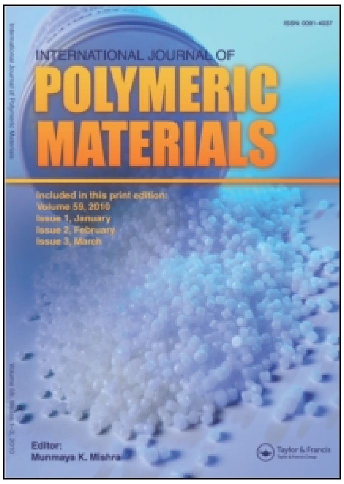

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The Kinetics of the Three-Dimensional Photopolymerization of Some Dimethacrylates: The Microheterogenous Model

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The kinetics of photopolymerization of oligodimethacrylate and diethylene glycol diacrylate at the wide range of photoinitiator concentration was investigated. We found the dependences between the intensity of the UV-irradiation and of the thickness of photocomposition on layer and kinetic parameters. Experimental date were compared with kinetic model of the photoinitial three-dimensional polymerization. It was determined that kinetic model allows us to describe the process of three-dimensional polymerization in the whole range of conversion. Molar extinction coefficient of photoinitiator and quantum yield of the decomposition, rate constants of homo (k_1)- and heterophase (k_2) process were estimated. It was determined that k_1 is influenced by the dimethacrylate properties and k_2 is a constant value for the whole investigated systems.

Keywords: Photopolymerization; kinetics; dimethacrylates; microheterogeneous model

EXPERIMENTAL, RESULTS AND DISCUSSION

The polymers of the dimethacrylates are used in production of optical and of the medical materials [1].

The process of three-dimensional polymerization of di(meth)acrylats 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 the homophase and heterophase process. Homophase process is running in the volume of liquid oligomer, and heterophase process is running the interphase layer on the boundary of the solid polymer-liquid oligomer 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 the 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 photopolymerization MDF-2 ($M—[O(CH_2—CH_2O)_2—C(O)C_6H_4—C(O)]_2—O—(CH_2—CH_2 O)_2—M$, where $M—CH{=}C(CH_3)—C(O)—$). These data are obtained at wide variation of the initiator concentration (c_0), intensity of the UV-illumination (I_0), and thickness of the layer of the polymerization composition (l). It is established that kinetic model allows us to describe the process of three-dimensional polymerization to extreme extents of transformation, based on four parameters; molar coefficient of extinction of photoinitiator (ε), quantum yield of its decomposition (γ), rate constants homo- and heterophase processes (see Table).

In present work we compare the kinetic model of three-dimensional polymerization with the experimental data, obtained by studying the kinetics of the photoinitial by diizopropiloxyazetophenon (DIPAF) polymerization of the oligomer OKM-2($M O(CH_2)_2—O—C(O)—O—(CH_2)_2—O—(CH_2)_2O—C(O)—O—(CH_2)_2—M$) and monomer DEGDA($CH_2{=}CH—C(O)—O—(CH_2)_2—O—(CH_2)_2—O—C(O)—CH{=}CH_2$).

Method of the experiments is described in [4].

The experimental results are shown as kinetic curves in form of dependences of integral relative depth of polymerization $P = \Gamma/\Gamma_0$ which represents the depth ratio of polymerization Γ to its limit Γ_0 reached at time t. Part of the experimental data is represented on Figure 1. As we see kinetic curves of the polymerization OCM-2 and DEGDA have a clear S-shape, which is typical for the three-dimensional polymerization process. Unlike MDF-2 [4], OCM-2 and DEGDA the maximum rate of the process, which corresponds to the point of inflection on kinetic curve, is observed at conversion $P \ll 1/2$.

According to elaborated algorithm [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 or condition of constancy of the photoinitiation rate.

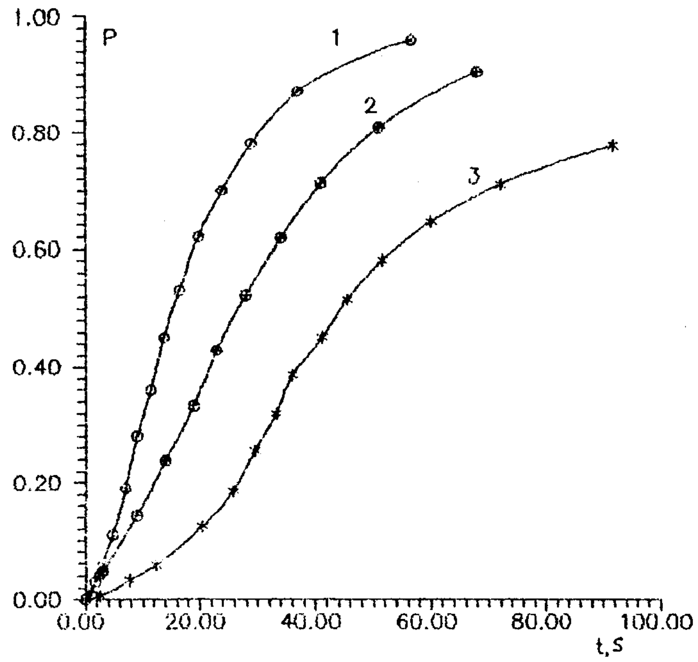

FIGURE 1 Experimental kinetic curves $P = f(t)$ of DEGDA (1) and OCM-2 (2 and 3) at $E_0 = 40.6$ W/m^2: 1. $c_0 = 0.06$M, $l = 4 \cdot 10^{-5}$m; 2. $c_0 = 0.02$M, $l = 4 \cdot 10^{-5}$m; 3. $c_0 = 0.06$M, $l = 30 \cdot 10^{-5}$m.

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

$$\frac{dP}{dt} = l^{-1}\left[2K_1\left(\frac{\gamma I_0}{\varepsilon c_0}\right)^{1/2}(1-e^{-y_0/2})(1-P) + K_2\gamma I_0(1-e^{-y_0})P(1-P)\right] \qquad (1)$$

where $y_0 = \varepsilon c_0 l$.

By analyzing the extremum 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:

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

where

$$A = (K_2 + 2K_1)(\gamma I_0 \varepsilon c_0)^{1/2}(1 - e^{y_0})(1 - e^{-y_0/2}) \qquad (3)$$

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

$$W_0/(1-P_0)^2 = (K_2\gamma I_0/l)[1-\exp(-\varepsilon c_0 l)] \qquad (4)$$

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

According to (4) at small thickness of the layer ($y_0 = \varepsilon c_0 l \ll 1$) the relation $W_0/(1-P_0)^2$ must be a linear function of concentration of the photoinitiator: $W_0/(1-P_0)^2 \approx k_2\gamma\varepsilon c_0 I_0$ and at large thickness of the layer (l) does not depend on it: $W_0/(1-P_0)^2 \approx k_2\gamma I_0/l$. From Figure 2 we see, that at $l \to 0$ values $W_0/(1-P_0)^2$ diverge proportionally to concentration of photoinitiator and at $l \to \infty$ 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 the

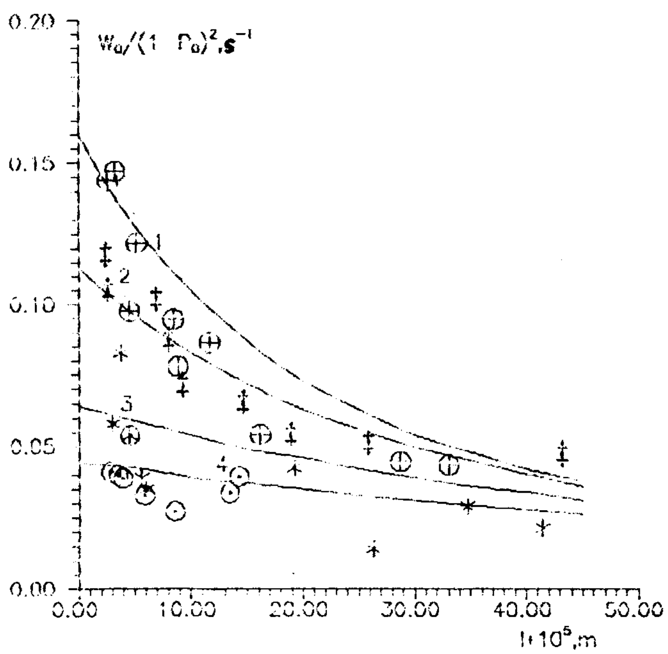

FIGURE 2 Relationship of $W_0/(1-P_0)^2$ from the thickness of layer l of OCM-2 at different concentrations of photoinitiator c_0, M = 0.16 (1); 0.06 (2); 0.4 (3); 0.2 (4).

linear function of the power of the UV-illumination, falling on the surface.

The calculated relationships between $W_0/(1-P_0)^2$ and l. presented in Figures 2 and 3 with continuous lines are obtained with the following selection of the parameters of equation (4); ($E_0 = 40.6$ W/m^2): $k_2\gamma I_0 = 1.74\cdot 10^{-5}$s for OCM-2 and $1.9\cdot 10^{-5}$s for DEGDA.

Using the relationship [4] $l_0 = 2.5\cdot 10^{-6} E_0$ mol·quant/m^2·s, we find $k_2\gamma = 0.174$m^3/mol for OCM-2 and 0.19 m^3/mol for DEGDA.

The comparison of the experimentally found values of parameter A in (2) with the calculated dependence A from l in (3) are represented in Figure 3.

Note that the dependence of experimentally found values of parameter A from l. are correlate well with the expression (3), according to which the increase of thickness of the layer parameter A must decrease from $A_0 = (\gamma I_0 \varepsilon c_0)^{1/2}/k_1$ at $l \to 0$ to $A = A_0/2$ at $l \to \infty$. Consequently,

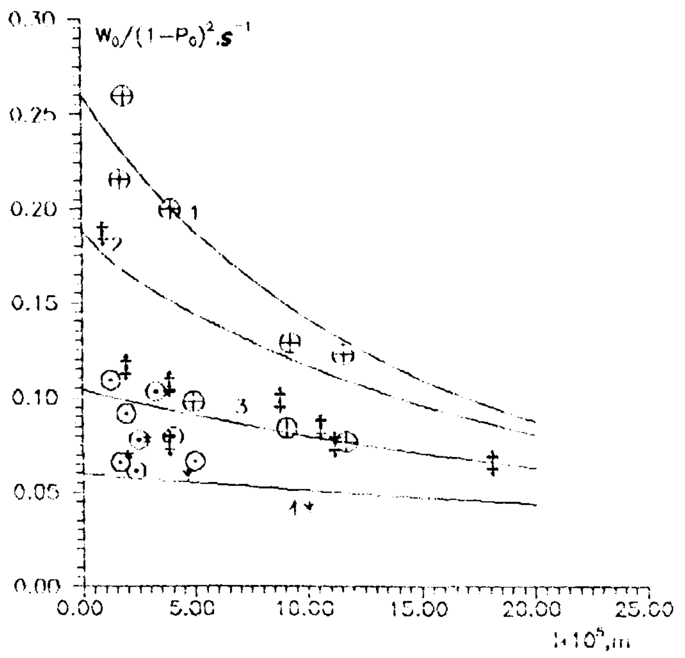

FIGURE 3 Relationship of $W_0/(1-P_0)^2$ from the thickness of layer l of DEGDA at different concentrations of photoinitiator c_0, M = 0.08 (1); 0.06 (2); 0.3 (3); 0.2 (4).

the calculated dependence of A from l obtained at values $k_1\gamma^{1/2} = 0.04$ $(\mathrm{m^3/mol{\cdot}s})^{1/2}$ for OCM-2 and 0.06 $(\mathrm{m^3/mol{\cdot}s})^{1/2}$ for DEGDA.

The estimate of quantum yield from the experimental data led in second approximation of the model of infinitesimally small thickness layer, which is based on condition ($y_0 = \varepsilon c_0 l \ll 1$). This model takes into account the dependence of the rate of photoinitiation on time, and the kinetic equation of polymerization assumes the form [4]:

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

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

The analysis (5) of maximum normalized rate of the polymerization $dP/(1-P)dt$, established the following connection between the ordinate P_2 and the rate W_2 which correspond 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 $dP/(1-P)dt$:

$$P_2 = W_2/\gamma\varepsilon I_0 - 1/2A_0 \tag{6}$$

Figure 4 shows the interpretation of the experimental data, which satisfy the approximation of the endlessly thickness layer ($y_0 = \varepsilon c_0 l \ll 1$) in form of kinetic curves ln) $=f(t)$. 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. These data and the calculated values of A allowed us to estimate the quantum yield of photoinitiation using (6). By means of (6) we then estimated the constants of the rate of homophase (k_1) and heterophase (k_2) process of polymerization.

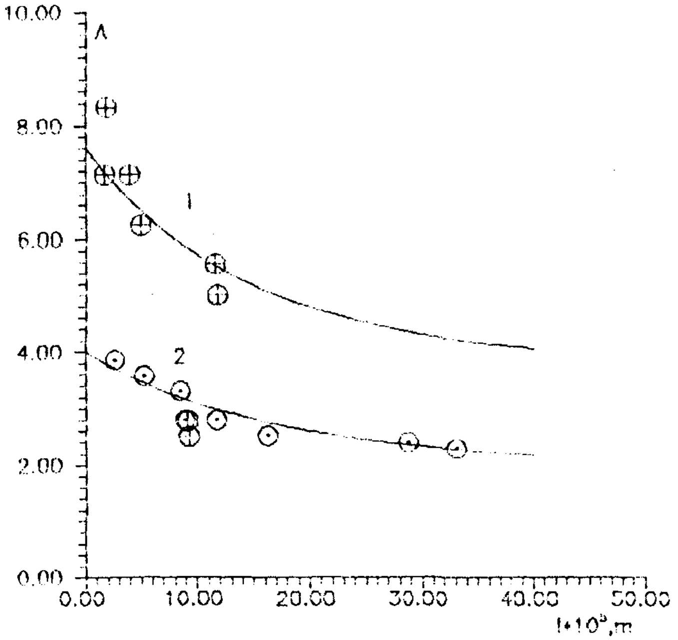

FIGURE 4 Experimental (points) and calculated an equation (line) dependences A from the thickness of layer l of DEGDA (1, $c_0 = 0.08$ M; $E_0 = 40.6$ W/m^2), OCM-2 (2, $c_0 = 0.08$ M; $E_0 = 40.6$ W/m^2).

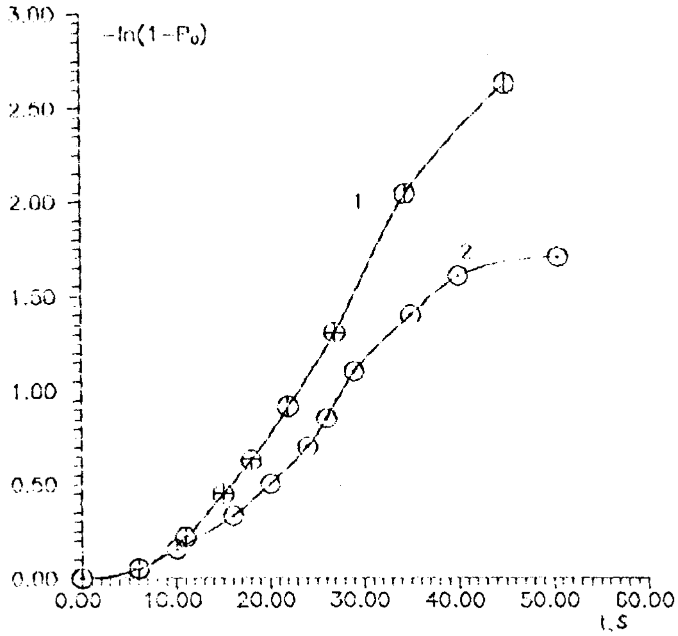

FIGURE 5 Interpretation of the experimental data in form of kinetic curves $\ln(1\text{-}P) = f(t)$: 1. $c_0 = 0.06$ M, $l = 2 \cdot 10^{-5}$ m, OCM-2; 2. $c_0 = 0.06$ M, $l = 1 \cdot 10^{-5}$ m, DEGDA.

The estimates of the constants of the kinetic model of three-dimensional polymerization of the investigated di(meth)acrylats are presented the Table below.

These values of OCM-2 and DEGDA were considered in equation (5) of the model of infinitesimally small thickness layer and the kinetic curves $P = f(t)$ were computed. Figure 6 shows that the calculated dependences $P = f(t)$ agree well with the experimental data.

TABLE I The kinetic parameters three-dimensional photopolymerization di(meth)acrylats in microheterogenous model

di(meth)-acrylats	*molecular mass*	$k_1 \cdot 10^2$ $(m^3/mol \cdot s)^{1/2}$	$k_2 \cdot 10$ m^3/mol	ε $m^3/mol \cdot m$	γ
MDF-2	714	0.8	2.4	87	0.9
OCM-2	418.5	4.3	2.1	160	0.85
DEGDA	214	6.4	2.3	160	0.84

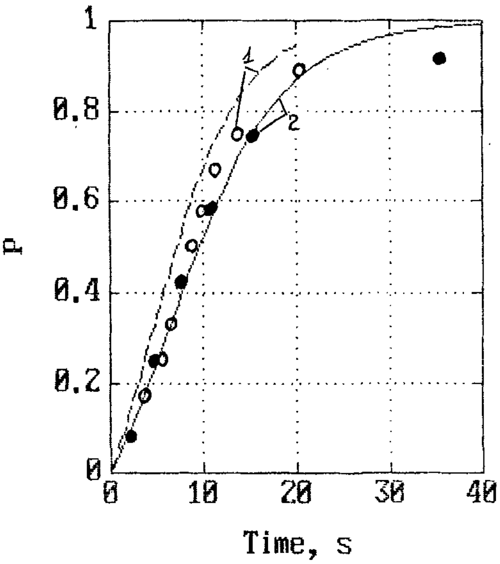

FIGURE 6 Computorcalculated on 5 (points) and experimental (line) dependences $P = f(t)$: 1. $c_0 = 0.06\,\mathrm{M}$, $l = 1 \cdot 10^{-5}\,\mathrm{m}$, DEGDA ; 2. $c_0 = 0.06\,\mathrm{M}$, $l = 2 \cdot 10^{-5}\,\mathrm{m}$, OCM-2.

It should be noted that the values of the molar coefficient of the extinction obtained by us ($\varepsilon = 87\ \mathrm{m^3/mol \cdot m}$ and $\varepsilon = 160\ \mathrm{m^3/mol \cdot m}$) greatly exceed the values determined from UV-spectrum at wavelength $\lambda = 340\,\mathrm{nm}$, which corresponds to maximum absorption band of DIPAF [5]. This weakly expressed band of absorption is situated on the descending branch of the wide and stronger absorption band with $\lambda = 280\,\mathrm{nm}$ of both di(meth)acrylats, where molar coefficient the extinction DIPAF in this bond is almost two times higher than that of the band $\lambda = 340\,\mathrm{nm}$.

It is possible that, the experimentally determined value of the molar coefficient of extinction determined by us represent λ is the effective amount, reflects not only the superposition of values ε of all wavelengths taking part in decomposition of photoinitiator, but also the sensibilizing capacity of di(meth)acrylats. The values of the quantum yield of the photoinitiator around one confirms this supposition.

According to obtained estimates (see table), the constant of rate k_2 of the heterophase process practically does not depend on the nature of di(meth)acrylats, whereas the constant of rate of homophase process k_1 increases with the decrease of the molecular mass and density of monomer. As far as [3]: $k_1 \approx k_{pf}/k_{tf}^{1/2}$ and $k_2 \approx k_{pm}/k_{tm}$. k_{pf} and k_{pm} is constants chain growth rate, with k_{tf} and k_{tm} being respectively the rates of its cut-off in homophase and heterophase processes, the observed trend may reflect that, rate growth the constants (k_{pf} and k_{tf}) and the chain cut-off of constants (k_{pm} and k_{tm}), are functions of the molecular mass and density of di(meth)acrylats. This is possible if both reactions, that is the growth and the chain cut-off processes in liquid phase and in heterophase are diffusion controlled. Negligible difference in values k_1 for di(meth)acrylate OCM-2 and diacrylate DEGDA confirms this.

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