in these cases.

Thus, the lack of rigorous solution to stationary regimes of the equation of heat conduction with a real source of heat release requires modification of the problem in such a manner that the approximate solution be consistent with the stationary regime which is practically implemented. Various methods of modification with analysis of the initial and boundary conditions for the equation of heat conduction were comprehensively treated in the monograph.[6] The theory of combustion most widely uses a modification proposed in Ref. 4. In this case, the true rate of heat release $QV$ in Eqn (1) is replaced by an effective source $QV_e$, which is equal to zero near the initial temperature $T_0$ and to the true source $QV$ otherwise, *i.e.*

$$V_e = \begin{cases} 0 \text{ at } T_0 \leqslant T < T_1 \\ V \text{ at } T_1 \leqslant T < T_k. \end{cases} \tag{9}$$

In the conditions (9), $T_1$ is the 'cut-off' temperature of the heat release source, *i.e.*, it is admitted that at $T_0 < T < T_1$ the rate of heat release is zero. Clearly, replacement of $V$ by $V_e$ excludes the effect of the reaction on the stationary regime of the reaction front propagation and, therefore, the stationary solution to problem (1) with the boundary conditions (3) does exist, being unique.[4] However, it should be noted that the modification proposed in Ref. 4 is appropriate if the solution to the problem is virtually independent of 'forcedly' introduced parameter $T_1$. For this reason, a thorough study [5] of the dependence of the bulk combustion rate ($\dot{m}$) on $T_1$ (the source 'cut-off' temperature) was performed taking an irreversible first-order reaction in a gas at Lewis numbers equal to unity ($Le = D/\chi = 1$). The scale factor $\dot{m}_*$ was calculated in the narrow reaction zone approximation. By analogy with Ref. 5, the dependence of the ratio $\dot{m}/\dot{m}_*$ on the source 'cut-off' temperature was calculated for frontal radical polymerization of vinyl monomers. To this end, a numerical study was performed of the system of equations, which describes the changes in the temperature ($T$) and concentrations of the initiator ($I$), monomer ($M$) and macroradicals ($R$) under conditions of one-dimensional polymerization front propagation:

$$c\rho\frac{\partial T}{\partial t} = \lambda\frac{\partial^2 T}{\partial x^2} + Q\frac{\partial M}{\partial t}, \tag{10}$$

$$-\frac{\partial I}{\partial t} = -W_i = fk_iI, \tag{11}$$

$$-\frac{\partial M}{\partial t} = k_pRM, \tag{12}$$

$$\frac{\partial R}{\partial t} = fk_iI - k_tR^2, \tag{13}$$

where $W_i$ is the initiation rate and $f$ is the initiation efficiency (for simplicity, from this point on we set $f = 1$).

The initial and boundary conditions for the system of equations (10)–(13) are as follows:

$$t = 0,\ T(x) = T_0,\ I = I_0,\ M = M_0,\ R = 0$$

for any $0 < x < +\infty$;

$$x = -\infty\ ;\ T = T_s;\ \left.\frac{\partial T}{\partial x}\right|_{x \to +\infty} = 0 \quad \text{for any } t, \tag{14}$$

here $T_s$ is the temperature of the external source.

The system of differential equations (10)–(13) with the conditions (14) was solved numerically using the finite difference method in explicit form as well as the kinetic and thermal physical parameters characteristic[56–62] of radical polymerization of vinyl monomers.

The scale factor $\dot{m}_*$ was the expression for the bulk velocity of stationary front propagation derived[18] in the framework of the narrow reaction zone approximation with inclusion of the gel effect for frontal polymerization of methyl methacrylate.

The results of numerical calculations [$\gamma = R_g T_k^2/E(T_k - T_0)$] are presented in Fig. 1. The curve (by analogy with the results reported in Ref. 5) exhibits three clearly seen characteristic portions of changes in the dependence of $\dot{m}/\dot{m}_*$ on $T_1$ in the form of dimensionless temperature $(T_1 - T_0)/(T_k - T_0)$. As $T_1$ approaches the initial temperature ($T_0$) of the reaction medium, the $\dot{m}/\dot{m}_*$ ratio abruptly increases. This behaviour of the $\dot{m}/\dot{m}_* \to \infty$ at $T_1 \to T_0$ ratio is equisignificant to the fact that polymerization begins simultaneously at all points $x$. Therefore, the $\dot{m}/\dot{m}_*$ ratio formally tends to infinity; however, from informal point of view, the system (13)–(17) has no wave solutions.

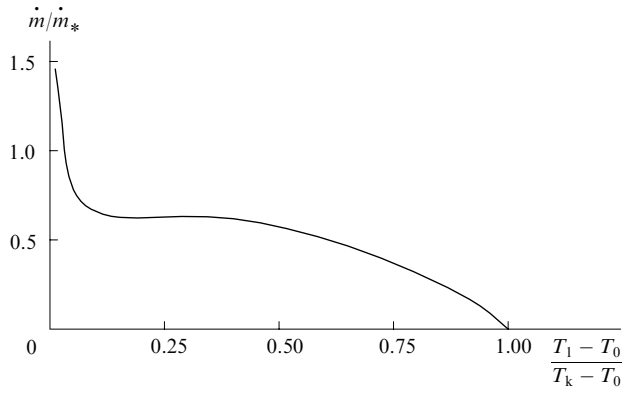



**Figure 1.** Dependence of $\dot{m}/\dot{m}_*$ ratio on dimensionless temperature (source 'cut-off') $T_1$ at $\gamma = 0.025$ and $\Gamma = 0.014$.

At high temperatures, the $\dot{m}/\dot{m}_*$ ratio decreases as a consequence of inadmissibility of the forced setting of the rate of heat release at high temperatures equal to zero, because the reaction rate is high.

At temperatures corresponding to a well-defined plateau in the curve shown in Fig. 1, the polymerization front propagation velocity is independent of the 'cut-off' temperature $T_1$. Therefore, by analogy with combustion in the modified problem the $T_1$ values should be chosen in the temperature range corresponding to the plateau. Thus, based on Fig. 1, one can suggest that the modification[4] is also suitable for frontal radical polymerization of vinyl monomers.

Other types of modification of the problem of stationary combustion front with the corresponding boundary conditions and their analysis have been considered in detail in the monograph[6] (see above) and we thus leave them out of consideration.

## III. The polymer–monomer equilibrium, the limiting polymerization temperature and the degree of conversion

For many processes of bulk radical polymerization of vinyl monomers, the chain propagation step is considered irreversible because the equilibrium concentration of monomer ($M_{eq}$) at the chosen temperatures of isothermal polymerization is negligible compared to its bulk concentration. For instance, the equilibrium concentrations of styrene and methyl methacrylate are $10^{-6}$ and $10^{-3}$ mol litre$^{-1}$, respectively, at room temperature.

For high-temperature polymerization regimes (adiabatic, frontal, *etc.*), where the running temperature of the medium significantly increases in the course of polymerization, the role of the reversible reaction may appear to be quite important. Because of this the velocity of propagation of the methyl methacrylate polymerization front is sometimes calculated with inclusion of polymer–monomer equilibrium (see, *e.g.*, Ref. 28). Therefore, in order to assess the reliability of the published results[17–19,21,25] and to carry out further theoretical studies of frontal polymerization, one should establish how the equilibrium stage of the chain propagation reaction affects the kinetics of high-temperature polymerization regimes, the limiting degree of conversion and, correspondingly, the front propagation velocity. Clearly, this requires that the three-stage scheme (6)–(8) of radical polymerization, which already includes the chain propagation reaction (7), be augmented with the depolymerization

$$\mathrm{R} + \mathrm{M} \underset{k_d}{\overset{k_p}{\rightleftharpoons}} \mathrm{R},$$

where $k_d$ is the rate constant for the depolymerization reaction.

With allowance for the depolymerization reaction, the rate of monomer consumption is given by

$$\frac{dM}{dt} = -k_p RM + k_d R = -k_p R\left(M - \frac{1}{K}\right), \tag{15a}$$

where $K = k_p/k_d$ is the equilibrium constant of polymerization.

In thermodynamic equilibrium, the rates of the forward and reverse reactions are equal and therefore one has

$$\frac{dM}{dt} = 0 \quad \text{and} \quad \frac{1}{K} = M_{eq}.$$

Then, expression (15a) can be re-written in the form:

$$\frac{dM}{dt} = -k_p R(M - M_{eq}). \tag{15b}$$

An increase in the reaction temperature affects the polymerization rate in a complex manner, because it is determined by the competing action of temperature on the rate constant for chain propagation and on the equilibrium

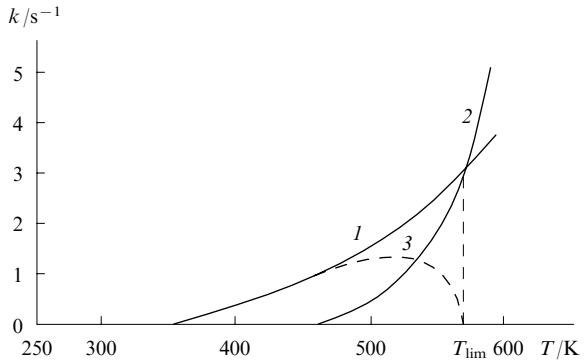



**Figure 2.** Temperature dependence of $k_pM$ (*1*), $k_d$ (*2*) and $k_pM-k_d$ (*3*) for styrene polymerization.[61]

concentration of the monomer. This is just the reason for the fact that the polymerization rate[61] decreases (Fig. 2) starting at a particular temperature and that the rates of the forward and reverse reactions become equal to each other from the very beginning of the polymerization process as a certain critical temperature is attained. Clearly, in this case the polymerization is impossible and the corresponding critical temperature is called the limiting polymerization temperature ($T_{lim}$). At temperatures below $T_{lim}$, the polymerization–depolymerization equilibrium can be analyzed using the expression for the change in the Gibbs free energy

$$\Delta G = \Delta G^\circ + R_g T \ln \Pi, \tag{16}$$

where $\Pi$ is a polynomial similar to the equilibrium constant (it includes the reactant activities in a nonequilibrium rather than equilibrium state; in equilibrium, one has $\Delta G = 0$ and $\Pi = K$). The parameter $\Delta G^\circ$ is the change in the Gibbs free energy of the monomer–polymer mixture under standard conditions (for monomer: a liquid state or 1 M solution; for polymer: an amorphous state, a crystalline state with low degree of crystallinity or a 1 M solution with respect to the repeating unit of the polymer).

The change in the Gibbs free energy in the standard state is given by

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \tag{17}$$

The quantities $\Delta H^\circ$ and $\Delta S^\circ$ are related to temperature as follows:

$$\Delta H^\circ_T = \Delta H^\circ_{298} + \int_{298}^{T} \Delta C_p \mathrm{d}T,$$
$$\Delta S^\circ_T = \Delta S^\circ_{298} + \int_{298}^{T} \frac{\Delta C_p}{T} \mathrm{d}T, \tag{18}$$

where $\Delta C_p$ is the specific heat at constant pressure difference between the monomer and polymer. The $\Delta H^\circ$ and $\Delta S^\circ$ values for a number of monomers are listed in Table 1.

Usually, the $\Delta C_p$ value is at most 42 J mol$^{-1}$ K$^{-1}$; therefore, $\Delta H^\circ$ and $\Delta S^\circ$ vary insignificantly as the temperature rises and, to a first approximation, $\Delta G^\circ$ can be treated as a linear function of temperature.

Most polymerization processes are exothermic ($\Delta H < 0$) and accompanied by the loss of entropy ($\Delta S < 0$). The parameter $\Delta G$ increases with temperature and becomes equal to zero at the limiting polymerization temperature. Then, taking into account Eqns (16) and (17), one gets

$$\Delta G^\circ = \Delta H^\circ - T_{lim}\Delta S^\circ = -R_g T_{lim} \ln K. \tag{19}$$

From Eqn (19) one has for $T_{lim}$

$$T_{lim} = \frac{\Delta H^\circ}{\Delta S^\circ - R_g \ln K} \tag{20}$$

In most cases, the polymerization of vinyl monomers is characterized by rather high $T_{lim}$ values. Table 2 lists the $\Delta G^\circ$ and $T_{lim}$ values for a number of monomers.

If polymerization of vinyl monomers proceeds under non-isothermal conditions (adiabatic, frontal polymerization, *etc.*), the limiting degree of conversion is determined by the kinetic features of the radical polymerization process rather than polymer–monomer thermodynamic equilibrium. This can be substantiated using experimental data on adiabatic initiated and bulk thermal polymerization of styrene.[61,62] It was shown[19,25,62] that the degree of conversion attained under conditions of adiabatic dicyclohexyl peroxydicarbonate-initiated polymerization of styrene, methyl methacrylate and n-butyl methacrylate is 0.4–0.45, whereas adiabatic thermal polymerization of styrene is

**Table 1**. Standard enthalpies and entropies of polymerization of monomers at 298 K.[61,63–67]

| Monomer | Phase state | | $-\Delta H^\circ$ /kJ mol$^{-1}$ | $-\Delta S^\circ$ /J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|
| | monomer | polymer | | |
| Acrylamide | aqueous solution | aqueous solution | 83 | – |
| Acrylic acid | the same | the same | 77.1 | – |
| Acrylonitrile | liquid | amorphous | 76.7 | – |
| Acrolein | " | " | 80.0 | – |
| Butadiene | " | " | 73.8 | 85.9 |
| Vinyl acetate | " | " | 89.3 | 109.8 |
| Isoprene | " | " | 75.0 | 101.4 |
| Methacrylic acid | " | " | 42.3 | – |
| Methacrylamide | aqueous solution | aqueous solution | 56.2 | – |
| Methyl methacrylate | liquid | amorphous | 58.2 | 117.4 |
| Styrene | " | " | 70.0 | 104.8 |
| α-Methylstyrene | " | " | 35.4 | 104.0 |
| Tetrafluoroethylene | " | " | 155.0 | 112.3 |

**Table 2**. $\Delta G^\circ$ and $T_{lim}$ values for polymerization of monomers.[a]

| Monomer | $-\Delta G^\circ$ /kJ mol$^{-1}$ | $T_{lim}$ /K |
|---|---|---|
| Styrene | 38.5 | 670 |
| Tetrafluoroethylene | 121.5 | 1370 |
| Methyl methacrylate | 20.1 | ~470 |
| α-Methylstyrene | 4.2 | 340 |

[a] All monomers listed are liquids while all polymers listed are amorphous substances.

characterized by nearly 100% conversion. Indeed, the kinetic scheme (6)–(8) allows the limiting degree of conversion in isothermal radical polymerization of vinyl monomers to be written as follows:

$$\alpha_{lim} = 1 - \exp\left[2k_{p0}\left(\frac{1}{k_{t0}k_{i0}}\right)^{1/2} I_0^{1/2} \exp\left(-\frac{E_{ef}}{R_g T}\right)\right].$$

Since for most monomers that are polymerized by the radical mechanism the exponent on the right side of this equation is much less than unity, one gets $\alpha_{lim} \approx 1$.

For adiabatic radical polymerization the equation determining the limiting polymerization temperature and, therefore, the degree of conversion,[19,62] has the form:

$$2k_{p0}\left(\frac{2}{k_{i0}k_{t0}}\right)^{1/2} \frac{1}{I_0^{1/2}} = -\frac{R_g T_{lim}^2}{E_{ef}(T_a - T_{lim})} \exp\left(-\frac{E_{ef}}{R_g T}\right) + \\ + \frac{R_g T_0^2}{E_{ef}(T_a - T_0)} \exp\left(\frac{E_{ef}}{R_g T_{lim}}\right),$$

where $T_a$ is the temperature of adiabatic heating reaction of the reaction mixture at 100% consumption of monomer.

The dependence of the limiting degree of conversion on the initial initiator concentration calculated using this equation is shown in Fig. 3. As can be seen, at low initiator concentrations the parameter $\alpha_{lim}$ abruptly increases and reaches a value of about 0.5. This behaviour can be explained by the fact that, owing to high activation energy of initiator decomposition, the initiator is completely consumed long before a 100% consumption of the monomer is attained. Therefore, further increase in the initiator concentration starting with $4 \times 10^{-2}$ mol litre$^{-1}$ has little effect on the limiting degree of conversion.

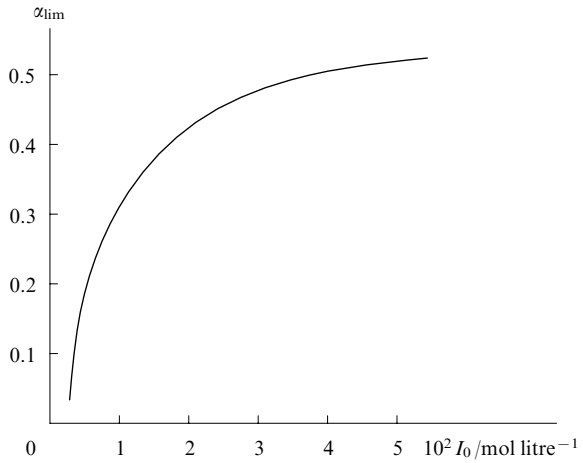



**Figure 3.** Effect of initial initiator concentration on the degree of polymerization.[62]

Numerical calculations for the system of kinetic equations derived from the three-stage kinetic scheme (6)–(8) taking account of Eqn (15b) showed that the polymer–monomer equilibrium has almost no effect on the limiting degree of conversion. This suggests that for all high-temperature regimes of radical polymerization (in particular, frontal polymerization), the reversibility of the chain propagation stage characteristic of most types of radical polymerization of vinyl monomers can be ignored.

## IV. The narrow reaction zone approximation in theory of frontal polymerization

The theory of frontal polymerization mainly uses the narrow reaction zone approximation[4] to determine the stationary propagation velocity of thermal waves. It should be noted that this technique proved itself in solving various problems in theory of the reaction front propagation. This is due to two factors, a high activation energy of the chemical reaction ($E/R_g T_k \gg 1$) and a zero or first order of the reaction with respect to reactants. However, in the case of frontal radical polymerization the overall order of the reaction is greater than unity, while the effective activation energies are low (60–100 kJ mol$^{-1}$); as a consequence, the reaction zone may appear to be not narrow. Therefore, if one deals with propagation of the polymerization front, the temperature range in which most part of monomer undergoes conversion into polymer, depends on kinetic factors, *e.g.*, the order of the reaction with respect to monomer and initiator, the activation energies and the rate constants for chain initiation and chain propagation. Thus, frontal polymerization can proceed in the narrow reaction zone regime (polymerization at nearly constant temperature close to the adiabatic heating temperature) or in the broad reaction zone regime (polymerization under continuous increase in the temperature of the medium).

Noteworthy is a wide application of the principle of quasi-stationary concentrations (QSC) in studies on radical polymerization.[56–60] Therefore, in developing the theory of radical frontal polymerization one should establish the conditions for applicability of two fundamental approximations:

— the QSC principle and
— the narrow reaction zone approximation.

It was shown[62] that the QSC principle is not always applicable under conditions of adiabatic polymerization of vinyl monomers. At the same time, the applicability of the QSC principle and its accuracy under the frontal polymerization conditions are determined by the particular (narrow or broad) type of the reaction zone.[17,25,68,69] Therefore, prior to discussing the applicability of the QSC principle to frontal radical polymerization of vinyl monomers one should analyze quantitative relations between the temperature and conversion profiles.

## V. Analysis of the conversion and temperature profiles under frontal radical polymerization conditions

Following Refs 17, 5, 68 and 69, we will consider frontal radical polymerization obeying the three-stage scheme (6)–(8), which includes the initiation by initiator decomposition, chain propagation and bimolecular chain termi-

nation by the recombination mechanism. The kinetic scheme (6)–(8) does not include chain transfer to monomer, polymer and solvent with subsequent regeneration of radicals, because these reactions, except for very rare cases, have no effect on the concentration of macroradicals and hence, on the polymerization rate.

The system of differential equations (10)–(13) with the conditions (14) was solved numerically using the kinetic and thermal physical parameters characteristic of radical polymerization of vinyl monomers. Figure 4 presents the temperature and conversion profiles along the direction of propagation of the polymerization front.

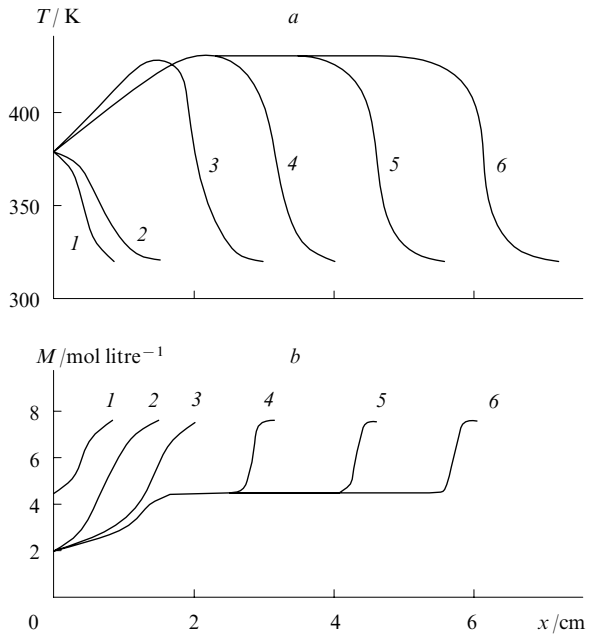



**Figure 4.** The temperature (*a*) and monomer concentration (*b*) profiles along the direction of propagation of the reaction front.[19]
Time/s: 200 (*1*), 800 (*2*), 1600 (*3*), 2400 (*4*), 3000 (*5*), 3600 (*6*);
$I_0 = 10^{-2}$ mol litre$^{-1}$, $M_0 = 8$ mol litre$^{-1}$.

As can be seen, layers near the reactor inlet are heated by an external heat source ($T_s = 380$ K), which leads to polymerization in these layers. As the polymerization develops, a fraction of heat released is transferred to the neighbouring layers where polymerization is initiated and, thus, at a distance of 2 to 3 cm from the reactor inlet the external heat source no longer plays a significant role. From this instant on propagation of the polymerization front is due to exothermicity of the reaction in a self-sustained regime characterized by constant values of the degree of conversion, maximum heating temperature and the front propagation velocity along the whole length of the reactor. In the steady-state frontal polymerization the degree of conversion is determined by the consumption of initiator.[17,19,62] A comparison of curves *1* and *2* in Fig. 5*a*,*b*, which characterize the steady-state frontal polymerization, shows that the width † of the reaction zone ($\Delta x_M$) is much

† It is accepted that the width of the reaction zone and the width of the range of temperature changes are intervals along the reaction front coordinate ($x$) that cover conversion of the most part of monomer ($\Delta x_M$) and temperature changes from the maximum to the initial value ($\Delta x_T$), respectively.

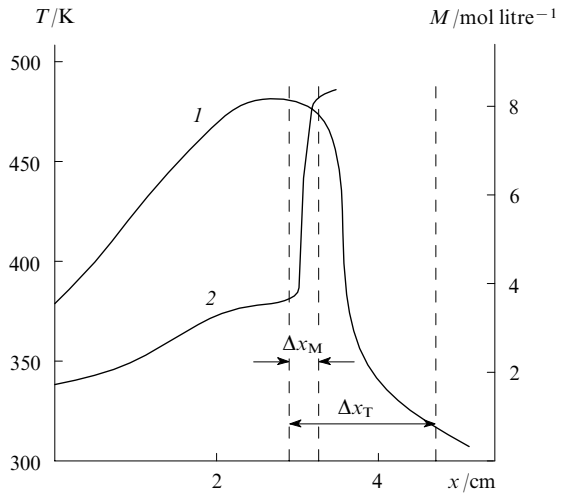



**Figure 5.** The temperature (*1*) and conversion (*2*) profiles on stationary segment of the polymerization wave.
Dashed lines denote the width of the reaction zone ($\Delta x_M$) and the width of the range of temperature changes ($\Delta x_T$).[69]

smaller than that of the region in which the temperature changes ($\Delta x_T$). The bulk of the monomer reacts at temperatures close to the maximum heating temperature of the reaction mixture. In this case, the reaction zone is narrow because the polymerization occurs at the maximum heating temperature.

To study how various kinetic parameters affect the width of the reaction zone, the system of equations (10)–(13) with conditions (14) was solved numerically using various data sets including the rate constants for and activation energies of reactions, the monomer and initiator concentrations and the orders of the reactions with respect to monomer and initiator.

Based on the analysis of the results of numerical calculations, it was concluded [17,69] that the reaction zone remains narrow upon variation of the rate constants and the monomer and initiator concentrations within reasonable limits. Only if the orders of the reaction with respect to monomer and initiator increase and the effective activation energy of polymerization decreases, the reaction zone is broadened.

As an example, Fig. 6 presents the dependence of the $\Delta x_M/\Delta x_T$ ratio on the formal order of reaction with respect to monomer ($n$). At $n = 0$ or 1, the reaction zone is narrow. If $n > 1$, the reaction zone is broadened and polymerization

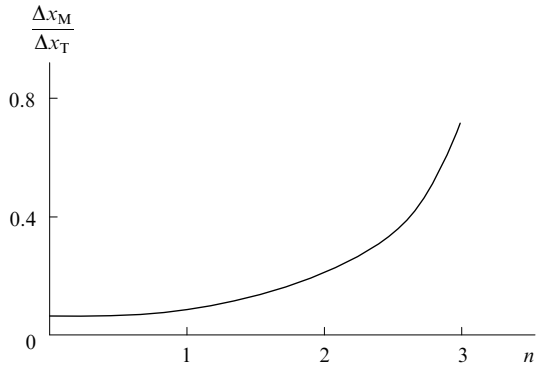



**Figure 6.** Dependence of the $\Delta x_M/\Delta x_T$ ratio on the formal order of reaction with respect to monomer.

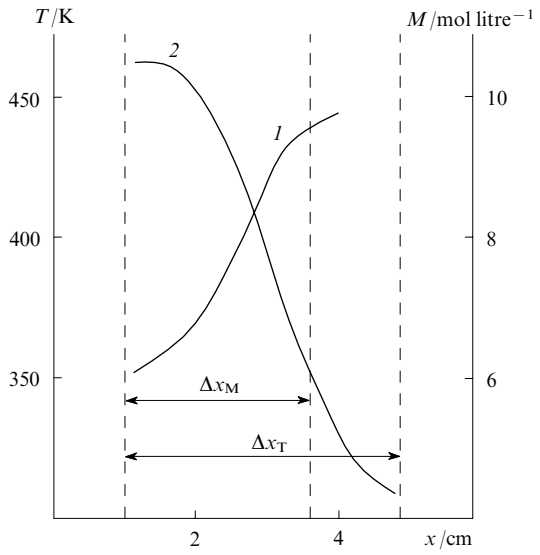



**Figure 7.** The temperature (*1*) and conversion (*2*) profiles; formal order of reaction with respect to monomer equals 3.[69]

proceeds at variable temperatures. To illustrate the notion 'broad reaction zone', Fig. 7 shows the conversion and temperature profiles; as can be seen, $\Delta x_M$ and $\Delta x_T$ are commeasurable quantities.

One should expect that broad reaction zones are possible if frontal radical polymerization of vinyl monomers involves thermal polymerization as a stage. Therefore, it is convenient to consider the formation of broad reaction zones taking thermal polymerization of styrene as an example (polymerization of many vinyl monomers can be thermally initiated). The case in point was not considered in the available studies on radical polymerization under conditions of propagation of the reaction front. Meanwhile, thermal initiation can play a significant role in conducting polymerization in similar thermal regimes, because the adiabatic heating temperature can be as high as hundreds of degrees under these conditions.

The kinetic equation for the rate of thermal polymerization (the initiation rate is proportional to the $n$th power of the monomer concentration) with allowance for the QSC approximation for macroradicals has the form [62]

$$\frac{d\alpha}{dt} = k_{ef}(1-\alpha)^{(n+2)/2} M_0^{n/2}. \qquad (21a)$$

Here $\alpha = (M_0 - M)/M_0$, $k_{ef} = k_p[k_i^1/k_{tan}(\alpha)]^{1/2}$is the effective rate constant for polymerization, $k_i^1$ is the rate constant for thermal initiation, $k_{tan}(\alpha)$ is the rate constant for bimolecular chain termination, which depends on the degree of conversion owing to gel effect.[62]

$$k_{tan}(\alpha) = k_t\mu(\alpha),\ \mu(\alpha) = \begin{cases} 1, & \text{if } \alpha \leqslant \alpha_g \\ \exp[b(\alpha-\alpha_g)], & \text{if } \alpha > \alpha_g, \end{cases} \qquad (22)$$

where $\alpha_g$ is the degree of conversion corresponding to the onset of gel effect and $b$ is the coefficient of proportionality. Taking into account expression (22) and the Arrhenius-type dependence of the effective rate constant for polymerization on temperature

$$k_{ef} = k_0 \exp\left(-\frac{E_{ef}}{R_g T}\right)$$

Eqn (21a) can be re-written as follows:

$$\frac{d\alpha}{dt} = k_0 M_0^{n/2}(1-\alpha)^{(n+2)/2}\exp\left(-\frac{E_{ef}}{R_g T}\right)\exp\left[\frac{b(\alpha-\alpha_g)}{2}\right]. \qquad (21b)$$

At $n > 1$, the use of the narrow reaction zone approximation to determine the stationary velocity of the reaction front is incorrect.[70, 71] However, these studies concerned systems (combustion of condensed media) characterized by retardation with the development of the reaction. Clearly, retardation itself causes the reaction zone to broaden irrespective of the order of a particular reaction.

The limits of applicability of the narrow reaction zone approximation in the presence of accelerating factors (*e.g.*, gel effect in the case of radical polymerization of vinyl monomers) have not been considered in the literature. Therefore, one should assess their dependence on the order of reaction taking thermal polymerization of vinyl monomers under conditions of propagation of the reaction front as an example. To this end, the stationary velocity of the reaction front was determined [72] using both the narrow and broad reaction zone approximations. The results obtained were also compared with those of numerical solution to Eqn (21b) and the equation of heat conduction (10) with the following boundary and initial conditions:

$$t = 0,\ T(x) = T_0;\ T(x=0) = T_i,\ \left.\frac{\partial T}{\partial x}\right|_{x=l} = 0 \text{ for any } t > 0,$$

$T_i$ is the initiation temperature of frontal polymerization and $l$ is the length of the sample.

First, we will consider thermal polymerization in the absence of gel effect ($\alpha = 0$). The stationary velocity of the polymerization front ($u$) is compared with the results of numerical calculations ‡ ($u'$) in Fig. 8.

In the absence of gel effect (Fig. 8, curves *1*, *3*) at $n = 1$, better results for the stationary velocity of the front propagation are obtained using the narrow reaction zone approximation (curve *1*). At $n > 1$, the reaction zone is not narrow and more correct results are obtained using the broad reaction zone approximation (curve *3*).

The gel effect causes the polymerization rate to increase. In this case, the region of applicability of the narrow reaction zone approximation is extended (curve *2*). Therefore, unlike propagation of the reaction front in a condensed medium with self-inhibition,[70, 71] this method can be used not only at $n = 1$, but also at $n > 1$. The broad reaction zone approximation in the presence of gel effect can be applied at $n \geqslant 3.5$ (curve *4*).

The dependences of the stationary velocity of the front propagation on the monomer concentration and initial temperature for thermal polymerization of styrene [72] are shown in Fig. 9.

From Fig. 9 *b* it follows that, irrespective of the initiation mechanism, $u$ changes in parallel with the monomer

‡ Equations (10) and (13) with corresponding initial and boundary conditions were solved numerically using the kinetic and thermal physical parameters taken from Refs 56–62 and 72 for $n = 1, 2, 3$. The kinetic parameters used for $n = 4, 5, \ldots$ were the data on thermal polymerization of styrene [62] with the trimolecular initiation mechanism.

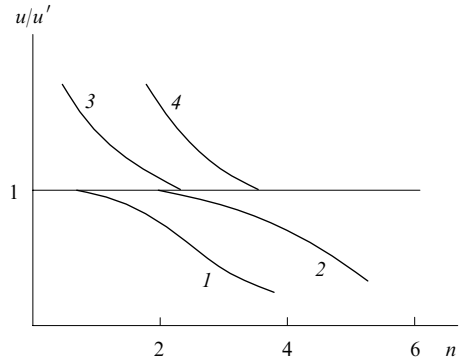



**Figure 8.** Dependence of the $u/u'$ ratio on the order of reaction; $u$ was obtained from analytical calculations using expressions for the stationary velocity of the polymerization front in the narrow (*1*, *2*) and broad (*3*, *4*) reaction zone approximation in the absence (*1*, *3*) and in the presence (*2*, *4*) of gel effect; $u'$ was obtained by numerical methods.[72]

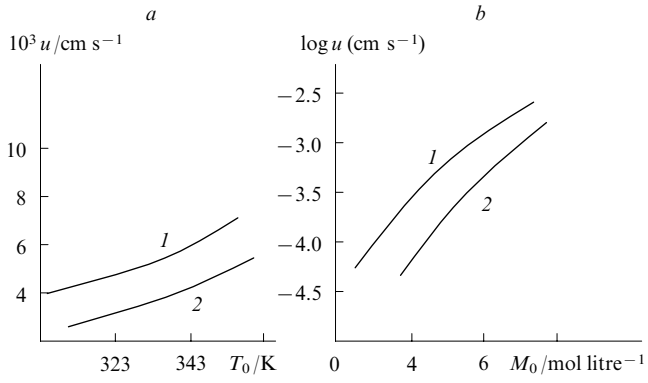



**Figure 9.** Effect of initial temperature (*a*) and monomer concentration (*b*) on the stationary velocity of the front propagation for bimolecular (*1*) and trimolecular (*2*) initiation mechanisms.[72]

concentration. However, the stationary velocity is higher in the case of bimolecular initiation.

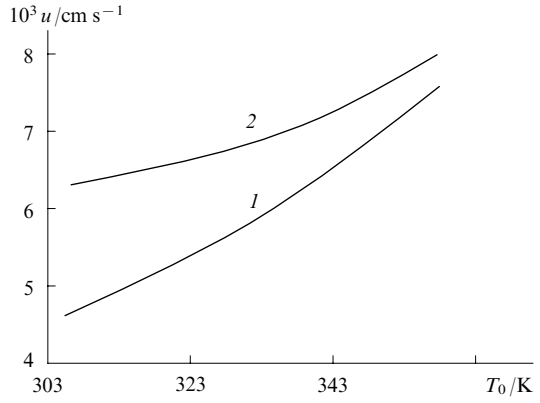



**Figure 10.** Effect of initial temperature of the medium on the stationary velocity of the front propagation in the absence (*1*) and in the presence (*2*) of gel effect.[72]

From the results obtained in Refs 17 and 72 it follows that in the polymerization of n-butyl methacrylate (the case of pronounced gel effect) the gel effect strongly affects the stationary velocity only at low temperatures and becomes less pronounced on raising the initial temperature (Fig. 10). Therefore, at temperatures close to 350 K the stationary velocity is not affected by the gel effect.

## VI. The principle of quasi-stationary concentrations: physical prerequisites

The Bodenstein–Semenov[73,74] QSC principle is widely used to solve various kinetic problems. However, rigorous mathematical substantiation of this technique in particular cases is difficult.[75–78] The situation becomes even more complicated for processes occurring under non-isothermal conditions.

Application of the QSC principle to isothermal radical polymerization of vinyl monomers is physically substantiated.[56–60] In particular, since the rate of the change in the concentration of macroradicals is much lower than the polymerization rate, *i.e.*, $|\mathrm{d}R/\mathrm{d}t| \ll |\mathrm{d}M/\mathrm{d}t|$, in the equation for the concentration of macroradicals

$$\frac{\mathrm{d}R}{\mathrm{d}t} = k_\mathrm{i}I - k_\mathrm{t}R^2 \tag{23}$$

one can assume that $\mathrm{d}R/\mathrm{d}t \approx 0$. This gives the following expression for the quasi-stationary concentration of macroradicals ($\bar{R}$):

$$\bar{R} = \left(\frac{k_\mathrm{i}I}{k_\mathrm{t}}\right)^{1/2}. \tag{24}$$

As a constant initiation rate ($k_\mathrm{i}I$ = const), the solution to Eqn (23) has the form:

$$R(t) = \left(\frac{k_\mathrm{i}I}{k_\mathrm{t}}\right)^{1/2} \mathrm{th}(k_\mathrm{i}Ik_\mathrm{t})^{1/2}t\,.$$

Based on expressions (23) and (24), one gets:

$$\frac{R(t)}{\bar{R}} = \mathrm{th}(k_\mathrm{i}Ik_\mathrm{t})^{1/2}t\,. \tag{25}$$

Analysis of Eqn (25) shows that if the average lifetime of growing polymer chains ($t_\mathrm{ch} \approx 1/(k_\mathrm{i}Ik_\mathrm{t})^{1/2}$) is much shorter than the characteristic time of polymerization [$t_\mathrm{p} \approx 1/k_\mathrm{p}\bar{R} = (1/k_\mathrm{p})(k_\mathrm{t}/k_\mathrm{i}I)^{1/2}$], *i.e.*, $t_\mathrm{ch} \ll t_\mathrm{p}$, one gets $R(t)/\bar{R} = 1$ and the QSC principle is valid. From inequality $t_\mathrm{ch} \ll t_\mathrm{p}$ it follows that

$$\frac{k_\mathrm{t}}{k_\mathrm{p}} \gg 1. \tag{26}$$

Relationship (26) is the necessary condition for application of the QSC principle. If the initiation rate varies in the course of polymerization, an additional requirement is needed, according to which the average lifetime of growing macromolecules should be much shorter than the time taken for complete consumption of initiator ($t_\mathrm{i}$). Since $t_\mathrm{i} \sim 1/k_\mathrm{i}$, from the condition $t_\mathrm{i} \gg t_\mathrm{ch}$ one gets

$$\frac{(Ik_\mathrm{t})^{1/2}}{k_\mathrm{t}} \gg 1. \tag{27}$$

Thus, simultaneous meeting the inequalities (26) and (27) based on physical considerations makes it possible to apply the QSC principle to non-isothermal radical polymerization of vinyl monomers.

Attempts to mathematically substantiate rigorous use of the QSC principle were reported.[75–78] A final solution to this problem for reversible chain reactions occurring under non-isothermal conditions is presented in Refs 76 and 77. In the case of irreversible reactions, situations with nearly-zero eigenvalues are possible. This requires additional studies on the applicability of the QSC principle. For instance, the limits of applicability of the QSC principle to adiabatic radical polymerization were determined.[62] Mathematically, here one deals[62] with the peculiar features mentioned above. In this connection, we will briefly outline the applicability of the QSC principle to adiabatic and frontal polymerization of vinyl monomers.[17, 62, 69]

## VII. The principle of quasi-stationary concentrations for adiabatic radical polymerization

As above, we will consider a three-stage (initiation, chain propagation and bimolecular chain termination) polymerization obeying the kinetic scheme (6)–(8). The relative deviation of the true concentration of macroradicals from the quasi-stationary value is characterized[62] by the parameter $\Delta = (R/\bar{R}) - 1$.

If $x = R/\bar{R}$, one has

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{1}{\bar{R}}\frac{\mathrm{d}R}{\mathrm{d}t} - \frac{R}{\bar{R}}\frac{1}{\bar{R}}\frac{\mathrm{d}\bar{R}}{\mathrm{d}t}. \tag{28}$$

Taking account of Eqn (23), the first term on the right side of Eqn (28) can be written as follows:

$$\frac{1}{\bar{R}}\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{k_\mathrm{i}I - k_\mathrm{t}x^2\bar{R}^2}{\bar{R}} = (1-x^2)k_\mathrm{t}\bar{R} = \\ = -\Delta(1+x)\sqrt{k_\mathrm{t}(t)k_\mathrm{i}(t)I(t)}\,. \tag{29}$$

The second term in Eqn (28) can be transformed as follows:

$$\frac{1}{\bar{R}}\frac{\mathrm{d}\bar{R}}{\mathrm{d}t} = \frac{\mathrm{d}(\ln\bar{R})}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\frac{1}{2}\left(\ln\frac{k_\mathrm{i}}{k_\mathrm{t}} + \ln I\right) = \\ = \frac{1}{2}\frac{1}{RT^2}(E_\mathrm{t} - E_\mathrm{i})\frac{\mathrm{d}T}{\mathrm{d}t} - \frac{1}{2}k_\mathrm{i}\,. \tag{30}$$

Now, substituting relationships (29) and (30) into Eqn (28) with allowance for $\mathrm{d}\Delta/\mathrm{d}t = \mathrm{d}x/\mathrm{d}t$, one gets the following equation for $\Delta$:

$$\frac{\mathrm{d}\Delta}{\mathrm{d}t} = -\Delta(1+x)\alpha(t) + \frac{1+\Delta}{2}\psi(t)\,,$$

where

$$\alpha(t) = \sqrt{k_\mathrm{t}(t)k_\mathrm{i}(t)I(t)};\ \psi(t) = \frac{1}{RT^2}(E_\mathrm{t} - E_\mathrm{i})\frac{\mathrm{d}T}{\mathrm{d}t} + k_\mathrm{i}(t);$$

here $\mathrm{d}T/\mathrm{d}t$ is the rate of temperature changes in the course of polymerization. In was shown[62] that if

$$Yt = \sqrt{k_\mathrm{t}(t)k_\mathrm{i}(t)I(t)}\,t \gg 1,\ Z = \sqrt{\frac{k_\mathrm{t}(t)}{k_\mathrm{i}(t)I(t)}} \ll 1, \tag{31}$$

one has $\Delta \to 0$, *i.e.*, the quasi-stationary approximation can be applied to non-isothermal radical polymerization.

A drawback of the criterial conditions (31) is that in each particular case one should have the temperature-*vs.*-time curve and the temperature dependences of the rate constants for the chain initiation and chain termination reactions. However, this drawback is compensated by the fact that the QSC principle for quasi-adiabatic and adiabatic radical polymerization can be used with a preset accuracy provided that the inequalities (31) hold. It is of importance that the inequalities (31) make it possible to evaluate, prior to consumption of initiator, the initiator concentration at which the QSC principle is still applicable.

Indeed, numerical analysis of the system of differential equations describing the three-stage adiabatic radical polymerization showed[62] that at $Yt \geqslant 10^2$ and $Z \leqslant 10^{-3}$ the QSC principle can be used with high accuracy (error less than 2%) (Fig. 11; as can be seen, curves *1* and *2* match each other).

Now, based on the aforesaid and following known concepts,[17, 25, 68, 69] we will consider the applicability of the QSC principle to frontal radical polymerization of vinyl monomers.

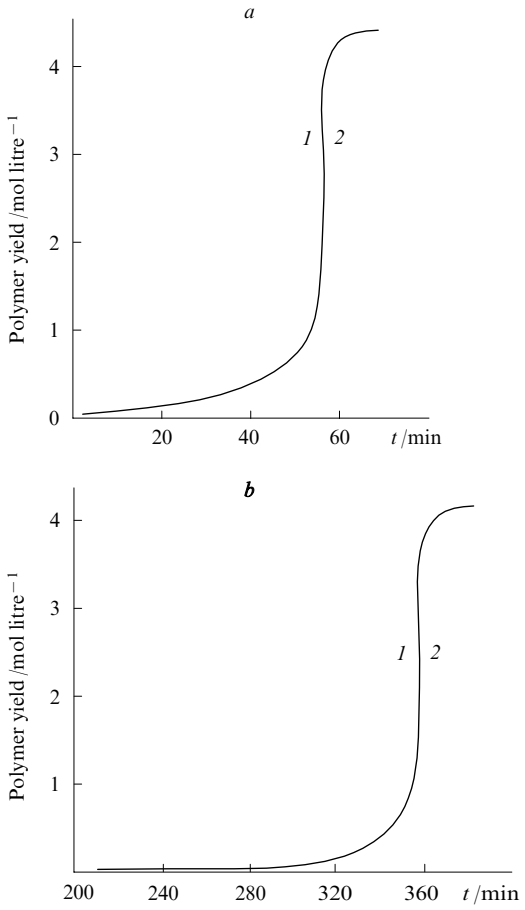



**Figure 11.** Polymer yield plotted *vs.* time: styrene (*a*) and methyl methacrylate (*b*). The kinetic curves were plotted at $\mathrm{d}R/\mathrm{d}t = 0$ (*1*) and $\mathrm{d}R/\mathrm{d}t \neq 0$ (*2*).[62]

## VIII. The principle of quasi-stationary concentration for frontal radical polymerization

It is appropriate to perform further analysis of the solution to the system (10)–(13) with the initial and boundary conditions (14) for stationary polymerization front in dimensionless variables:[17, 69]

$$\theta = \frac{E_{ef}}{R_g T_*^2}(T - T_*),\ \theta_0 = \frac{E_{ef}}{R_g T_*^2}(T_0 - T_*);$$

$$E_{ef} = E_p - \frac{1}{2}(E_t - E_i);\ \tau = \frac{t}{t_*};$$

$$\xi = \frac{x}{x_*};\ x_*^2 = \frac{\lambda t_*}{c\rho};\ t_* = \frac{\gamma}{k_{ef}\exp(-E_{ef}/R_g T_*)M_0^{1/2}};$$

$$\gamma = \frac{c\rho\beta T_*}{QM_0};\ \beta = \frac{RT_*}{E_{ef}};$$

$$k_{ef} = k_p\left(\frac{k_i}{k_t}\right)^{1/2};\ \alpha = \frac{M_0 - M}{M_0};\ i = \frac{I_0 - I}{I_0};\ r = \frac{R}{R_0};\ b = \frac{I_0}{M_0}; \quad (32)$$

$$B = \frac{k_{t0}\exp\left[(E_{ef} - E_t)/R_g T_*\right]M_0^{1/2}}{k_{ef}};$$

$$\Gamma = \frac{k_{p0}\exp\left[(E_{ef} - E_p)/R_g T_*\right]M_0^{1/2}}{k_{ef}};$$

$$\eta = \frac{B}{\Gamma^2} = \frac{k_{i0}\exp\left[(E_{ef} - E_i)/R_g T_*\right]}{k_{ef}M_0^{1/2}};$$

$$S_0 = \frac{E_p}{E_{ef}};\ S_1 = \frac{E_i}{E_{ef}};\ S_2 = \frac{E_t}{E_{ef}};\ z = \xi + u\tau,$$

where $T_*$, $t_*$, $x_*$ are the scaling temperature, time, and coordinate, respectively; and $u$ is the dimensionless velocity of the polymerization front.

Having integrated the stationary equation of heat conduction (10) over $z$ with allowance for Eqn, (12) and notations (32) and assuming that $(dT/dx)\big|_{\substack{x=0\\x=+\infty}} = 0$, one gets

$$\frac{d\theta}{dz} = \frac{u[\gamma(\theta - \theta_0) - \alpha]}{\gamma},$$
$$\theta_k = \theta_0 + \frac{\alpha_k}{\gamma}, \quad (33)$$

where $\theta_k = \theta(+\infty)$, $\alpha_k = \alpha(+\infty)$ are the final temperature and degree of conversion. Here, $\theta_k$ and $\alpha_k$ are unknowns which should be determined along with the front velocity $u$. It is this feature that makes the problem in question different from related problems treated conventionally.

From the system of equations (10)–(13) it follows that $\theta(z)$ is a monotonic function of $z$; therefore, the stationary problem with allowance for relations (33) has the form:

$$\frac{d\alpha}{d\theta} = \frac{\omega\Gamma\varphi_0(\theta)(1-\alpha)r}{\Omega(\theta,\alpha)}, \quad (34)$$

$$\frac{dr}{d\theta} = \omega\frac{b\eta\varphi_1(\theta)(1-i) - B\varphi_2(\theta)r^2}{\Omega(\theta,\alpha)}, \quad (35)$$

$$\frac{di}{d\theta} = \omega\eta\frac{\varphi_1(\theta)(1-i)}{\Omega(\theta,\alpha)}, \quad (36)$$

$$\omega = \frac{\gamma^2}{u^2},\ \Omega(\theta,\alpha) = \gamma(\theta - \theta_0) - \alpha,$$
$$\theta = \theta_0,\ \alpha = r = i = 0,$$
$$\theta = \theta_k,\ \alpha = \alpha_k,\ r = 0,\ i = 1, \quad (37)$$

$$\varphi_j(\theta) = \begin{cases} 0 \text{ at } \theta_0 \leqslant \theta \leqslant \theta_0 + \delta \\ \exp\left(\dfrac{S_j\theta}{1+\beta\theta}\right) = [\varphi(\theta)]^{S_j} \text{ at } \theta > \theta_0 + \delta;\ j = 0, 1, 2, \end{cases}$$

where $\varphi_j(\theta)$ ($j$ = 0, 1, 2) are continuous functions of $\theta$; $S_1 > 1$, $S_1 > S_2$ and $\delta$, as above, is the 'cut-off' of the source.

The problem described by Eqns (34)–(36) and conditions (37) was called the complete problem.[68, 69] Using the QSC principle, it is reduced to the system of equations

$$\frac{d\alpha}{d\theta} = \frac{\omega b^{1/2}\varphi_0(\theta)(1-\alpha)(1-i)^{1/2}}{\Omega(\theta,\alpha)}, \quad (38)$$

$$r = \frac{1}{\Gamma}\left[\frac{b\varphi_1(\theta)(1-i)}{\varphi_2(\theta)}\right]^{1/2}, \quad (39)$$

$$\frac{di}{d\theta} = \omega\eta\frac{\varphi_1(\theta)(1-i)}{\Omega(\theta,\alpha)}, \quad (40)$$

$$\theta = \theta_0,\ \alpha = i = 0,$$
$$\theta = \theta_k,\ \alpha = \alpha_k,\ i = 1, \quad (41)$$

which is called [17, 69] the quasi-stationary problem.

A comparison of the systems of equations (34)–(37) and (38)–(41) shows that the quasi-stationary system (38)–(41) can be derived from the complete system (34)–(37) as an asymptotics with respect to a small parameter ($\varepsilon$) at the derivative in Eqn (35). The system with the small parameter can be derived by representing, *e.g.*, $\Gamma$ and $B$ as $\Gamma = \bar{\Gamma}/\varepsilon$, $B = \bar{B}/\varepsilon^2$, where $\varepsilon \ll 1$ and $\bar{\Gamma}$ and $\bar{B}$ are of the order of unity. Having introduced a variable $v = r/\varepsilon$, the system (34)–(36) is transformed to

$$\frac{d\alpha}{d\theta} = \omega\frac{\bar{\Gamma}\varphi_0(\theta)(1-\alpha)v}{\Omega(\theta,\alpha)},$$
$$\varepsilon\frac{dv}{d\theta} = \frac{\omega b\eta\varphi_1(\theta)(1-i) - \bar{B}\varphi_2(\theta)v^2}{\Omega(\theta,\alpha)},$$
$$\theta = \theta_0,\ \alpha = v = i = 0.$$

Let us denote:

$$A_1 = \frac{k_t}{k_p} \gg 1;\ A_2 = \left(\frac{I_0 k_t}{k_i}\right)^{1/2} \gg 1, \quad (42)$$

where $k_t$, $k_p$, and $k_i$ are the rate constants at the temperature of isothermal process. When polymerization is conducted under non-isothermal conditions, $A_1$ and $A_2$ are functions of temperature and vary over a wide range.[43] Taknig account of notations (42), one gets

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

Under frontal polymerization conditions, it is convenient to use as $T_*$ the temperature at which the heat release function reaches its maximum value, *i.e.*, the maximum heating temperature at which $A_1$ and $A_2$ usually have nearly minimum values. Therefore, if conditions (42) are met for the whole range of temperature variation during the polymerization process, by virtue of the relations $\Gamma = \bar{\Gamma}/\varepsilon$, $B = \bar{B}/\varepsilon^2$, $\alpha \ll 1$ one can assume that the QSC approximation will lead to good results.

The complete and quasi-stationary problems were numerically solved using different sets of kinetic and thermal physical parameters characteristic of radical polymerization of vinyl monomers. The dimensionless velocities ($u$) of the front propagation and the finite temperatures ($\theta_k$) were compared. The relative deviations of solutions to the quasi-stationary and complete problems were evaluated:

$$\Delta u = \frac{u - u_0}{u_0} \times 100\%,$$

$$\Delta\theta = \frac{\theta_k - \theta_{k0}}{\theta_{k0}} \times 100\%,$$

where $u$ and $\theta_k$ are the velocity of the front propagation and the final temperature for the complete problem, respectively, and $u_0$ and $\theta_{k0}$ are the corresponding parameters for the quasi-stationary problem. Using parameters providing a narrow reaction zone and an accuracy of determination of the stationary dimensionless velocity of the polymerization front of 0.01%, it was found that $\Delta u = 0.02\%$ and $\Delta\theta = 0.063\%$. The dimensionless system of equations included $\varepsilon \approx 10^{-6}$. Next, the parameters were changed in such a manner that the coefficient $\varepsilon$ was equal to $10^{-4}$, $10^{-2}$, and 1; the corresponding $\Delta u$ and $\Delta\theta$ values are respectively (in %): 1.8 and 1.8; 8 and 22; and 20 and 97. The dependences of $\Delta u$ and $\Delta\theta$ on some kinetic parameters are shown in Figs 12 and 13.

Figure 12 shows that $\Delta u$ slightly increases while $\Delta\theta$ decreases as the $I_0/M_0$ ratio increases. However, the dependence of both quantities on the $I_0/M_0$ ratio is so weak that the quasi-stationary approximation holds to an accuracy of 1% in the studied interval of changes in this ratio.

Numerical calculations of the influence of the activation energies of initiator decompositon, chain propagation and bimolecular chain termination reactions on $\Delta u$ and $\Delta\theta$ were reported.[17,69] Analysis of the results obtained showed that

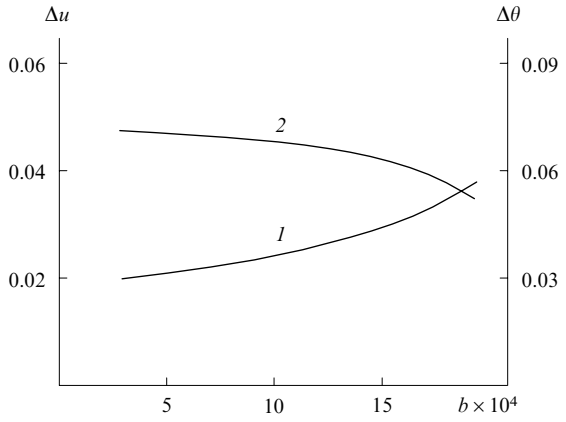



**Figure 12.** $\Delta u$ (*1*) and $\Delta\theta$ (*2*) plotted *vs.* parameter $b$.[69]

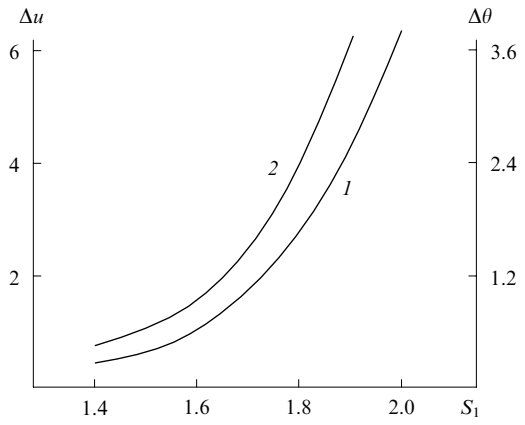



**Figure 13.** $\Delta u$ (*1*) and $\Delta\theta$ (*2*) plotted *vs.* parameter $S_1$.[69]

if $E_i \geqslant (125-140)$ kJ mol$^{-1}$ and the $E_p$ and $E_t$ values are characteristic of radical polymerization, the quasi-stationary approximation is highly accurate. If $E_i < 125$ kJ mol$^{-1}$ and $E_{ef} \leqslant 80$ kJ mol$^{-1}$, the quasi-stationary approximation 'works' poorer. As an example, Fig. 13 shows how the parameter $S_1$ affects the $\Delta u$ and $\Delta\theta$ values at $E_i = 80$ kJ mol$^{-1}$. At $S_1 \leqslant 1.55$, the dependence of $\Delta u$ and $\Delta\theta$ on $S_1$ is weak, but in the region $S_1 > 1.6$ the $\Delta u$ and $\Delta\theta$ values rapidly increase.

When the solutions to the complete and quasi-stationary problems coincide with sufficient accuracy, the reaction zone is usually narrow.[68] In this case, polymerization proceeds close to the maximum heating temperature.

Analysis of the temperature and conversion profiles revealed broadening of the reaction zone starting with $E_{ef} \leqslant 76$ kJ mol$^{-1}$; this is the reason for an increase in the relative deviations $\Delta u$ and $\Delta\theta$ (see Fig. 13).

Apart from Eqns (10)–(13), the kinetic model for polymerization was studied numerically[69] using an increased formal order of reaction with respect to monomer. Here, Eqn (12) has the form

$$-\frac{dM}{dt} = k_p R M^n .$$

The cases $n = 2$, 3 were considered with the same kinetic and thermal physical parameters as those used for the system of differential equations (10)–(13). For the dimensionless system of equations (34)–(36), it was found that an increase in $n$ causes the small parameter $\varepsilon$ to increase, which directly affects the $\Delta u$ and $\Delta\theta$ values (Fig. 14).

Analysis of the temperature and conversion profiles shows that an increase in the relative deviations $\Delta u$ and $\Delta\theta$ is accompanied by broadening of the temperature interval where monomer is consumed.

Summing up, analysis of the results reported in Refs 17 and 69 shows that

— for narrow reaction zones, meeting the criterial conditions (42) allows the QSC principle to be applied with necessary accuracy;

— for broad reaction zones, the inequalities (42) 'work' poorer, which affects the accuracy of the quasi-stationary approximation.

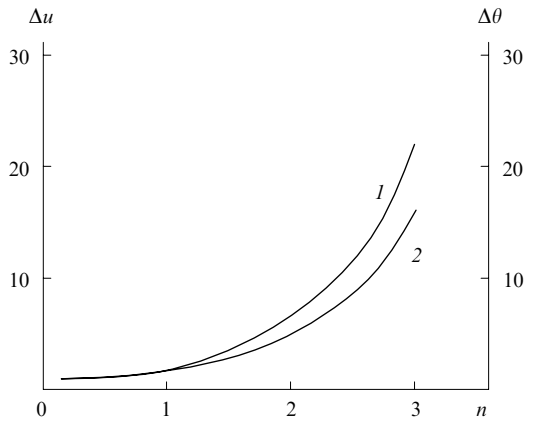



**Figure 14.** $\Delta u$ (*1*) and $\Delta\theta$ (*2*) plotted *vs*. formal order of reaction with respect to monomer.[69]

In the latter cae, it is more appropriate to use the criterial conditions (31) of the QSC principle, which are used for adiabatic radical polymerization of vinyl monomers.[62]

* * *

Thus, analysis of seminal studies on the combustion of gas mixtures and condensed media and their comparison with the published data on frontal polymerization showed that the steady-state approximation for frontal radical polymerization is met with high accuracy.

When studying the propagation dynamics of the polymerization front, the polymer yield, the stability of frontal regimes, *etc*., the depolymerization reaction in the monomer – polymer equilibrium can be ignored. At the same time, no data on the effect of this reaction on the molecular-mass characteristics of polymers formed under frontal radical polymerization have been reported so far.

Particular examples of narrow and broad reaction zones were demonstrated using published data. Quantitative analysis of physical criteria underlying the QSC principle allowed the limits of its applicability to frontal radical polymerization to be evaluated.

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