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KINETIC MODEL OF PHOTOINITIATED COPOLYMERIZATION OF MONOFUNCTIONAL MONOMERS TILL HIGH CONVERSIONS

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Abstract. Regularities of kinetics of photoinitiated copolymerization till high conversions in the systems of monofunctional methacrylate comonomers (hydroxyethyl methacrylate (HEMA), glycidyl methacrylate (GMA)) have been investigated by laser interferometry in a wide range of experimental factors (molar ratio of comonomers, photoinitiator concentration, intensity of UV-irradiation). Kinetic model of photoinitiated copolymerization of methacrylates till high conversions has been proposed on the basis of microheterogeneity conception of the polymerization process.

Keywords: kinetic model, copolymerization, photoinitiator

1. Introduction

Copolymers on the basis of various by nature and functionality acrylate and methacrylate monomers are of increasingly wide use in different industries of national economy. It causes a great interest for investigation of copolymerization processes of acrylates and methacrylates. In particular, a lot of researches are devoted to polymerization processes which take place at UV-irradiation since copolymers obtained by photochemical technologies are used in polygraphy for manufacturing of printing boards and plates, integral schemes in radio- and microelectronics, optical discs, holograms, as organic basis of stomatological materials *etc*. [1, 2]. Most of these works have experimental character and deal with the influence of the acrylate monomers structure and reactive medium nature on kinetics of their polymerization and copolymerization as well as on properties of the obtained products. For example, in [3-4] it was shown that nature of solvent, viscosity and pH of reactive medium, temperature, pressure *etc*. significantly affect the value of copolymerization rate constants. Some authors [5-8] investigated the influence of additives (diluents, stable radicals, fillers) on kinetic features of photopolymerizing acrylate systems.

However, statistically significant data from kinetics of photoinitiated copolymerization till high conversions, which would serve as an experimental base for kinetic model of the process derivation, are practically absent.

Regularities of kinetics of photoinitiated copolymerization for the initial stage of the process, that is at conversions, when polymerizing system remains homogeneous and is monomer-polymer phase, may be satisfactorily described by the known Mayo-Walling equation. Theoretical description of copolymerization kinetics till high conversions seems to be more complicated, since it is necessary to take into account the division of the system at microphase level.

According to the conception of microheteogeneity of polymerizing system [1, 9] the process is assumed to pass till high conversions in three reaction zones: in monomer-polymer phase, in polymer-monomer one which precipitates from monomer-polymer phase in the form of micrograins, and in the interphase layer. On its basis kinetic models for homopolymerization of mono- and bifunctional monomers have been obtained.

As the development of this direction in the present work kinetics of photoinitiated copolymerization of monofunctional methacrylates till high conversions has been investigated. On the basis of above-mentioned conception the kinetic model for quantitative description of these processes have been suggested.

2. Experimental

2.1. Initial Substances

For experimental researches the following materials were chosen:

2,3–epoxypropyl (methacrylate glycidyl methacrylate) (GMA)

$$CH_2=C-C(O)-O-CH_2-CH-CH_2$$
$$\quad\quad |\quad\quad\quad\quad\quad\quad\quad\quad \backslash\ /$$
$$\quad\quad CH_3\quad\quad\quad\quad\quad\quad\quad O$$

reagent grade (Fluka) with the following characteristics: assay $\geq$ 97 %, *FW* 142.16, d_4^{20} 1.075, n_d^{20} 1.450, *bp* 465–470 K;

2–hydroxyethyl methacrylate (HEMA)

$CH_2=C(CH_3)-C(O)-O-CH_2-CH_2-OH$
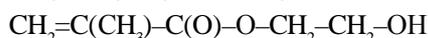
reagent grade (Aldrich) with the following characteristics: assay $\geq$ 97 %, *FW* 130.14, d_4^{20} 1.073, n_d^{20} 1.453, *bp* 330–345 K.

Monomers were purified by mixing them with activated Al_2O_3 powder and subsequent centrifugation [1].

2,2–dimethoxy–1,2–diphenylethane–1–on (IRGACURE 651) reagent grade (Fluka), assay $\geq$ 98 %, *FW* 156.30, d_4^{20} 1.210, *mp* 330–344 was used as photoinitiator.

2.2. Experimental Technique

Stationary kinetics of photoinitiated copolymerization of methacrylates to high conversions was studied by laser interferometry (modification of dilatometric method) [2]. Photocompositions were placed under covering medical glass (with the aim to prevent the inhibitive effect of oxygen). The UV-irradiation of the system was performed by means of a mercury-quartz lamp DRT-400.

During the experiments the current (H_t) as well as maximal (H_o) shrinkage of polymerizing composition layer have been determined. The ratio between the current shrinkage and the maximal one was accepted as the relative integral polymerization depth (conversion): $P = H_t/H_o$. The kinetic curves of stationary copolymerization were obtained in co-ordinates: conversion *vs* time.

3. Results and Discussion

3.1. Kinetic Regularities of Copolymerization of Monofunctional Methacrylates till High Conversions

Kinetics of photoinitiated copolymerization of monofunctional monomers HEMA and GMA to high conversions was studied at molar ratio of components 4:1, 2:1, 1:1, 1:2 and 1:4. For every system kinetic curves were built at two concentrations of photoinitiator (1 and 2 mol %) and at three intensities of UV-irradiation (7, 17 and 48 W/m^2). In Figs. 1-2 the integral kinetic curves of methacrylates copolymerization and their differential anamorphoses are presented.

All integral kinetic curves, regardless of the composition of the polymerizing system and conditions of
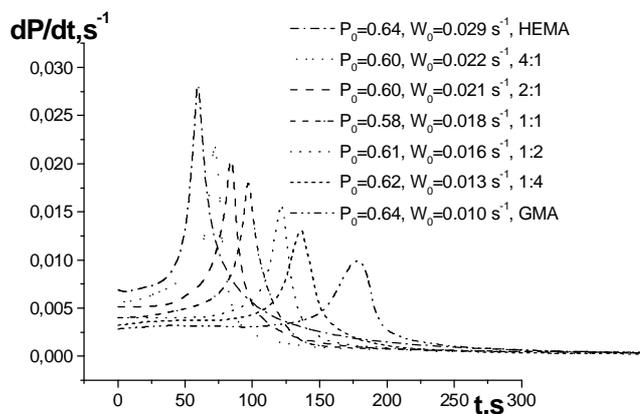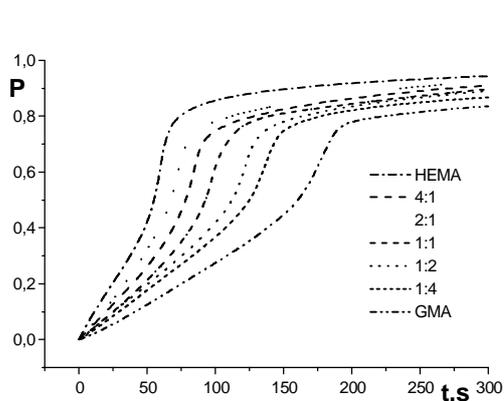
a)
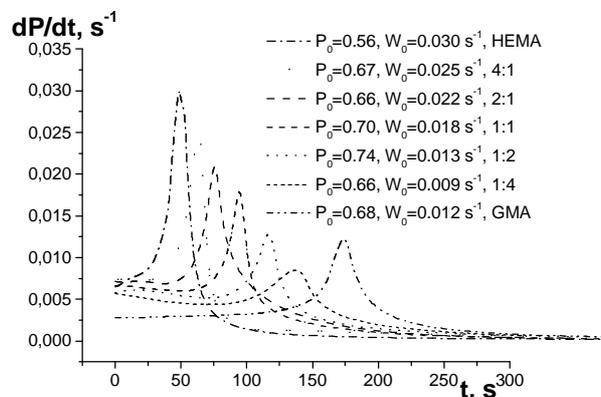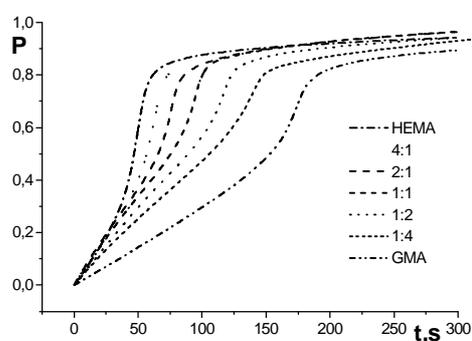
b)
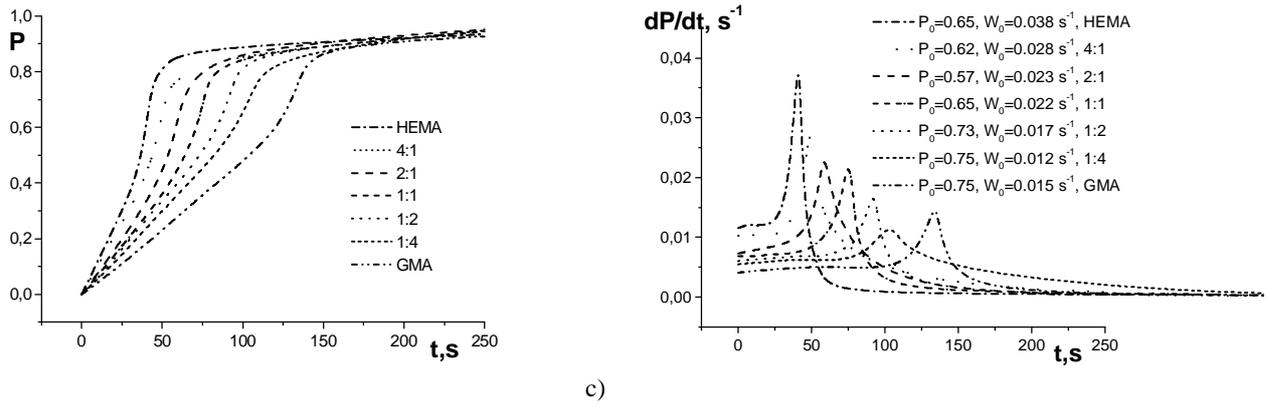
Fig.1. Integral kinetic curves and their differential anamorphoses of photoinitiated copolymerization of HEMA – GMA system depending on its composition (IRGACURE 651 2.0 mol %, $T = 293$ K)
a) $E_o = 7$ W/m²; b) $E_o = 17$ W/m²; c) $E_o = 48$ W/m²
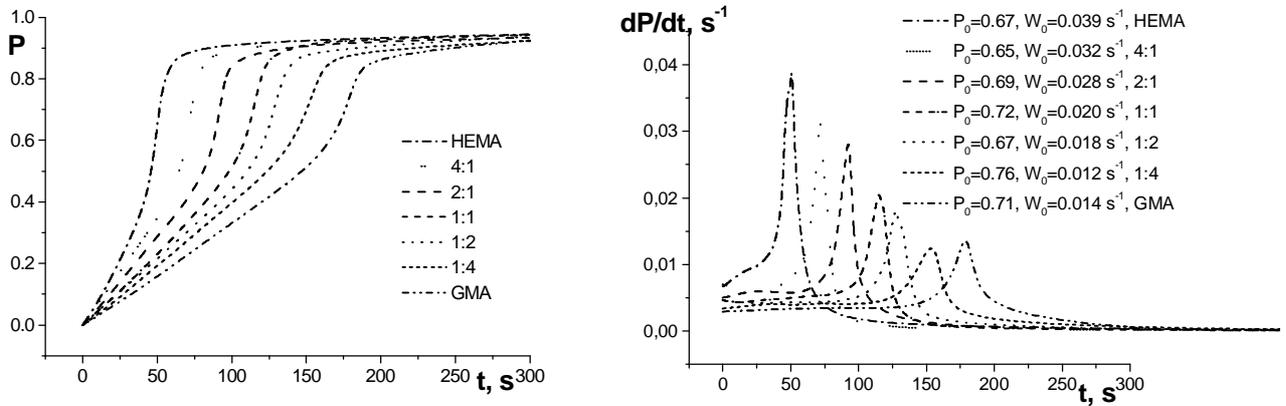
Fig. 2. Integral kinetic curves and their differential anamorphoses of photoinitiated copolymerization of HEMA – GMA system depending on its composition (IRGACURE 651 1.0 mol %, $T = 293$ K, $E_o = 48$ W/m²)

the carrying out process, are typically *S*-shaped and consist of the protracted, practically linear initial part, the short one that reflects the intensive process of autoacceleration and the protracted part that reflects the slow process of autobraking. However, with increasing of the ratio HEMA:GMA appropriate diminishing of the beginning of the autoacceleration stage conversion P_v^o, conversion P_o at maximal copolymerization rate W_o during autoacceleration stage, and increasing of W_o are observed.

These results show that it is possible to describe kinetics of monofunctional monomers copolymerization in terms of conception of three reaction zones taking into account the features of copolymerization in every reaction zone.

3.2. Main Principles of the Kinetic Model

1. Polymerizing system is homogeneous that is monomer-polymer phase (MPP) up to the conversion P^*, at which solubility of comonomer in monomer solution is maximal. The process of copolymerization takes place in it after the classic kinetic scheme with square chain termination:

chain propagation
$$A_i + R_j \xrightarrow{k_{pij}} R_i , \ i = 1,2 , \quad P \le P* \quad (1)$$
chain termination
$$R_i + R_j \xrightarrow{k_{tij}} \text{product}, \ i = 1,2 , \ P \le P* \quad (2)$$
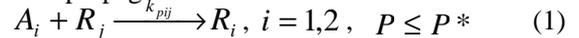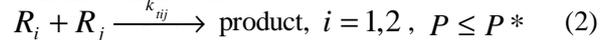
Specific copolymerization rate W_{vi} of *i*-monomer may be described using the well-known Mayo-Walling equation

$$w_{v_i} = \frac{(k_{pii}k_{pij}[A_{vi}]^2 + k_{pij}k_{pji}[A_{vi}][A_{vj}])v_{in}^{1/2}}{\{k_{tii}(k_{pij}[A_{vi}])^2 + 2k_{tij}k_{pij}k_{pji}[A_{vi}][A_{vj}] + k_{tjj}(k_{pji}[A_{vj}])^2\}^{1/2}} \quad (3)$$

where $[A_{vi}]$ is *i*- monomer concentration in MPP.

According to (3) copolymerization rate ($W_{vi} + W_{vj}$) must be the quenching function of time, while experimental kinetic curves at this part are practically linear. Probably, with increase of polymer concentration in MPP and respective increase of its viscosity the rate constant k_t of the square chain termination decreases due to the growth of contribution of macroradicals diffusion braking.

2. At the achievement of critical conversion P^* at the moment of time t^* monomer-polymer phase becomes saturated with copolymer. At some oversaturation polymer-

monomer phase (PMP) precipitates from MPP in the form of nuclei, that is a solid solution of monomers in copolymer. After spontaneous formation of PMP nuclei oversaturation of MPP with copolymer practically disappears, that is why subsequent copolymerization process is accompanied only by the growth of PMP nuclei.

Appearance of the polymer-monomer phase creates two new reaction zones: a volume of PMP and interphase layer at MPP and PMP interface. Let us designate reaction zones volumes as v_v, v_s and v_{vs}, and their volume fractions regarding to the general volume v_o of the system $-j_v$, j_s and j_{vs}, respectively. The volume v_{vs} and, respectively, the volume fraction j_{vs} of interphase layer are complicated functions of the processes of formation, growth and aggregation of PMP micrograins. At the stage of micrograins growth, when $j_v >> j_s$, it is possible to expect $j_{vs} \sim j_s$; at the stage of aggregation, when $j_v << j_s$, on the contrary, $j_{vs} \sim j_v$. In general case, in view of probability of contact between white and black balls in a vessel, it is possible to approximate the connection between j_{vs}, j_v and j_s by the function

$$j_{vs} \cong F_v j_v j_s \qquad (4)$$

where the proportion coefficient F_{vs} depends on fractal characteristics of micrograins (both PMP and MPP), their number and the thickness of interphase layer [9, 10].

It is possible to assume, that the volume of the interphase layer is sufficiently small and the condition $j_{vs} << j_v + j_s$ takes place so that $j_v + j_s \cong 1$. Then it is conveniently to consider j_s as the only variable and to rewrite correlation (4) in the form of:

$$j_{vs} \cong F_{vs}(1 - j_s) j_s \qquad (5)$$

3. In the microheterogeneous system at $P \geq P^*$ and $t \geq t^*$ the specific rate of i-monomer expense is determined as the contribution of every reaction zone:

$$-\frac{d[A_i]}{dt} = w_{vi}(1 - j_s) + w_{vsi} F_{vs}(1 - j_s) j_s + \langle w_{si} \rangle j_s \qquad (6)$$

On the contrary to w_{vi} and w_{vsi} that are specific copolymerization rates on i-component in volumes of MPP and interphase layer which are homogeneous, $\langle \omega_{si} \rangle$ is the specific rate of copolymerization on i-component in micrograins of PMP, averaged by their volume and times of precipitating of PMP portion.

4. Interphase layer at MPP and PMP interface differs from MPP by considerably smaller segmental and, respectively, transmission mobility of macroradicals, which increases the contribution of the diffusion braking into square chain termination with respective abrupt decrease of its rate constant. Nevertheless, let us accept [11], that square chain termination remains dominant, and the kinetic scheme of copolymerization in interphase layer keeps its classic form (1) and (2). Consequently, specific copolymerization rate on i-monomer in interphase layer

may be described using Mayo-Walling equation (3) with substantially changed k_p and especially k_t.

In the polymer-monomer phase the segmental and transmission mobilities of macroradicals decrease so that the dominant process of chain termination is "desactivation" of macroradicals at trapping them by the polymeric matrix [12-14]. From formal-stoichiometric position such type of chain termination is linear on macroradicals and is indicated as an act of macroradical propagation which leads into a trap. Therefore the kinetic scheme of the linear chain termination can be expressed as [9-11]:

$$
A_i + R_j
\begin{array}{c}
\overset{k_{pij}}{\nearrow} R_i \\
\underset{k_{tij}}{\searrow} \{R_i\}
\end{array}
\qquad (7)
$$
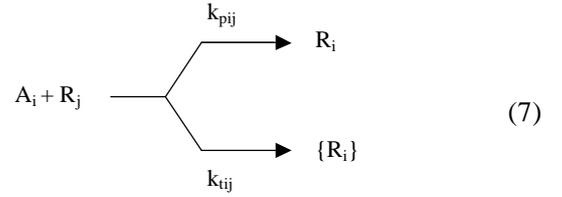
k_{tij} is the function of k_{pij} and of the traps concentration [9, 15].

The equation of polymerization rate in the multicomponent system for kinetic scheme (7) has been obtained in the general form by the routes method [9, 16]. According to it in a partial case of copolymerization we get:

$$w_{si} = \frac{(k_{pii}k_{pij}[A_{si}]^2 + k_{pij}k_{pji}[A_{si}][A_{sj}])v_{in}}{k_{tii}k_{pij}[A_{si}]^2 + (k_{tij}k_{pij} + k_{tji}k_{pij})[A_{si}][A_{sj}] + k_{tij}k_{pji}[A_{sj}]^2} \qquad (8)$$

Here, however, the concentrations of monomers $[A_{si}]$ are different on PMP micrograins volume and depend not only on the time of precipitating of this PMP portion, copolymerization rate in it but also on the rate of coming of this monomer from MPP into PMP.

5. Let us consider the situation in the moment of time $t \geq t^*$. In the interval $t + dt$ the elementary volume of PMP will precipitate from PMP, equal to $v_o dj_s$. It is possible to accept, that it is homogeneous in composition and specific copolymerization rate in it obeys Eq. (8). To the moment of time $t \geq t$, that is in the interval $t - t$, the average specific copolymerization rate in the given elementary volume will be equal to

$$\overline{w_{si}} = \frac{1}{t - t} \int_t^t w_{si} dt \qquad (9)$$

The contribution of the elementary volume $v_o dj_s$, which has precipitated in the moment of time $t \geq t^*$, into integral copolymerization rate in PMP on i-component is equal to

$$\overline{w_{si}} dj_s = \frac{dj_s}{t - t} \int_t^t w_{si} dt \qquad (10)$$

Intergrating (10) from 0 till φ_s on the left, from t^* till t on the right according to the theorem about a mean, we get

$$\langle w_{si} \rangle j_s = \int_{t*}^{t} \frac{dj_s}{dt} \frac{dt}{t-t} \int_{t}^{t} w_{si} dt, \quad t* \le t \qquad (11)$$

One more variable appears as a result, which charactrizes the rate $d\varphi_s/dt$ of polymer-monomer phase precipitating. For its determination let us write down the change of number of i-monomer moles dn_{vi} in MPP at the time dt:

$$-dn_{vi} = v_v w_{vi} dt + v_{vs} w_{vsi} dt + [A_{si}] dv_s \qquad (12)$$

Two first items give i-monomer expense due to copolymerization in MPP and in the interphase layer, the third one – due to the monomer transition into PMP. On the other hand, at the change of PMP composition and volume we have

$$dn_v = v_v d[A_{vi}] + [A_{vi}] dv_v \qquad (13)$$

Comparing (12) and (13), we find

$$-(1-j_s) d[A_{vi}] = w_i dt - ([A_{vi}] - [A_{si}]) dj_s \qquad (14)$$

For shortening let us designate the copolymerization rate in MPP and in the interphase layer as w_i:

$$w_i = w_{vi}(1-j_s) + w_{vsi} F_{vs}(1-j_s) j_s \qquad (15)$$

Having summarized the balance equation (14) on both monomers, we obtain

$$-(1-j_s)(d[A_{vi}] + d[A_{vj}]) = (w_i + w_j)dt -$$
$$-([A_{vi}] - [A_{si}] + [A_{vj}] - [A_{sj}])dj_s \qquad (16)$$

It is possible to assume, that in a monomer-polymer phase, saturated with polymer, the copolymerization process changes the ratio between monomers concentrations so that $d[A_{vi}] \cong -d[A_{vj}]$. Equating the right part of (16) according to this condition to zero, we get

$$\frac{dj_s}{dt} = \frac{w_i + w_j}{[A_{vi}] - [A_{si}] + [A_{vj}] - [A_{sj}]} \qquad (17)$$

Here $[A_{vi}]$ and $[A_{si}]$, respectively, are i-monomer concentrations in MPP and PMP in the moment of precipitating of given portion $d\varphi_s$ of polymer-monomer phase. We can assume, that distribution of monomer between MPP and given PMP portion $d\varphi_s$ is practically equilibrium and obeys the relation

$$[A_{si}] = [A_{vi}] L_i \qquad (18)$$

where L_i is the distribution coefficient.

6. In two-phases polymerizing system for the complete description of the process kinetics the rates of monomers expense in every phase must be known, taking into account the rate of precipitating of PMP from MPP, which is determined by expression (17).

The expression for the rate of i-monomer concentration in MPP change we find from (14):

$$-\frac{d[A_{vi}]}{dt} = \left\{ w_i - ([A_{vi}] - [A_{si}]) \frac{dj_s}{dt} \right\}/(1-j_s) \qquad (19)$$

The rate of i-monomer concentration change in PMP we find from the following relations. Increase dn_{si} of i-component moles number in PMP in time dt will be:

$$dn_{si} = -\langle w_{si} \rangle v_s dt + [A_{si}] dv_s \qquad (20)$$

On the other hand, setting the concentration of i-monomer averaged on volume PMP in given moment of time t, we can write down

$$dn_{si} = [\overline{A_{si}}] dv_s + v_s d[\overline{A_{si}}] \qquad (21)$$

Comparing (20) and (21), we get

$$-\frac{d[\overline{A_{si}}]}{dt} = \left\{ \langle w_{si} \rangle j_s - ([A_{si}] - [\overline{A_{si}}]) \frac{dj_s}{dt} \right\}/j_s \qquad (22)$$

As according to (18) $[A_{si}]$ is a function of $[A_{vi}]$, four equations like (19) and (22) together with (17) completely describe 5 independent variables: $[A_{vi}]$, $[\overline{A_{si}}]$ and φ_s. Let us show, that it takes place, bringing equations (19) and (22) to the balance equation (6), that describes i-monomer expense in the whole system.

The current i-monomer concentration $[A_i]$ counted on the whole system volume is equal to

$$[A_i] = [A_{vi}](1-j_s) + [\overline{A_{si}}] j_s \qquad (23)$$

Taking into account the change φ_s in time we have

$$\frac{d[A_i]}{dt} = (1-j_s) \frac{d[A_{vi}]}{dt} + j_s \frac{d[\overline{A_{si}}]}{dt} -$$
$$- ([A_{vi}] - [\overline{A_{si}}]) \frac{dj_s}{dt} \qquad (24)$$

Substituting into (24) expressions (19) and (22) for $d[A_{vi}]/dt$ and d/dt, respectively, and taking into account designation (15), we obtain (6). Thus, equations (19), (22) and (17) make up the complete system of differential equations, that describe copolymerization kinetics in three reaction zones of two-phases polymerizing system.

4. Conclusions

The experimental material on kinetics of photoinitiated copolymerization of monofunctional methacrylates till high conversions allowed to suggest the kinetic model of the process in general form on the basis of the conception of microheterogeneity of polymerizing system, which takes into account copolymerization features in three reaction zones: monomer-polymer and polymer-monomer phases and at interphase layer.

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КІНЕТИКА ФОТОІНІЦІЙОВАНОЇ КОПОЛІМЕРИЗАЦІЇ МОНОФУНКЦІОНАЛЬНИХ МОНОМЕРІВ ДО ГЛИБОКИХ КОНВЕРСІЙ

Анотація. *Закономірності кінетики фотоініційованої кополімеризації до глибоких конверсій в системах монофункціональних метакрилових комономерів (гідроксиетилметакрилат (ГЕМА), гліцидилметакрилат (ГМА)) досліджені методом лазерної інтерферометрії у широкому діапазоні зміни експериментальних факторів (мольні співвідношення комономерів, концентрація фотоініціатора, інтенсивність УФ-опромінення). На основі концепції мікрогетерогенності полімеризаційного процесу запропонована кінетична модель фотоініційованої кополімеризації метакрилатів до глибоких конверсій.*

Ключові слова: *кінетична модель, кополімеризація, фотоініціатор.*