

Kinetic Model of Block Photopolymerization of Glycidyl Methacrylate to High Conversion

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ABSTRACT: The kinetics of glycidyl methacrylate block polymerization to high conversion was experimentally investigated with variations of the photoinitiator concentration, temperature, and power of UV illumination. The kinetic curves of this polymerization process contain three characterized sections of coordinates of "conversion–time," namely: The first one is practically linear to a conversion of ≈ 0.5 , the second represents, by itself, the autoacceleration

process, and the third presents the autodeceleration process. An additional peculiarity of such a polymerization process is poor reproduction of the kinetic measurements. This reproduction does not correspond to instrumental error. Derivation of a kinetic model for block linear polymerization was done. This model is, quantitatively, in good agreement with all the data of the experimental material. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3556–3569, 2002

INTRODUCTION

The kinetics of mono- and multifunctional polymerization to high conversion is characterized by both general and differential peculiarities of the process. The main general ones are (1) the S-like shape of the kinetic curves, indicating the presence of autoacceleration and autodeceleration processes; (2) a great posteffect, that is, being dark after UV illumination, stopping the postpolymerization process observed from the autoacceleration stage; and (3) a high (to 10^{-1} mol/m³) concentration of radicals discovered by EPR spectroscopy "in situ" until the end of the polymerization process.^{1–8}

Two main conceptions have been formulated with the aim of explanation of such peculiarities for the polymerization process to high conversion. The first is based upon the diffusion-controlled character of elementary reactions assigned to the classic kinetic scheme. That is why the kinetic equation of the initial stage of the process is a starting point in the diffusion-controlled reaction (DCR) conception. The parameters of the above-mentioned equation are functions of the current state of the monomer–polymeric solution.⁹

There are different variants of the DCR conception, differing one from the other, taking into account the physical factors and the details of the diffusion control

description of the elementary reaction rate. As a rule, attention has been paid mainly to bimolecular chain termination. The constant rate of chain termination is considered to be a function of the macroradicals' mobility, length,^{9–14} and free volume^{12–15,17} or the characteristic viscosity of the monomer–polymeric system. However, with the aim of explanation, the autodeceleration stage presence, the efficiency of initiation, and the constant rate chain propagation appear in the range of the macroradical mobility function variants.^{12,15,18} The second conception or microheterogeneous model^{1,18–22} is based upon the principle that, in process kinetics, in its initial stage, there is no homophase polymerization in the liquid monomer–polymeric solution, but a heterophase one, proceeding on the boundary of the "liquid monomer–solid polymer" microgranules under gel-effect conditions.

Microheterogeneity of a polymerizing system, that is, the presence of solid polymer micrograins in it with limited conversion in a liquid monomeric phase or, after phase inversion, of microdrops of a liquid monomer distributed in solid polymeric matrix, is a factor proved by both direct and indirect experimental methods. This is why microheterogeneity for a polymerizing system was not disputed even in works^{2,7,10,15} which were observed to DCR conception. Quite the reverse, this factor is taken into account for explanation of the high concentration of radicals stored via polymerization proceeding at the expense of their trapping⁶ by a solid polymeric matrix. In that work, where the peculiarities of polymerization at the high conversion can be explained by changing the chemical mechanism of chain termination, that is, by transition

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TABLE I
Characteristic Parameters of Glycidyl Methacrylate Polymerization Kinetics at the Photoinitiator Concentration $c_0 = 0.5\%$ (by mass), $T = 283\text{ K}$, $E_0 = 37.4\text{ W/m}^2$, and Different Thickness of the Layer

No.	Thickness of layer $l \times 10^4$ (m)	Time of maximum rate coming (s)	Conversion of maximum rate (P_0)	Maximum rate of process (s^{-1})	Rate of the linear site (s^{-1})
1	1.3	760	0.74	4.0	0.74
2	1.5	740	0.74	2.7	0.89
3	1.8	780	0.8	4.5	0.83
4	2.0	720	0.72	3.4	0.81
5	2.3	720	0.75	4.3	0.76

from a quadratic to a linear one, the latter also is considered as the physical elimination of active radicals, their transformation captured, "frozen," or "locked" by the solid polymeric matrix.^{5,7} From this point of view, the difference between a microheterogeneous model and DCR conception consists only in whether to consider the microheterogeneity of the polymerizing system as an essential important factor determining the main peculiarities of polymerization to high conversion.

Generally, the kinetic model of block three-dimensional (3D) polymerization of multifunctional monomers based upon the microheterogeneity of the polymerizing system conception and especially the role of the interface layer on the "liquid monomer–solid polymer" boundary has been represented in works.^{23–26} The starting principles include that the observed rate of polymerization is a sum consisting of the rate of the homophase process proceeding in a volume of a liquid monomer according to a classic kinetic scheme with the quadratic chain termination and the rate of the heterophase process proceeding under gel-effect conditions; clusters of a solid polymer in a liquid monomeric phase and clusters of a liquid monomer in a solid polymeric matrix are characterized by the structure of mass fractals; and the gel effect in the interface layer decreases the rate of chain termination and the transition of control under it up to chain propagation rate. Linear chain termination plays the role of an active radical self-burial act observed in computer experiments accordingly to the theory of self-avoiding walks.^{27,28}

The obtained kinetic equations for stationary and non-stationary (so-called postpolymerization) processes,^{25,26} both qualitatively, explain all the main peculiarities of block 3D polymerization to high conversion and also were quantitatively proved on a wide range of experimental materials in regard to the kinetics of photoinitiated polymerization of dimethacrylates. This permitted, for the first time, a numerical estimate of the constant rates of linear chain termination.²⁹ In the presented work, a quantitatively kinetic model for linear block polymerization to high conversion is proposed on the basis of experimental material in regard to the kinetics of photoinitiated polymerization of gly-

cidyl methacrylate obtained in a wide range of variational parameters.

EXPERIMENTAL

The kinetics of glycidyl methacrylate (2,3-epoxypropyl methacrylate) photoinitiated polymerization was studied using a laser interferometric plant in thick layers of $0.5\text{--}2 \times 10^{-4}\text{ m}$ in the presence of a photoinitiator, 2,2-dimethoxy-2-acetophenone (ketal) $\text{C}_6\text{H}_5\text{—C}(\text{OCH}_3)_2\text{—C}(\text{O})\text{—C}_6\text{H}_5$, under UV illumination of a mercurial quartz lamp DRT-400. The technique of the experiment was described in more detail in ref. 23.

The concentration of the photoinitiator (0.5–3.0% by mass), temperature (10–30°C), and power E_0 of UV illumination (37.4–65 W/m^2) on the surface of the photocomposition layer were varied.

The selected experimental kinetic curves of glycidyl methacrylate polymerization are represented in Figure 2 as a dependence of conversion upon time. As we can see from the point locations, the instrumental error at the individual kinetic curve is rather small. However, comparison of the individual kinetic curves between each other (see Table I) shows scattering of the characteristic parameters (e.g., the maximal rate W_0 of the process on the autoacceleration stage, conversion P_0 and time t_0 of achievement W_0 , and also the rate W_1 of an initial linear section of the kinetic curve). Such scattering essentially exceeds the error of each individual experiment. At the same time, the scattering of the characteristic parameters represented in Table I fully shows the level of the influence of the layer thickness l of the photopolymerizing composition via ranges of its changing. The poor reproduction of kinetic measurements or "whims" of the process are well known^{30,31} and they are a result of the fluctuating sensitivity of the polymerization process, especially on an autoacceleration stage. That is why the results consisting of the five to eight kinetic curves represented in Figure 2 were obtained in the narrow limits of the layer thickness, changing for each set of the assigned parameters (starting concentration of the photoinitiator, temperature, and power of UV illumination).

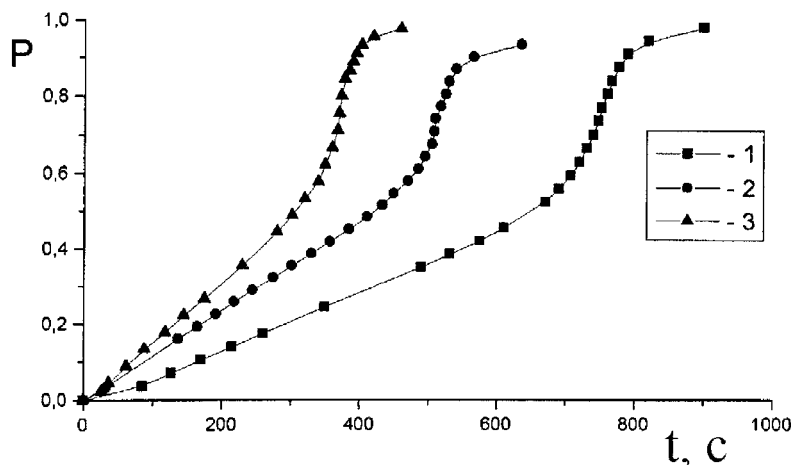


Figure 1 Typical kinetic curves of glycidyl methacrylate polymerization for photoinitiator concentrations: (1) 0.5%; (2) 1.5%; (3) 3.0% (by mass); $T = 283$ K; $E_0 = 37.4$ W/m².

RESULTS AND DISCUSSION

Discussion of experimental data and formulating the starting positions of the kinetic model

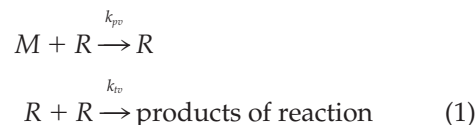
The represented experimental data indicate one more general peculiarity of linear and 3D polymerization processes, namely, poor reproduction of the kinetic measurements does not correspond to the instrumental error. This proves a high fluctual sensitivity of these processes, especially on the autoacceleration stage. However, let us also note the essential differences in the kinetics of linear and 3D polymerization: Contrary to 3D polymerization, the autoacceleration stage at the linear one begins only at the achievement of high conversion, in this case, at $P > 1/2$. As we can see from Figures 1 and 2, this conversion does not depend upon the photoinitiator concentration and the power of UV illumination and slightly increases (see Fig. 1) with increasing temperature. Up to conversion $P \approx 1/2$, the practically linear section of the kinetic curve is observed, although, according to classic kinetics, the rate of polymerization should be twice decreased.

The inflection point of the kinetic curve or conversion P_0 , which corresponds to the maximal rate of the process, for 3D polymerization, for instance, dimethacrylates,^{24,25} is less than or equal to 0.5; for linear polymerization, $P_0 > 0.5$ and is in the range of 0.7–0.75. This value of P_0 practically does not depend upon the parameters of the process.

The maximal rate W_0 of the process for linear polymerization depends less upon the concentration of the photoinitiator and the power of UV illumination in a similar interval of layer thickness than for the 3D polymerization of dimethacrylates.^{24,25} The differences in the kinetics of linear and 3D polymerization mean that the kinetic model of linear polymerization cannot be a simple copy of a kinetic model for 3D polymerization, but should contain in it some common peculiarities.

On the basis of the above, let us formulate the main basic positions of a kinetic model for linear polymerization to high conversion:

1. To the monomer concentration $[M_v^0]$, corresponding to conversion $P_v^0 = [M_0] - [M_v^0]/[M_0]$, where $[M_0]$ is the initial concentration of the monomer in the block, the polymerizing system is monophasic and represents, by itself, the solution of the polymer in the monomer; let us name this solution conditionally as the monomer–polymeric phase (MPPh). The MPPh polymerization process proceeds in accordance with the classic kinetic scheme with quadratic chain termination:



The linear dependence of conversion upon time in the MPPh is explained by partial diffusion control at the linear chain termination.

2. At the achievement of conversion P_v^0 , the monomer–polymeric solution becomes saturated relative to the polymer, and at some supersaturation, the new polymer–monomer phase (PMPH) is selected from it. It represents, by itself, the saturated solution of a monomer in a polymer with the concentration of the monomer $[M_s^0]$, which corresponds to conversion P_s^0 : $P_s^0 = ([M_0] - [M_s^0])/[M_0]$.

Concentrations of the monomer $[M_v^0]$ in the MPPh and $[M_s^0]$ in the PMPH are functions of the nature of the monomer–polymeric system and temperature. The supersaturation of the MPPh disappears after the spontaneous origin of the PMPH embryos, needed for the origin of the new phase. That is why the polymerization process is further accompanied only with the

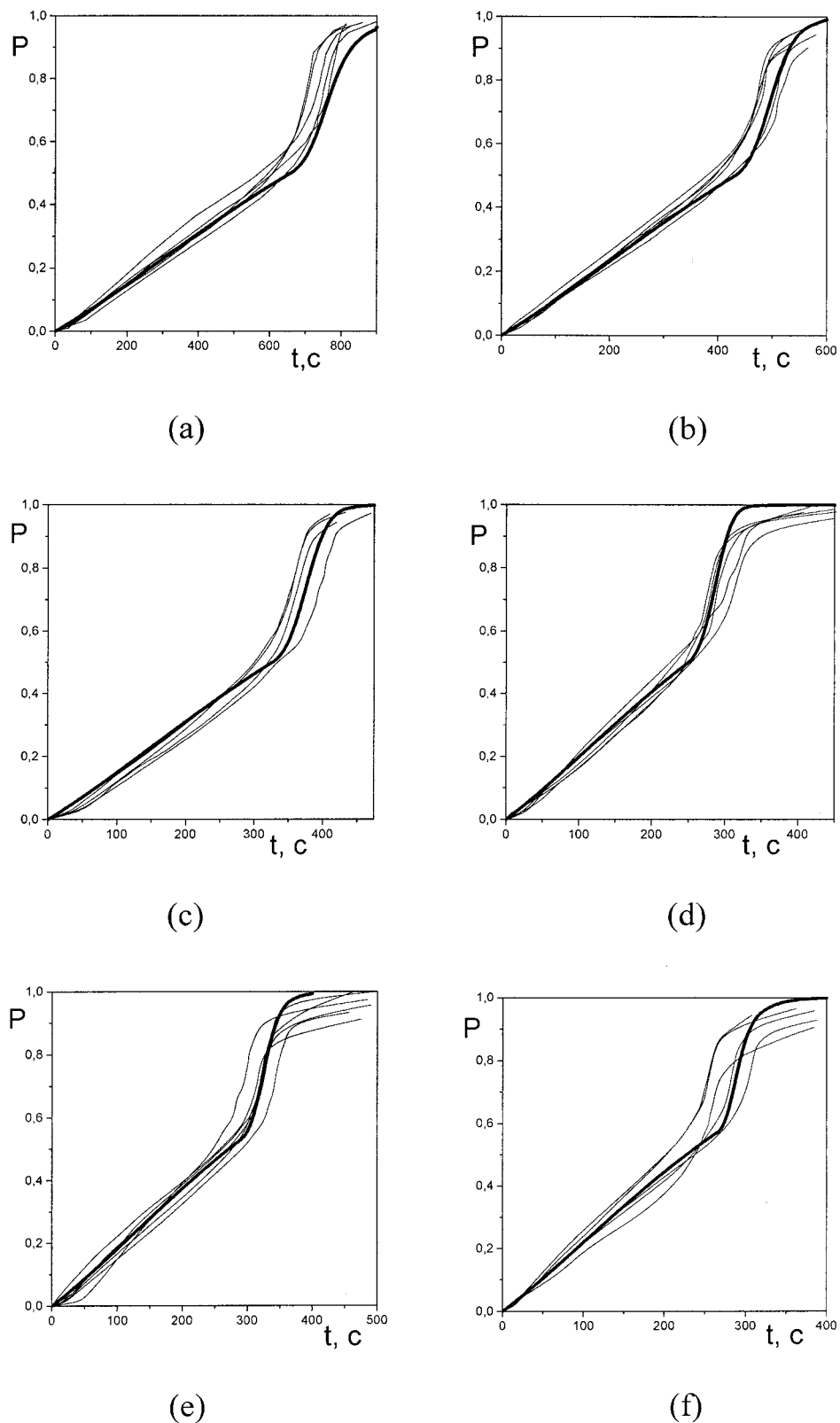


Figure 2 Comparison of the (thin lines) experimental data and (bold lines) calculated data in accordance with eqs. (61)–(64) of kinetic curves of glycidyl methacrylate photopolymerization in variants:

Variant	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
Photoinitiator concentration (% mass)	0.5	1.5	3.0	3.0	3.0	3.0
Power of UV illumination ($E_0, W/m^2$)	37.4	37.4	37.4	65	37.4	37.4
Temperature (K)	283	283	283	283	293	303

propagation of arisen embryos or micrograins of the PMPH.

3. The photoinitiator is distributed between the MPPH and the PMPH nonuniformly, but in equilibrium, that is, in accordance with the law of substance distribution between two phases. Since the PMPH is rather viscous, the effects of mixing inside the micrograins can be neglected; that is why the concentration of the photoinitiator will be a variable on a radius of micrograins in accordance with the time of a given micrograin-layer selection.
4. In the case of a microheterogeneous system, polymerization proceeds in three reactionary zones, namely, in a saturated monomer-polymeric solution, in an interphase layer on the boundary of the MPPH and micrograins of the PMPH, and in a "solid" (conditionally) polymer-monomeric solution.
5. In the MPPH, polymerization proceeds in accordance with the same classic kinetic scheme (1), but at a constant concentration $[M_v^0]$ of the monomer and viscosity of the solution. Only the concentration of the photoinitiator and volumetric parts (ϕ_v) of the MPPH are varied.
6. In the case of an interphase layer on the boundary of the MPPH and the PMPH, polymerization proceeds accordingly to the scheme (1), but the constant rate of linear chain termination k_{tvs} is different. It is connected with the fact that "solid" PMPH creates an especially ordered structure of the nearest reactionary space, in which there is sharply reduced transmitting and segmental mobility of the macroradicals. Let us accept that the concentration of the monomer and photoinitiator in the interphase layer are equal or proportional to their concentration in the MPPH.

The volume and, respectively, the volumetric part of the interphase layer are the complete function of the propagation and aggregation process (stage of monolithization¹) of the PMPH micrograins. The volumetric part of the interphase layer will be proportional to the volumetric part ϕ_s of the PMPH, namely, $\phi_{vs} \sim \phi_s$ only while $\phi_v \gg \phi_s$ is on the stage of micrograin propagation; at the end of the monolithization stage, when $\phi_v \ll \phi_s$, it is the opposite: $\phi_{vs} \sim \phi_v$. Supposing that micrograins of the PMPH are the mass fractals for which the fractal dimensions of surface and volume coincide^{32,33} and using the probability of contact in the model of black and white balls in accordance with ref. 23, we approximate the relationship among ϕ_{vs} , ϕ_v , and ϕ_s by use of the approximate function

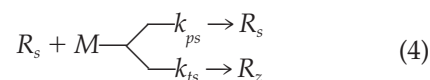
$$\phi_{vs} \cong F_{vs} \phi_v \phi_s \quad (2)$$

where the coefficient of proportionality F_{vs} de-

pends upon the fractal characteristics of the micrograins of the PMPH in the MPPH and the microdrops of the MPPH in the PMPH, their number, and the thickness of the interphase layer. In an approximation when the volume of the interphase layer is small and the relationships $\phi_{vs} \ll \phi_v + \phi_s$ and $\phi_v + \phi_s \approx 1$ are fulfilled, we obtained (3) instead of (2):

$$\phi_{vs} \cong F_{vs} \phi_s (1 - \phi_s) \quad (3)$$

7. Polymerization in the polymer-monomeric phase is characterized by two main peculiarities: First, it proceeds under a gel-effect condition, at which, by virtue of a sizable loss of transmitting and segmental mobility of the macroradicals, control of the rate of chain termination passes to the rate of its propagation. This means that the acts of chain development and its termination take place as two different outcomes of the interaction of the active radical R_s with the functional group of the monomer leading to the formation of an active radical (propagation of chain) or a frozen one, in accordance with the terminology of refs. 24 and 25, the so-called self-burial, that is, an inactive radical R_z (linear chain termination). This can be represented by the scheme



From a stationary condition upon active radicals R_s , it follows that the specific rate of polymerization in the PMPH is equal to

$$w_s = (k_{ps}/k_{ts})v_{is} \quad (5)$$

where v_{is} is a specific rate of initiation in the PMPH and k_{ps}/k_{ts} is the chain length.

The second, via polymerization proceeding in the PMPH, new polymeric phase, that is, a polymer with limited conversion near 1, cannot be allocated as an independent phase, since a great viscosity of the PMPH takes place. That is why polymerization inside micrograins of the PMPH can be considered as a glass transition process, leading to reduction of the reactive volume of the PMPH. The glass transition process of micrograins develops nonuniformly upon the radius of the micrograin in accordance with the different times given of its layer selection. That is why the summarized rate of polymerization in the PMPH will be characterized with an integral character.

Obtaining the kinetic model

Homogeneous system

Polymerization proceeds in a homophase system in accordance with the classic kinetic scheme (1) to the

monomer concentration $[M] \geq [M_v^0]$ or conversion $P \leq P_v^0$ with a specific rate:

$$-d[M]/dt = k_{pv}[M]v_{iv}^{1/2}/k_{iv}^{1/2} \quad (6)$$

where v_{iv} is the initiation rate. Via conversion P , the polymerization rate is described by the expression

$$dP/dt = k_{pv}(1 - P)v_{iv}^{1/2}/k_{iv}^{1/2} \quad (7)$$

The weak gel effect, which is exhibited as a linear section of the kinetic curve up to the autoacceleration stage, is caused by partial diffusion control upon the rate of quadratic chain termination. That is why we represent the constant rate k_{iv} of chain termination in the following form:

$$1/k_{iv} = 1/k_c + 1/k_d \quad (8)$$

where k_c and k_d are constant rates of termination, controlled by the chemical act of radical interaction and diffusion delivery to them to the point of interaction accordingly.

The viscosity η_v of the MPPh is described by the linear function in the interval $0 \leq P \leq P_v^0$:

$$\eta_v = \eta_0 \left(1 + \frac{\eta_v^0 - \eta_0}{\eta_0 P_v^0} P \right) \quad (9)$$

where η_0 and η_v^0 are viscosities of the pure monomer in the block and the monomer-polymeric solution, respectively, at $P = P_v^0$. Accepting k_d as inversely proportional to the viscosity of the solution ($k_d \eta = \text{const}$), we can rewrite

$$\frac{1}{k_d} = \left(1 + \frac{\eta_v^0 - \eta_0}{\eta_0 P_v^0} P \right) / k_d^0 \quad (10)$$

where k_d^0 is a constant rate of radical diffusion in the monomer.

By combining eqs. (8) and (10), we have

$$1/k_{iv} = (1 + aP)/k_{iv}^0 \quad (11)$$

where

$$1/k_{iv}^0 = 1/k_c + 1/k_d^0 \quad (12)$$

$$a = k_{iv}^0(\eta_v^0 - \eta_0)/k_d^0 \eta_0 P_v^0 \quad (13)$$

Thus, k_{iv}^0 is a constant rate of chain termination in a pure monomer ($P = 0$). With substitution of (11) into (7), the rate of polymerization in the MPPh at $P \leq P_v^0$ will be described by the equation

$$dP/dt = (k_{pv}/k_{iv}^0)^{1/2}(1 - P)(1 + aP)^{1/2}v_{iv}^{1/2}, \quad P \leq P_v^0 \quad (14)$$

Microheterogeneous system

At $P \geq P_v^0$, polymerization proceeds in the three reactionary zones and that is why its rate is described by the sum

$$-d[M]/dt = w_v\varphi_v + w_{vs}\varphi_{vs} + \langle w_s \rangle \varphi_s \quad (15)$$

were w_v and w_{vs} are specific rates of the process in a saturated monomer-polymeric solution and the interphase layer on the boundary of the MPPh and the PMPH, respectively; $\langle w_s \rangle$ is the average specific rate of polymerization in the PMPH per volume of micrograins. Instead of (15), we can write

$$dP/dt = w_v\varphi_v/[M_0] + w_{vs}\varphi_{vs}/[M_0] + \langle w_s \rangle \varphi_s/[M_0] \quad (16)$$

The contribution $(dP/dt)_v = w_v\varphi_v/[M_0]$ of the polymerization process proceeding in the MPPh into a summarized rate is described by the same eq. (14), but at the constant value of $P = P_v^0$ and variable $\phi_v = 1 - \phi_s$:

$$(dP/dt)_v = (k_{pv}/k_{iv}^0)^{1/2}(1 - P_v^0)(1 + aP_v^0)^{1/2}(1 - \varphi_s)v_{iv}^{1/2} \quad (17)$$

The specific rate of polymerization in the interphase layer is described by the classic eq. (6), but with the constant rate of termination k_{ivs} , in which the contribution of diffusion control has been considerably increased, we obtained

$$w_{vs} = -d[M]/dt = (k_{pv}/k_{ivs}^{1/2})[M_{vs}]v_{ivs}^{1/2} \quad (18)$$

While phases coexist, $k_{ivs} = \text{const}$. Accepting that in the interphase layer the concentration of the monomer $[M_{vs}]$ is proportional to $[M_v^0]$ ($[M_{vs}] = k_m[M_v^0]$) and that the initiation rate v_{ivs} is proportional to v_{iv} ($v_{ivs} = k_v v_{iv}$), let us describe the contribution of polymerization rates in the interphase layer $(dP/dt)_{vs} = w_{vs}\rho_{vs}/[M_0]$ into summarized kinetics, taking into account (3), by the next expression:

$$(dP/dt)_{vs} = k_2(1 - P_v^0)\varphi_s(1 - \varphi_s)v_{iv}^{1/2} \quad (19)$$

where

$$k_2 = (k_p/k_{ivs}^{1/2})F_{vs}k_mk_v \quad (20)$$

k_2 is an effective constant rate of polymerization in the interphase layer. Summarizing (17) and (19), namely, $(dP/dt)_v + (dP/dt)_{vs} = (dP/dt)_{v+vs}$, we obtained

$$(dP/dt)_{v+vs} = k_1(1 - P_v^0) \times [(1 + aP_v^0)^{1/2} + k_2\varphi_s/k_1](1 - \varphi_s)v_{iv}^{1/2} \quad (21)$$

where

$$k_1 = k_p/k_{iv}^{0.5} \quad (22)$$

The magnitude $(dP/dt)_{v+vs}$ determines the rate of the new PMPH selection from the MPPH. Let us determine the connection between them. In the moments of time t and $t + dt$, the monomer's quantity in the MPPH is equal to $[M_v^0](1 - \phi_s)$ and $[M_v^0](1 - \phi_s - d\phi_s)$, respectively. The monomer's quantity passed into the PMPH for time dt equal to $[M_s^0]d\phi_s$. At the expense of copolymerization into the MPPH and the interface layer, $d[M]_{v+vs}$ was reacted. From the balance, it follows that $-d[M]_{v+vs} = ([M_v^0] - [M_s^0])d\phi_s$. Thus, we have

$$(dP/dt)_{v+vs} = (P_s^0 - P_v^0)d\phi_s/dt \quad (23)$$

Comparing (21) and (23), let us rewrite the latter relative to $d\phi_s/dt$:

$$\frac{d\phi_s}{dt} = \frac{1 - P_v^0}{P_s^0 - P_v^0} k_1 \left[(1 + aP_v^0)^{1/2} + \frac{k_2}{k_1} \varphi_s \right] (1 - \varphi_s)v_{iv}^{1/2} \quad (24)$$

In turn, we can describe the summarized rate of the process in a microheterogeneous system as

$$dP/dt = (P_s^0 - P_v^0)d\phi_s/dt + \langle w_s \rangle \varphi_s / [M_0] \quad (25)$$

Let us return to $\langle w_s \rangle$, which is the average specific rate of polymerization in the volume of micrograins of the PMPH, even though t_v^0 is the time needed for the achievement of conversion P_v^0 in the MPPH and for the appearance of the PMPH embryos. Let us take this time as the emanating point, assuming that $t_v^0 = 0$ is the beginning of the new phase separation. Let us consider the element $d\phi_s$, which was allocated from the MPPH in the moment of time $t \geq 0$. In this moment, the concentration of the monomer in it was equal to $[M_s^0]$, and the part $1 - \beta$ of the glass-transitioned, so-called inactive part of the polymer with limited conversion is equal to zero. In the moment of time $\tau \geq t$, the part of the nonglass-transitioned matter at the expense of polymerization is equal to $\beta \geq 0$. So, in the moment of time τ , the specific rate of polymerization in the element volume $d\phi_s$, separated in a moment of time t , is equal to

$$-d[M]_s/d\tau = w_s\beta \quad (26)$$

where β is a function $\tau - t$ and a specific rate w_s of the process.

In this case, in a moment of time t , by removing the unit volume of the PMPH $-\beta = 1$, the amount of a monomer is equal to its concentration $[M_s^0]$. In a moment of time $\tau > t$, we obtained $\beta < 1$, and the amount of a monomer in a unit volume is equal to $[M_s^0]\beta$. Via time $d\tau$, the $d[M_s]$ of a monomer will be reacted and remain in a nonglass-transitioned part of the unit volume $[M_s^0](\beta + d\beta)$. It follows from this that $d[M_s] = [M_s^0]d\beta$ or

$$d[M_s]/d\tau = [M_s^0]d\beta/d\tau \quad (27)$$

Comparing (26) and (27), we obtained

$$d\beta/\beta = -w_s d\tau/[M_s^0] \quad (28)$$

With the photoinitiator concentration variations being constant as a result of its photodecomposition, we accept that v_{is} and, respectively, w_s in accordance with (5) do not depend upon the time interval $\tau - t$ after removing the given unit of the PMPH volume. That is why, by integrating (28) in accordance with condition $\beta = 1$ in a moment of time t for removing the PMPH, we have

$$\beta = \exp\{-w_s(\tau - t)/[M_s^0]\} \quad (29)$$

The summary rate of polymerization in the removed unit $d\phi_s$ of the PMPH volume is equal to

$$-\frac{d[M_s]}{d\tau} d\phi_s = w_s\beta d\phi_s \quad (30)$$

Let us to substitute (29) into (30) with the replacement $d\phi_s = [(d\phi_s)/(dt)]dt$ in its right part and integrate (30) upon ϕ_s on the left and upon t on the right, taking into account the fact that, in accordance with the mean-value theorem, we have

$$-\int_0^{\varphi_s} \frac{d[M_s]}{d\tau} d\phi_s = -\left\langle \frac{d[M_s]}{d\tau} \right\rangle \varphi_s = \langle w_s \rangle \varphi_s \quad (31)$$

and we obtained

$$\langle w_s \rangle = \frac{1}{\varphi_s} \int_0^{\tau} w_s \exp\left\{-\frac{w_s}{[M_s^0]}(\tau - t)\right\} \frac{d\varphi_s}{dt} dt \quad (32)$$

It follows from this that the rate contribution $(dP/dt)_s = \langle w_s \rangle \varphi_s / [M_0]$ of the polymerization process into the PMPH in a microheterogeneous system can be determined by the expression

$$\left(\frac{dP}{d\tau}\right)_s = \int_0^{\tau} \frac{w_s}{[M_0]} \exp\left\{-\frac{w_s}{[M_s^0]}(\tau - t)\right\} \frac{d\varphi_s}{dt} dt \quad (33)$$

The general kinetic equation of polymerization in a microheterogeneous system at $P \geq P_v^0$ can be done as follows:

$$\frac{dP}{d\tau} = (P_s^0 - P_v^0) \frac{d\varphi_s}{d\tau} + \int_0^\tau \frac{w_s}{[M_0]} \times \exp\left\{-\frac{w_s}{[M_s^0]}(\tau - t)\right\} \frac{d\varphi_s}{dt} dt \quad (34)$$

At this time, we can write, in accordance with (5), the following:

$$w_s/[M_0] = k_3 v_{is}, \quad w_s/[M_s^0] = k_3 v_{is}/(1 - P_s^0) \quad (35)$$

where

$$k_3 = k_{ps}/k_{ts}[M_0] \quad (36)$$

Equations (24) and (34) (taking into account that $dt = d\tau$) represent, by themselves, the kinetic model of polymerization in a microheterogeneous system in the integral-differential form. We will obtain the integrated form of the kinetic model if we rewrite

$$P = P_v^0(1 - \varphi_s) + \langle P_s \rangle \varphi_s \quad (37)$$

where $\langle P_s \rangle$ is the average conversion in the PMPH in the present moment of time τ .

As was shown earlier, the amount of a monomer in the unit volume of the PMPH, taking into account the share of β of its nonglass-transitioned part, is equal to $[M_s] = [M_s^0]\beta$ or

$$[M_s] = [M_s^0] \exp\left\{-\frac{w_s}{[M_s^0]}(\tau - t)\right\} \quad (38)$$

By multiplying the left part of eq. (38) on $d\varphi_s$ and the right one on $[(d\varphi_s)/(dt)]dt$ and by integrating it, taking into account the mean-value theorem, we obtain

$$\langle [M_s] \rangle = \frac{[M_s^0]}{\varphi_s} \int_0^\tau \exp\left\{-\frac{w_s}{[M_s^0]}(\tau - t)\right\} \frac{d\varphi_s}{dt} dt \quad (39)$$

Its follows from this that

$$\langle P_s \rangle = 1 - \frac{1 - P_s^0}{\varphi_s} \int_0^\tau \exp\left\{-\frac{w_s}{[M_s^0]}(\tau - t)\right\} \frac{d\varphi_s}{dt} dt \quad (40)$$

Thus, the integral kinetic model of polymerization in a microheterogeneous system can be represented in accordance with the (37) and (40) as follows:

$$P = P_v^0 + (1 - P_v^0)\varphi_s - (1 - P_s^0) \int_0^\tau \exp\left\{-\frac{w_s}{[M_s^0]}(\tau - t)\right\} \frac{d\varphi_s}{dt} dt \quad (41)$$

The difference between the rates of initiation v_{iv} in an MPPH and v_{is} in a PMPH is determined by the initiator distribution character between the two phases in the moment of the PMPH being removed from the MPPH and also by the absence of mixing the inside grains of the PMPH. We obtained, at the equilibrium distribution of the initiator, the following ratio:

$$c_s/c_v = L \quad (42)$$

where L is a coefficient of distribution, and c_v and c_s , respectively, the molar-volumic concentrations of the initiator in the MPPH and removal of the PMPH in the present time.

Let us assume that the initiator concentration in the MPPH in the moment of time τ is equal to $c_v(1 - \varphi_s)$. In the moment of time $\tau + d\tau$, we shall obtain, respectively, $(c_v + dc_v)(1 - \varphi_s - d\varphi_s)$; at this time, the initiator concentration transported via time $d\tau$ in the PMPH, is equal to $c_s d\varphi_s$. It follows from this that $-c_v d\varphi_s + (1 - \varphi_s)dc_v + c_s d\varphi_s = 0$. We obtained (43) by the replacement of $c_s = c_v L$. So,

$$dc_v/c_v = (1 - L)d\varphi_s/(1 - \varphi_s) \quad (43)$$

Let us integrate eq. (43) according to the condition that, in the starting moment of the first portions of removing the PMPH ($\varphi_s = 0$), the initiator concentration in the MPPH was equal to c_v^0 . Then, we have

$$c_v = c_v^0/(1 - \varphi_s)^{1-L} \quad (44)$$

$$c_s = Lc_v^0/(1 - \varphi_s)^{1-L} \quad (45)$$

So, the rates of initiation at the thermodecomposition of the initiator in a microheterogeneous system can be as follows:

$$v_{iv} = f_{iv} k_d c_v^0/(1 - \varphi_s)^{1-L} \quad (46)$$

$$v_{is} = f_{is} k_d L c_v^0/(1 - \varphi_s)^{1-L} \quad (47)$$

where k_d is a constant rate of the initiator decomposition and f_{iv} and f_{is} are coefficients of initiation in the MPPH and the PMPH accordingly.

Equations (24), (34)–(36), (46), and (47) represent, by themselves, the kinetic model of thermoinitiated polymerization in a microheterogeneous system at $P \geq P_v^0$. The variant of the photoinitiated polymerization is considerably complicated, since, in this case, it is nec-

essary to take into account the presence of a gradient of the light exposure on the layer of the photopolymerizing composition, which reduces, accordingly, to that the rates of polymerization and conversion are functions not only time, but also of the coordinates of a layer x from an illuminated surface ($x = 0$) and appear, thus, in differential performances of the process in a layer x , $x + dx$. The transition from the differential characteristics $P(x, t)$ and $\partial P(x, t)/\partial t$ to the experimentally determined, that is, averaged on a layer of photopolymerizing composition, $P(t)$ and $dP(t)/dt$, is carried out via integrated transformations:

$$P(t) = \frac{1}{\ell} \int_0^\ell P(x, t) dx, \quad \frac{dP(t)}{dt} = \frac{1}{\ell} \int_0^\ell \frac{\partial P(x, t)}{\partial t} dx \quad (48)$$

where l is a thickness of the layer.

With the dynamics of the initiator decomposition in the homogeneous phase taken into account, the light illumination gradient is described by a system of nonlinear differential equations in partial derivatives:

$$\partial c / \partial t = -\gamma \epsilon c J, \quad \partial J / \partial x = -\epsilon c J \quad (49)$$

Here, $J = J(x, t)$ and $c = c(x, t)$ are the light intensity and the photoinitiator concentration in layer x ; $x + dx$ is from an illuminated surface in the moment of time t ; ϵ is the molar factor of the photoinitiator extinction; and γ is the quantum yield of the initiator photodecomposition.

The decision of (49) is well known³⁴ and leads to the following expression of the initiator photodestruction differential rate:

$$\partial c(x, t) / \partial t = \gamma \epsilon J_0 \exp\{\gamma \epsilon J_0 t - \epsilon c_0 x\} \div [1 + \exp\{-\epsilon c_0 x\}(\exp\{-\epsilon J_0 t\} - 1)]^2 \quad (50)$$

where J_0 is the intensity of falling light upon the surface of the polymerizing composition and c_0 is the initial concentration of the photoinitiator. However, eq. (50), in the full form, can be used only for the polymerization in the MPPh until $P = P_v^0$. That is why in the analysis of the obtained kinetic models to high conversion the simplifications are used in the variant of the photoinitiated polymerization.

First, let us to assume that the characteristic time of the photoinitiator decomposition $t_d = (\gamma \epsilon J_0)^{-1}$ is considerably more than the time t of the polymerization; therefore, we can neglect the changing of the photoinitiator concentration via time (typical approximation for long-chain processes), taking that $c = c_0$. Second, by neglecting the microheterogeneity of the system, let us accept that $\partial J / \partial x = -\epsilon c_0 J$, and after that, we shall obtain $J = J_0 \exp\{-\epsilon c_0 x\}$ and, respectively,

$$-[\partial c(x) / \partial t] = \gamma \epsilon c_0 J_0 \exp\{-\epsilon c_0 x\} \quad (51)$$

Third, taking into account that the thickness of layer l for the photopolymerizing composition and, respectively, its optical densities $\epsilon c_0 l$ are small in our experiments, let us assume that the obtained kinetic models will be approximately adequate in the variant of the photoinitiated polymerization in the case when we use no differential rate of the photoinitiator decomposition accordingly to (51) but an average one upon the layer. Under the definition of average values (51), we obtain

$$-\left\langle \left(\frac{dc}{dt} \right)^{1/2} \right\rangle = \frac{1}{\ell} (\gamma \epsilon c_0 J_0)^{1/2} \int_0^\ell \exp\{-\epsilon c_0 x / 2\} dx \quad (52)$$

$$-\left\langle \frac{dc}{dt} \right\rangle = \frac{\gamma \epsilon c_0 J_0}{\ell} \int_0^\ell \exp\{-\epsilon c_0 x\} dx \quad (53)$$

Therefore,

$$-\left\langle \left(\frac{dc}{dt} \right)^{1/2} \right\rangle = \frac{2}{\ell} \left(\frac{\gamma J_0}{\epsilon c_0} \right)^{1/2} (1 - \exp\{-\epsilon c_0 \ell / 2\}) \quad (54)$$

$$-\left\langle \frac{dc}{dt} \right\rangle = \frac{\gamma J_0}{\ell} (1 - \exp\{-\epsilon c_0 \ell\}) \quad (55)$$

It follows from (54) and (55) that, at the small relative density of the layer, we will obtain $\epsilon c_0 l \ll 1$, $-\langle (dc/dt)^{1/2} \rangle = (\gamma \epsilon c_0 J_0)^{1/2}$, $-\langle dc/dt \rangle = \gamma \epsilon c_0 J_0$, and, at the large optical density, $\epsilon c_0 l \gg 1$, $-\langle (dc/dt)^{1/2} \rangle = (2/l)(\gamma \epsilon c_0 J_0)^{1/2}$, and $-\langle dc/dt \rangle = \gamma J_0/l$. Thus, the observed order upon photoinitiation at the quadratic chain termination can be varied from 1/2 to -1/2, and at the linear chain termination, from 1 to 0 depending on the thickness of layer l or its optical density $\epsilon c_0 l$. But, at the same time, the order upon UV illumination intensity is always equal to 1/2 or 1.

As we can see from the experimental data, the order upon photoinitiation at the initial linear sections of the kinetic curves is similar, but less than 0.5. This means that the approximation of the infinitely thick layer $\epsilon c_0 l \ll 1$ in our experiments is not strictly enough. That is why, taking into account that l is small and varies in a narrow range accordingly to the previous analysis, we use the average approximations instead of strict expressions (54) and (55):

$$-\langle (dc/dt)^{1/2} \rangle = (\gamma J_0)^{1/2} (\epsilon c_0)^m \quad (56)$$

$$-\langle dc/dt \rangle = \gamma J_0 (\epsilon c_0)^{2m} \quad (57)$$

where $0 < m < 1/2$.

TABLE II
Parameters of Proposed Kinetic Model for the Different Temperatures

Temperature (K)	\bar{k}_1	\bar{k}_2	\bar{k}_3	P_v^0	P_s^0	a	L	m
283	0.020	0.50	2.40	0.50	0.80	6.5	0.50	0.4
293	0.024	0.6	2.87	0.53	0.76	6.5	0.55	0.4
303	0.029	0.72	3.45	0.57	0.73	6.5	0.60	0.4

Introducing the further factors of f_v and f_s , we obtain the next equation for a homogeneous polymerizing system at $P \leq P_v^0$:

$$\langle v_{iv}^{1/2} \rangle = (\gamma_v J_0)^{1/2} (\epsilon c_0)^m \quad (58)$$

For a microheterogeneous polymerizing system at $P \geq P_v^0$, taking into account expressions (44) and (45) at the replacement $c_v^0 = c_0$, we obtain

$$\langle v_{iv}^{1/2} \rangle = (\gamma_v J_0)^{1/2} (\epsilon c_0)^m / (1 - \varphi_s)^{m(1-L)} \quad (59)$$

$$\langle v_{is}^{1/2} \rangle = \gamma_s J_0 (\epsilon c_0 L)^{2m} / (1 - \varphi_s)^{2m(1-L)} \quad (60)$$

where $\gamma_v = f_v \gamma$ and $\gamma_s = f_s \gamma$ are quantum yields of photoinitiation in the MPPh and the PMPh, respectively.

By substituting the $v_{iv}^{1/2}$ and v_{is} in kinetic models (14), (24), (34), and (35) upon their average analogs on layers (58)–(60), we have finally obtained the following equation for the variant of photoinitiated polymerization in a homogeneous system at $P \leq P_v^0$, $t \leq t_v^0$:

$$\frac{dP}{dt} = \bar{k}_1 J_0^{1/2} c_0^m (1 - P)(1 + \alpha P)^{1/2} \quad (61)$$

We obtained the following expressions at $P_v^0 \leq P$, $t_v^0 \leq t$ in the case of a microheterogeneous system:

$$\frac{d\varphi_s}{d\tau} = \frac{1 - P_v^0}{P_s^0 - P_v^0} \bar{k}_1 (J_0)^{1/2} c_0^m \left[(1 + \alpha P_v^0)^{1/2} + \frac{\bar{k}_2}{\bar{k}_1} \varphi_s \right] \times (1 - \varphi_s)^{1-m\alpha} \quad (62)$$

$$\frac{dP}{d\tau} = (P_s^0 - P_v^0) \frac{d\varphi_s}{d\tau} + \bar{k}_3 J_0 (c_0 L)^{2m} U(\tau) \quad (63)$$

$$U(\tau) = \int_0^\tau (1 - \varphi_s)^{-2m\alpha} \exp \left\{ -\frac{\bar{k}_3 J_0}{1 - P_s^0} \left(\frac{c_0 L}{(1 - \varphi_s)^\alpha} \right)^{2m} \times (\tau - t) \right\} \frac{d\varphi_s}{dt} dt \quad (64)$$

where $\alpha = 1 - L$, and

$$\bar{k}_1 = k_1 \gamma_v^{1/2} \epsilon^m = k_p \gamma_v^{1/2} \epsilon^m / (k_{tv}^0)^{1/2} \quad (65)$$

$$\bar{k}_2 = k_2 \gamma_v^{1/2} \epsilon^m = k_p F_{vs} k_m k_v \gamma_v^{1/2} \epsilon^m / (k_{tvs})^{1/2} \quad (66)$$

$$\bar{k}_3 = k_3 \gamma_s \epsilon^{2m} = k_p \gamma_s \epsilon^{2m} / k_{ts} [M_0] \quad (67)$$

Let us rewrite the integral eqs. (40) and (41) as follows:

$$\langle P_s \rangle = 1 - [(1 - P_s^0) V(\tau) / \varphi_s] \quad (68)$$

$$P = P_v^0 + (1 - P_v^0) \varphi_s - (1 - P_s^0) V(\tau) \quad (69)$$

$$V(\tau) = \int_0^\tau \exp \left\{ -\frac{\bar{k}_3 J_0 (c_0 L)^{2m}}{(1 - P_s^0)(1 - \varphi_s)^{2m\alpha}} (\tau - t) \right\} \frac{d\varphi_s}{dt} dt \quad (70)$$

Calculation results

The calculated kinetic curves were compared with the experimental data in Figure 2, and as we can see, they are in good agreement with them. The calculations were done with the use of the parameters of the constants of a model represented in Table II. Among these parameters, the part, for example, \bar{k}_1 , a , P_v^0 and m , was simply estimated upon the initial sections of the kinetic curves. Other ones were selected "manually" with the aim of obtaining a satisfactory agreement with the experimental data via all ranges of the controlled parameters of process variation. As we can see from Table II, with the exception of $a = 6.5$ and $m = 0.4$, the other parameters of the kinetic model are functions upon temperature, but, at the same time, all of them do not depend upon the photoinitiator concentration and the intensity of the illumination. The values of the constants \bar{k}_1 , \bar{k}_2 , and \bar{k}_3 were increased uniformly 20% with an increasing temperature to 10°C, which corresponds to the effective activation energy of ≈ 12.6 kJ/mol. In accordance with the experimental data [see Fig. 2(c,e,f)], the conversion P_v^0 in the saturated the MPPh with the increase in temperature is also increased, which can be considered as polymer solubility propagation in the monomer with increasing temperature. Similarly, we can expect the monomer solubility in the polymer to increase and that leads to the P_s^0 diminution with increasing temperature. The factor of the photoinitiator distribution L between the MPPh and the PMPh is increased at the expense of the above-said effect.

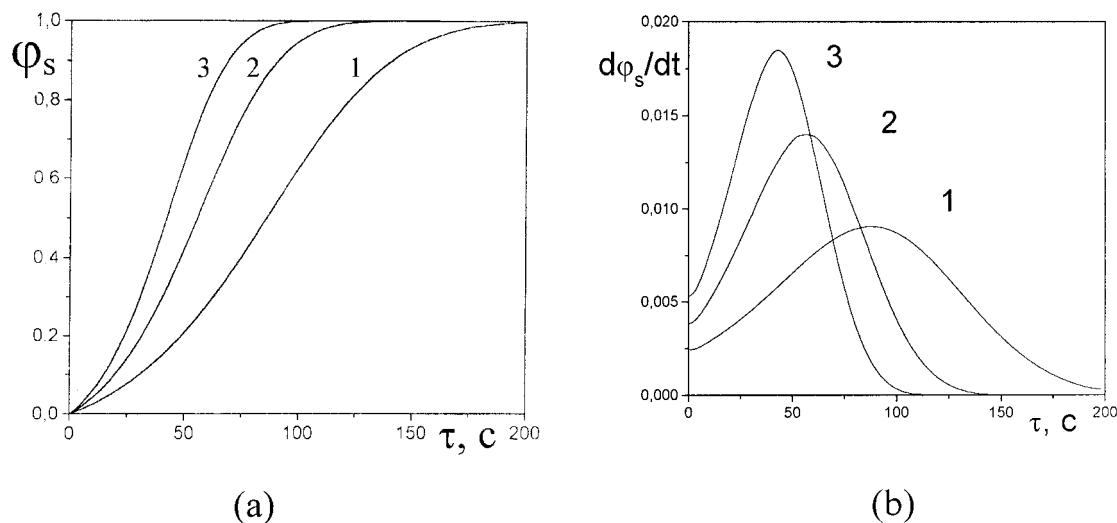


Figure 3 Dependencies calculated via eq. (62) and at various concentrations of photoinitiator (percent by mass) in the microheterogeneous system: (1) 0.5%; (2) 1.5%; (3) 3%. $E_0 = 37.4 \text{ W/m}^2$; $T = 283 \text{ K}$.

The intensity of the falling UV illumination (J_0) upon the surface of the polymerizing composition was calculated, taking into account its power $E_0 \text{ (W/m}^2\text{)}$, in approximation, that it concentrated on the conditional wavelength $\lambda = 340 \text{ nm}$: $J_0 = 2.83 \times 10^{-6} E_0 \text{ mol} \times \text{quant/m}^2 \times \text{s}$. The starting concentrations of the photoinitiator $c_0 = (\text{percent by mass}) = \rho_m/M_{in}$ and the monomer in the block $[M_0] = \rho_m/M_m$ (where $\rho_m = 1.04 \times 10^6 \text{ g/m}^3$ is the density of the monomer and $M_{in} = 256$ and $M_m = 142 \text{ g/mol}$ are the molecular masses of the initiator and the monomer, respectively) expressed in the units mol/m^3 . The given choice of the dimensions J_0 , c_0 , and also $[M_0]$ determines the numerical values $\bar{k}k_1$, \bar{k}_2 , and \bar{k}_3 and are represented in Table II. From our point of view, taking into account the experimental data error, the accordance between them and the calculated one can be estimated as satisfactory and it can be considered that the proposed kinetic model quantitatively explains the main peculiarities of the photoinitiated linear polymerization to high conversion in the layers with small optical densities.

Characterized peculiarities of the linear polymerization into microheterogeneous system

The experimental data represented as a conversion dependence upon time do not permit one to select the separate components of the linear polymerization process, to estimate their share into the summary rate of the process, or to underline its characterized peculiarities. The kinetic model gives this possibility.

Let us consider the most interesting stage of polymerization in the microheterogeneous system, that is, from the moment of polymer–monomer phase extraction: The kinetic data of the PMPH from the MPPH extraction are represented in Figure 3 by the calculated, accordingly to (62), dependencies ϕ_s and $d\phi_s/dt$

upon time. The represented calculated results show that the maximum rate $(d\phi_s/dt)_{\max}$ of the PMPH from the MPPH extraction is observed practically at the same value $\phi_{s(\max)} = 0.525$ at all concentrations of the photoinitiator. From the analysis of (62) on the function $d\phi_s/d\tau$, the extremum follows that, at the equilibrium distribution of the photoinitiator between the MPPH and the PMPH, that is, at $L = 1$, the maximum value $d\phi_s/d\tau$ should be observed at $\phi_{s(\max)} \leq 0.5$; at this time, the equality sign is fulfilled accordingly to condition $\bar{k}_1 \ll \bar{k}_2$, at which the main share into $(d\phi_s/d\tau)_{\max}$ brings the polymerization rate into the interphase layer, whose maximum is determined by the function $\phi_s(1 - \phi_s)$. Under the same conditions, $\bar{k}_1 \ll \bar{k}_2$, but at the nonequilibrium photoinitiator distribution ($L < 1$), the maximum rate of polymerization in the interphase layer according to function $\phi_s(1 - \phi_s)^\beta$, where $\beta = 1 - m\alpha$, is achieved at the value $\phi_{s(\max)} = 1/(1 + \beta)$, that is, at $\phi_{s(\max)} = 0.555$. The lesser value $\phi_{s(\max)} = 0.525$ in the numerical calculations indicates that the condition $\bar{k}_1 \ll \bar{k}_2$ (\bar{k}_1 is 25 times less than \bar{k}_2) is not completely fulfilled and brings into the value $(d\phi_s/d\tau)_{\max}$ a small, but noticeable, share in the process of polymerization in liquid the MPPH.

Figure 4 compares the calculated summarized rate $dP/d\tau$ (63) and its constituents, namely, $(dP/d\tau)_{v+vs} = (P_s^0 - P_v^0)d\phi_s/d\tau$ is the summarized rate of polymerization in the MPPH and the interphase layer on the boundary of the MPPH and the PMPH and also $(dP/d\tau)_s = \bar{k}_3 J_0 (c_0 L)^{2m} U(\tau)$ is the polymerization rate in the PMPH. The maximum values $(dP/d\tau)_{v+vs}$ are observed at the same times as $d\phi_s/d\tau$; the maximum values $(dP/d\tau)_s$ are observed at later times. The summarized rate of the process $dP/d\tau$ at small t from the beginning of the PMPH extraction is completely determined by $(dP/d\tau)_{v+vs}$, and at the large τ , that is, on the finished

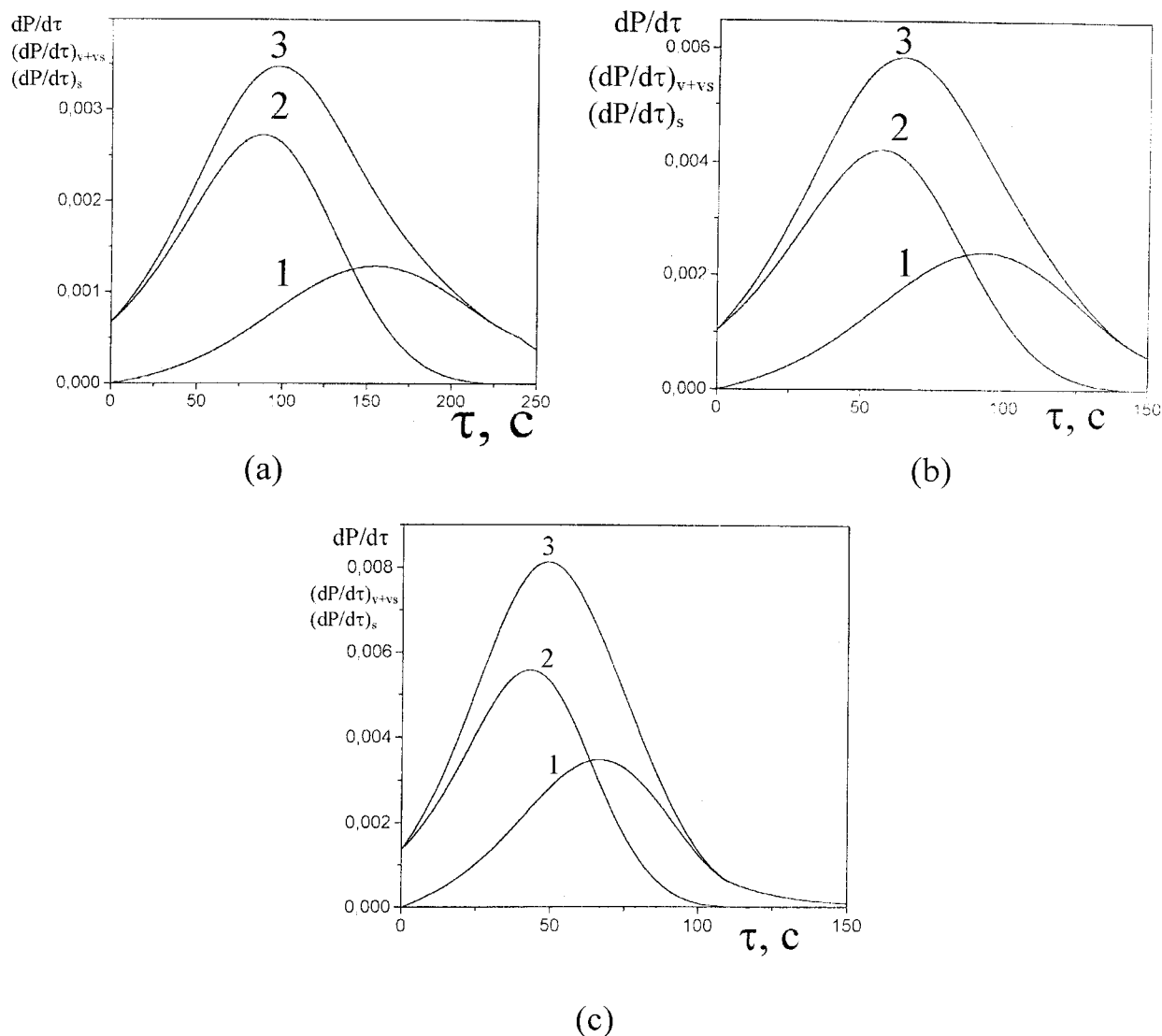


Figure 4 (Curve 3) Calculated dependencies via eqs. (62) and (63) and also the summary polymerization rate $dP/d\tau$ in the microheterogeneous system and its components, namely, (curve 1) $(dP/d\tau)_s$, the polymerization rate in the volume of the PMPh and (curve 2) $(dP/d\tau)_{v+vs}$, polymerization rate in volume of the MPPh and interphase layer on the boundary of an MPPh and a PMPh.

stage of the polymerization process, by the rate $(dP/d\tau)_s$ of polymerization in the PMPh. An extreme of the summarized rate $dP/d\tau$ of the polymerization via time is located between extremes $(dP/d\tau)_{v+vs}$ and $(dP/d\tau)_s$ but is considerably near to an extreme $(dP/d\tau)_{v+vs}$. In another case, the main share (up to 70%) into the maximum value $dP/d\tau$ gives $(dP/d\tau)_{v+vs}$. However, with increasing of the photoinitiator concentration, this share decreased slowly and the share $(dP/d\tau)_s$ increased. When the extreme $dP/d\tau$ is slightly shifted relative to the extreme $d\phi_s/d\tau$, the values $\phi_s^0 > \phi_{s(\max)}$ correspond to maximum values $dP/d\tau$. The calculated data give a value $\phi_s^0 = 0.625$ as well as $\phi_{s(\max)}$, one practically not depending upon the photoinitiator concentration. Thus, the conversion P_0 , corresponding to the maximal rate of polymerization, is determined, in our case, by the equation $P_0 \approx P_s^0(1 - 0.625) + \bar{P}_s^0$

0.625, where \bar{P}_s^0 is the average value of conversion into the PMPh in the moment of time corresponding to the maximum $dP/d\tau$.

The dependence of the calculated values \bar{P}_s accordingly to (68) upon the time at various photoinitiator concentrations is represented in Figure 5. The values \bar{P}_s^0 , corresponding to the maximal rates of the summarized process, are very slightly increased (from 0.85 to 0.87) with an increasing photoinitiator concentration. From this follows that the magnitudes P_0 should also be increased with the photoinitiator concentration increasing from ≈ 0.72 at $c_0 = 0.5\%$ (by mass) to 0.74 at $c_0 = 3\%$ (by mass). The experimental data do not allow one to observe of this weak effect.

Even though the first order upon the photoinitiator, taking into account the gradient of illumination on the layer of the polymerizing composition decreasing to

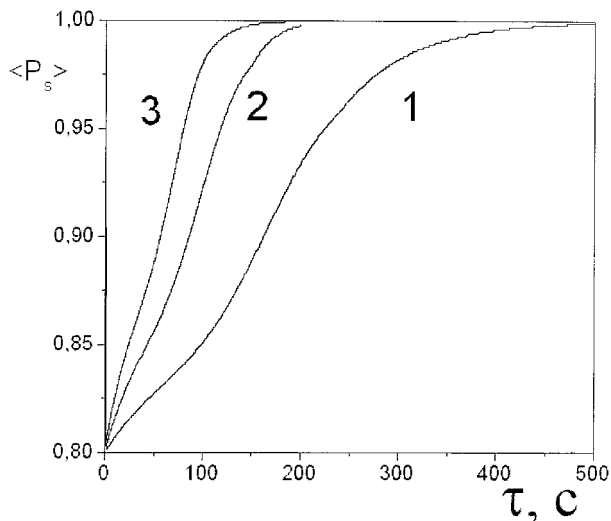


Figure 5 Average conversion into the PMPH calculated dependencies via eq. (68) at different concentrations of the photoinitiator c_0 (% mass): (1) 0.5%; (2) 1.5%; (3) 3.0%. $E_0 = 37.4 \text{ W/m}^2$; $T = 283 \text{ K}$.

$2m = 0.8$, is installed into the kinetic equation of the polymerization process in the PMPH: The rate $(dP/d\tau)_s$ is increased 2.7 times when increasing the photoinitiator concentration up to six times (see Fig. 4). It connected with fact that the comultiplicant before the integral $U(\tau)$ is increased with the increasing photoinitiator concentration in the rate expression $(dP/d\tau)_s$ for polymerization in the PMPH, but the integral $U(\tau)$ is decreased. The behavior of the integral $V(\tau)$ is similar. Their behaviors via time at the different photoinitiator concentrations are shown in Figure 6.

Two extreme cases are possible depending upon the rate ratios into the PMPH and the MPPH and the interphase layer. If the PMPH separation rate is con-

siderably faster than the polymerization rate into the PMPH, we would obtain the average conversion into the PMPH equal to $(\bar{P}_s \approx \bar{P}_s^0)$, practically to the values $\rho_s \approx 1$. This conversion is equal to the the PMPH separating rate. The kinetic curve of the process should be characterized in this case with a long slow tail to polymerization into the PMPH at $\rho_s \approx 1$.

Conversely, if the rate of polymerization into the PMPH is considerably higher than the rate of the PMPH separation, then the average conversion into the PMPH will be equal to $\bar{P}_s = \approx 1$. In this case, the polymerization process is simultaneously finished in all reactionary zones in accordance with the condition $\rho_s \approx 1$ and $P \approx 1$ and the kinetic curve will not have a long slow tail. This variant approximates the kinetics of linear polymerization up to a 3D one, at which the polymer with limiting conversion $P_s^0 \approx 1$ is selected in the solid phase at once.

CONCLUSIONS

The main peculiarity of linear polymerization is that this chemical process proceeds in a medium, the properties of which sharply vary until the transition into a new phase state. We cannot obtain a quantitative kinetic model of the process with not taking into account the above-said circumstance, that is, using the formalism of diffusion control upon the quadratic chain-termination rate only.

The microheterogeneity of a polymerizing system in the case of 3D polymerization is observed at very low conversions and is not an experimentally proven fact. Theoretically, this fact can be explained both thermodynamically (as a poor coexistence of a network polymer with a monomer) and kinetically (by the small

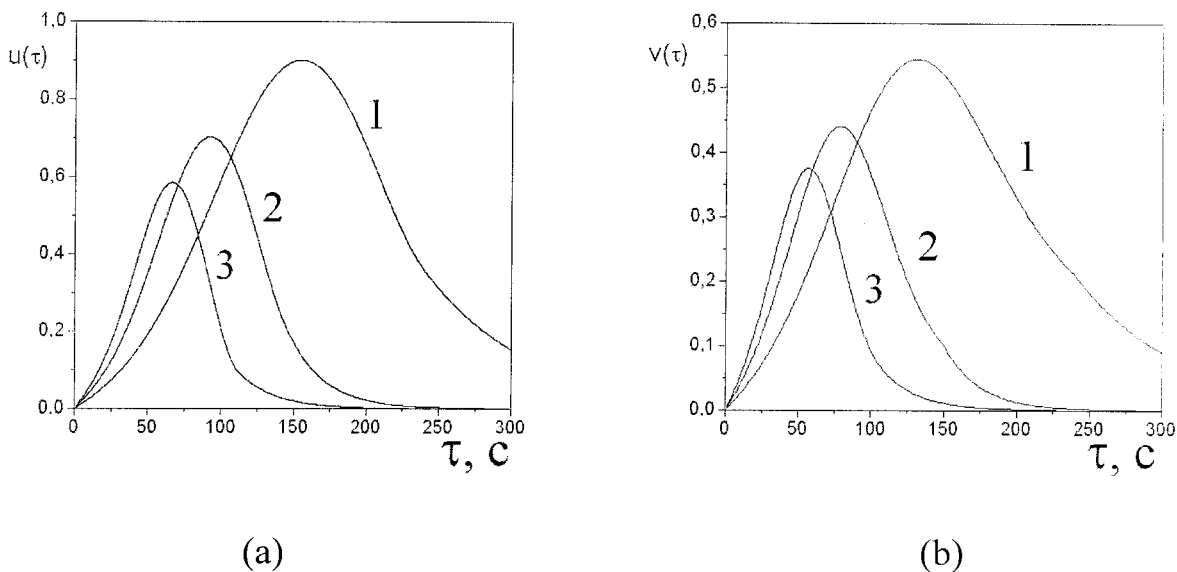


Figure 6 Calculated, in accordance with eqs. (64) and (70), behavior of integrals $U(\tau)$ and $V(\tau)$ via time at different concentrations of the photoinitiator c_0 (% mass): (1) 0.5%; (2) 1.5%; (3) 3.0%; $E_0 = 37.4 \text{ W/m}^2$; $T = 283 \text{ K}$.

viscosity of the monomer block and the solubility of a polymer, which is little).

The observed generality (e.g., the increasing order upon the initiator) of the kinetic peculiarities for block polymerization to high conversion, of matrix photopolymerization,³⁵ and of polymerization in the presence of porous fillers³⁶ or at adsorption immobilization on the carrier surface of the polymeric initiator³⁷ indicates that the solid phase creates the special ordered structure of the nearest reactionary space, in which the transmitting and segmental mobility of the macroradicals are sharply reduced. That is why polymerization in the ordered reactionary space can proceed in accordance with other kinetic regularities than in the liquid monomer space.

Such an idealized conception of two reactionary zones (liquid monomer phase and interphase layer on the boundary of a "liquid monomer–solid polymer") allowed one to obtain the quantitative kinetic model of stationary and nonstationary processes for 3D polymerization and to explain their special peculiarities.^{23–25} The same conception, but for the three reactionary spaces, is used in the presented work for construction of a kinetic model for stationary linear polymerization. However, for linear polymerization, even at conversion P_v^0 , corresponding to the limited solubility of a polymer in a monomer, the microphase separation of a system cannot be characterized with a so-unambiguous character, as in a 3D polymerization one. Two factors hinder this process, namely, first, a large thermodynamic compatibility of the linear polymer with the monomer and, second, the high viscosity of the monomer–polymer solution at conversion P_v^0 . Therefore, instead of the strict microphase distribution, we have the glass transition process of a polymerizing system, that is, the process of initiation, propagation, and confluence of fluctuations of both density and structure, which, conditionally, can be named as microvolumes of the polymer–monomer phase. Since the fluctuation microvolumes possess a higher structural ordering than the "liquid monomer–polymeric phase," they and their diffusion-spray part (so-called interphase layer) are reactionary spaces with other kinetics of polymerization than in the liquid monomer–polymer solution. Despite the formality and idealism of this concept, it allows to one obtain the kinetic model of the linear polymerization process quantitatively, corresponding to all sets of experimental data.

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