

Monomolecular Chain Termination in the Kinetics of Dimethacrylate Postpolymerization

Y. G. Medvedevskikh,¹ A. R. Kytsya,¹ L. I. Bazylyak,¹ A. M. Bratus,¹ A. A. Turovski,¹
G. E. Zaikov²

¹Physical Chemistry and Technology of Combustible Minerals Department, L. V. Pisarzhevsky Institute of Physical Chemistry, National Academy of Sciences of the Ukraine, 3a Naukova Str., Lviv 79053, Ukraine

²N. Emmanuel Institute of Biochemical Physics, Russian Academy of Sciences, 4 Kosygin Str., Moscow 117977, Russia

Received 5 March 2003; accepted 14 July 2003

ABSTRACT: The kinetics of postpolymerization (after ultraviolet illumination was stopped) for a number of dimethacrylates that differed by nature and molecular mass was experimentally studied over a wide range of temperatures. A series of kinetic curves that differed by the starting conversion of the dark period of time was obtained for every temperature. The proposed kinetic model of the process is based on the following main principles: (1) the process at an interface on the liquid monomer–solid polymer (micrograins) boundary takes a main share of the kinetics of postpolymerization; (2) chain termination at an interface is monomolecular, is controlled by the chain propagation rate, and represents by itself the self-burial act of active radicals in the conformation trap; and (3) monomolecular chain termination is characterized by a wide spectrum of character-

istic times and that is why the function of the relaxation is described by Kohlrausch's stretched exponential law. The obtained kinetic equation was in good agreement with all of the sets of experimental data. This permitted us to estimate the rate constant of chain termination (k_t) and to determine the scaling dependence of k_t on the molar-volumetric concentration of the monomer in bulk $[M_0]$. We assumed that the stretched exponential law and scaling dependence k_t from $[M_0]$ were characterized by common peculiarities, namely, a wide range of characteristic times of relaxation possessed by a property of the fractal set. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2376–2382, 2004

Key words: chain

INTRODUCTION

Postpolymerization, or the so-called nonstationary dark process of polymerization, proceeding after ultraviolet (UV) illumination is stopped gives us important information about the chemical mechanism of chain-termination elementary reactions. In the experimental data, a series of general regularities^{1–4} exists both for monofunctional and multifunctional monomers: (1) the rate and polymerization degree depend appreciably on the starting conversion of the dark period; (2) the number-average molecular mass of the polymer is propagated via the polymerization process, and the concentration of radicals detected by EPR spectroscopy *in situ* is insignificantly decreased or is constant; and (3) there are two sections on the kinetic curve: a rapid and short section and a slow and long one. The previous discussion permits us to suppose that radicals initiating the postpolymerization process are sharply distinguished by characteristic times of life (τ_t 's). Maybe that is why three variants of postpoly-

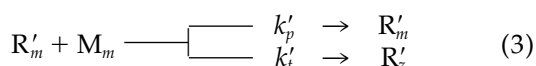
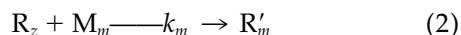
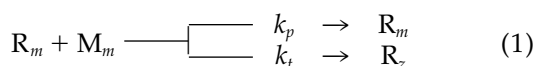
merization kinetic descriptions based on bimolecular, linear, and mixed-chain termination checked in ref. 5 showed that kinetic models with only bimolecular or linear chain termination agreed less satisfactorily with the experimental data than their combination, representing by itself mixed-chain termination and permitting the introduction of at least two radical τ_t 's. It is supposed also in ref. 5 that the postpolymerization process proceeds with the same rate in the all volumes of the polymerizing system.

However, the kinetic models of stationary and nonstationary (dark) processes of photoinitiated polymerization proposed in refs. 6–8 were based on imaging about the microheterogeneity of the polymerizing system and its two reactive zones. That is why the observed rate of polymerization (ω) is a sum of the rate of the homophaseous process proceeding in the volume of the liquid monomer in accordance with the classic kinetic scheme with the bimolecular chain-termination and that of the heterophaseous process proceeding in the interface layer on the liquid monomer–solid polymer (micrograins) boundary under gel-effect conditions with monomolecular chain termination: $\omega = \omega_v\phi_v + \omega_m\phi_m$, where ϕ_v and ϕ_m are the volumetric parts of the liquid monomer phase and the interface layer, respectively, and ω_v and ω_m are the corresponding specific rates of polymerization.

Correspondence to: G. E. Zaikov (chembio@sky.chph.ras.ru).

Contract grant sponsor: STCU; contract grant number: 1447.

However, this takes into account the derivation of kinetic model for the postpolymerization in which radicals in the liquid phase are characterized with little times of life and cannot play a remarkable part in the postpolymerization process. So, that is why the rate of postpolymerization is completely determined by the rate of the heterophaseous process in the interface layer: $\omega \cong \omega_m \phi_m$. With the aim of taking into account the difference between the radical τ_i 's, the authors of ref. 8 proposed a kinetic scheme of the process in the interface layer as primary [eq. (1)] and secondary [eq. (3)] chains with the monomolecular chain termination and two τ_i 's, namely, $\tau_1 = (k_t[M_m])^{-1}$ and $\tau_2 = (k_t'[M_m])^{-1}$:



The main peculiarity of the schemes in eqs. (1) and (3) is the fact that the rate of monomolecular chain termination is controlled by the rate of chain propagation (w_p) because acts of chain propagation and chain termination represent by themselves two different results of the interactions of active radicals (R_m and R_m') with the functional group of the monomer, leading to the formation again of active radicals (so-called chain propagation) or their freezing^{3,9} or trapping^{4,10} (monomolecular chain termination), that is, leading to formation of nonactive radicals (R_z and R_z'). Elementary eq. (2) represents by itself the reaction of the secondary active radicals (R_m') initiation from the primary frozen ones (R_z).

Although the kinetic schemes in eqs. (1)–(3) are idealized, they can be explained from the physical point of view. This physical sense is based on the generality of the kinetic regularities of polymerization at an interface (including specifically the first-order on the initiator) and, for example, bulk polymerization,¹¹ polymerization in the presence of porosity filler,¹² or at the adsorbed immobilization on the surface of the carrier of the polymeric initiator.¹³ This generality means that the solid phase creates the specially ordered structure of the nearest reactive space in which the translational and segmental mobilities of the macroradicals are sharply decreased. Such a structure is similar to a system of weak interactions between other microreactors^{11–15} in which every chain termination is determined by w_p in a such manner that the decay of radicals represents by itself a self-burial act.⁸

The kinetic schemes of postpolymerization in eqs. (1)–(3) describes well the experimental kinetic curves.

This permitted us first to estimate the numerical values of the rate constants for monomolecular chain termination ($k_t \approx 10^{-5}$ m³/mol s and $k_t' \approx 10^{-6}$ m³/mol s) and to ascertain the scaling dependencies ($k_t \approx [M_0]^{-m}$, $k_t' \sim [M_0]^{-n}$, $m = 1.5$, $n = 2.5$, where $[M_0]$ is the molar-volumetric concentration of the monomer in bulk).¹⁶ The aforementioned dependencies did not agree with the kinetic schemes in eqs. (1)–(3) with two τ_i 's of macroradicals life because they indicated a wide spectrum of τ_i 's. Also, if we assumed that the self-burial act of the active radical represents by itself the act of chain propagation, we needed to at least estimate the activated nature (k_t). That is why, in this work, the temperature dependence of the postpolymerization rate for a range of dimethacrylates was experimentally studied, and a stretched exponential law (in accordance with ref. 17) is used for the description of the kinetics of the process.

EXPERIMENTAL

The kinetics of dimethacrylate postpolymerization, namely, MGPh-9 [M—O—(CH₂CH₂O)₃—C(O)—C₆H₄—C(O)—(OCH₂CH₂)₃—O—M], OCM-2: [M—O—(CH₂CH₂O)—C(O)—(CH₂—CH₂O)₂—C(O)—O—(CH₂CH₂O)—O—M], TGM-3: [M—O—(CH₂—CH₂—O—)₃—M—], and DMEG: [M—O—CH₂—CH₂—O—M—], where M is CH₂=C(CH₃)—C(O)—, were studied in the range 5–50°C, and also 1,4-butandioldimethacrylate was studied at 20°C.

Experiments were carried out on the interferometric laser plant; we measured the current contractions (H_s) and limited achieved contractions (H_0 's) of the layer of photopolymerizing composition. With the ratio of the aforementioned contractions taken into account, the relative degree of polymerization (or conversion) was determined, namely, $P = H/H_0$.

Integral UV illumination of a DRT-400 lamp (with a luminous flux of 37.4 W/m²) falling upon the surface of the photopolymerizing composition was used for the experiments. UV illumination was stopped at a defined stage of the luminous polymerization process prolonging the registration of the contraction of the composition layer under dark conditions; after that, UV illumination was switched on, which provided the end of the polymerization process and allowed us to proceed with the determination of the final contraction (H_0). With the aforementioned value of H_0 taken into account, the thickness of the layer was determined. The previously mentioned thickness of the photocomposition layer was varied in the range 0.5–3.0 × 10⁻⁴ m. 2,2-Dimethoxy-1,2-diphenylethane-1-one was used as a photoinitiator of the process at its starting concentration of 1 mass %.

Typical experimental kinetic curves of the postpolymerization are represented on Figure 1 as the depen-

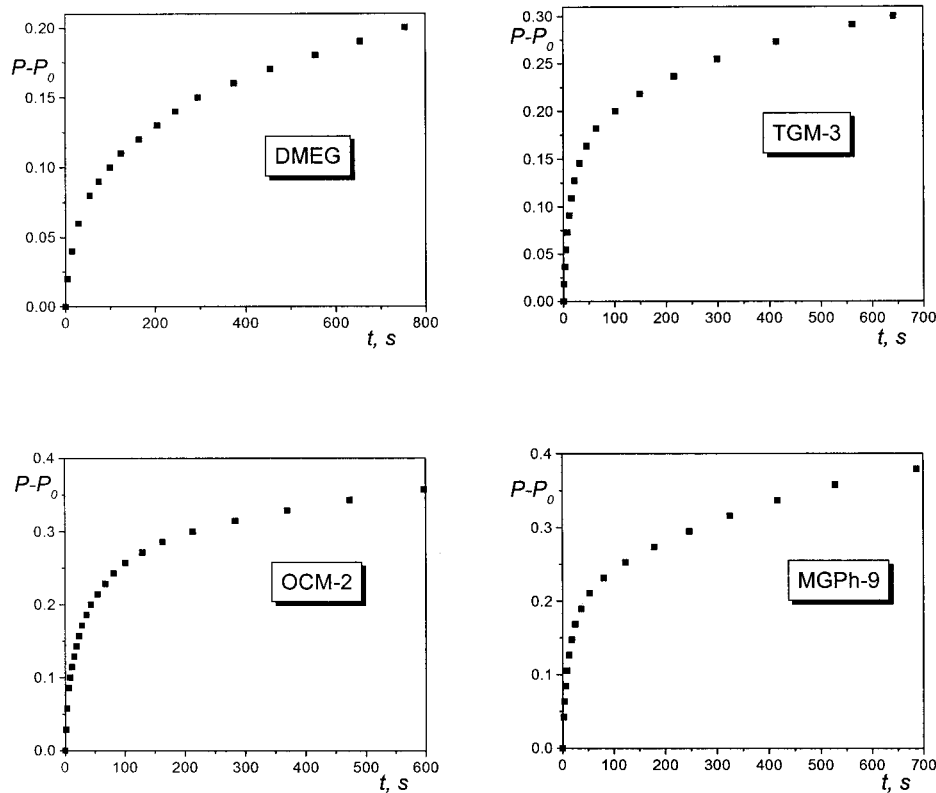


Figure 1 Typical experimental kinetic curves of dimethacrylate postpolymerization at 15°C

dence of the conversion ($P - P_0$) increment from the time (t) of the dark period.

RESULTS AND DISCUSSION

Let us be limited only by the kinetic scheme in eq. (1) for a description of the postpolymerization kinetics. In accordance with the aforementioned scheme, w_p and the rate of monomolecular chain termination (w_t) can be determined by the following equations:

$$w_p = k_p[M_m][R_m] \quad (4)$$

$$w_t = k_t[M_m][R_m] \quad (5)$$

So, the rate of the radical's concentration changing under dark conditions is equal to

$$d[R_m]/dt = -k_t[M_m][R_m] \quad (6)$$

If we assume that $[M_m]$ is approximately constant, we obtain

$$[R_m] = [R_{m0}] \exp(-\beta t) \quad (7)$$

where $[R_{m0}]$ is the starting concentration of radicals in the reactive zone for the dark period of time and the parameter

$$\beta = k_t[M_m] \approx \tau_t^{-1} \quad (8)$$

determines the radical τ_t , or the relaxation time.

In accordance with the starting principle in ref. 8, we assumed that the process at the interface played the main part in the kinetics of postpolymerization; as a result

$$-d[M]/dt = w_m \phi_m = w_p \phi_m \quad (9)$$

where $[M]$ is the molar-volumetric concentration of the monomer calculated on the whole volume of system.

ϕ_m is approximated by the function⁶⁻⁸

$$\phi_m \approx h(F_s/F_v)\phi_s(1 - \phi_s) \approx h(F_s/F_v)P(1 - P) \quad (10)$$

where ϕ_s is the volumetric part of the solid polymeric phase, h is the thickness of the interface layer, F_s/F_v is the ratio of the fractal characteristic of the surface and the volume of micrograins of the solid polymeric phase into a liquid monomeric one or microdrops of liquid monomeric phase into a solid polymeric matrix.

By combining eqs. (4), (7), and (10) into (9) and expressing the rate of process in the units of conversion as $dP/dt = -(d[M]/dt)/[M_0]\Gamma_0$, where Γ_0 is the

final degree of double-bond conversion in the solid polymeric phase, we obtain

$$dP/dt = k_p[M_m][R_{m0}]h(F_s/F_v)P(1-P)\exp(-\beta t) \quad (11)$$

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

$$(dP/dt)_{t=0} \equiv w_0 = k_p[M_m][R_{m0}]h(F_s/F_v)P_0(1-P_0) \quad (12)$$

represents by itself the starting rate of postpolymerization for the dark period of time.

With eq. (12) taken into account, eq. (11) for the determination of the postpolymerization rate can be represented as

$$\frac{dP}{dt} = w_0 \frac{P(1-P)}{P_0(1-P_0)} \exp(-\beta t) \quad (13)$$

As we expected, eq. (13) with a single $\tau_t = \beta^{-1}$ satisfactorily describes only the starting rapid and short section of the experimental kinetic curve. This means that monomolecular chain termination is characterized with a wide spectrum of relaxation times. That is why the stretched exponential law was used for the full description of the kinetic curve. In accordance with this law, the function of relaxation is written as follows:

$$\psi(t) = A \exp(-bt)^\gamma, \quad 0 < \gamma < 1 \quad (14)$$

Namely, $0 < \gamma < 1$ gives the effect of the stretched exponential to eq. (14).

The stretched exponential law in the form of eq. (14) was proposed by Kohlrausch (see ref. 17) first in 1864 for the description of materials creeping and was used by Williams and Watts¹⁸ in 1970 for the analysis of the dielectric relaxation of polymers. The aforementioned law describes the different types of relaxation mainly in nonordered systems, in which spatial inhomogeneity forms the hierarchy of relaxation times, subordinating to the properties of the fractal set.¹⁹

By setting the effect of the stretched exponential into eq. (13), we obtain

$$\frac{dP}{dt} = w_0 \frac{P(1-P)}{P_0(1-P_0)} \exp(-\beta t)^\gamma \quad (15)$$

The integral form of eq. (15) does not have the simple analytic view, and that is why integral kinetic curves $P-P_0 = f(t)$ (see Fig. 1) were numerically differenced for comparison of eq. (15) with the experimental data. After this, differential kinetic curves [$dP/dt = f(t)$] were obtained; typical examples of such curves are represented on Figure 2 by points. On the basis of the

comparison of these obtained curves and eq. (15) by the optimization method, all three constants of eq. (15) were found, namely, w_0 , β , and γ . As we discovered, the spread in numerical values for parameter γ from 0.5 to 0.7 was less satisfactory at the optimization selection of all of the parameters in the experimental series. This could be explained by the fact that the most important section of the kinetics curve for estimation of parameter γ , namely, slow and long, was characterized by low values of dP/dt and played little part in the functional of number squared of the calculated deviations from the experimental ones. Fixing the parameter γ showed that the minimal standard error at the estimation of w_0 and β was observed at the value $\gamma = 0.6$. That is why all of experimental curves [$dP/dt = f(t)$] were compared with eq. (15) at a fixed value $\gamma = 0.6$ with optimization only on two parameters, namely, w_0 and β . A comparison of the calculated examples (lines) in accordance with eq. (15) and experimental (points) kinetic curves is represented on Figure 2. In all of the cases, satisfactory correspondence took place between the experimental and calculated data according to the eq. (15) kinetic curves.

As mentioned earlier,^{6,7} the experimental error at the construction of the separate kinetic curve of postpolymerization was sufficiently small. This is proven by the location of the points in Figure 1. At the same time, the spread in kinetic curves under the same experimental conditions considerably exceeded the error of the individual kinetic curve. This phenomenon is well-known as a bad reproduction of the kinetic measurements and, in accordance with the author's mind,^{6,7} represented by itself direct proof of the microheterogeneity of the polymerizing system, the fluctuated mechanism of the formation and propagation of a solid polymeric phase and interface layer on the liquid monomer–solid polymer boundary, and also its active role via postpolymerization. That is why 3–10 kinetic curves were obtained for each experimental condition. From these curves, we averaged the kinetic parameters of the process. In such a way, the statistical truth of the obtained estimations was stepped up. For example, we can see in Table I the values of the parameter β obtained from individual kinetic curves and also results of their average. We can see from Figure 3 that despite the spread in values of parameter β , these values did not depend on the starting conversion (P_0) of the dark period. The same picture was observed for other experimental conditions.

Average β values for the investigated dimethacrylates at different temperatures are represented in Table II. The interpretation of these data in Arrhenius coordinates is shown in Figure 4; the corresponding linear equations of the regression are also presented in Figure 4. The activation energies of the k_t values were calculated in accordance with the previous equations and are presented in Table III.

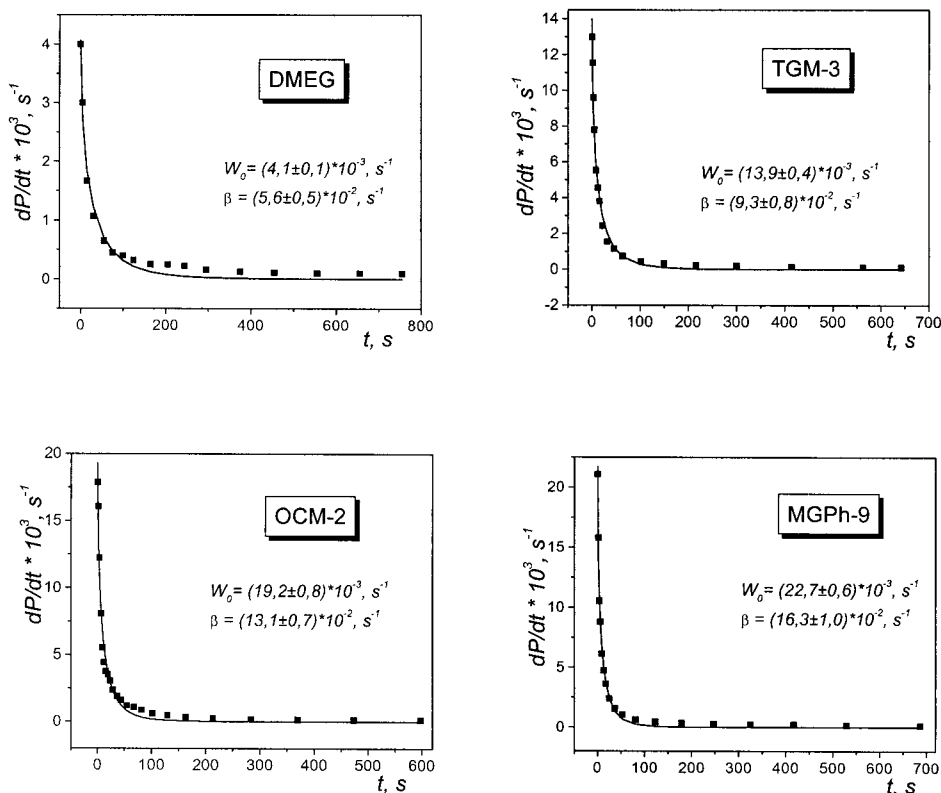


Figure 2 Interpretation of the experimental kinetic curves of dimethacrylate postpolymerization in the differential form (points) and compared with ones calculated by eq. (15) (lines) at 15°C.

As we can see from these data, the activation energies of the k_t values for the three dimethacrylates (OCM-2, MGPh-9, and TGM-3) were similar to each other and equal to 6.7–7.6 kJ/mol; the value for DMEG was 11.6 kJ/mol. So, monomolecular chain termination represented by itself the activated process, and low values of activation energies were considerably less than the activation energies of viscous flow (e.g., for OCM-2 and MGPh-9, these values were ~55 and 44 kJ/mol, respectively) and did not agree with the accepted assumption, according to which the monomolecular w_t was controlled by its w_p , and, as follows from this, monomolecular chain termination cannot be considered as a passive freezing of the active radical.

TABLE I
Nature of the Spread for the Parameters w_0 and β Calculated via Eq. (15) for the Postpolymerization of DMEG at 15°C

	P_0	τ (s)	$w_0 \times 10^3 (s^{-1})$	$\beta \times 10^2 (s^{-1})$
1	0.30	650	4.0 ± 0.1	5.7 ± 0.4
2	0.29	700	3.7 ± 0.1	4.6 ± 0.3
3	0.16	650	3.4 ± 0.1	7.4 ± 0.7
4	0.22	750	4.1 ± 0.1	5.6 ± 0.5
5	0.19	700	3.6 ± 0.2	5.5 ± 0.6
6	0.21	750	3.2 ± 0.1	5.3 ± 0.6 5.7 ± 0.9

With the aim of decreasing the element of randomness in the estimation of parameter β during the interpretation of the scaling dependence, we also calculated β and k_t from $[M_0]$, and values of β at temperature at 20°C on the basis of linear equations of regression. These values ($\beta k_t = \beta/[M_0]$ at 20°C) were calculated with the assumption that concentration of the monomer in the interface layer was near to its concentration in the bulk, namely, $[M_m] \cong [M_0]$. The obtained results are also given in Table III.

When the results of this work were compared with a kinetic model with the stretched exponential law

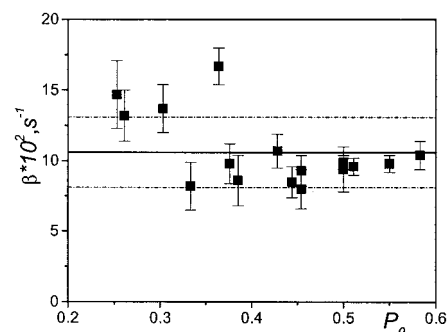


Figure 3 Values of the β parameter calculated by the optimization method at different starting conversions of postpolymerization for the dimethacrylate TGM-3 at 15°C.

TABLE II
Average Values of Parameter β Accordingly to Kinetic Eq. (15) Calculated from Experimental Data for Dimethacrylate Postpolymerization at Different Temperatures

Temperature (°C)	$\beta \times 10^2$ (s ⁻¹)				
	DMEG	BDMC	TGM-3	OCM-2	MGPh-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

values of k_t and those in ref. 16 according to a kinetic scheme with two τ_i 's and the exponential law of relaxation, they practically coincided. For example, values of k_t for BDMC were 2.2 and 1.4×10^{-5} m³/mol s, values for OCM-2 were 5.0 and 3.6×10^{-5} m³/mol s, and values for MGPh-9 were 7.3 and 5.2×10^{-5} m³/mol s. So, both kinetic models, despite their differ-

ences, led to corresponding estimations of k_t . This means that the main peculiarity of dimethacrylate postpolymerization was monomolecular chain termination according to the scheme in eq. (1).

The interpretation of the scaling dependence of calculated β values from $[M_0]$ is represented in Figure 5. If we designate this dependence as $\beta \approx [M_0]^{1-\xi}$, in

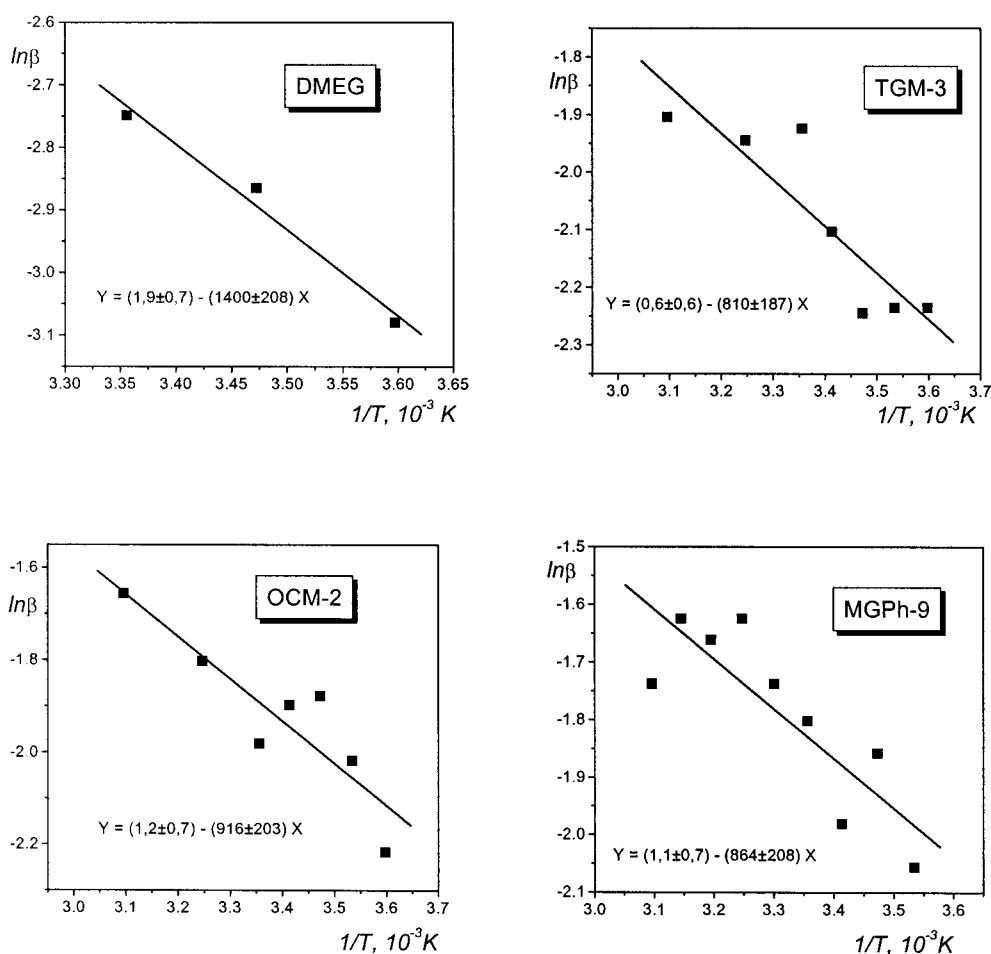


Figure 4 Temperature dependencies of the β parameter in the coordinates of the Arrhenius equation.

TABLE III
Kinetic Constants of Dimethacrylate Postpolymerization

Dimethacrylate	[M] (g/mol)	[M] ₀ (mol/m ³)	$\bar{\beta} \times 10^2$ (s ⁻¹)	$\bar{k}_t \times 10^5$ (m ³ /mols)	E _A (kJ/mole)	k _p ρ ₀ ^ξ
DMEG	0.198	5297	6.2	1.17	11.6	19.4
BDMC	0.226	4526	9.8	2.16	—	27.6
TGM-3	0.286	3814	12.2	3.20	6.7	30.6
OCM-2	0.418	2890	14.6	5.05	7.6	30.4
MGPPh-9	0.566	2060	15.1	7.33	7.2	25.1

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

accordance with the linear equation of regression (see Fig. 5), we obtain $1 - \xi = -0.86 \pm 0.27$. As follows from this, the scaling dependence $k_t \approx [M_0]^{-\xi}$ and $\xi = 1.86 \pm 0.27$ are true for a constant w_t .

As previously mentioned, the scaling dependence $k_t \approx [M_0]^{-\xi}$ was determined earlier in ref. 16 despite the fact that postpolymerization kinetics in this work was described on the basis of the kinetic schemes in eqs. (1)–(3) with two τ_t 's of relaxation. This means that the scaling dependence $k_t \approx [M_0]^{-\xi}$ was determined by fundamental factors but not by the choice of postpolymerization kinetics equation [exponential law with two τ_t 's of relaxation based on the schemes in eqs. (1)–(3) or the stretched exponential law based only on the scheme in eq. (1)]. However, the stretched exponential law demands the spectrum of τ_t 's of relaxation possessed by properties of the fractal set.¹⁹ The scaling form $k_t \sim [M_0]^{-\xi}$ is also directed on this fact. So, we

conclude that a relation between the scaling form and the stretched exponential law exists. Maybe, that is why $1/\xi \approx \gamma$; however, this needs special theoretical discussion.

References

- Garina, E. S.; Kuznietsova, T. M.; Zubov, V. P.; Kabanov, V. A. Dokl AN USSR 1973, 209(2), 380.
- Shen, J.; Tian, Y.; Wong, G. Sci China 1990, 33, 1046.
- D'yachkov, A. N.; Efimov, A. L.; Efimov, A. L. Vysokomol Soedin A 1983, 25, 2176.
- Zhu, S.; Tian, Y.; Mamielles, A. E. Macromolecules 1990, 23, 1144.
- Andrzejewska, E.; Bogacki, M. B.; Andrzejewski, M. Macromol Theory Simul 2001, 10, 842.
- Medvedevskikh, J. G.; Zagladko, E. A.; Turovski, A. A.; Zaikov, G. E. Int J Polym Mater 1999, 43, 157.
- Zagladko, E. A.; Medvedevskikh, J. G.; Turovski, A. A.; Zaikov, G. E. Int J Polym Mater 1998, 39, 227.
- Medvedevskikh, J. G.; Zagladko, E. A.; Turovski, A. A.; Zaikov, G. E. Russ Polym News 1999, 4(3), 33.
- Efimov, A. L.; Bugrova, T. A.; D'yachkov, A. I. Vysokomol Soedin B 1992, 25, 2176.
- Kurdikar, D. L.; Peppas, N. A. Macromolecules 1981, 27, 4084.
- Ivanov, V. B.; Romaniuk, A. P.; Shybanov, V. V. Vysokomol Soedin B 1993, 35, 119.
- Min'ko, S. S.; Luzinov, I. A.; Smirnov, B. P. Vysokomol Soedin 1990, 32, 750.
- Min'ko, S. S.; Sydorenko, A. A.; Voronov, S. A. Vysokomol Soedin 1995, 37, 1403.
- Ivanchev, S. S.; Dmitrenko, A. B.; Krupnyk, A. M. Vysokomol Soedin A 1998, 30, 1951.
- Stepanian, A. O.; Zaremsky, M. Y.; Olenin, A. V. Dokl AN USSR 1984, 274(3), 655.
- Medvedevskikh, Y. G.; Zaglad'ko, E. A.; Bratus' A. N.; Turovskiy, A. A. Dokl AN USSR 2000, (10), 148.
- Montroll, E. W.; Bendler, J. T. J Stat Phys 1984, 34, 129.
- Williams, G.; Watts, D. C. Trans Faraday Soc 1970, 66, 80.
- Shlezinger, M.; Klafter, J. In Abstracts of the International Symposium on Fractals in Physics; Myr: Moscow, 1988; p 553.

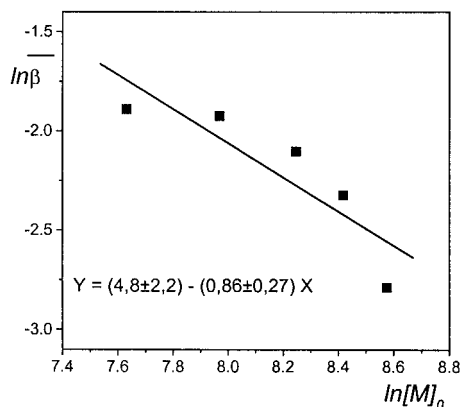


Figure 5 Dependence of calculated values of the $\bar{\beta}$ parameter at 20°C on $[M_0]$ of dimethacrylate in bulk.