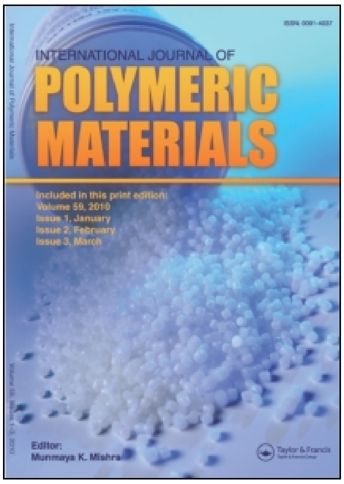

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The Kinetics of theThree-dimensional Photopolymerization of Some Diacrylates

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The kinetics of photopolymeryzation of diacrylates: diethylene glycol(DEGDA)-, 1,4-butanediol-, 1,6-hexanediol- and dipropylene glycol diacrylate at a wide range of photoinitiator concentration and thickness of the layer of the polymerization composition was investigated. We found the dependencies between the maximum rate of the process and the thickness of photocomposition layer and kinetic parameters. Experimental data were compared with a kinetic model of the photoinitiated three-dimensional polymerization. It was determined that the kinetic model allows us to describe the process of three-dimensional polymerization over the whole range of conversion. Molar extinction coefficient of photopolymerization (ε) and quantum yield of the photoinitiator decomposition (γ), rate constants of homo

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*Corresponding author.

(k_1)- and heterophase (k_2) process were estimated. It was determined that the constants k_1 and k_2 of the investigated diacrylates are first order. Quantum yields (γ) of the decomposition of photoinitiator are about 1.0.

EXPERIMENTAL, RESULTS AND DISCUSSION

The polymers of the dimethacrylates and the diacrylates are used in the production of optical and medical materials [1]. The process of three-dimensional polymerization of diacrylates is characterized by peculiarities, which are qualitatively explained by the microheterogeneous model [2]. The quantitative interpretation of these processes was introduced in paper [3] under the following assumption:

- The rate of the three-dimensional polymerization is the sum of the rates of homophase and heterophase processes. Homophase process is running in the volume of liquid oligomer, and heterophase process is running in the interphase layer in the regime of the gel-effect. The cut-off rate is controlled by its growth rate;
- The initiator is uniformly distributed between the phases and the interphase layer;
- Clusters of the solid polymer in liquid oligomer phase and clusters of the liquid oligomer in solid polymeric matrix have a fractal structure.

The interpretation of the suggested kinetic model for the variant of the photoinitiated polymerization, that takes into consideration the gradient of illumination on the layer of photoinitiated composition, concentration gradient of photoinitiator and conversion of the monomer is shown in [4]. Here the theoretical model of the process is compared with the experimental data of polymerization MDF-2:

$$\begin{aligned}&M\text{—}[O(CH_2\text{—}CH_2O)_2\text{—}C(O)\text{—}C_6H_4\text{—}C(O)]_2\\&\text{—}O\text{—}(CH_2\text{—}CH_2O)_2\text{—}M,\end{aligned}$$

where M: $CH_2{=}C(CH_3)\text{—}C(O\text{—})$.

These data were obtained at wide variation of the initiator concentration (c_0), intensity of the UV-illumination (E_0) and thickness of the layer of the polymerization composition (1). It was established that the kinetic model allows us to describe the process of the three-dimensional polymerization to extreme extents of transformation, based on four parameters: molar coefficient of extinction of photo-initiator (ε), quantum yield of its decomposition (γ), rate constants of the homo (k_1)- and heterophase (k_2) processes (see Tab. I).

In the present work we compared the kinetic model of three-dimensional polymerization with the experimental data, obtained by studying the kinetics of the polymerization of the following diacrylate monomers, photo initiated by 2,2-dimetoxy-2-phenilacetophenone (ketal):

(a) diethylene glycol diacrylate (DEGDA):

$$CH_2{=}CH{-}CO{-}O{-}(CH_2)_2$$
$$-O{-}(CH_2)_2{-}O{-}C(O){-}CH{=}CH_2$$

(b) 1,4-butanediol diacrylate:

$$CH_2{=}CH{-}CO{-}O{-}(CH_2)_4{-}O{-}CO{-}CH{=}CH_2$$

(c) 1,6-hexanediol diacrylate:

$$CH_2{=}CH{-}CO{-}O{-}(CH_2)_6{-}O{-}CO{-}CH{=}CH_2$$

(d) dipropylene glycol diacrylate:

$$CH_2{=}CH{-}CO{-}O{-}(CH_2)_3$$
$$-O{-}(CH_2)_3{-}O{-}CO{-}CH{=}CH_2.$$

TABLE I Kinetic parameters for the three-dimensional photopolymerization of diacrylates

Diacrylate	*Molecular mass*	$k_1 * 10^2$ $m^3/(mol\ s)^{1/2}$	$k_2 * 10^2$ m^3/mol	ε $m^3/mol * m$	γ
1,4-butanediol diacrylate	198	5.2	7.2	760	1.0
diethyleneglycol diacrylate(DEGDA)	214	3.8	8.0	830	1.0
1,6-hexanediol diacrylate	226	4.4	5.7	870	1.0
dipropyleneglycol diacrylate	242	3.5	6.1	900	1.0

The experiments were performed with a laser interferencial apparatus. Method of the experiments is described in detail in [4]. The experimental results are shown as kinetic curves in the form of dependences of integral relative depth of polymerization $P = H/H_0$ which represents the depth ratio of polymerization H to its limit H_0 reached at time t. Part of the experimental data is represented in Figure 1. As we can see, the kinetic curves of the diacrylates polymerization have a clear S-shape, which is typical for the three-dimensional polymerization process. The maximum rate of the process, which corresponds to the point of inflection in the kinetic curve, is observed at conversion $P < 1/2$ for all diacrylates.

According to the elaborated algorithm of [4], let us compare the obtained experimental results with the first approximation of the general kinetic model, which corresponds to the initial stage of the process, *i.e.*, condition of constancy of the photoinitiation rate.

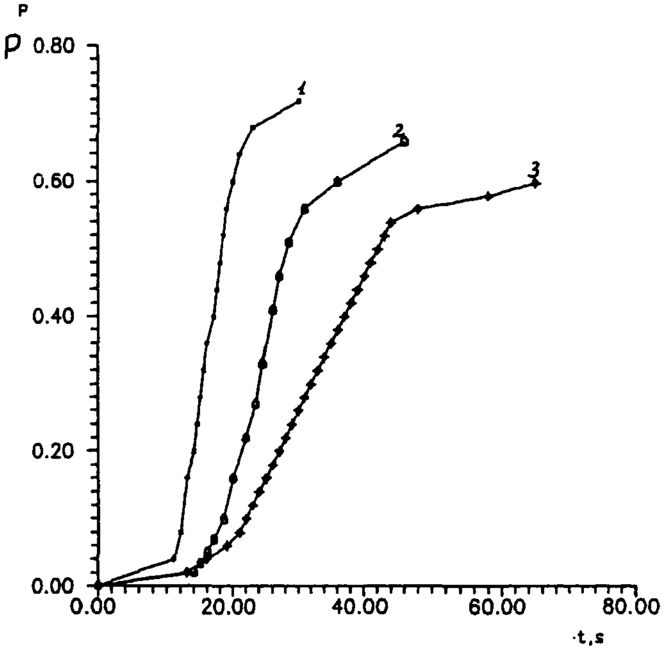

FIGURE 1 Experimental kinetic curves $P - f(t)$ of DEGDA at $E_0 - 37.4\ \mathrm{W/m^2}$, $C_0 - 0.04\ \mathrm{M}$; $1 - l - 2.6 \times 10^{-5}\ \mathrm{m}$; $2 - l - 5.15 \times 10^{-5}\ \mathrm{m}$; $3 - l - 8.36 \times 10^{-5}\ \mathrm{m}$.

In this approximation the integral rate of polymerization, $W = dP/dt$, is described by the equation:

$$dP/dt = l^{-1}[2k_1(\gamma I_0/\varepsilon c_0)^{1/2}(1 - \exp(-y_0/2))(1 - P) + k_2\gamma I_0(1 - \exp(-y_0))P(1 - P)] \quad (1)$$

where $y_0 = \varepsilon c_0 l$.

By analyzing the limits of (1) we find the expression for the conversion P_0, which corresponds to the point of inflection of the kinetic curve and maximum rate of the process:

$$P_0 = (A-1)/2A \quad (2)$$

where

$$A = (k_2 + 2k_1)(\varepsilon\gamma I_0 c_0)^{1/2}(1 - \exp(y_0))(1 - \exp(-y_0/2)) \quad (3)$$

Using Eqs. (1) and (2) in (3), we obtained the boundary between the maximum rate of the polymerization process W_0 and the ordinate of the point of inflection in the kinetic curve P_0:

$$W_0/(1 - P_0)^2 = (k_2\gamma I_0/l)[1 - \exp(-\varepsilon c_0 l)] \quad (4)$$

The dependence of the experimentally found values of $W_0/(1 - P_0)^2$ on the thickness of the layer l of the photopolymerizing composition at different concentrations of the photoinitiator are shown in Figures 2 and 3.

According to Eq. (4), at small thickness of the layer ($y_0 = \varepsilon c_0 l < 1$) the relation $W_0/(1 - P_0)^2$ must be a linear function of the concentration of the photoinitiator: $W_0/(1 - P_0)^2 = \varepsilon\gamma k_2 c_0 I_0$ and at large thickness of the layer (l) does not depend on it: $W_0/(1 - P_0)^2 = \gamma k_2 I_0/l$. From Figures 2 and 3 we see, that as $l \to 0$ values $W_0/(1 - P_0)^2$ diverge proportionally to concentration of photoinitiator and at $l \cong 15 \times 10^{-5}$ m converge showing the independenced $W_0/(1 - P_0)^2$ from l. In conformity with (4) and experimental data for all l, the relation $W_0/(1 - P_0)^2$ is a linear function of the power of the UV-illumination falling on the surface.

Using the relationship between $W_0/(1 - P_0)^2$ and l, the parameters $[\gamma k_2]$ and ε of the Eq. (4) were calculated. The calculated relationships between $W_0/(1 - P_0)^2$ and l presented in Figures 2 and 3 with

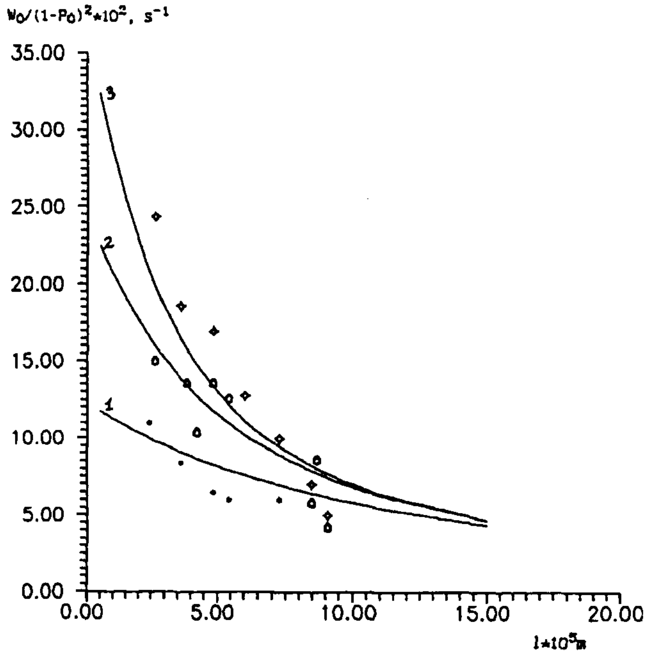

FIGURE 2 Relationship of $W_0/(1-P_0)^2$ from the thickness of layer l of 1,6-hexanediol diacrylate at different concentration of photoinitiator C_0: 1 – 0.02 M; 2 – 0.04 M; 3 – 0.06 M.

continuous lines are obtained with the following selection of the parameters of Eq. (1): rate constants of homo-(k_1) and heterophase (k_2) process. The estimate of quantum yield from the experimental data led to a second approximation of the model at infinitesimally small layer thickness, which is based on the condition ($y_0 = \varepsilon c_0 l < 1$). This model takes into account the dependence of the rate of photoinitiation on time, and the kinetic equation of polymerization assumes the form [4, 5]:

$$dp/dt = k_1(\varepsilon\gamma c_0 I_0)^{1/2}(1-P)\exp(-\tau/2) + k_2\varepsilon\gamma c_0 I_0 P(1-P)\exp(-\tau) \qquad (5)$$

where $\tau = \varepsilon\gamma I_0 t$.

The analysis (5) of maximum normalized rate of the polymerization $dP/(1-p)dt$, established the following connection between the

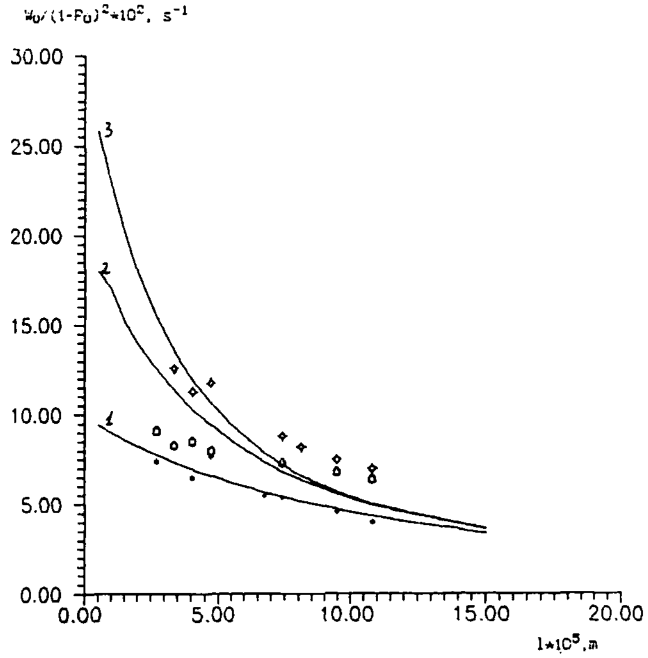

FIGURE 3 Relationship of $W_0/(1-P_0)^2$ from the thickness of layer l of dipropyleneglycol diacrylate at different concentration of photoinitiator C_0: 1 – 0.02 M; 2 – 0.04 M; 3 – 0.06 M.

ordinate P_2 and the rate W_2 which corresponds to the point of inflection of the kinetic curve of the form $-\ln(1-P)=f(t)$ and corresponds to the maximum normalized rate of polymerization $dP/(1-P)dt$:

$$P_2 = W_2/\gamma\varepsilon I_0 - 1/2A_0 \quad \text{where} \quad A_0 = k_2/k_1(\varepsilon\gamma c_0 I_0)^{1/2} \tag{6}$$

$$A_0 = 1/1 - 2P_0 \tag{7}$$

Figure 4 shows the interpretation of the experimental data, which satisfy the approximation of an infinitely thick layer ($y_0 = \varepsilon c_0 l < 1$), in the form of kinetic curves $-\ln(1-P_0)=f(t)$. On the ordinate of inflection, the tangent of slope values in $(1-P_2)$ and $dP/(1-P)dt$ were found, from which P_2 and W_2 were calculated:

$$-d\ln(1-P_2)/dt = W_2/(1-P_2) \tag{8}$$

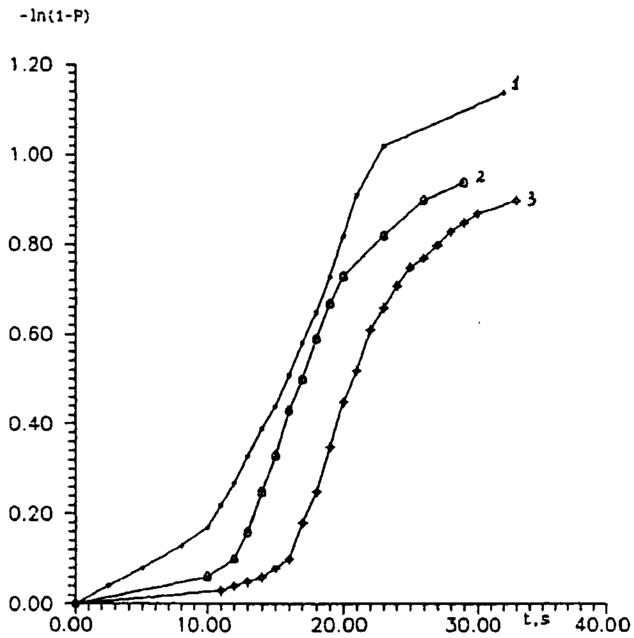

FIGURE 4 Interpretation of the experimental data in form of kinetic curves $-\ln(1-P)-f(t)$ of DEGDA, $C_0-0.04$ M; $1-l-2.6 \times 10^{-5}$ m, $2-l-5.15 \times 10^{-5}$ m, $3-l-8.36 \times 10^{-5}$ m.

These data and the calculated values of the relationship tween $W_0/(l-P_0)^2$ and the thickness of the layer (l) allowed us to estimate the quantum yield of photoinitiation (γ) using (6, 7):

$$\gamma = 2W_2/\varepsilon I_0[2(P_2 - P_0) + 1] \qquad (9)$$

By transformation of (6) we estimated the constants of the rate of homophase (k_1) and heterophase (k_2) processes of polymerization. The estimates of the constants of the kinetics of three-dimensional polymerization of the investigated diacrylates are presented the Table I below.

According to the estimates obtained (see table), the constants of rate k_1 of the homophase process for the diacrylates is practically independent of the nature of diacrylates, but increases with the decrease in the molecular mass and density of the monomer. In paper [5] the rate constants k_1 for some dimethacrylates: OCM-2

($k_1 = 0.043\,\mathrm{m}^3/(\mathrm{mol\,s})^{1/2}$, mol.mass = 418) and MDF-2 ($k_1 = 0.008\,\mathrm{m}^3/(\mathrm{mol\,s})^{1/2}$, mol. mass = 714) were obtained. As we may see, the rate constants of the homophase process k_1 increase with the decrease of the molecular mass and density of the monomer.

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