

# Kinetics of Bimolecular Radical Decay in Different Polymeric Matrices

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**ABSTRACT:** Using electron spin resonance spectroscopy, we have studied the kinetics of the bimolecular decay of methacrylic macroradicals in networked and unnetworked polymeric matrices. We have determined that macroradical decay in the entire range of temperatures (20–70°C) is definitely ordered to a second-order kinetic reaction equation. We have estimated the activation parameters of the process. Using Smolukhovskiy's and Einstein's equations and the fractal dependence of the conformation radius of the macroradical on its polymeriza-

tion degree, we have obtained an equation for the constant of bimolecular radical decay under diffusion conditions. This equation is in good agreement with all the experimental data and possesses a commonness permitting its use in the analysis of bimolecular chain termination in different reaction zones via polymerization processes until high conversions. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 4047–4053, 2007

**Key words:** kinetics; matrix; ESR

## INTRODUCTION

Of the three factors determining the kinetics of polymerization, that is, the initiation rate, chain propagation, and chain termination, the last factor is the most sensitive to changes in the phase state of the polymerization system. It is connected to the possibility of diffusion braking bimolecular chain termination. However, the role and sensitivity of diffusion braking bimolecular chain termination during different polymerization stages until high conversions remain unclear, and the experimental and theoretical estimations are often contradictory.<sup>1–5</sup>

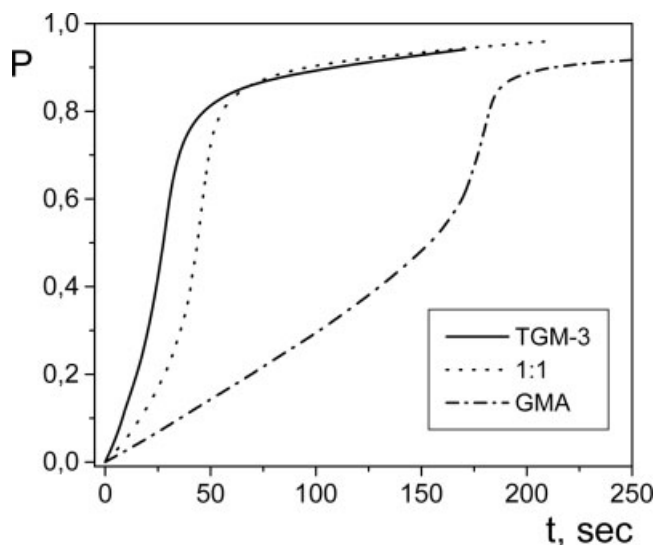
According to the conception of different reaction zones<sup>6–8</sup> resulting from the microheterogeneity conception of polymerization systems,<sup>9</sup> the polymerization of polyfunctional monomers in the early stages is concentrated in two reaction zones, the monomeric phase and the interfacial phase at the border (the liquid monomer and micrograins of the polymeric matrix), with the conversion practically limited by the monomer. The process in the interfacial phase provides the main contribution to the total polymerization kinetics at the autoacceleration stage. In this interfacial phase, because of the sharply de-

creasing translational and segmental mobility of the macroradicals, the chain termination is monomolecular, so chain propagation leads to macroradical trapping by the polymeric matrix or its freezing.<sup>3,5</sup>

Studying the postpolymerization kinetics of dimethacrylates,<sup>8,10–12</sup> that is, the polymerization process after the UV illumination is ended, is needed to determine that the monomolecular chain termination is ordered according to Kohlrausch's stretched exponential law and allows us to numerically evaluate the rate constant of monomolecular chain termination ( $k_t$ ) in the range of  $1 \times 10^{-5}$  to  $5 \times 10^{-5}$  m<sup>3</sup>/mol s for different dimethacrylates. The theoretical inference<sup>8,13</sup> of the stretched exponential law also permits us to explain the fractal dependence of  $k_t$  on the molecular weight of dimethacrylates or the molar volume concentration.

For the polymerization of monofunctional (meth)acrylates, because of the visible solubility of the polymer in the monomer with the formation of a monomer–polymer solution and of the monomer in the polymer with the formation of a solid polymer–monomer solution, the monomer–polymer phase, polymer–monomer phase, and the interfacial phase at the boundary of these phases are by the reaction zones. The theoretical description<sup>13,14</sup> of the polymerization kinetics satisfactory agrees with the experimental results. We assume that chain termination in the monomer–polymer phase and in the interfacial phase is bimolecular; the initial linear section of the kinetic

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**Figure 1** Kinetic curves of the photoinitiated polymerizations of TGM-3, GMA, and their equimolar mix. The photoinitiator concentration was 2 mol %, and the UV-illumination intensity was  $17 \text{ W/m}^2$ .

curve of the polymerization up to the autoacceleration stage shows the bimolecular chain termination constant decreasing at the expense of a reinforcing contribution of the diffusion braking as the polymer concentration in the polymeric matrix increases. In the interfacial phase, the diffusion braking of the bimolecular chain termination rate becomes dominant.

Studying the kinetics of the dark postpolymerization of a monofunctional monomer at starting conversions of  $P \geq 0.7$ , which corresponds to the rate maximum in the autoacceleration stage, leads to the conclusion that in the solid polymer–monomer phase, the chain termination is monomolecular and is ordered to the stretched exponential law. The values of the monomolecular chain termination rate constants are of the same order ( $10^{-5} \text{ m}^3/\text{mol s}$ ) as those of dimethacrylates.<sup>8,13</sup>

Monomolecular chain termination, as the self-burial of an active radical, under chain propagation shows the worth of polymerization kinetics in that case if the bimolecular chain termination rate for radical decay is considerably less than the monomolecular chain termination rate; this is possible with sharply decreasing transmission and segmental mobility of the macroradicals.

Because during the polymerization process in bulk limited conversion of the monomer is never achieved ( $P = 100\%$ ) and, as a rule, is equal to  $P = 85\text{--}90\%$ , the analysis of the rate of bimolecular decay of macroradicals that have accumulated in the polymeric matrix until the end of the process is interesting not only for the estimation of the diffusion mobility of macroradicals in polymeric matrices of different natures but also because it can provide important information needed

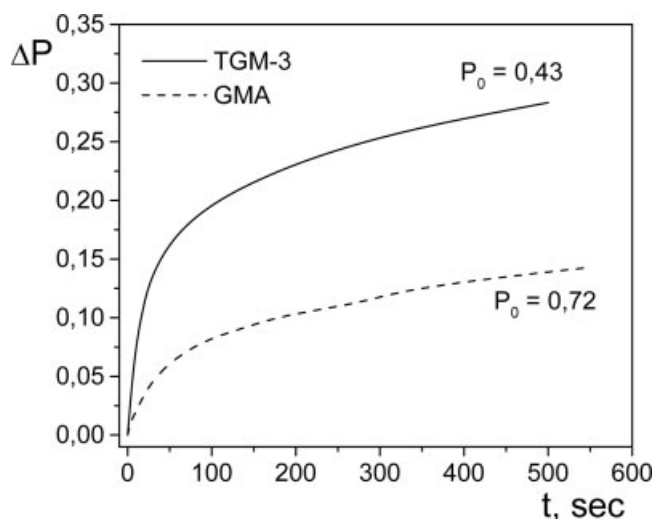
for understanding the chemical mechanism of the polymerization in different reaction zones.

The top-ranked method for studying the kinetics of macroradical bimolecular decay in polymeric matrices is electron spin resonance (ESR) spectroscopy. A number of works<sup>15–19</sup> in this direction have, however, an episodic character, both in the insufficiency of the experimental material and in the theoretical interpretation.

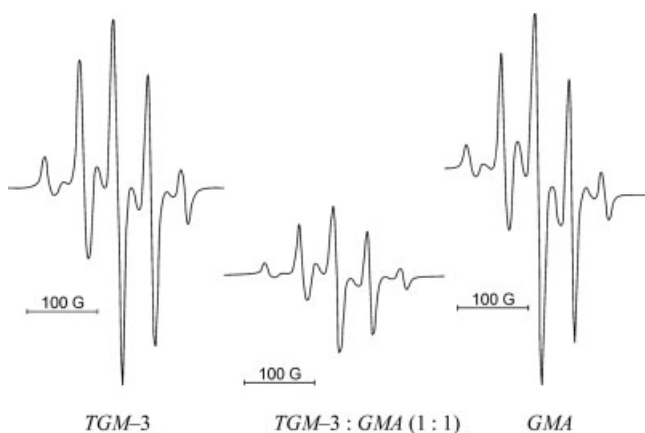
In this article, we report experimental data for the kinetics of the bimolecular decay of macroradicals in three polymer matrices based on a bifunctional dimethacrylate [triethylene glycol dimethacrylate (TGM-3), a monofunctional glycidyl methacrylate [2,3-epoxypropylmethacrylate (GMA)], and their equimolar mix (1 : 1). Investigations have been carried out in a wide range of temperatures ( $20\text{--}70^\circ\text{C}$ ) and have permitted us to estimate the activation parameters of the process. The kinetic curves of photoinitiated polymerizations of TGM-3, GMA, and 1 : 1 TGM-3/GMA until high conversions and the kinetic curves of the postpolymerization of these two monomers are presented in this article for comparison with the aforementioned data.

## RESULTS

Kinetic curves of the polymerization and postpolymerization were recorded with a laser interferometric plant determining the contraction of the thin layer (to 0.1 mm) of the photocomposition (the monomer plus the photoinitiator Irgacure 651, Merck-Schuchardt Co., Germany) under a medical glass cover versus time. The results of these investigations are presented as the dependence of the integral relative conversion (Fig. 1) or its increment in the dark period (Fig. 2)



**Figure 2** Kinetic curves of the postpolymerization of GMA and TGM-3 at  $20^\circ\text{C}$ . The digits on the curves correspond to the starting conversions of the dark period.



**Figure 3** ESR spectra of methacrylic radicals in different polymeric matrices.

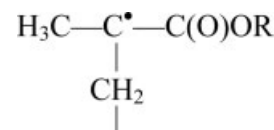
versus time. A comparison of the kinetic curves of the photoinitiated polymerizations of dimethacrylate TGM-3 and monomethacrylate GMA as well as 1 : 1 TGM-3/GMA (Fig. 1) neatly shows their formal difference. The main factor is the long initial stage of the polymerization with a practically constant rate before the autoacceleration stage of GMA. This is evidence of a gradual reduction of the constant of bimolecular chain termination at the expense of an increase in the contribution of the diffusion braking with changes in the monomer–polymer solution composition. Moreover, the kinetic curve of the polymerization of the 1 : 1 TGM-3/GMA system is more like the kinetic curve of the TGM-3 polymerization than the kinetic curve of the GMA polymerization.

On the contrary, the kinetic curves of the TGM-3 and GMA postpolymerization (see Fig. 2) are characterized by similar forms and the same characteristic time of approximately  $10^3$  s; this indicates the resemblance of the postpolymerization processes in the interfacial layer (for TGM-3) and the polymer–monomer phase (for GMA), which according to ref. 13 is determined by a general chemical mechanism of monomolecular chain termination.

ESR spectroscopy investigations have been carried out with an AE 4700 microwave spectrometer (Lviv, Ukraine) with the frequency of the electromagnetic field in the resonator at 9.49 MHz. The photocomposition (2 mol % photoinitiator 2,2-dimethoxy-2-phenylacetophenone) was put in a quartz test tube and UV-illuminated at a power of  $48 \text{ W/m}^2$  for 30 min. After this, the sample was cooled with water at  $10\text{--}12^\circ\text{C}$  and was put in a thermostat with a working temperature in the range of  $20\text{--}70^\circ\text{C}$ .

The concentration of the paramagnetic centers was determined via the area under the absorption curve of the ESR signal.<sup>20</sup> The calibration of the device was performed with a standard sample, namely, diphenyl picryl hydroxyl in benzene, with a concentration of paramagnetic centers of  $3.37 \text{ mol/m}^3$ .

Typical ESR spectra of paramagnetic centers in the systems of TGM-3, GMA, and their equimolar mix are presented in Figure 3. They are similar in form and correspond to the spectrum of the methacrylic radical:<sup>21</sup>



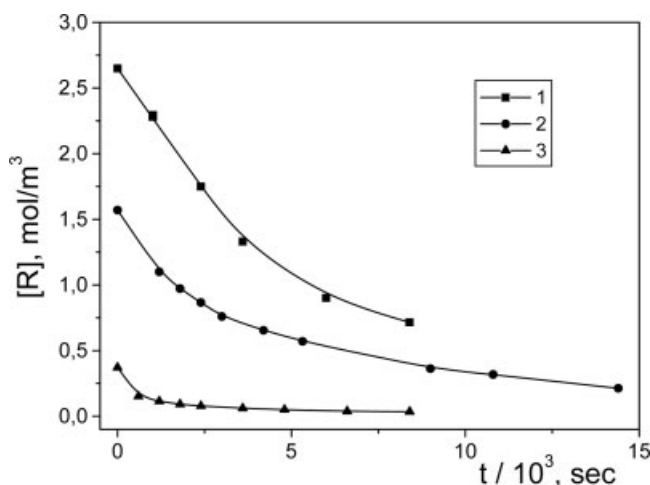
ESR spectra (e.g., the width of the peak at half of its height) are practically not reduced with time; this is evidence that the dispersity of the macroradicals with respect to their lengths and states in the polymeric matrix is not reflected in their spectral characteristics.

Kinetic data confirm this fact. The starting kinetic curves of radical decay presented in Figure 4 are typical for all temperatures, although their characteristic times at the temperature change from  $20$  to  $70^\circ\text{C}$  are reduced by about 4 orders. The presentation of the experimental data in the coordinates of the following second-order reaction (see Fig. 5) supports a bimolecular mechanism for their decay that is not complicated by the presence of a monomolecular mechanism (as noted in ref. 19) or by the dependence of  $k_t$  on time (as observed in ref. 18):

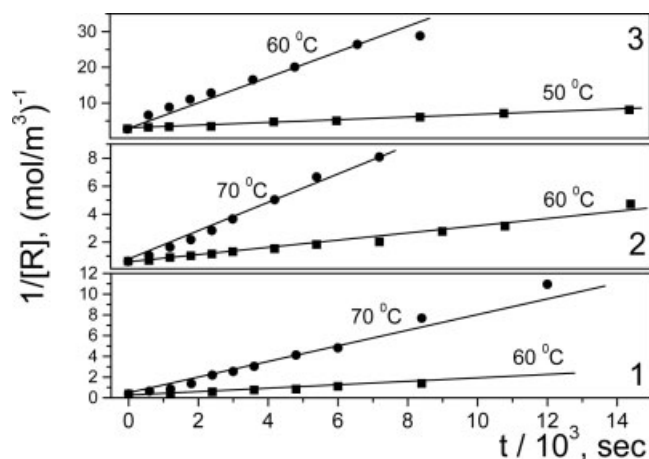
$$\frac{1}{[\text{R}]} = \frac{1}{[\text{R}]_0} + k_t t \quad (1)$$

where  $[\text{R}]_0$  and  $[\text{R}]$  are the initial radical concentration and the radical concentration at time  $t$ .

The results for  $k_t$ , calculated in accordance with eq. (1) for all investigated polymeric matrices at different temperatures, are presented in Table I. The numerical values of the parameters of the Arrhenius equation were determined on the basis of the temperature de-



**Figure 4** Starting kinetic curves of the radical decay at  $60^\circ\text{C}$  in the polymeric matrices: (1) TGM-3, (2) TGM-3/GMA (1 : 1), and (3) GMA.



**Figure 5** Presentation of the kinetic curves of radical decay in different polymeric matrices in the coordinates of the second-order equation: (1) TGM-3, (2) TGM-3/GMA (1 : 1), and (3) GMA.

pendence of  $k_t$  (see Fig. 6; this is presented in Table I):

$$k_t = k_0 \exp\left\{-\frac{E}{RT}\right\} \quad (2)$$

where  $k_0$  is a pre-exponential factor,  $E$  is the activation energy,  $R$  is the gas constant, and  $T$  is the temperature. Both the high values of  $E$  for the radical decay process and the high values of  $k_0$  for the Arrhenius equation, as well as the presence of a correlation between them, call particular attention to this. Such high values of  $E$  refute the possibility of controlling the rate of radical decay by the rate of chain propagation at the expense of the residual monomer in the polymeric matrix and confirm the diffusion control of the process.

## DISCUSSION

Despite a number of ESR spectroscopy investigations of the radical decay processes in different polymeric matrices, their theoretical discussion has been mainly

qualitative and often is limited by the determination of the formal kinetic characteristics. The experiments presented in this work, because of their systematic character, permit us to carry out a theoretical analysis of the bimolecular decay of radicals in polymeric matrices on a quantitative level. This analysis is based on the numerical estimation of  $k_t$  for the bimolecular decay of radicals and its activation parameters.

The relation between the rate constant of the bimolecular decay of radicals under diffusion conditions is described by the Smolukhovsky equation:

$$k_{ij} = 4\pi(r_i + r_j)(D_i + D_j)N_A \quad (3)$$

where  $N_A$  is Avogadro's number. This equation represents the rate of two particles meeting with radii  $r_i$  and  $r_j$  and diffusion coefficients  $D_i$  and  $D_j$  at their single concentrations.

Let us correct eq. (3), starting from the position that macroradical decay takes place only when the paramagnetic centers are at a distance sufficient for chemical interactions. This distance is the statistical length of the free-chain Kuhn segment or length  $a$  of the chain link; that is why we assume that  $r_i = r_j = a$ . As previously noted, the effects of the dispersion of the macroradicals on the sizes and values of the diffusion coefficient ( $D$ ) practically are not shown in the kinetic results, and this permits us to also assume  $D_i = D_j = D$ . Under these conditions, the Smolukhovsky equation is as follows for  $k_t$  for the bimolecular decay of radicals under diffusion conditions:

$$k_t = 16\pi a D N_A \quad (4)$$

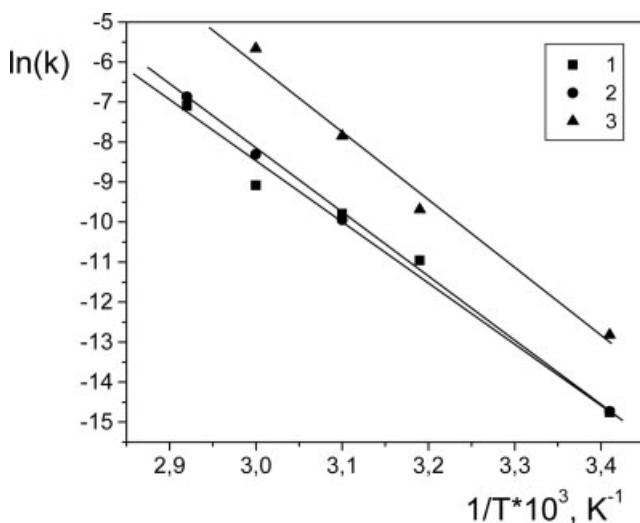
$D$  for the macroradical can be described with the Einstein equation:

$$D = r^2/2t^* \quad (5)$$

where  $t^*$  is the characteristic time of the macroradical transfer at a distance equal to its size  $r$  and  $r$  represents by itself the conformation radius.

**TABLE I**  
Experimental and Calculated Kinetic Parameters of Bimolecular Radical Decay

System	$T$ (K)	$k_t$ ( $\text{m}^3/\text{mol s}$ )	$E$ (kJ/mol)	$k_0$ ( $\text{m}^3/\text{mol s}$ )	$\Delta S^*/R$	$T_s$ (K)
TGM-3	293	$3.9 \times 10^{-7}$	122.2	$2.7 \times 10^{15}$	18.0	817
	313	$1.7 \times 10^{-5}$				
	323	$5.6 \times 10^{-5}$				
	333	$1.1 \times 10^{-4}$				
	343	$8.3 \times 10^{-4}$				
TGM-3/GMA	293	$4.0 \times 10^{-7}$	131.0	$8.4 \times 10^{16}$	21.4	735
	323	$4.8 \times 10^{-5}$				
	333	$2.5 \times 10^{-4}$				
	343	$1.0 \times 10^{-3}$				
GMA	293	$2.7 \times 10^{-6}$	142.3	$4.9 \times 10^{19}$	27.8	616
	313	$6.2 \times 10^{-5}$				
	323	$3.9 \times 10^{-4}$				
	333	$3.5 \times 10^{-3}$				



**Figure 6** Dependence of the constant rate of radical decay in the polymeric matrices on the temperatures in the coordinates of the Arrhenius equation: (1) TGM-3, (2) TGM-3/GMA (1 : 1), and (3) GMA.

In diluted solutions,  $r$  of a polymeric chain is described as a function of the average chain length ( $N$ ) by the Flory fractal expression<sup>22</sup> according to strict self-avoiding random-walk statistics:<sup>23</sup>

$$r = aN^{3/5} \quad (6)$$

We suppose that with some error this expression is applicable also to the determination of the characteristic volume of a macroradical in a polymeric matrix.

The forward movement of macroradicals, especially in a polymeric matrix, cannot be realized except in light of the consistency of the movements of its links (segmental movement), that is, according to the reptation mechanism of De Gennes.<sup>24</sup> Then,  $t^*$  of the macroradical transfer for distance  $r$  can be determined with the following considerations. Every link of the chain should move  $r/a$  steps at the macroradical transfer at distance  $r$ , and the general number of the steps will be equal to  $Nr/a$ . Introducing characteristic time  $\tau$  for every step, we obtain

$$t^* = Nr\tau/a \quad (7)$$

where  $\tau$  is the time of the elementary transition of a chain link from one state to another. For this reason, it can be described in accordance with the absolute reaction rate theory via the following expression:

$$\tau^{-1} = \frac{kT}{h} \exp\left\{\frac{\Delta S^*}{R}\right\} \exp\left\{-\frac{E}{RT}\right\} \quad (8)$$

where  $E$  and  $\Delta S^*$  are the activation energy and entropy of the step of the chain link.

By combining eqs. (4)–(8) we obtain

$$D = \frac{a^2}{2N^{2/5}} \frac{kT}{h} \exp\left\{\frac{\Delta S^*}{R}\right\} \exp\left\{-\frac{E}{RT}\right\}, \quad (9)$$

$$k_t = \frac{8\pi a^3 N_A}{N^{2/5}} \frac{kT}{h} \exp\left\{\frac{\Delta S^*}{R}\right\} \exp\left\{-\frac{E}{RT}\right\} \quad (10)$$

By comparing eq. (10) with the Arrhenius equation [eq. (2)], we have

$$k_0 = A \exp\left\{\frac{\Delta S^*}{R}\right\} \quad (11)$$

where

$$A = \frac{8\pi a^3 N_A}{N^{2/5}} \frac{kT}{h} \quad (12)$$

Knowing  $A$  and the experimental value of  $k_0$ , we can calculate  $\Delta S^*$ :  $\Delta S^*/R = \ln(k_0/A)$ . For the numerical estimation of  $A$  according to eq. (12), we assume the most probable values of  $N$  (1024; i.e.,  $N^{2/5} = 16$ ) and  $a$  ( $1.86 \times 10^{-10}$  m, which was taken for polystyrene) at 323 K. With these values of the parameters, we have obtained  $A = 4.1 \times 10^7$  m<sup>3</sup>/mol s. Next, the activation entropies are calculated as  $\Delta S^*/R$ , which is presented in Table I.

As we can see, between  $\Delta S^*$  and  $E$ , there is some connection. To discover the physical sense of this connection, let us take into account that according to eqs. (8) and (10),  $E$  of the chain link transition from one state to another one can be considered the formation energy of the free volume ( $a^3$ ) in the polymeric matrix; in this volume, segmental movement proceeds freely, that is, without additional energy expense. Therefore,  $E$  in the general case can be assumed to be proportional to the enthalpy of sublimation ( $\Delta H_S$ ):  $E \sim \Delta H_S$ . Let us assume that the free activation energy ( $\Delta G^*$ ) of the segmental movement is also proportional to the free sublimation energy ( $\Delta G_S$ ) of the polymer:  $\Delta G^* \sim \Delta G_S$ .

In agreement with the principle of free-energy linearity, we can assume

$$\Delta G^* = \alpha \Delta G_S \quad (13)$$

where  $\alpha$  is a transition coefficient ( $0 < \alpha \leq 1$ ).

Therefore, we also have

$$\Delta S^* = \alpha \Delta S_S, \quad E = \alpha \Delta H_S \quad (14)$$

where  $\Delta S_S$  is the entropy of sublimation.

Under the presented external pressure, there is a sublimation temperature ( $T_S$ ), at which the sublimation of the polymer is the equilibrium phase transition (i.e.,  $\Delta G_S = 0$  and  $\Delta S_S = \Delta H_S/T_S$ ). If the difference between  $T$  and  $T_S$  is not great and the derivative  $\partial \Delta S_S / \partial T$  is equal to  $\Delta C_{ps}$  (where  $\Delta C_{ps}$  is the change in

**TABLE II**  
**Calculated Values of the Characteristic Time of the Segmental Movement ( $\tau$ ), the Diffusion Coefficient of the Macroradicals in the Polymeric Matrices ( $D$ ), and the Pressure of the Saturated Vapor of the Polymer Above the Polymeric Matrices ( $P$ )**

$T$ (K)	TGM-3			TGM-3/GMA			GMA		
	$\tau$ (s)	$D$ (m <sup>2</sup> /s)	$P$ (Pa)	$\tau$ (s)	$D$ (m <sup>2</sup> /s)	$P$ (Pa)	$\tau$ (s)	$D$ (m <sup>2</sup> /s)	$P$ (Pa)
293	15.6	$6.5 \times 10^{-22}$	$1.1 \times 10^{-9}$	17.8	$5.5 \times 10^{-22}$	$0.9 \times 10^{-9}$	3.1	$3.1 \times 10^{-21}$	$5.2 \times 10^{-9}$
313	0.6	$1.6 \times 10^{-20}$	$2.6 \times 10^{-8}$	0.6	$1.7 \times 10^{-20}$	$2.8 \times 10^{-8}$	$7 \times 10^{-2}$	$1.3 \times 10^{-19}$	$2.2 \times 10^{-7}$
323	0.1	$6.9 \times 10^{-20}$	$1.1 \times 10^{-7}$	0.1	$8.2 \times 10^{-20}$	$1.3 \times 10^{-7}$	$1.3 \times 10^{-2}$	$6.9 \times 10^{-19}$	$1.2 \times 10^{-6}$
333	$3 \times 10^{-2}$	$2.7 \times 10^{-19}$	$4.4 \times 10^{-7}$	$2.5 \times 10^{-2}$	$3.5 \times 10^{-19}$	$5.7 \times 10^{-7}$	$2.5 \times 10^{-3}$	$3.4 \times 10^{-18}$	$5.8 \times 10^{-6}$
343	$9 \times 10^{-3}$	$9.7 \times 10^{-19}$	$1.6 \times 10^{-6}$	$6.3 \times 10^{-3}$	$1.4 \times 10^{-18}$	$2.3 \times 10^{-6}$	$5.6 \times 10^{-4}$	$1.5 \times 10^{-17}$	$2.5 \times 10^{-5}$

the polymer heat capacity at sublimation), then  $\Delta S_S$  at the transition from  $T_S$  to  $T$  can be neglected, and we can also assume that at the presented temperature, the next equality takes place:

$$\Delta S_S = \Delta H_S / T_S \quad (15)$$

At that time, taking into account eq. (14), we obtain

$$\Delta S^* = \frac{E}{T_S} \quad (16)$$

The values of  $T_S$  under the presented external pressure have been calculated with the estimations of  $\Delta S^*$  and  $E$  and are presented in Table I. The values of  $T_S$  and their dependence on the nature of the polymeric matrix correspond to the physical sense found in the determination of  $T_S$ . Although the  $E$  values of the bimolecular decay of radicals in polymeric matrices are arranged as  $E_{\text{TGM-3}} < E_{\text{TGM-3/GMA}} < E_{\text{GMA}}$ , the values of  $T_S$  obey the reverse order:  $T_{S,\text{TGM-3}} > T_{S,\text{TGM-3/GMA}} > T_{S,\text{GMA}}$ .  $T_{S,\text{TGM-3/GMA}}$  is about half of the sum of  $T_{S,\text{TGM-3}}$  and  $T_{S,\text{GMA}}$ .

$\tau$  can be calculated with the values of  $T_S$ :

$$\tau^{-1} = \frac{kT}{h} \exp \left\{ -\frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_S} \right) \right\} \quad (17)$$

$D$  for macroradicals in polymeric matrices can be calculated as follows:

$$D = D_0 \exp \left\{ -\frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_S} \right) \right\} \quad (18)$$

According to eq. (9), we find that

$$D_0 = \frac{a^2}{2N^{2/5}} \frac{kT}{h} \quad (19)$$

where  $D_0$  is the diffusion coefficient at the sublimating temperature ( $T_S$ ).

In agreement with the previously accepted values of  $N$  and  $A$ , we have obtained  $D_0 = 6 \times 10^{-8}$  m<sup>2</sup>/s. The calculations of  $\tau$  and  $D$ , presented in Table II, give us an idea of the ranges of these values and their changes with the temperature.

To emphasize once more the physical validity of the values of  $T_S$ , the pressure of the saturated vapor of the polymer ( $P_S$ ) above the polymeric matrix ( $P$ ) has been calculated in the experimental range of temperatures under the assumption of  $\alpha = 1$  (i.e.,  $\Delta H_S = E$  and  $P_S = 10^5$  Pa) according to the Claudius–Klapeyron equation:

$$\ln \frac{P}{P_S} = -\frac{\Delta H_S}{R} \left( \frac{1}{T} - \frac{1}{T_S} \right) \quad (20)$$

The results of the calculation are presented in Table II, which lists low values of  $P$ , and this does not disagree with the known properties of the polymers.

As we can see from Table II, the calculated values of  $\tau$ ,  $D$ , and  $P$  essentially depend on the nature of the polymeric matrix: in networked polymeric matrices TGM-3 and TGM-3/GMA, they practically coincide; however, in a linear polymeric matrix,  $\tau$  is greater, and  $D$  and  $P$  are less by 1 order.

## THEORETICAL PREDICTION

Unfortunately, we do not know literature estimations of  $D$  and  $r$  in polymeric matrices, but those estimations of  $D$  and  $r$  obtained by us (Table II) differ by some orders from known estimations of these parameters for liquid-diluted solutions of polymers.<sup>22</sup> Besides, as noted earlier, the Flory expression [eq. (6)] is definitely applicable only to polymeric chains in diluted solutions. That is why it is interesting to extrapolate this approach to the field of diluted solutions and to obtain estimations of  $D$  and  $\tau$  that can be compared with experimental data. This also permits us to estimate  $k_t$  for diluted solutions and the possible contribution of diffusion braking to the rate of bimolecular chain termination.

In agreement with the developed approach, for the estimation of  $D$  and  $\tau$  in diluted solutions with eqs. (17) and (18), it is necessary to accept  $E = \alpha \Delta H_k$ , where  $\Delta H_k$  is the evaporation enthalpy, and  $T_S$  must be changed to  $T_k$ , which is the boiling temperature of the solvent at a given external pressure. In this way, we obtain for diluted solutions the following:

$$\tau^{-1} = \frac{kT}{h} \exp\left\{-\frac{\alpha\Delta H_k}{R}\left(\frac{1}{T} - \frac{1}{T_k}\right)\right\} \quad (21)$$

$$D = D_0 \exp\left\{-\frac{\alpha\Delta H_k}{R}\left(\frac{1}{T} - \frac{1}{T_k}\right)\right\} \quad (22)$$

$D_0$  is determined by eq. (19) and is definitely applicable to polymeric chains in diluted solutions.

It follows from the same position that a constant rate of bimolecular chain termination under diffusion conditions in diluted solutions [as follows from eq. (10)] can be described by the following equation:

$$k_t = A \exp\left\{-\frac{\alpha\Delta H_k}{R}\left(\frac{1}{T} - \frac{1}{T_k}\right)\right\} \quad (23)$$

where  $A$  is determined by eq. (12).

Let us assume the same estimations,  $D_0 = 6 \times 10^{-8} \text{ m}^2/\text{s}$  and  $A = 4.1 \times 10^7 \text{ m}^3/\text{mol s}$ , that were obtained earlier. Toluene was used as a solvent, for which the enthalpy of boiling was 37.99 kJ/mol and the boiling temperature was 383.6 K. Because the transfer coefficient  $\alpha$  was unknown, we assumed it was equal to 1.

Calculations at room temperature (293 K) yielded the following values:  $\tau = 10^{-11} \text{ s}$ ,  $D = 10^{-9} \text{ m}^3/\text{s}$ , and  $k_t = 10^6 \text{ m}^3/\text{mol s}$ . Thus,  $\tau$  and  $D$  are in good agreement with the experimental data.

In the initial stages of the polymerization, that is, in diluted solutions, the rate constant of bimolecular chain termination has been estimated to be  $10^2$ – $10^4 \text{ m}^3/\text{mol s}$ . Comparing these data with the obtained value of  $k_t = 10^6 \text{ m}^3/\text{mol s}$ , we can affirm that in diluted solutions bimolecular chain termination is not limited by the diffusion conveyance of the macroradicals.

However, if we take into account the diapason change of  $k_t$  from  $10^6$  for diluted solutions to  $10^{-7} \text{ m}^3/\text{mol s}$  for polymeric matrices at room temperature, at high concentrations of the polymer in liquid monomer–polymer and solid polymer–monomer phases and also in interfacial layers on the boundary of their division, the most probable are the diffusion conditions of bimolecular chain termination. However, between the two mechanisms of chain termination (i.e., a bimolecular mechanism at the expense of radical decay and a monomolecular mechanism at the expense of chain propagation and freezing of the active center of the radical in the trap of the polymeric matrix), a quicker mechanism will be found. Let us compare the rates of these processes, using  $k_{t1}$  and  $k_{t2}$  as the rate constants of monomolecular and bimolecular chain termination. Then, the rates of these processes are equal to  $v_1 = k_{t1}[\text{M}][\text{R}]$  and  $v_2 = k_{t2}[\text{R}]^2$ , respectively, where  $[\text{M}]$  is the concentration of the monomer in the reaction zone. We can obtain the condition  $v_1 > v_2$  at  $k_{t1} > k_{t2}[\text{R}]/[\text{M}]$ . Taking into account that  $k_{t1}$  is  $10^{-5} \text{ m}^3/\text{mol s}$  according to the data in ref. 13,  $k_{t2}$  is  $10^{-7} \text{ m}^3/\text{mol s}$  according to the data in

Table I, and the ratio  $[\text{R}]/[\text{M}]$  is equal to  $10^{-2}$ , we have  $v_1 \gg v_2$ . That is why the postpolymerization process is determined by  $k_{t1}$  for bimolecular chain termination.

## CONCLUSIONS

The proposed theoretical approach to the description of the kinetics of bimolecular decay of macroradicals in polymeric matrices possesses a sufficient degree of generality to be used for the estimation of diffusion control of chain termination in different reaction zones, which are formed in the polymerization process until high conversions.

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