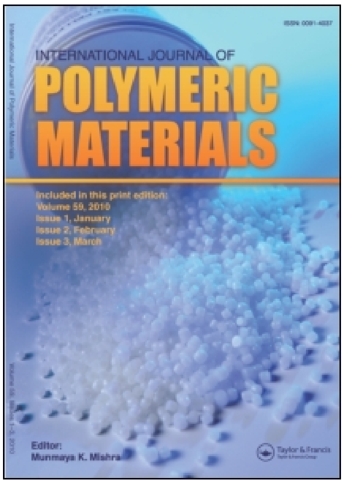

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Kinetics of the Three-dimensional Photopolymerization

Ju. G. Medvedevskikh[a]; E. A. Zagladko[a]; A. A. Turovski[a]; G. E. Zaikov[b]
[a] Department of Pisarzhevski, Institute of Physical Chemistry, Ukrainian Academy of Sciences, Lviv, Ukraine [b] Emmanuel Institute of Biochemistry and Physics, Russian Academy of Sciences, Moscow, Russia

To cite this Article Medvedevskikh, Ju. G. , Zagladko, E. A. , Turovski, A. A. and Zaikov, G. E.(1999) 'Kinetics of the Three-dimensional Photopolymerization', International Journal of Polymeric Materials, 43: 1, 157 — 168
To link to this Article: DOI: 10.1080/00914039908012131
URL: http://dx.doi.org/10.1080/00914039908012131

Intern. J. Polymeric Mater., 1999, Vol. 43, pp. 157–168
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Kinetics of the Three-dimensional Photopolymerization

JU. G. MEDVEDEVSKIKH[a], E. A. ZAGLADKO[a],
A. A. TUROVSKI[a] and G. E. ZAIKOV[b,*]

[a] *Department of Pisarzhevski Institute of Physical Chemistry, Ukrainian Academy of Sciences, Naukova str., 3a, Lviv, 290053, Ukraine;*
[b] *Emmanuel Institute of Biochemistry and Physics, Russian Academy of Sciences, Kosygin str., 4, Moscow, 117977, Russia*

(Received 17 October 1997)

On the basis of the microheterogenous model and taking into account the light gradient the kinetic equation of the three-dimensional photoinitiated polymerization of the polyfunctional oligomers in block is obtained. The prediction of models for the initial stage of the process and endless thin layer – are correlated with the experimental data of photopolymerization of the bifunctional oligoacrylate, obtained within the wide range of values of photoinitiator concentration, thickness of the composition layer and the intensity of the light falling on its surface. In all cases the data predicted by the model correlate with the experimental observations. The following parameters of the model are found: coefficient of the photoinitiator extinction, quantum yield of its decay, constants of the rates of homophase and heterophase polymerization process. The comparison of the calculated set of parameters and experimental kinetic curves shows, the satisfactory correspondence of the suggested model including the fluctuation dependence of the rate of three-dimensional polymerization caused by the microheterogenity of the process.

Keywords: Photopolymerization; microheterogenic model; kinetic; the UV-radiation; polyfunctional oligomers

The polymers have for space applications have valuable use properties and are widely used in different technologies including the photochemical forming of complex items [1, 2].

The process of their synthesis depends; (i) on the mechanism of the process of the polymerization of the polyfunctional oligomers, which

---

* Corresponding author.

are explained in terms of the microheterogenic model [1], and (ii) on the gradient of lighting in the layer of the photopolymerizating composition, and (iii) gradients in concentrations of the photoinitiator of the oligomer and the depth of the photopolymerization.

. Short time of the process of the photopolymerization in such viscous environments as oligoacrylates allows us to neglect the action of the diffusion mass transfer on the indicated gradients. In this case the dynamics of the photodecomposition of the initiator is determined by the system of the nonlinear partial differential equations [3, 4],

$$\partial I/\partial X = -\varepsilon c I, \quad \partial c/\partial t = -\gamma \varepsilon c I, \tag{1}$$

where $I = I_0(x,t)$ and $c = c(x,t)$ – intensity of the lighting and the concentration of the photoinitiator in layer x, $x + dx$ from illuminated surface ($x = 0$) in the moment of time t; ε – molar extinction coefficient of the photoinitiator: γ – quantum yield, close to the coefficient of initiation by its sense.

The common solution of Eq. (1) is known [5, 6] and it is convenient to describe it using the dimentionless parameters $\tau = \gamma \varepsilon I_0 t$, $y = \varepsilon c_0 x$, where I_0 – Intensity of light which falls on the surface of the polymerizating composition, c_0 – initial concentration of the photoinitiator, which is assumed to be equal for all layers of the initial composition

$$c = c_0[1 + e^{-y}(e^{\tau} - 1)]^{-1}, \quad I = I_0 e^{\tau - y}[1 + e^{-y}(e^{\tau} - 1)]^{-1} \tag{2}$$

From (1) and (2) we obtain the expression for the rate of photoinitiation $v_i(x,t) = -\partial c/\partial t$:

$$V_i = c_0 I_0 e^{\tau - y}[1 + e^{-y}(e^{\tau} - 1)]^{-2} \tag{3}$$

In the previous work [7] based on the microheterogenous model we have suggested the following kinetic equation of the three-dimensional polymerization of the polyfunctional oligomers,

$$\partial p/\partial t = k_1(1-p)v_i^{1/2} + k_2 p(1-p)v_i \tag{4}$$

Here $p(x,t) = \Gamma(x,t)/\Gamma_0$ – relative depth of the polymerization in the layer x, $x + dx$ at the moment of time t, which is determined by the relation of the current depth of polymerization $\Gamma(x,t)$ to the limit $\Gamma_0(t \rightarrow\ )$; k_1 and k_2 – kinetic constants.

According to [7], the first constituent in (4) represents the rate of the process in the liquid oligomer phase, second in the interphase layer in the boundary solid polymer liquid oligomer.

As a rule, the experimentally measured parameters of the photoinitiated polymerization are not the differential rate of the process $\partial p/\partial t$, or relative depth of the polymerization P, but their integral, that is the average of the layer analogs. They are determined by the expressions:

$$W = dP/dt = \ell^{-1\ell}\int_0 (dp/dt)dx, \quad P = \ell^{-1\ell}\int_0 pdx, \tag{5}$$

where ℓ – thickness of the photopolymerization composition.

Using (3) and (4) in the integral convertion (5) and taking into account the theorem about the mean, the expression for the polyfunctional oligomers will be

$$W = \frac{dP}{dt} = k_1(1-P)\mathrm{Int}(1) + k_2P(1-P)\mathrm{Int}(2), \tag{6}$$

$$\mathrm{Int}(1) = 2\ell^{-1}\left(\frac{\gamma I_0}{\varepsilon c_0}\right)^{1/2}\left(\frac{e^{\tau}}{e^{\tau}-1}\right)^{1/2}\mathrm{arctg}\frac{(e^{\tau}-1)^{1/2}(1-e^{y_0/2})}{1+e^{-y_0/2}(e^{\tau}-1)}$$

$$\mathrm{Int}(2) = \ell^{-1}\gamma I_0(1-e^{-y_0})/[1+e^{-y_0}(e^{\tau}-1)].$$

where $y_0 = \varepsilon c_0 \ell$ – initial optical density of the layer.

EXPERIMENTAL DATA AND THEIR ANALYSIS USING THE SUGGESTED KINETICS MODEL

The photoinitiated polymerization of the α-methakryloil-ω-methakryloildiethyleneglykoloxy-Oligodiethyleneglycolphthalate (MDF-2) with the known characteristics [8] was studied on the interphotometrical laser device [2] measuring the current and extreme $(t \rightarrow\ )$ concentration of the layer of composition. From their relation the relative integral depth of the polymerization was calculated $P = H/H_0$. The photoinitiator used was the 2,2-diisopropoxyacetophenone.

The initial concentration of the photoinitiator c_0, the thickness of the photopolymerizated composition the intensity E_0 of the integral UV-radiation of the lamp DRT-400 were varied.

The value ℓ was found on the extreme of concentration of the layer, using the expression $\ell = H_0/h$; coefficient of the contraction $h = 0.065$ was calculated from the relation of the densities of the liquid oligomer and the solid polymer [1].

The surface of the layer of the composition was protected from the oxidation by the 0.15 mm thick glass. This also prevented the deformation at the reflection point of the laser ray, caused by the strains on the boundary of the division of the liquid and solid phases at frontal character of the process [3, 9].

A part of the obtained experimental results is presented on Figure 1 as the dependence of the relatice integral depth of polymerization *vs* time.

They have a clear S-like shape with the ordinate of the point of the inflection neat $P = 1/2$ which practically independent from the intensity of the UV-radiation, concentration of the photoinitiator and the thickness of the layer of composition.

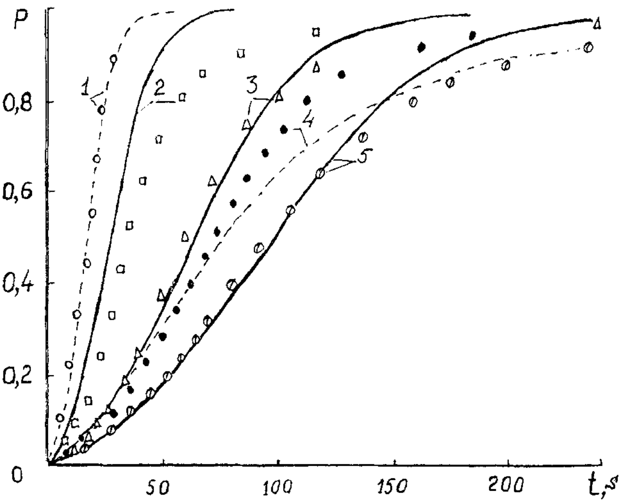

FIGURE 1 Experimental (points) and calculated (dashed lines) on Eq. (13), continuous lines on Eq. (6) the kinetic curves of photopolymerization MDF-2 $E_0 = 40.6\,\mathrm{J/m^2{\cdot}s}$, c_0, mol/l = 0.105 (1 – 3,5), 0.021 (4); ℓ, mm = 0.03(1), 0.15(2), 0.55(3), 0.12(4), 0.86(5).

However the general situation of the kinetic curves depends on these parameters particularly of the thickness of the layer.

The comparison of the experimental data with the general kinetic model (6) is difficult. Therefore two approximation are considered. The first one is based on the assumption $c = c_0$, $v_i = \text{const}$, which is justified for the long chain processes at condition $\tau \ll 1$. Consequently this approximation may be considered as the model of the initial stage of the process [10]. Using the condition $\tau \ll 1$ in (6), we obtain

$$\frac{dP}{dt} = \ell^{-1}\left[2K_1\left(\frac{\gamma I_0}{\varepsilon c_0}\right)^{1/2}(1 - e^{-y_0/2})(1 - P) + k_2\gamma I_0(1 - e^{-y_0})P(1 - P)\right]. \tag{7}$$

Analysing (7) for the extremes of the function, we find that the ordinate P_1 of the point of the inflection of kinetic curve should be determined by the relation

$$P_1 = (A - 1)/2A, \tag{8}$$

where

$$A = k_2(2k_1)^{-1}(\gamma\varepsilon c_0 I_0)^{1/2}(1 - e^{-y_0})/(1 - e^{-y_0/2}) \tag{9}$$

According to the experimental data $P_1 \simeq 1/2$ and using (8) it follows that $A \gg 1$. This leads to the expression for the maximum rate of the photopolymerization $W_0 = (dP/dt)_0$, which corresponds to the point of the inflection of the kinetic curve;

$$W_0 = (k_2\gamma I_0/4\ell)[1 - \exp(-y_0)] \tag{10}$$

As follows from (10) at given concentration of the photoinitiator c_0 and small thickness of the layer of the composition ($y_0 = \varepsilon c_0 \ell \ll 1$), the maximum rate of the photopolymerization must have the first order on initiatior: $W_0 \simeq k_2\gamma\varepsilon c_0 I_0/4$; but at great thickness of the layer ($y_0 = \varepsilon c_0 \ell \gg 1$)–zero: $W_0 \simeq k_2\gamma I_0/4\ell$.

Experimental data shown on Figure 2 confirm this dependence: at $\ell \to 0$ the values W_0 depend on the concentration of the photoinitiator, but at $\ell \to \infty$ they approach, showing the independence of W_0 from c_0.

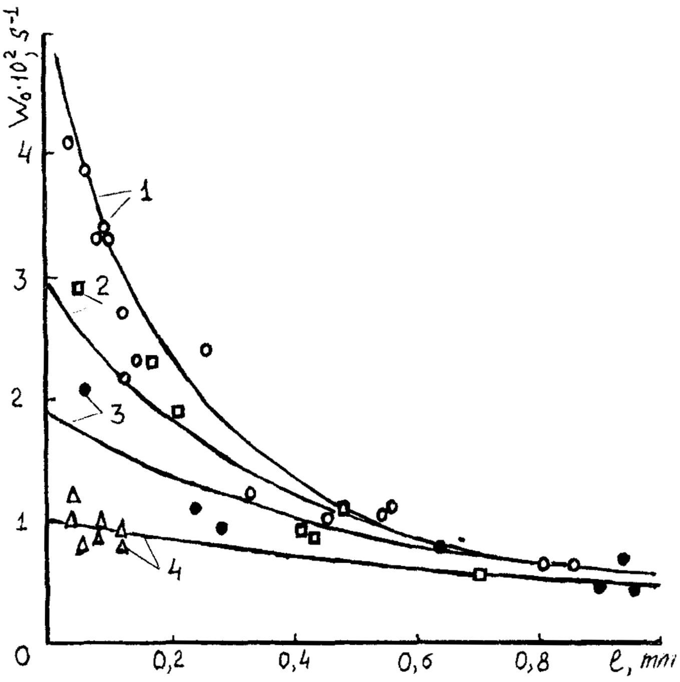

FIGURE 2 Experimental (points) and calculated on Eq. (10) (continuous lines) dependence of maximum rate w_0 of photopolymerization MDF-2 from thickness c_0, mol/l = 0.105(1); 0.064(2); 0.040(3); 0.021(4); $E_0 = 40.6\,\mathrm{J/m^2{\cdot}s}$.

However, the maximum rate of the process is the linear function of the intensity of the UV-radiation, falling on the surface of the composition.

The calculated dependences of W_0 from ℓ are shown in Figure 2 by solid lines. These data were obtained by the following set of parameters in the Eq. (10): $k_2\gamma I_0 = 2.2{\cdot}10^{-5}\,\mathrm{s}$ (at $E_0 = 40.6\,\mathrm{J/m^2 s}$) and $\varepsilon = 87\,\mathrm{m^3/mol{\cdot}m}$.

The given value of the molar coefficient of the extinction is almost 7 times higher than the value, obtained from UV-spectrum of wavelength $\lambda_{\max} \simeq 340\,\mathrm{nm}$, which correspond to the maximum of the absorption band [11].

This band occurs on the falling branch of the wide and larger absorbtion band with $\lambda_{\max} \simeq 280\,\mathrm{nm}$, which corresponds to the coefficient of the extinction almost two orders more, than at $\lambda_{\max} \simeq 280\,\text{nm}$.

The experimentally determined molar coefficient of extinction $\varepsilon = 87\,\text{m}^3/\text{mol}\cdot\text{m}$ based on our kinetic measurements is probably the super position for all wavelengths which take part in decomposition of the photoinitiator in the integral spectrum of the lamp.

We believe that the given experimental estimate of ε reflects also the influence of the absorbing capacity of the oligomer which appears also as a wide band with $\lambda_{\max}$ near 280 nm.

As far as it is impossible to indicate the wavelength of the UV-radiation, which leads to decomposition of the photoinitiator, we selected arbitrarily the average wavelength between 280 and 300 nm, which led to $J_0 = 2.5\cdot10^{-6}E_0\,\text{mol}\cdot\text{quant/m}^2\cdot\text{s}$. Using the values $k_2\gamma I_0 = 2.2\cdot10^{-5}\text{c}$ at $E_0 = 40.6\,\text{J/m}^2\cdot\text{s}$ this allowed us to estimate $k_2\gamma = 0.22\,\text{m}^3/\text{mol}$.

Equation (7) at $A \gg 1$ after integration has the form:

$$\ln[(1 + AP)/(1 - P)] = k_2\gamma I_0(1 - e^{-y})t/\ell = 4W_0t \qquad (11)$$

This offers the possibility of estimating the parameter A from experimental data by the relation

$$A = \exp(4W_0t_{1/2}) - 2, \qquad (12)$$

in which $t_{1/2}$ – time of attainment of the ordinate $P = 1/2$ on the kinetic curve.

Since the errors in determining W_0 and $t_{1/2}$ are included into the exponent, the estimate of A using (12) has a significant experimental error.

Figure 3 shows, the dependence of A from ℓ, which agrees with the expression (9), according to which the increase of the thickness of the layer parameter A must decrease from value $A_0 = k_2(\gamma\varepsilon c_0 I_0)^{1/2}/k_1$ at $\ell = 0$ to value $A = A_0/2$ that by a factor of two.

The calculated dependence of A from ℓ (Fig. 3), was obtained at value $A_0 = 25$, that led to: $k_1\gamma^{1/2} = 8.4\cdot10^{-3}(\text{m}^3/\text{mol}\cdot\text{s})^{1/2}$. The calculated values of parameters ε, $k_1\gamma^{1/2}$ and $k_1\gamma$ allow us to interpret the experimental data in coordinates of Eq. (11). The parameter A is calculated using Eq. (9).

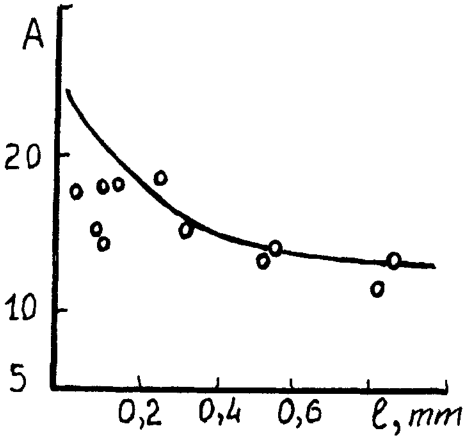

FIGURE 3 Experimental (points) and calculated on Eq. (9) (continuous lines) dependence of the parameter A from thickness of layer MDF-2 at $E_0 = 40.6\,\mathrm{J/m^2\cdot s}$, $c_0 = 0.105\,\mathrm{mol/l}$.

As shown in Figure 4 the initial plots of the kinetic curves are well linearized in coordinates of Eq. (11). The values of the slope tangent of the straight line plots are within the limits of the error of measured of values of $4W_0$.

The deviation of the experimental data from the straight line relation of the coordinates of Eq. (11) begins at values $P_k = 0.7 - 0.9$. Note, that higher values of ℓ correspond to smaller values of P_k. This allows us to conclude, that the observed deviation is caused by the neglect of the initial stage of the photoinitiation.

The estimate of the quantum yield γ from experimental data were made using the second approximation, which corresponds to the model of the endless thin layer [12]. Using the condition $y_0 = \varepsilon c_0 \ell \ll 1$. For the layer 0, 0 + dx accurate determination of the endless thin layer differential and integral characteristics of the process coincide. Therefore the rate of the photopolymerization may be described by the initial equation (4), in which $v_i = \gamma\varepsilon c_0 I_0 \exp(-\gamma\varepsilon I_0 t)$ and is the function of time.

Thus in the model of the endless thin layer

$$\frac{dP}{dt} = k_1(\gamma\varepsilon c_0 I_0)^{1/2}(1 - P)e^{-\tau/2} + k_2\gamma\varepsilon c_0 I_0 P(1 - P)e^{-\tau} \qquad (13)$$

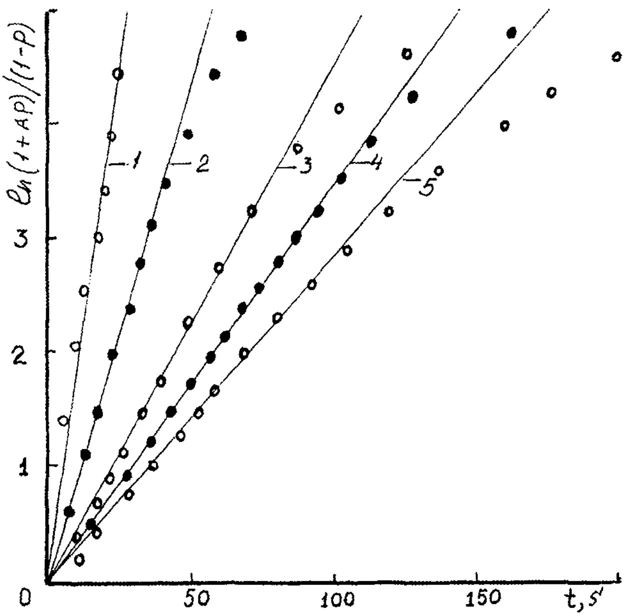

FIGURE 4 Interpretation of the experimental kinetic curves in coordinates Eq. (11) (numeration of the curves the same as on Fig. 1).

The analysis (13) on maximum normalized rate of photopolymerization which in terms of the accepted value $dP/(1-P)\,dt = -d\ln(1-P)/dt$ establishes the relationship between the ordinate P_2 and rate $W_2 = (dP/dt)$, which corresponds to the point of inflection of the kinetic curve of the shape $\ln(1-P) = f(t)$ and the maximum rate of the polymerization $(-d\ln(1-P)/dt)_{\max}$

$$P_2 = W_2/\gamma\varepsilon I_0 - 1/2A_0 \tag{14}$$

In Figure 5 are shown the experimental data in the form of the kinetic curves $\ln(1-P) = f(t)$ which satisfy the approximation of endless thin layer $y_0 = \varepsilon c_0 l \ll 1$. From the ordinate of inflection and slope tangents the values $\ln(1-P_2)$ and $(dP/(1-P)dt)_{\max}$ were found. This allowed us to calculate P_2 and W_2. With these and the calculated values A_0 allowed us to calculate $\gamma\varepsilon I_0$. The average of two calculations (Fig. 5) gave the value $\gamma\varepsilon I_0 \simeq 8\cdot10^{-3}$ at $I_0 = 10^{-4}$mol·quantum/m^2·s, thus $\gamma = 0.9$ is found. With the already known values $k_1\gamma^{1/2}$ and $k_2\gamma$

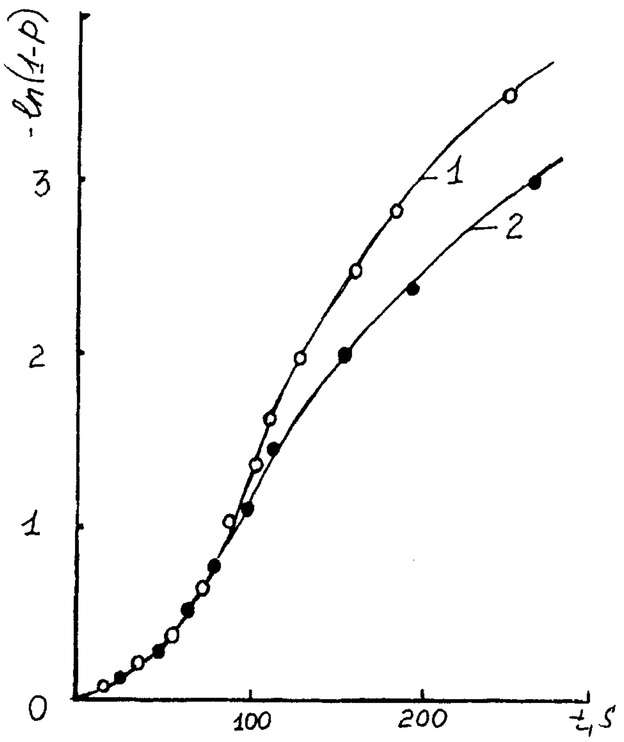

FIGURE 5 Interpretation of the experimental kinetic curves in coordinates, showing the presence of the maximum normalized rate of photopolymerization $E_0 = 40.6\,\mathrm{J/m^2 \cdot s}$, $c_0 = 0.021\,\mathrm{mol/l}$, ℓ, mm = 0.14(1); 0.09(2).

we can estimate the numerical values of two principal parameters of the initial kinetic equation: $k_1 = 8.8 \cdot 10^{-3} (\mathrm{m^3/mol \cdot s})^{1/2}$ and $k_2 = 0.24\,\mathrm{m^3/mol}$.

These values of k_1 and k_2, and also $\varepsilon = 87\,\mathrm{m^3/mol \cdot m}$ and $\gamma = 0.9$ were put in the approximate kinetic equation (13) of the model of endless thin layer and total kinetic equation (6) for the direct calculation $P = P(t)$ by numerical integration (13) and (6). The obtained calculated dependences $P = f(t)$ are correlated with experimental kinetic curves (Fig. 1). From this correlation appears that although the calculated dependences $P = f(t)$ do not coincide with experimental kinetic curves, the qualitative and quantitative correspondence between them is quite satisfactory. This and the found quantum yield of the photocomposition of the indicator are the important arguments in for the validity of the suggested kinetic models (4) and (6).

Another argument supporting this conclusion is found in the correlation or the numerical value k_1, found by us with those reported in literature.

Some of the differences between the calculated and experimental kinetic curves, represented on Figure 1, may be explained by the extimated kinetic constants k_1, k_2, ε and γ which agree with the experimental data. A more detailed analysis of the kinetic curves showed, however, that any of them can be described with a very small error using the individual set of the constants k_1, k_2, ε at $\gamma = 1$. Therefore, we concluded as we see, that the difference between the calculated and experimental relationship $P = P(t)$ is caused not only by the approximate estimate of the set of the kinetic constants, but has also deep physical reasons.

Note also that the instrumental error in construction of the individual kinetic curve in separate experiment is very small. This is seen from the arrangement of the experimental points arround the kinetic curve (see Figs. 1, 4 and 5).

The comparison of the individual kinetic curves shows the dispersion of parameters, which are calculated from this kinetic curve (for example the values W_0 on Fig. 2 and A in Fig. 3) which significantly exceeds the error of the separate experiment. This phenomenon is known for three dimensional polymerization and is reflected in poor reproducibility of kinetic measurements [13–15]. We maintain that the indicated feature of the three-dimensional polymerization is the direct approval of the microheterogenity of the process namely, the active role of the interphase layer between the liquid oligomer–solid polymer and the fluctuations in interphase formation during the stage of initiation of the solid polymer phase. This is reflected in the kinetic constant k_2, the numerical value of which depends on the relation of the fractal characteristics of the surface and the volume of the cluster of solid polymer phase in liquid oligomer and of the liquid oligomer in solid polymer matrix.

Since the contribution of the process of polymerization in the interphase is dominant, its fluctuational dependence is transferred also on the entire process.

References

[1] Berlin, A. A., Koroliov, G. V. and Kepheli, T. Ja. (1979). Acrylic Oligomers and their products. Moscow, Khimia. (Russian).

[2] Grishchenko, V. K., Maslyuk, A. F. and Gudsera, S. S. (1985). Liquid polymerizable Compositions. – Kiev; *Scientific Proceedings* (Russian).

[3] Ivanov, V. V. and Smirnov, B. R. (1991). *Vysokomal. Soed.*, **(B)33**, 807 (Russian).

[4] Treushnikov, V. M. and Janin, A. M. (1987). *J. Science and Proceedings of Photography and Film*, **32**, 308 (Russian).

[5] Ovchinnikov, V. M. and Kharstiev, V. E. (1965). *J. Experimental and Theoretical Physics*, **49**, 315 (Russian).

[6] Borovich, B. A., Zuev, V. S. and Krokhin, O. N. (1965). *J. Experimental and Theoretical Physics*, **49**, 315 (Russian).

[7] Medvedevskikh, Ju. G., Zagladko, E. A. and Turovski, A. A., *Chemical Physics*.

[8] Treushnikov, V. M., Esin, S. A. and Zueva, T. A. (1995). *Vysokomol. Soed.*, **(A)37**, 1973 (Russian).

[9] Medvedevskikh, Ju. G. and Berlin, Ar. A. (1992). *Theoretical and Experimental Chemistry*, **28**, 420 (Russian).

[10] Medvedevskikh, Ju. G. and Simonenko, V. V. (1992). *J. Physical Chemistry*, **66**, 1432 (Russian).

[11] Shibanov, V. V., Basyljuk, K. F. and Marshalok, I. I. (1993). *Vysokomol. Soed.*, **(A)35**, 115 (Russian).

[12] Medvedevskikh, Ju. G. and Simonenko, V. V. (1992). *J. Physical Chemistry*, **66**, 1656 (Russian).

[13] Entsyklopedija polimerov, Vol. 2, 185 - Moscow (1974) (Russian).

[14] Kolegov, V. I. (1995). *Vysokomol. Soed.*, **(A)37**, 1973 (Russian).

[15] Treushnikov, V. M., Zelenskova, N. B. and Oleinik, A. V. (1987). *J. Science and Proceedings in Photography and Film*, **32**, 308 (Russian).