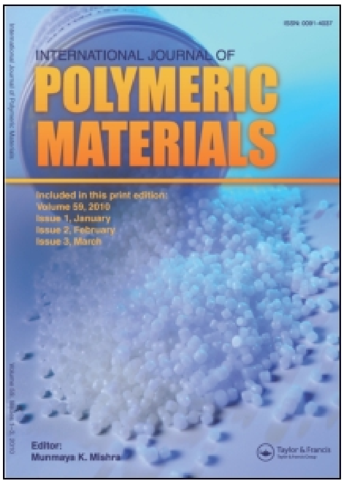

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Kinetics of Three-dimensional Block Polymerization

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A kinetic model of three-dimensional block-polymerization of multifunctional monomers until high state of conversions has been suggested. The model is based on the conception of microheterogeneity of the polymerizing system and a special role of the interphase layer on the border of solid polymer–liquid monomer. The initial assumptions are: (a) the observed polymerization rate is a sum of rates of homophase process taking place in the volume of liquid monomer according to the classical kinetic scheme with the quadratic chain termination, and of a heterophase process taking place in the inter-phase layer in the regime of gel-effect; (b) the clusters of solid polymer in the liquid monomer phase and clusters of liquid monomer in a solid polymer matrix have a fractal structure; (c) the gel-effect in the interphase layer is related to the radical decay rate decrease, and transition of the chain termination control to the rate of chain propagation control. Because of this, the kinetic scheme of the process in the interphase layer incorporates only the elementary reactions of chain propagation which also fulfill the functions of the active radicals decay reactions in the act of their deactivation and function of the reaction initiation of the secondary active radicals from the 'frozen' state as the result of their growth into the reaction zone. The obtained kinetic equations for the stationary and nonstationary regime of the process explain all the basic features of the block-polymerization until high states of conversion.

Keywords: Block-polymerization; Kinetics; 3-dimension; Microheterogeneity

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INTRODUCTION

The investigation of mono- and multifunctional monomer polymerization kinetics till high conversion showed common features of these processes which are in disagreement with the classical kinetic scheme of polymerization which is satisfactory for the initial stage of polymerization. The first feature is the S-shape of the kinetic curves which reflect the dependence of polymerization state on time. Such dependence is characteristic for the autocatalytic reactions. The maximal rate of polymerization corresponds to the transition point on the curve. The last one shows the existence of the process auto-acceleration stage. The maximum occurs also for the case of a relative polymerization rate what shows the existence of an autoretardation stage at which the process rate is decreasing faster than the decrease of monomer concentration [1].

The second feature is based on the pronounced 'post-effect', *i.e.*, on the "dark" (after turning off the UV-light irradiation) postpolymerization process taking place from the beginning of the autoacceleration stage and continuing till the full conversion in some cases [2, 3]. The kinetic curve of the postpolymerization consists of two parts: the first one is fast and short, the second one is slow and prolonged [4–6]. This allows to assume that the postpolymerization process is leading by two types of radicals sharply differing in their life time periods. The polymer molecular mass (MM) is increasing in the post-polymerization process. Sometimes it is reflected in the existence of a second maximum on the molecular mass distribution curve [5]. Incorporation of a chain exchange agent reduces the polymer molecular mass both in the light and in the dark polymerization regimes [2, 4]. The third feature is a high, up to $10^5\,\mathrm{mol/m^3}$ radical concentration determined by EPR-spectroscopy *in situ* at the polymerization end [7, 8]. In the stationary light process regime, a noticeable accumulation of radicals starts from the auto-acceleration stage. In the postpolymerization the radical concentration decreases insignificantly or remains constant. The radical decay becomes noticeable only at relatively high temperatures, > 60°C and the kinetics of the process in some cases is described as a first order reaction. Thus, the radical characteristic life spans determined by EPR-spectroscopy *in situ* at the end of polymerization process are significantly higher than the periods of time of the stationary light and the non-stationary dark processes. Hence, they do not drive the polymerization and are radicals of the third type [7]. To explain the polymerization features till the high conversions two basic concepts are used. The first one is based on a diffusion-controlled character of elementary reactions of the polymerization process given by the classic kinematic scheme. Because of this, in the concept of the diffusion-controlled reactions (DCR) the basis is the known kinetic equation of the initial process stage. The parameters of the process are described, however, as being a function of the current state of monomer-polymer solution [9].

There are different types of the DCR concept varying by taking into consideration various physical factors and details of analytical description of the diffusion control over the rate of elementary reactions. As a rule, the attention is paid mainly to bimolecular chain termination of rate constant which is considered to be a function of macroradicals mobility, their length [9–14], free volume [12, 15–17], or the characteristic viscosity [4, 18] of the monomer-polymer solution. In some variants [12, 15, 18], for the macroradicals mobility functions the initiation efficiency and the chain propagation rate constant are also accepted. Although all the variants of the DCR concept can, in principle, affect the stationary kinetics of polymerization till high conversions, they need to divide the whole process over arbitrary intervals and use for them various mechanisms of diffusion control and corresponding to them analytical dependencies including the empirical ones. The second concept or the micro-heterogeneous model [1, 19–22] is based on the assumption that the basic input into the process kinetics already on the beginning stages is made not by the homophase polymerization in the liquid monomer-polymer solution but by the heterophase one taking place on the boundary of the solid polymer–liquid monomer in the gel-effect regime.

At least for the multi-functional monomers, the microononuniformity of the polymerizing system (*i.e.*, existence of micro-grains of solid polymers in the liquid monomer phase or, after phase inversion, presence of monomer micro-drops distributed in the solid polymer matrix) is a fact proven by both direct experimental methods and indirect methods [1, 19–22]. Because of this, even in the works using the DCR concept, the factor of polymerizing system nonuniformity is not denied [2, 7, 10, 15]. On the contrary, the factor is attractive in explaining the high radical concentration accumulating in the course of polymerization by trapping [6] them in the solid polymeric matrix [7, 15]. In the works where the polymerization features till the high conversions are explained by changing of the chain termination mechanism, *i.e.*, by transition from quadratic to linear, the last one is also considered as a physical exception of active radicals transforming them into trapped, frozen, inactive immobile state by the solid polymer matrix [5, 7]. From this point of view, the difference between micro-heterogeneous model and DCR concept is based on the consideration whether to acknowledge or not that microheterogenety is the main factor determining the features of the polymerization process till high conversions. On the qualitative level, the micro-heterogeneous model is not worse than the DCR concept, however the difficulties of its quantitative treatment were seemed to be unresolvable. Only in the work [23] we have developed a kinetic equation of the stationary process of block polymerization based on the micro-heterogeneous model. The equation was satisfactorily checked on examples of photo-initiated polymerization several di(meth)acrylates [24, 25]. In this work the initial assumption were formulated as following: – the observed polymerization rate is a sum of the homophase polymerization process taking place in the volume of liquid monomer according to the (1) – (2) classical kinetic scheme with a quadratic chain termination, and the rate of heterophase process taking place in the interphase layer on the boundary solid polymer – liquid monomer in the gel-effect regime;

- the clusters of solid polymer in a liquid monomer phase and clusters of liquid monomer in a solid polymeric matrix have a fractal structure;
- the catalytic role of the interphase layer, *i.e.*, the gel-effect, is showing up in decreasing the rate of radicals decay and in transition from chain termination rate control to the control of chain propagation rate.

The suggested kinetic equation has the following type:

$$dp/dt = k_1(1-p)v_i^{1/2} + k_2p(1-p)v_i \tag{1}$$

where: $p = \Gamma/\Gamma_0$, – a relative state of polymerization determined through the polymerization state at a given time moment,

$\Gamma = ([M]_0 - [M])/[M]_0$ and a maximally achievable polymerization state $\Gamma = ([M]_0 - [M]_{00})/[M]_0$, at $t \to \infty$; $[M]_0$, $[M]$ and $[M]_{00}$, are initial, at a given time, and the end monomer concentrations relative to the volume of the whole system correspondingly; k_1 and k_2, are kinetic constants; v_i, – initiation rate. Equation (1) was obtained from the initial one:

$$w = \varphi_V w_V + \varphi_m w_m \qquad (2)$$

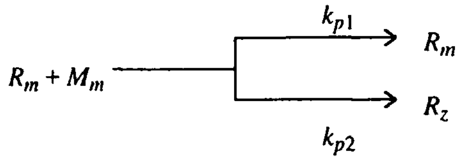
where: φ_v and φ_m are the volume fractions of liquid monomer phase and inter-phase layer respectively and w_v and w_m, are specific polymerization rates related to them. The relationship between $w = dM/dt$ and dp/dt is given as $dp/dt = w/[M]_0\Gamma_0$. Thus, the first products in (1) and (2) are polymerization rates in the liquid monomer phase, and the second ones – in the interphase layer. By preparing the Eqs. (1) and (2), the fact was taken into account that already at the beginning stage of block polymerization (at $\Gamma = 0{,}01$) the liquid monomer phase becomes saturated relative to the new polymer phase but the saturation concentration was low. Because of this, the monomer concentration $[M]_v$ in saturated monomer–polymer solution is constant with time and practically equal to the initial one: $[M]_v = [M]_0$. On the contrary, the volume fraction of liquid phase, p is a variable factor and it is changing with the polymerization state, $\varphi_v = 1 - p$

According to the classical scheme

$$\begin{aligned} &M_v + R_v \xrightarrow{k_{pv}} R_v \\ &R_v + R_v \xrightarrow{k_{tv}} \text{termination product} \end{aligned} \qquad (3)$$

the specific rate of a process in liquid phase is described by the following expression: $w_v = k_{pv}[M]_v(v_i/k_{tv})^{1/2}$ in which k_{pv} and k_{tv} are rate constants of chain propagation and chain termination respectively. Taking into account the expressions $\varphi = 1 - p$ and $[M]_v = [M]_0$, the input of homophase process into the summary process is determined by the first product of Eq. (1). In this case, $k_1 = k_{pv}/\Gamma_0 k_{tv}{}^{1/2}$.

Because the interphase layer is in transition state between the phases of constant compositions – solid polymer with $\Gamma = \Gamma_0$ and liquid monomer with $\Gamma = 0$ and, hence, the properties practically do not depend on the state of polymerization. Only the volume fraction of inter-phase layer, φ_m is changing: due to increase in size and number of clusters of new polymeric phase and their aggregation it should originally increase with polymerization, and then decrease. To describe the dependence of φ_m on the state of polymerization in work [23], the approximation $\varphi_m = h(F_s/F_v)p(1-p)$ was used. In this function h is the interphase thickness, and F_s and F_v, are, respectively, fractal characteristics of clusters surface and volume. The analysis performed in [23] allowed to assume that the most probable cause of gel-effect in the interphase layer is a transition from the chain termination rate control to the chain propagation rate control [9, 10, 12]. This means, that the acts of chain propagation and chain termination are the result of two different interactions of active radical R_m, with monomer functional group. One radical interaction leads to reproduction of the active radical and, hence, to chain propagation, and the other interaction leads to formation of a frozen, inactive radical, R_z what can be represented by the following scheme:



(4)

In respect to the chain propagation reaction, acknowledging the existence of gel-effect in the inter-phase layer means only that k_{p1}, can not be equal to k_{pv}. For initiation reaction, the gel-effect is convenient to consider [15] through the change of the initiation coefficient, f. In this assumption, the ratio between the rates of initiation in the interphase layer and in the liquid monomer volume can be written as $v_{im}/v_{iv} = f_{im}/f_{iv}$. Taking as a reference in the interphase layer, the rate of initiation in liquid phase $v_i = v_{iv}$, the rate of initiation will be $v_{im} = (f_{im}/f_{iv})v_i$.

From the stationary condition of active radicals R_m it follows that in the interphase layer the specific rate of polymerization equals $w_m = k_{p1}(f_m/f_v)v_i/k_{t1}$. Taking into account the volume fraction of the inter-phase layer $\varphi_m = h(F_s/F_v)p(1-p)$, the input of heterophase process into the summary one will be determined by the second product of the Eq. (1). In this case $k_2 = h(F_s/F_v)(f_m/f_v)k_{p1}/k_{t1}\,[M]_0\Gamma_0$. As can be seen, the kinetic parameters k_1 and k_2 in Eq. (1) do not depend on the state of polymerization. Their constancy is confirmed by the quantitative correspondence of Eq. (1) to the experimental data of the stationary kinetics of photoinitiated polymerization of di(meth)acrylate monomers till maximal states of conversion [24, 25]. However, comparison of the suggested model with experimental data on the dark postpolymerization indicates the incompleteness of the kinetic Schemes (3) and (4). Based on the model, it is not possible to explain the existence of two characteristic portions of the postpolymerization kinetic curve and the increase of the average molecular mass of polymer in the dark process.

RESULTS AND DISCUSSION

In the kinetics Schemes (3) – (4) there are two radicals leading the chains. The R_v radicals have a life time in the liquid monomer phase at least two-three orders of magnitude lower than the characteristic times of postpolymerization. Because of this the R_v radicals cannot provide a noticeable input in the postpolymerization process. The performance of active radicals R_m in the interphase layer with life time $\tau_1 = (k_{t1}[M]_m)^{-1}$where $[M_m]$, is the monomer concentration in the interphase layer, can explain the existence of the first, fast and short portion of kinetic curve of postpolymerization but not the second, slow and prolonged one.

Let us accept the point of view made in [5] that the frozen radicals, R_z, are responsible for the prolonged and slow postpolymerization. The participation of the radicals in the creation of the secondary chains can be represented by the following schemes:

$$R_z + M_m \xrightarrow{k_m} R''_m \qquad (5)$$

$$R''_m + M_m \begin{cases} \xrightarrow{k_{p2}} R''_m \\ \xrightarrow{k_{t2}} R''_z \end{cases} \qquad (6)$$

The meaning of (5) is an elementary reaction of creation of the secondary active radicals, R''_m, based on which secondary chain with linear termination is built. However, reaction (5) cannot be the chain transmission reaction because this contradicts the observed experimental increase of the average polymer molecular mass in the post-polymerization process. Hence, reaction (5) should be considered as an act of "shooting" [26] of the frozen radical R_z into an active zone of the interphase layer. In this case, when the length of primary chains is $\nu_1 = k_{p1}/k_{t1}$ and the length of secondary chains $\nu_2 = k_{p2}/k_{t2}$ the average length of primary frozen radicals will be equal to ν_1, and the secondary frozen radicals will be $\nu_1+\nu_2$. This will explain the increase of average polymer molecular mass in the dark process at period of times higher than the life time τ_1 of the primary active radicals. At controlling the rate of linear chain termination and rate of its propagation, the act of chain propagation, for example of the primary chain (4) relative to radicals with the average length ν_1 *i.e.*, R_z, is the act of their decay. From here, the following relation should be valid. $k_{p1}[R_z] = k_{t1}[R_m]$. Because of this,

$$[R_z] = (k_{t1}/k_{p1})[R_m] = [R_m]/\nu_1 \tag{7}$$

From the same considerations, for the secondary chain (6), we have:

$$[R''_z] = (k_{t2}/k_{p2})[R''_m] = [R''_m]/\nu_2 \tag{8}$$

According to (4)–(6), the kinetics of active primary and secondary radicals accumulation in the inter- (15) (16) phase layer is described by the following equations:

$$d[R_m]/dt = v_{im} - k_{t1}[M_m][R_m] \tag{9}$$

And

$$d[R''_m]/dt = k_m[M_m][R_z] - k_{t2}[M_m][R''_m] \tag{10}$$

Denoting:

$$\beta = k_{t1}[M_m], \quad \gamma = k_{t2}[M_m]. \tag{11}$$

We will rewrite (9) and (10) taking into account also (7) as follows:

$$d[R_m]/dt = v_{im} - \beta[R_m] \tag{12}$$

$$d[R''_m]/dt = k_m[M_m][R_z] - \gamma[R''_m] \tag{13}$$

Let us first discuss the stationary process kinetics in the interphase layer assuming $d[R_m]/dt = d[R''_m]/dt = 0$. Then, we will have

$$[R_m] = v_{im}/\beta, \quad [R''_m] = (k_m/k_{p1})v_{im}/\gamma \tag{14}$$

As it is seen, the value (k_m/k_{p1}) in the right hand side expression of (14) plays a role of the efficiency of the second chain initiation due to initiator decomposition in interphase layer reaction. The characteristic polymerization rate in the interphase layer due to primary and secondary chains propagation is then,

$$w = k_{p1}[M_m][R_m] + k_{p2}[M_m][R''_m] \tag{15}$$

After incorporation of the R'_m and R''_m values from (14) into (15) and taking into account (11), we have

$$w_m = (k_{p1}/k_{t1} + k_m k_{p2}/k_{p1}k_{t2})v_{im} \tag{16}$$

From here it follows that the input of the process in the inter-phase layer into the summary process again will be represented by the second product in (1) but at different determination of kinetic parameter k_2:

$$k_2 = h(F_s/F_v)(f_m/f_v)(k_{p1}/k_{t1} + k_m k_{p2}/k_{p1}k_{t2})/[M]_0\Gamma_0 \tag{17}$$

Thus, the kinetic Schemes (4)–(6) keeps the former shape of stationary process (1) and changes only the physical meaning of the k_z parameter. At this, according to (16), the effective length of a chain in the interphase layer will be $v_m = \nu_1 + (k_m/k_{p1})\nu_2$.

Let us discuss now the non-stationary kinetics of the dark post-polymerization. Because the input of homophase process into the summary one in the post-polymerization process must be insignificant (as it was noted above), we will analyze only the kinetics in the interphase layer by assuming $w = \varphi_m w_m$. In the dark regime $v_{im} = 0$. The solution of (12) and (13) can be as follows:

$$[R_m] = (v_{im0}/\beta)\exp(-\beta t) \tag{18}$$

$$[R''_m] = [(k_m/k_{p1})v_{im0}/(\beta - \gamma)][-\exp(-\beta t) + (\beta/\gamma)\exp(-\gamma t)] \qquad (19)$$

Here, time t is determined from the beginning, of the dark period of time, $t = 0$, and v_{im0} is the rate of initiation in the inter-phase layer at the end of the stationary light period corresponding to the beginning of the dark period of time. At this, $[R_m]_0 = v_{im0}/\beta$ and $[R''_m]_0 = (k_m/k_{p1})v_{im0}/\gamma$ – the initial radicals concentrations for the period of postpolymerization.

By incorporating (18) and (19) into (15) and taking into account (16), we obtain an expression for the characteristic postpolymerization rate:

$$w_m = (w_{m0}/(\beta - \gamma))[((1 - \alpha)(\beta - \gamma) - \alpha\gamma)\exp(-\beta t) + \alpha\beta\exp(-\gamma t)] \qquad (20)$$

Here, w_{m0} is the initial postpolymerization rate determined according to (16) for the end of the stationary light period at $v_{imt} = v_{im0}$; the parameter α characterizes the relative input of the secondary chain in the summary kinetics in the interphase layer and is determined by the expression:

$$\alpha = (k_m k_{p2}/k_{p1}k_{t2})/(k_{p1}/k_{t1} + k_m k_{p2}/k_{p1}k_{t2}) \qquad (21)$$

In accordance with the characteristic periods of time of the fast and short, slow and prolonged portions of the kinetic curve of postpolymerization which are determined by the life time of primary radicals $R_m(\tau = \beta^{-1})$ and secondary ones $R''_m(\tau = \gamma^{-1})$, it is possible to assume that $\beta \gg \gamma$ which gives a simpler form of Eq. (20):

$$w_m = w_{m0}[(1 - \alpha)\exp(-\beta t) + \alpha\exp(-\gamma t)] \qquad (22)$$

By again neglecting the input of the homophase process into the postpolymerization, its rate expressed in units of relative conversion can be described as:

$$dp/dt = k_2 p(1 - p)v_{i0}[(1 - \alpha)\exp(-\beta t) + \exp(-\gamma t)] \qquad (23)$$

where k_2 is determined according to (17). In the case of photoinitiated polymerization, the parameters v_{i0}, p, and dp/dt are functions not only of time but also of coordinate of the layer x from the lighted surface ($x = 0$) *i.e.*, they are considered as the differential characteristics of the process in the layer x, $x+dx$. The transition from differential characteristics $p(x, t)$ and $dp(x, t)/dt$ to the experimentally determined ones, *i.e.*, to those averaged through the layer of the photopolymerizing composition, $P(t)$ and $dP(t)/dt$ are obtained by the integral transformations [20]:

$$P(t) = L^{-1}\int_0^L p(x,t)dx, \quad dP(t)/dt = L^{-1}\int_0^L (dp(x,t)/dt)dx \tag{24}$$

where: L is the layer thickness. The differential rate of photoinitiation as function of layer coordinate x and time, t is described by expression [24]:

$$V_i = C_0 J_0 \exp(\tau - y)[(1 + \exp(-y)(\exp(t) - 1)]^{-2} \tag{25}$$

in which: $y = \varepsilon c_0 x$, $\tau = \gamma_v \varepsilon J_0 t''$; C_0–initial for light period ($t' = 0$) concentration of photo-initiator; J_0–light intensity irradiating the composition surface;–molar photoinitiator extinction coefficient: γ_v–quantum efficiency of photoinitiation; t''–light period of time. At the end of the light period of time ($t'' = t_0''$) the differential rate of photoinitiation have value v_{i0} which is determined (25) at $\tau = \gamma_v \varepsilon J_0 t_0''$.

By treating (23) τ_0 according to the theorem of averages we obtain

$$\begin{aligned} dP/dt = (k_2 P(1 - P)[(1 - \alpha)e^{-\beta t} + \alpha e^{-\gamma t}] \\ \gamma_v J_0(1 - \exp(-y_0))/(L[1 + \exp(-y_0)(\exp(\tau_0) - 1)]) \end{aligned} \tag{26}$$

where: $y_0 = e\ C_0\ L$– initial optical density of the layer. At $t = 0$ (the beginning of the dark period), we have $P = P_0$ and

$$\begin{aligned} W_{m0} = (dP/dt)_{t=0} = (k_2 P_0(1 - P_0) \\ \gamma_v J_0(1 - \exp(-y_0))/(L[1 + \exp(-y_0)(\exp(\tau_0) - 1)]) \end{aligned} \tag{27}$$

By using (27) we will give (26) a simpler shape:

$$dP/dt = (P(1 - P)W_{m0}[(1 - \alpha)\exp(-\beta t) + \alpha \exp(-\gamma t)])/P_0(1 - P_0) \tag{28}$$

By comparison with experimental data on post-polymerization represented by kineticcurves of the type $P = P(t)$ the integral form of (28) is more convenient:

$$\ln P(1-P_0)/P_0(1-P) = [W_{m0}[(1-\alpha(1-e^{-\beta t}))/\beta + \alpha(1-e^{-\gamma t})/\gamma]]/P_0(1-P_0) \tag{29}$$

CONCLUSIONS

The suggested kinematic model in the form of (l) or (23), (28) or (29), based on assumption of micro-heterogeneity of polymerizing system and a special role of the interphase layer on the boundary of solid polymer–liquid monomer, satisfactorily explains all the listed above features of block polymerizations till high conversions including the S-shape character of the stationary kinetic curves [23–25], the average MM increase in the postpolymerization process, and the existence in the process of at least two characteristic periods determined by the lifetime of active primary and secondary radicals in the interphase layer. Besides, the model explain the increased radical concentration in stationary light process due to constant incorporation into solid polymer matrix of frozen radicals types R'_z and R''_z. Note also, that although the polymerization process in the interphase layer kinetic scheme is significantly simplified and formalized, it uses a simple physical explanation. The explanation is based on the generality of kinetic regularities of polymerization in the interphase layer, and for example, matrix photopolymerization [27], polymerization in presence of porous fillers [28], or at adsorption immobilization on the surface of polymer initiator carrier [29]. The generality shows that the solid phase creates a special ordered structure of nearest reaction space in which the translation and segmental mobility of macroradicals are sharply reduced. Such structure is similar to the system of microreactors [26–30] weakly interactive with each other in each of which the chain termination is determined by its rate of propagation so that the radical delay is an act of their self-burying which can be found in the model of non-intersecting random walk [31]. A comparison of the suggested model with experimental data on photo-initiated postpolymerization of di(meth)acrylate monomers will be presented in the next paper.

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