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Linear Chain Termination in the Kinetics of Postpolymerization of Dimethacrylates

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Abstract—The kinetics of postpolymerization (after turning off UV irradiation) of various dimethacrylates differing in their nature and molecular weight was studied over a wide range of temperatures. For each temperature, a series of kinetic curves, varying in the initial conversion during a dark period, was obtained. The proposed kinetic model is based on the following assumptions. The process in the interphase layer at the liquid monomer–solid polymer boundary has the most significant contribution to the kinetics of postpolymerization. Chain termination in the interphase layer occurs by the unimolecular reaction, is controlled by the chain growth rate, and presents the act of "self-burying" of an active radical in a conformational trap. A wide spectrum of characteristic times is inherent in unimolecular chain termination, and the relaxation function is described by the Kohlraush' stretched exponential law. The rate law obtained agrees well with experimental data. This fact made it possible to estimate the rate constants (k_t) and the activation energies of chain termination and to establish the scale dependence of k_t on the molar concentration $[M_0]$ of the monomer in a block. It is suggested that both the stretched exponential law and the scale k_t–$[M_0]$ dependence are due to a wide spectrum of characteristic times of relaxation exhibiting the properties of a fractal set.

INTRODUCTION

Postpolymerization or dark polymerization under unsteady-state conditions, which proceeds after turning off UV irradiation, provides valuable information on the mechanism of the elementary reactions of chain termination. The relationships obtained for monofunctional monomers have much in common with those for polyfunctional monomers [1–4]: (1) The rate and degree of postpolymerization substantially depend on the initial conversion during the dark period. (2) In the course of postpolymerization, the average molecular weight of a polymer increases, and the concentration of radicals detected by the *in situ* EPR method only slightly decreases or remains constant. (3) Two portions can be recognized in the kinetic curve of postpolymerization, which correspond to the quick and slow (prolonged) processes, respectively. This fact suggests that radicals carrying out postpolymerization differ drastically in their characteristic lifetimes.

Probably because of this, there exist three variants of kinetic description of postpolymerization based on the quadratic, linear, and mixed chain termination [5]. They show that the kinetic models with only quadratic or only linear chain termination describe the experimental data more poorly than models based on their combinations with mixed chain termination, which makes it possible to introduce at least two characteristic lifetimes. It was also suggested that polymerization occurs at the same rate in the entire volume of the polymerizing system [5].

Conversely, the kinetic models of photoinduced polymerization under steady-state and unsteady-state (dark) conditions that were proposed in [6–8] are based on the idea of microheterogeneity of the polymerizing system with two reaction zones. Therefore, the observed rate of polymerization (ω) is the sum of the rates of the homophase process in the bulk of the liquid polymer via a classical kinetic scheme with the quadratic chain termination and the heterophase process in the interphase layer at the liquid monomer–solid polymer (micrograins) interface in the regime of the gel effect with linear chain termination: $\omega = \omega_v\varphi_v + \omega_m\varphi_m$, where φ_v and φ_m are the volume fractions of the liquid monomeric phase and respectively; ω_v and ω_m are the corresponding specific rates of polymerization.

However, when developing the kinetic model of postpolymerization, one usually assumes that radicals have a short lifetime in the liquid phase and insignificantly contribute to postpolymerization, so that the rate of the process is controlled by the rate of the heterophase reaction in the interphase layer: $\omega \cong \omega_m\varphi_m$. To take into account distinctions between the characteristic lifetimes of radicals, we previously proposed [8] a kinetic scheme of the process in the interphase layer involving the primary (I) and secondary (III) chains with linear chain termination and two characteristic times $\tau_1 = (k_t[M_m])^{-1}$ and $\tau_2 = (k'_t[M_m])^{-1}$:

$$R_m + M_m \begin{cases} \xrightarrow{k_p} R_m \\ \xrightarrow{k_t} R_z, \end{cases} \tag{I}$$

$$R_z + M_m \xrightarrow{k_m} R'_m, \tag{II}$$

$$R'_m + M_m \begin{cases} \xrightarrow{k'_p} R''_m \\ \xrightarrow{k'_t} R'_z. \end{cases} \tag{III}$$

The main feature of scheme (I)–(III) is that the rate of linear chain termination is controlled by the rate of chain growth, because the reactions of chain propagation and chain termination lead to two different results of interaction of the R_m and R'_m radicals with the functional group of a monomer. Thus, the former process gives rise to reactive radicals, and the latter one is responsible for freezing [3, 9] or trapping [4, 10] the radicals, i.e., for the formation of inactive radicals R_z and R'_z. Elementary reaction (II) initiates secondary active radicals (R'_m) from the initially frozen ones (R_z).

Although kinetic scheme (I)–(III) is very idealized, it has a simple physical interpretation based on the following facts. The similarity of the kinetics is observed for polymerization in the interphase layer (in particular, the first order of the reaction in an initiator) and, for example, for matrix polymerization [11], polymerization in the presence of porous fillers [12], or for adsorption immobilization of a polymeric initiator at the surface of a support [13]. The above similarity indicates that the solid phase presents a particular ordered structure of the nearest reaction space in which the translation and segmental mobility of macroradicals are sharply lowered. Such a structure is analogous to the system of weakly interacting microreactors [11–15]. In each of such microreactors, chain termination is determined by the chain growth rate so that the disappearance of radicals is the act of their "self-burying" [8].

The equation of the rate of postpolymerization derived from kinetic scheme (I)–(III) adequately describes the experimental kinetic curves. Based on these data, we were the first to determine the numerical values of the rate constants of linear chain termination ($k_t \sim 10^{-5}$ and $k'_t \sim 10^{-6}$ m^3 mol^{-1} s^{-1}) and to establish the scale dependences $k_t \sim [M_0]^{-m}$, $k'_t \sim [M_0]^{-n}$, where $m = 1.5$, $n = 2.5$, and $[M_0]$ is the monomer concentration in the block [16]. These scale dependences are inconsistent with kinetic scheme (I)–(III) involving two characteristic lifetimes for macroradicals, and point to a wide spectrum of characteristic times. Moreover, to accept the act of self-burying as a chain growth reaction, one should at least estimate the activation energy of chain termination. In this work, the temperature dependence of the postpolymerization rate was studied for various dimethacrylates. To describe the kinetics of the process, the stretched exponential law was used [17].

EXPERIMENTAL

We studied the kinetics of postpolymerization of the following dimethacrylates: {M–O–$(CH_2CH_2O)_3$–C(O)–C_6H_4–C(O)–$(OCH_2CH_2)_3$–O–M} (MGF-9), {M–O–(CH_2CH_2O)–C(O)–$(CH_2$–$CH_2O)_2$–C(O)–O–(CH_2CH_2O)–O–M} (OKM-2), {M–O–$(CH_2$–CH_2–O–$)_3$–M–} (TGM-3), and {M–O–CH_2–CH_2–O–M–} (DMEG) (where M = CH_2 = $C(CH_3)$–C(O)–) in the temperature range from 5 to 50°C. Postpolymerization of 1,4-butanedioldimethacrylate (BDMK) was also examined at 20°C.

The runs were performed in the interferometeric laser set. Actual (H) and limiting (H_0) contractions of the layer of the photopolymerizing composition were measured, and the relative degree of polymerization or the conversion $P = H/H_0$ were determined. Integral UV radiation of a DRT-400 lamp was used; the radiation power was equal to 37.4 W/m^2. At a certain stage of light-induced polymerization, we interrupted UV radiation and continued detecting the contraction of the composition layer in the dark. Then, we turned on UV radiation again, allowed polymerization to complete, and determined the limiting contraction H_0 from which we calculated the thickness of the layer of photocomposition [(0.5–3.0) × 10^{-4} m]. 2,2-Dimethoxy-2-phenyl acetophenone (1 wt %) was used as a photoinitiator.

Figure 1 shows typical experimental curves of postpolymerization presenting the dependence of a change in the conversion ($P - P_0$) on the time of the dark period (t).

RESULTS AND DISCUSSION

To describe the kinetics of postpolymerization, we used kinetic scheme (I), according to which the rates of chain growth (w_p) and linear chain termination (w_t) are determined by the following expressions:

$$w_p = k_p[M_m][R_m], \tag{1}$$

$$w_t = k_t[M_m][R_m]. \tag{2}$$

Consequently, the rate of change of the radical concentration in the dark period is equal to

$$d[R_m]/dt = -k_t[M_m][R_m]. \tag{3}$$

Putting $[M_m] \approx$ const, we have

$$[R_m] = [R_{m,0}]\exp\{-\beta t\}. \tag{4}$$

Here, $[R_{m,0}]$ is the initial (for the dark period) concentration of radicals in the reaction zone; parameter

$$\beta = k_t[M_m] \approx \tau_t^{-1} \tag{5}$$

determines the characteristic lifetime of radicals τ_t or the time of relaxation.

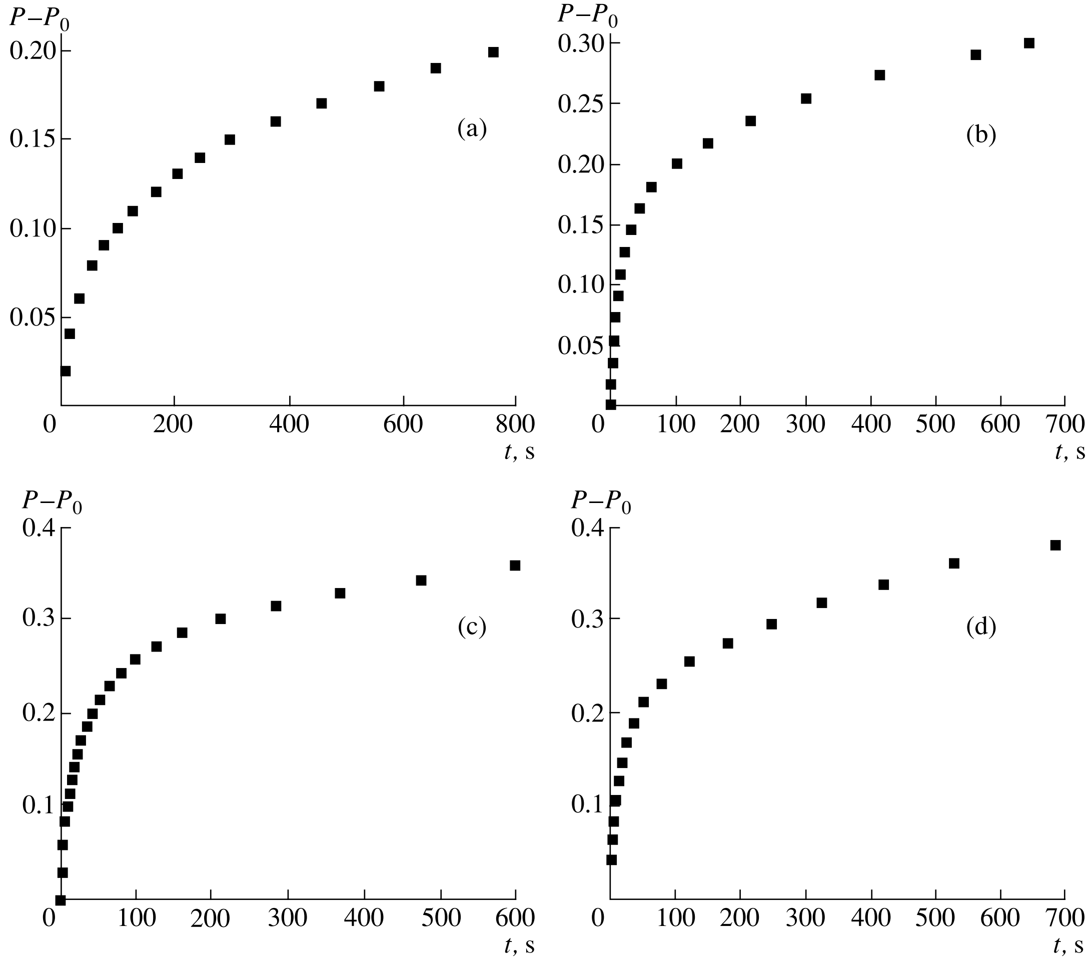

Fig. 1. Kinetic curves of postpolymerization of dimethacrylates at 15°C: (a) DMEG, (b) TGM-3, (c) OKM-2, and (d) MGF-9.

According to the initial assumption [8], the process in the interphase layer has the greatest contribution to the kinetics of postpolymerization, so that

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = w_{\mathrm{m}}\varphi_{\mathrm{m}} = w_{\mathrm{p}}\varphi_{\mathrm{m}}, \qquad (6)$$

where [M] is the monomer molar concentration calculated per overall volume of the system.

The volume fraction of the interphase layer φ_{m} was approximated by the function [6–8]

$$\varphi_{\mathrm{m}} \approx h(F_{\mathrm{s}}/F_{\mathrm{v}})\varphi_{\mathrm{s}}(1-\varphi_{\mathrm{s}}) \approx h(F_{\mathrm{s}}/F_{\mathrm{v}})P(1-P), \qquad (7)$$

where φ_{s} is the volume fraction of the solid polymeric phase, h is the thickness of the interphase layer, $F_{\mathrm{s}}/F_{\mathrm{v}}$ is the ratio of the fractal characteristics of the surface and the volume of micrograins of the solid polymeric phase in the liquid monomeric phase or the volume of microdrops of the liquid monomeric phase in the solid polymeric matrix.

Substituting formulas (1), (4), and (7) in Eq. (6) and expressing the rate of the process as $\mathrm{d}P/\mathrm{d}t = -(\mathrm{d}[\mathrm{M}]/\mathrm{d}t)/[\mathrm{M}_0]\Gamma_0$ (where Γ_0 is the limiting conversion in the solid polymeric phase), we obtain

$$\mathrm{d}P/\mathrm{d}t = k_{\mathrm{p}}[\mathrm{M}_{\mathrm{m}}][\mathrm{R}_{\mathrm{m,\,o}}]h(F_{\mathrm{s}}/F_{\mathrm{v}})P(1-P)\exp\{-\beta t\}. \qquad (8)$$

At $t = 0$, we have $P = P_0$ and

$$(\mathrm{d}P/\mathrm{d}t)_{t=0} \equiv w_0 = k_{\mathrm{p}}[\mathrm{M}_{\mathrm{m}}][\mathrm{R}_{\mathrm{m,\,o}}]h(F_{\mathrm{s}}/F_{\mathrm{v}})P_0(1-P_0). \qquad (9)$$

Expression (9) corresponds to the initial rate of polymerization in the dark period.

Equation (8) for the rate of postpolymerization can be written taking into account Eq. (9) in the form

$$\frac{\mathrm{d}P}{\mathrm{d}t} = w_0\frac{P(1-P)}{P_0(1-P_0)}\exp\{-\beta t\}. \qquad (10)$$

As expected, Eq. (10) with one characteristic time $\tau_{\mathrm{t}} = \beta^{-1}$ adequately describes only the initial (quick and short) portion of the experimental kinetic curve. This fact testifies that linear chain termination is characterized by a wide spectrum of relaxation times. In the subsequent consideration, we used the stretched exponential law for description of the overall kinetic curve.

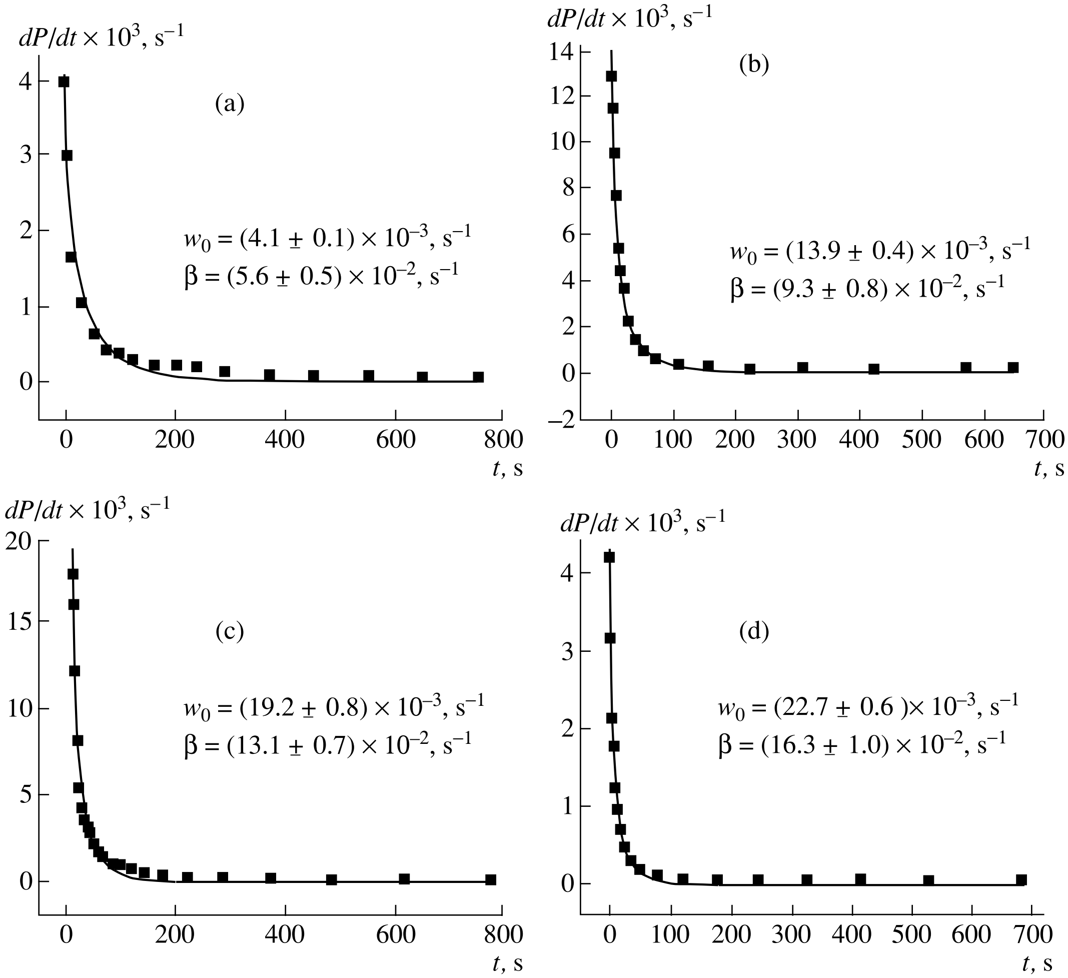

Fig. 2. Differential kinetic curves of postpolymerization of dimethacrylates at 15°C: (a) DMEG, (b) TGM-3, (c) OKM-2, and (d) MGF-9. Solid lines correspond to the calculations; points stand for the experimental values.

According to this law, the relaxation function is written in the form

$$\psi(t) = A\exp\{-bt\}^{\gamma}, \quad 0 < \gamma < 1. \qquad (11)$$

The values $0 < \gamma < 1$ make Eq. (11) the extended exponent.

In 1864, Kohlraush first proposed the stretched exponential law in the form of Eq. (11) for the description of material creep [17]. In 1970, this law was used in analysis of dielectric relaxation of polymers [18]. Then, it was found that the law is usable in the description of various types of relaxation, for the most part, in the disordered systems where spatial nonuniformity creates a hierarchy of relaxation times obeying the properties of the fractal set [19].

With the stretched exponential law, Eq. (10) can be transformed as follows:

$$\frac{\mathrm{d}P}{\mathrm{d}t} = w_0\frac{P(1-P)}{P_0(1-P_0)}\exp\{-\beta t\}^{\gamma}. \qquad (12)$$

The integral form of Eq. (12) has no simple analytical expression. To relate this equation to the experimental data, we numerically differentiated the integral kinetic curves ($P - P_0 = f(t)$) (see Fig. 1) and determined the w_0, β, and γ parameters from the differential kinetic curves (Fig. 2) by optimization. The least adequate results within one experimental series were obtained for the γ parameter (its values ranged from 0.5 to 0.7). The reason is that the slow and prolonged portion of the kinetic curve, which is the most important for the γ evaluation, exhibits low values of dP/dt and contributes only slightly to the function of squared deviations of the calculated and experimental values. The minimum standard errors in the estimation of w_0 and β were observed at $\gamma = 0.6$. Therefore, in further studies we correlated all experimental kinetic curves $\mathrm{d}P/\mathrm{d}t = f(t)$ with Eq. (12) at the fixed value $\gamma = 0.6$ with the optimization over two parameters (w_0 and β) only. Note that in all cases we obtain the adequate correlation between the experimental and calculated kinetic curves.

Table 1. Values of the w_0 and β parameters of Eq. (12) calculated from experimental data on postpolymerization of dimethacrylate DMEG at 15°C

P_0	τ, s	$w_0 \times 10^3$, s^{-1}	$\beta \times 10^2$, s^{-1}
0.30	650	4.0 ± 0.1	5.7 ± 0.4
0.29	700	3.7 ± 0.1	4.6 ± 0.3
0.16	650	3.4 ± 0.1	7.4 ± 0.7
0.22	750	4.1 ± 0.1	5.6 ± 0.5
0.19	700	3.6 ± 0.2	5.5 ± 0.6
0.21	750	3.2 ± 0.1	5.3 ± 0.6
$\beta \times 10^2$, s^{-1}			5.7 ± 0.9

Table 2. Average values of the β parameter of Eq. (12) calculated from the experimental data on postpolymerization of dimethacrylates at various temperatures

T, °C	$\beta \times 10^2$, s^{-1}				
	DMEG	BDMK	TGM-3	OKM-2	MGF-9
5	4.6 ± 2.3	–	10.7 ± 3.0	10.9 ± 3.0	–
10	–	–	10.7 ± 2.1	13.3 ± 2.1	12.8 ± 1.2
15	5.7 ± 0.9	–	10.6 ± 2.5	15.3 ± 2.1	15.6 ± 2.8
20	–	9.8 ± 7.1	12.2 ± 0.7	15.0 ± 2.0	13.8 ± 3.4
25	6.4 ± 2.8	–	14.6 ± 4.5	13.8 ± 2.6	16.5 ± 2.3
30	–	–	–	–	17.6 ± 2.2
35	–	–	14.3 ± 4.1	16.5 ± 4.0	19.7 ± 7.4
40	–	–	–	–	19.0 ± 4.4
45			–	–	19.7 ± 5.2
50	–	–	14.9 ± 4.0	19.1 ± 2.8	17.6 ± 6.1

As in the previous studies [6, 7], the experimental error in the construction of each individual kinetic curve of postpolymerization was small (see the localization of points in Fig. 1). At the same time, the scatter of the kinetic curves obtained under the same experimental conditions is considerably higher than the error in the individual kinetic curve. Such an unsatisfactory reproducibility of the kinetic measurements points to microheterogeneity of the polymerizing system, the fluctuation mechanism of the formation and development of the solid polymeric phase (and, correspondingly, the interphase layer at the liquid monomer–solid polymer boundary) and to its important role in polymerization [6, 7]. Because of the above phenomenon, we obtained from 5 to 10 kinetic curves under the same experimental conditions. The kinetic parameters found from these curves were averaged, and thus, the statistical reliability of the obtained parameters increased. Table 1 lists, for example, the β values calculated from individual kinetic curves and the averaged value. As can be seen from the data in Fig. 3, the β values are independent of the initial conversion P_0 in the dark period despite the marked dispersion of these values. Similar relationships were observed under different experimental conditions.

The average β values for the studied dimethacrylates at various temperatures are given in Table 2. Figure 4 presents these data plotted in the coordinates of the Arrhenius equation; there one can see the corresponding linear regression equations used to calculate the activation energies of the rate constants of linear chain termination presented in Table 3.

The activation energies of chain termination for three dimethacrylates (OKM-2, MGF-9, and TGM-3) are close in magnitude (6.7–7.6 kJ/mol), whereas the value of the activation energy for DMEG is higher and equal to 11.6 kJ/mol. Thus, linear chain termination is the activated process. The low values of the activation energy, which are considerably lower than those of the viscous flow (for example, ≈55 and 44 kJ/mol for OKM-2 and MGF-9, respectively) are consistent with the assumption that the rate of chain termination is controlled by the rate of chain growth. Consequently, linear chain termination cannot be considered as passive freezing of an active radical.

To decrease a contingency in evaluating the β parameter on treating the scale dependence of β and k_t

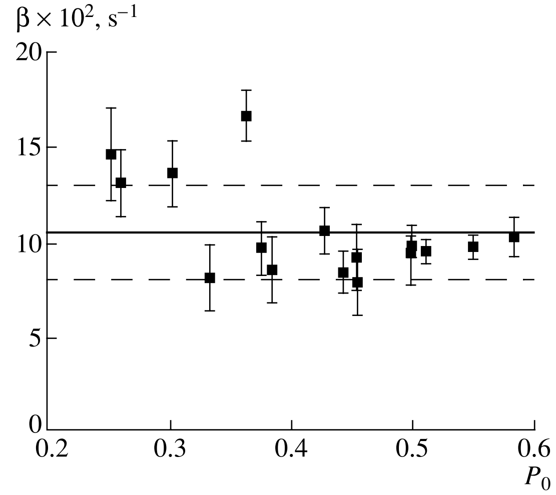

Fig. 3. Values of the β parameter calculated by the optimization method at various initial conversions of postpolymerization of TGM-3 at 15°C.

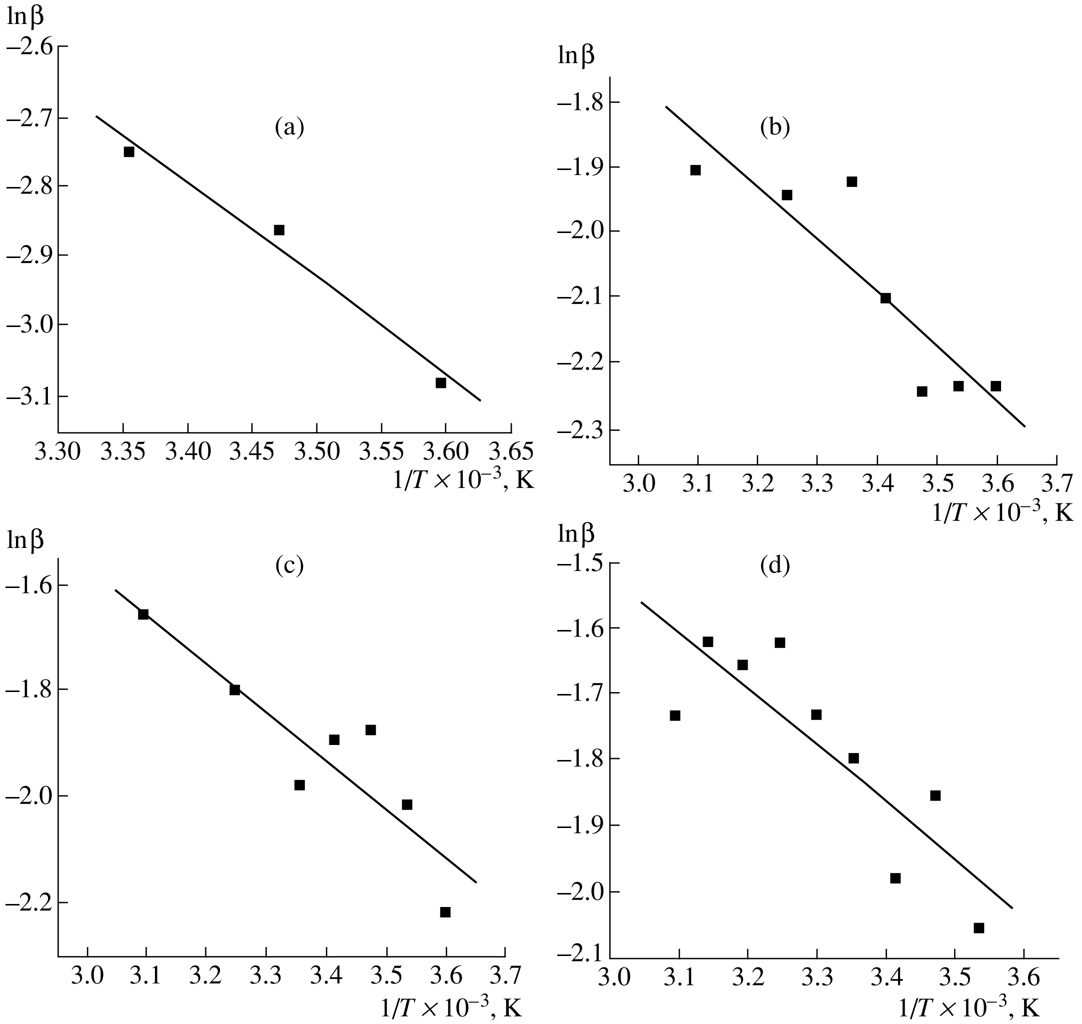

Fig. 4. Temperature dependences of the β parameter in the coordinates of the Arrhenius equation: (a) DMEG, (b) TGM-3, (c) OKM-2, (d) MGF-9.

on $[M_0]$, a regression estimate of β was made (20°C). Assuming that the monomer concentration in the interphase layer is close to that in the block ($[M_m] \cong [M_0]$), we calculated constants $k_t = \beta/[M_0]$ at 20°C. These data are also given in Table 3.

Note that the k_t values, which are determined in this work using the kinetic model with the stretched exponential law, virtually coincide with those calculated previously [16] from the kinetic model with two characteristic times and the exponential law of relaxation.

Table 3. Kinetic parameters of postpolymerization of dimethacrylates

Dimethacrylate	M, kg/mol	$[M]_0$, mol/m^3	$\bar{\beta} \times 10^2$, s^{-1}	$\bar{k}_t \times 10^5$, m^3 mol^{-1} s^{-1}	E_A, kJ/mol	$k_p\rho_0^{\xi}$
DMEG	0.198	5297	6.2	1.17	11.6	19.4
BDMK	0.226	4526	9.8	2.16	–	27.6
TGM-3	0.286	3814	12.2	3.20	6.7	30.6
OKM-2	0.418	2890	14.6	5.05	7.6	30.4
MGF-9	0.566	2060	15.1	7.33	7.2	25.1

Note: The $\bar{\beta}$ values are calculated at 20°C by the linear regression equations for the temperature dependence (Fig. 4): $\bar{k}_t = \bar{\beta}/[M_0]$; $k_p\rho_0^{\xi} = \bar{k}_t\rho_m^{\xi} = \bar{k}_t[M_0]^{\xi}$, where $\xi = 1.67$.

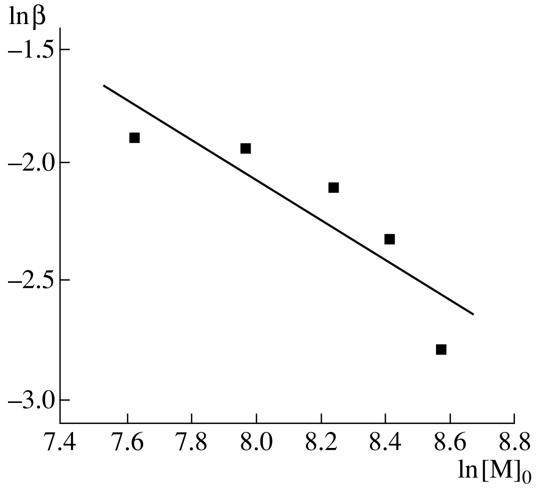

Fig. 5. Logarithmic dependence of the calculated values of the $\bar{\beta}$ parameter on the mole concentration of dimethacrylate in the block (20°C).

For example, the k_t values for the above two models are equal to 2.2 and 1.4 (BDMK), 5.0 and 3.6 (OKM-2), 7.3 and 5.2 (MGF-9) (all in the units of 10^{-5} m^3 mol^{-1} s^{-1}). Thus, both kinetic models give results that are in good agreement. This fact supports the main peculiarity of postpolymerization of dimethacrylates, namely, linear termination in terms of kinetic scheme (I).

Figure 5 presents the logarithmic dependence of the calculated β values on the monomer concentration in the block. With the proviso that $\beta \sim [M_0]^{1-\xi}$, we obtain the expression $1 - \xi = -0.86 \pm 0.27$ from the linear equation of regression (Fig. 5). Consequently, the scale dependence $k_t \sim [M_0]^{-\xi}$ takes place for the rate constant of linear chain termination, and $\xi = 1.86 \pm 0.27$.

As mentioned above, the scale dependence $k_t \sim [M_0]^{-\xi}$ was revealed previously in [16] where the kinetics of postpolymerization was described on the basis of the kinetic scheme (I)–(III) with two characteristic times of relaxation. Thus, the obtained dependence $k_t \sim [M_0]^{-\xi}$ is fundamental rather than due to the choice of the rate law of postpolymerization [the exponential law with two characteristic times of relaxation on the basis of scheme (I)–(III) or the stretched exponential law based on scheme (I) only]. However, the stretched exponential law requires the spectrum of characteristic times of relaxation, which has the properties of a fractal set [19]. The scale form $k_t \sim [M_0]^{-\xi}$ supports this statement. Consequently, a relation between the above scale dependence and the stretched exponential law should exist resulting in the expression $1/\xi \approx \gamma$. However, this point needs further theoretical investigation.

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