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KINETICS OF MACRORADICALS PROPAGATION AND DECAY IN POLYMERIC MATRIX OF 1,6-HEXANEDIOL DIACRYLATE

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Abstract. Dependence of acrylate macroradicals concentration in polymeric matrix of 1,6-hexanediol diacrylate on time within temperature range of 318–353 K has been investigated by means of ESR-spectroscopy. It has been established that experimental data do not linearize in coordinates of the equation of the second order reaction, that coordinates with bimolecular mechanism of macroradicals decay. It has been suggested, that the effect of decreasing the rate constant of bimolecular macroradicals decay in time is related with their propagation in chain propagation reaction. Kinetic equation obtained on this basis describes experimental data satisfactorily, that allowed to estimate quantitatively such parameters as the rate constants of chain propagation and termination in polymeric matrix, diffusion coefficient of macroradicals and characteristic time of segmental movement.

Key words: polymeric matrix, macroradical, chain propagation, chain termination, diffusion, segmental movement.

1. Introduction

Among three factors which determine kinetics of polymerization: initiation rate, chain propagation and chain termination rates, the latter is assumed to be the most sensitive to the changes of phase states of the polymerizing system. It is connected with the possibility of diffusion braking of bimolecular chain termination. However, the role and the significance of diffusion braking of bimolecular chain termination during different stages of polymerization and in different reaction zones are not cleared up, their experimental and theoretical estimations are often contradictory [1–5].

The analysis of macroradicals decay rate, piled up in polymeric matrix till the end of the photoinitiated polymerization process, can give the valuable information not only about the diffusion mobility of macroradicals, but also about connected with it structural properties of polymeric matrices of different nature, and, perhaps, about the peculiarities of the polymerization process in solid phase.

In this paper the experimental results on kinetics of macroradicals bimolecular decay in network polymeric matrix of 1,6-hexanediol diacrylate (GDDA) within the temperature range of 318–353 K are presented. The investigations were carried out by means of microwave spectrometer AE 4700 (Ukraine) at the electromagnetic field frequency in the resonator 9.49 *MHz*. The photocomposition (monomer GDDA + photoinitiator 2,2-dimethoxy-2-phenyl-acetophenone , 2 mol %) placed in a quartz test-tube was *UV*-illuminated at integral intensity of irradiation 48 W/m^2 during 30 min. Then the sample was cooled by water at 283–285 K and placed in a thermostat with the working temperature.

The typical *ESR*-spectrum of paramagnetic centers of acrylate macroradicals is presented in Fig. 1. The concentration of paramagnetic centers was determined by the area under the curve of *ESR*-signal absorption [6]. The calibration of the device was carried out using the standard sample (diphenylpicrylhydrazyl in benzene) with the concentration of paramagnetic centers of 3.37 mol/m^3.
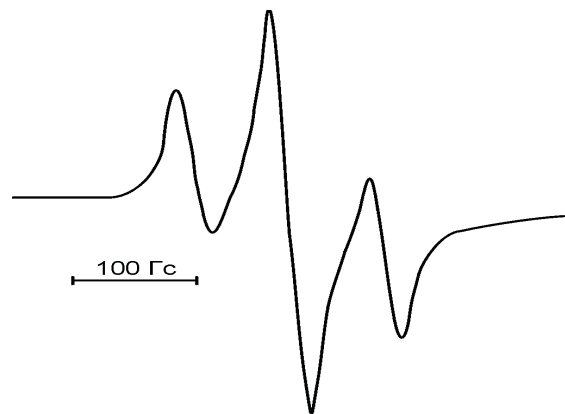

Fig. 1. ESR-spectrum of acrylate macroradicals in network polymeric matrix of 1,6-hexanediol diacrylate

2. Results and Discussion

As one can see from Fig. 2, the experimental data on the macroradicals concentration dependences $[R]$ vs time at all experimental temperatures do not linearize in coordinates of the equation of the second order reaction. The type of the obtained dependences indicates, that the effective rate constant of macroradicals bimolecular decay in polymeric matrix of 1,6-hexanediol diacrylate is the damped time function. It is commonly connected with the dispersion of macroradicals sizes and diffusion braking of the process at which the rate constant k_{tij} of the bimolecular encounting of i and j macroradicals is described by the Smolukhovsky equation

$$k_{tij} = 4\pi(r_i + r_j)(D_i + D_j)N_A, \qquad (1)$$

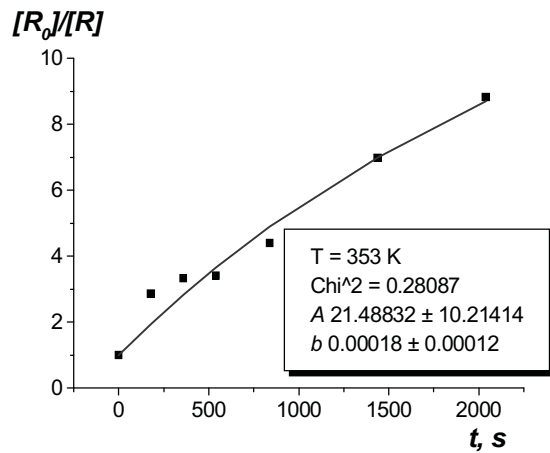where r_i and r_j are macroradicals sizes, D_i and D_j are their diffusion coefficients, N_A is Avogadro constant.

[R₀]/[R]

T = 318 K
Chi^2 = 0.00477
A 5.87049 ± 0.15313
b 0.00003 ± 0.00001

[R₀]/[R]

T = 323 K
Chi^2 = 0.02758
A 4.99335 ± 0.17763
b 0.000045 ± 0.00001

[R₀]/[R]

T = 333 K
Chi^2 = 0.32895
A 13.06552 ± 2.09113
b 0.00008 ± 0.00002

[R₀]/[R]

T = 343 K
Chi^2 = 0.39509
A 19.81017 ± 2.01021
b 0.00012 ± 0.00034

[R₀]/[R]

T = 353 K
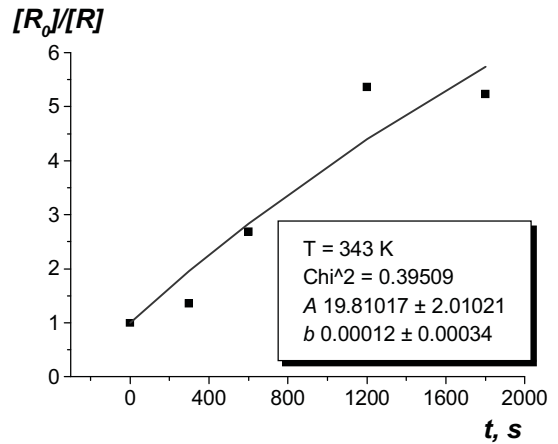Chi^2 = 0.28087
A 21.48832 ± 10.21414
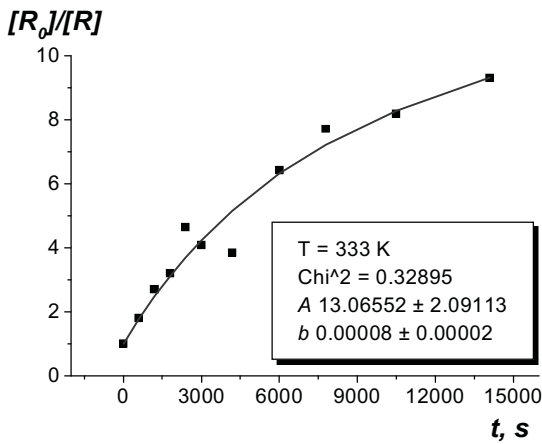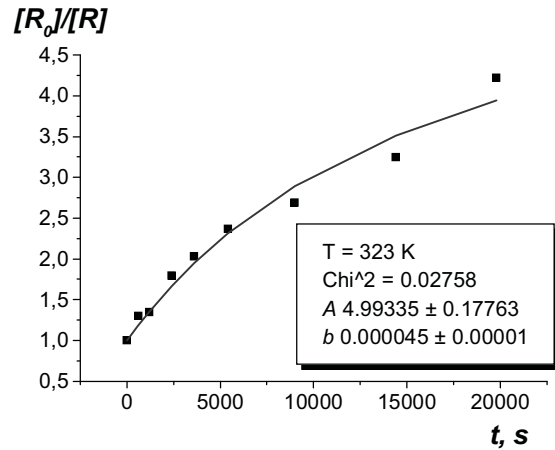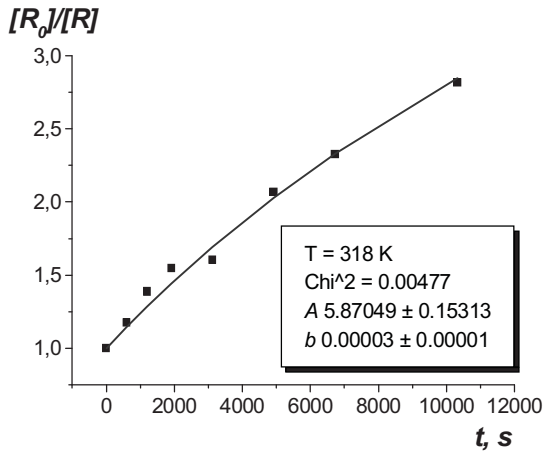b 0.00018 ± 0.00012

Fig. 2. Interpretation of experimental data (dots) of bimolecular macroradicals decay in polymeric matrix of 1,6-hexanediol diacrylate in coordinates of equation of the second order reaction and their description by means of kinetic equation (10) (solid lines)

Since according to (1), more mobile radicals decay more quickly, the effective rate constant k_t will diminish in time.

However, let us note the circumstances which allow to look at the fact of diminishing k_t in time from another point of view. First, the main features of *ESR*-spectra, for example, the peak width on the half of its height, do not change practically at all, consequently, the dispersion of macroradicals lengths and their states in polymeric matrix weakly affect the changes of their spectral characteristics in time. Secondly, dispersion of macroradicals is an inevitable phenomenon, however the effect of k_t decrease is not always observed. In particular, kinetics of macroradicals bimolecular decay in polymeric matrices of TGM-3 dimethacrylate (triethylene glycol dimethacrylate), GMA methacrylate (glycidyl methacrylate) and their copolymer TGM-3:GMA = 1:1, studied by us earlier [7], are well described within the limits of the second order reaction with the k_t value which is constant in time. Thirdly, it is known that the rate constant of chain propagation k_p of acrylates is considerably larger than that of methacrylates.

Above mentioned facts allow to assume, that decreasing the effective rate constant of bimolecular acrylate macroradicals decay in polymeric matrix of 1,6-hexanediol diacrylate may be caused by the process of macroradicals propagation till their collision and decay owing to the residual concentration of the monomer, which may be 10–15 % of the initial concentration at the photoinitiated polymerization in bulk. We will consider the experimental data just from this point of view.

Let us correct the Smolukhovsky equation (1), resulting from the fact that macroradicals decay will take place when paramagnetic centers appear on the distance, at which their chemical interaction will be possible. Such a distance equals to the length a of a chain monomer link; that is why we accept $r_i = r_j = a$. Ignoring the effect of macroradical dispersion, we have also $D_i = D_j = D$. Under such terms the equation (1) looks like

$$k_t = 16\pi a D N_A. \qquad (2)$$

Let us describe the rate of macroradicals decay and their propagation by means of equations

$$d[R]/dt = -k_t[R]^2, \qquad (3)$$
$$dN/dt = k_p[M]. \qquad (4)$$

Here $[R]$ and $[M]$ are molar-volumetric concentrations of macroradicals and monomer in polymeric matrix; N is the macroradical length, k_p is the rate constant of chain propagation.

According to self-avoiding random walks statistics the diffusion coefficient of macromolecules in concentrated solutions and melts is described by the formula [8]

$$D = a^2/2\tau(\rho/\rho_o)^{2.5} N^{2.4}, \qquad (5)$$

in which t is the characteristic time of segmental movement, responsible for the reptation mechanism of macromolecules diffusion, ρ/ρ_o is the ratio between the melt density and the density in the monomer link: $\rho_o = M_o/a^3 N_A$, where M_o is the molar mass of the monomer. We accept that the same ratio (5) will be true for the diffusion coefficient in the solid polymeric matrix with the characteristic time τ of the segmental movement correction.

Since $[R] \gg [M]$, at integration (4) we accept $[M] \cong$ const, that results in the expression

$$N = N_o(1 + bt), \qquad (6)$$

in which N_o is the average initial (at $t = 0$) length of macroradicals, and

$$b = k_p[M]/N_o. \qquad (7)$$

Substituting (6) into (5), and then into (2), we have

$$k_t = k_{to}/(1 + bt)^{2.4}, \qquad (8)$$

where

$$k_{to} = 8\pi a^3 N_A/\tau(\rho/\rho_o)^{2.5} N_o^{2.4}. \qquad (9)$$

Using (8), at integration (3) we obtain

$$[R_o]/[R] = 1 + A[1 - (1 + bt)^{1.4}], \qquad (10)$$

where

$$A = k_{to}[R_o]/1.4b. \qquad (11)$$

One can see from Fig. 2 that experimental data are described satisfactorily by the equation (10) at the parameters A and b selected by means of the optimization method. Their numerical values at different temperatures are presented in Table. Using them, the values of $k_{to} = 1.4bA/[R_o]$ were calculated, and they are given in Table too. Temperature dependences of k_{to} and b presented in coordinates of the Arrhenius equation (Fig. 3) allowed to find activation energies of the processes of bimolecular macroradicals decay $E_t = 76.3$ кJ/mol and chain propagation $E_p = 46.8$ кJ/mol.

For the estimation of numerical values of the rate constant k_p of macroradicals propagation (with the use of equation (7)), diffusion coefficient D, corresponding to the initial length N_o of macroradicals (by means of

Kinetic parameters of the processes of macroradicals propagation and decay in GDDA polymeric matrix
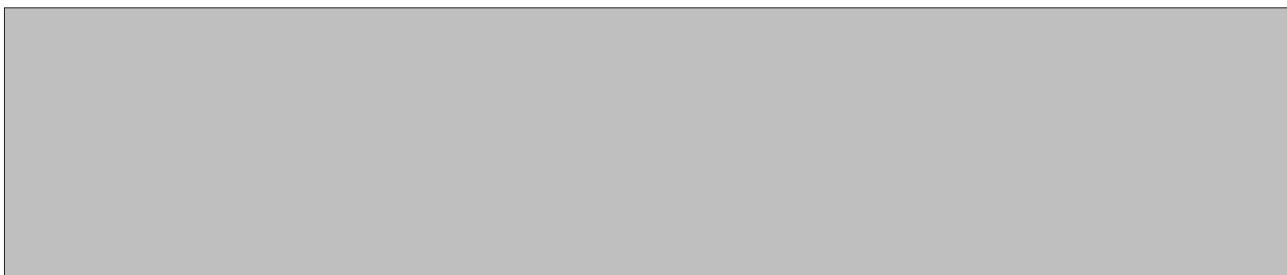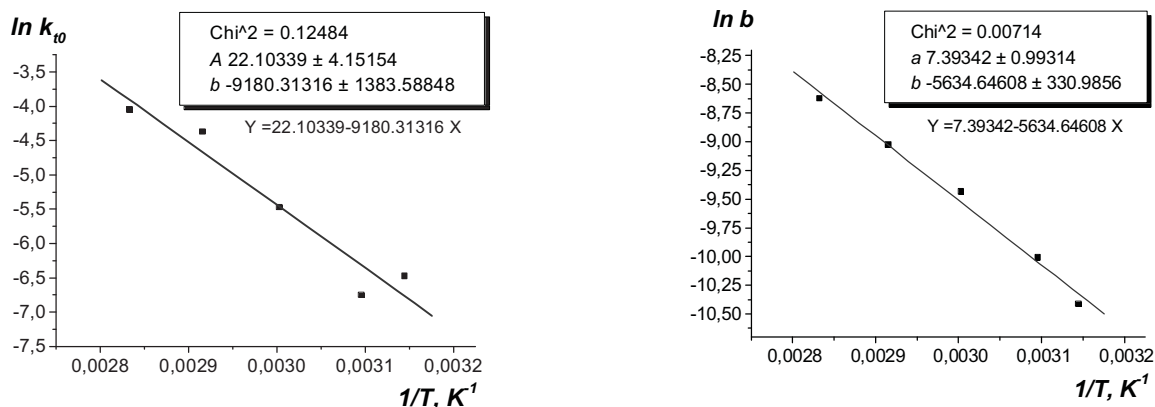
Fig. 3. Temperature dependence of parameters k_{to} and b in coordinates of the Arrhenius equation

equation (2) with the use of k_{to} values), and also the characteristic time τ of segmental movement (using equation (9)) it was accepted $a = 1.86 \cdot 10^{-10}$ m (as for styrene), $N_o = 10^3$, $[M] = 0.1[M]_o$, where $[M]_o$ is molar-volumetric monomer concentration in bulk: $[M]_o = c / M_o$; at $\rho = 1.024 \cdot 10^6$ g/m³ $M_o = 226$ g/mol. At these parameters a, ρ and M_o we have also $\rho /\rho_o = 1.76 \cdot 10^{-2}$. The results of calculations are shown in Table.

At the reptation mechanism of macromolecule diffusion transfer the characteristic time τ is the time of the elementary act transition of chain link from one state into another, that is why it may be described within the limits of absolute reaction rates theory by the expression

$$\tau^{-1} = \frac{kT}{h} \exp\{\Delta S^* / R\} \exp\{-E / RT\}, \qquad (12)$$

where $E = E_t = 76.3$ кJ/mol is activation energy determined experimentally, and ΔS^* is the activation enthropy of segmental movement. Having chosen the value of $\tau = 3.5 \cdot 10^{-5}$ s at T = 333 K we have calculated $\Delta S^*/ R = 8.3$ with the use of (12).

3. Conclusions

The calculated values of the diffusion coefficient of acrylate macromolecules in a polymeric matrix of GDDA, presented in the Table, are sufficiently exact, since calculating them while using experimental data it was necessary to set only one parameter a that is the length of the chain link. The calculation of k_p and τ values additionally required the numerical estimation of N_o – the average initial length of macroradicals. The true value of N_o can differ from the accepted value by the order. It means that the values of k_p are estimated with the deviation not smaller than one order, and the value of τ - with the deviation of two and more orders. Nevertheless, these estimations of k_p and τ are useful, since they show that in the polymeric matrix the rate constant of chain propagation is approximately by 2–3 orders smaller and the characteristic time of segmental movement is by 4–5 orders more than the corresponding values of k_p and τ in liquid phase. Mainly

it is connected with the abrupt increase of the activation energy of both chain propagation and segmental movement.

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КІНЕТИКА РОСТУ І ЗАГИБЕЛІ МАКРОРАДИКАЛІВ У ПОЛІМЕРНІЙ МАТРИЦІ 1,6-ГЕКСАНДІОЛДИАКРИЛАТУ

Анотація. *ЕПР-методом досліджена залежність концентрації акрилатних макрорадикалів у полімерній матриці 1,6-гександіолдиакрилату від часу в температурному інтервалі 318-353 К. Встановлено, що експериментальні дані не лінеаризуються в координатах рівняння реакції другого порядку, що відповідає бімолекулярному механізму загибелі макрорадикалів. Висловлено припущення, що ефект зниження константи швидкості бімолекулярної загибелі макрорадикалів у часі пов'язаний з їхнім ростом в реакції продовження ланцюга. Одержане на цій основі кінетичне рівняння задовільно описує експериментальні дані, що дозволило кількісно оцінити такі параметри, як константи швидкостей росту і обриву ланцюга в полімерній матриці, коефіцієнт дифузії макрорадикалів і характеристичний час сегментального руху.*

Ключові слова*: полімерна матриця, макрорадикал, ріст ланцюга, обрив ланцюга, дифузія, сегментальний рух*