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MECHANISM OF THE RADICAL LOSS IN γ -IRRADIATED POLYMETHYLMETHACRYLATE UNDER HYDROSTATIC PRESSURE

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Abstract: It has been shown that PMMA films which have been γ -irradiated up to 10Mrad, give a 9-component EPR spectrum and depending on the pressure P the rate constants of recombination of radicals decrease non-linearly. The activation volume V^* of radical loss is positive in the γ -irradiated PMMA and is 40-80 cm³/mol.

According to the data of the spin probe method it has been established that the reason for the non-linearity of pressure dependences of molecular mobility is a decrease with the compressibility pressure of β polymer. It is shown that these dependences become linear in the coordinates $1/V^*$ on p. At high pressures, the influence of γ -radiation on PMMA plays an important role in destructive processes.

Keywords: polymethylmethacrylate, hydrostatic pressure, polymerization, radiation, macroradical

1. Introduction

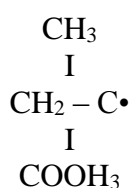
At present, new methods for polymerization of methylmethacrylate monomers (PMMA) are being developed, for example, by frontal polymerization [1]. The behavior of PMMA obtained under various influences can be significantly notable for the value of glass-transition temperature T_{gt} , for the kinetics of radical formation and other physico-mechanical characteristics. Within the exploitation of PMMA under hydrostatic conditions, it is often necessary to resort to additional stabilization of the polymer by introducing various chemical additives promoting the breakdown of free radicals [1, 2]. If we take into account that PMMA is widely used in electronic, atomic, cosmic technology and other fields of engineering and instrument-making [3], then the study of destruction and stabilization processes of PMMA under various types of influences (e^- - and γ -radiation) is of great importance.

The aim of this work is to study the formation and loss processes of radicals in γ -irradiated PMMA under hydrostatic pressure.

The use of high pressures (HP) while studying macroradical loss in γ -irradiated PMMA at different temperatures is an effective method of changing the molecular dynamics and free volume of the polymer [4-6].

2. Experimental part

The irradiated samples of PMMA gave 9-component EPR spectrum (fig.1), which is referred to as a terminal macroradical in the literature



EPR spectra were obtained at room temperature by using X-band EPR-spectrometer RADIOPAN. The spectrometer was equipped with a personal computer. The registration parameters of all the spectra were the same: microwave power – 2 mV, modulation amplitude – 4 G, scanning range – 1000 and 2000 G. While determining the concentrations of paramagnetic centers, manganese ions Mn^{2+} in MgO lattice and samples of stable diphenylpicrylhydrazine DPPH radical were used as a standard. The spectra analysis was carried out using the programs of Bruker Simphonia and Winep. The error in measuring the relative concentration of paramagnetic centers was 7-10%, but the absolute concentration – no less than 30-40%.

The samples were subjected to γ -irradiation up to dose 10Mrad on the installation RXM- γ from ^{60}Co source in the vacuum at 300K.

The obtained results were compared with the results of calculation and analysis of reactions of macroradical loss (from the EPR spectra) in other amorphous polymers obtained in [3-7].

3. Results and their discussion

The shape of the spectrum weakly depends on temperature and pressure (Fig. 1). The radical loss occurs above room temperatures at a noticeable rate. When the samples are annealed in the spectrum, lines from allylic (quartet), middle (doublet) and polyvinyl (singlet) macroradicals begin to appear.

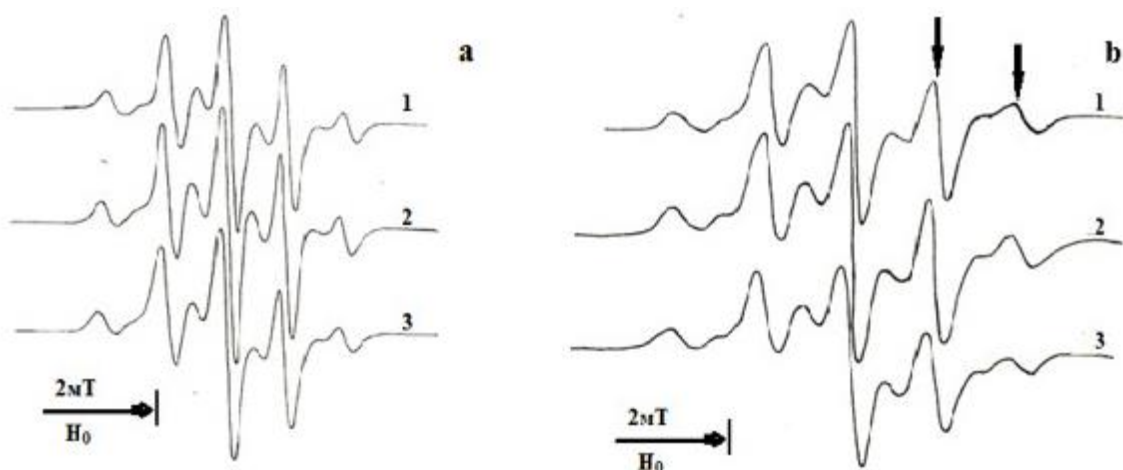


Fig.1. Change in EPR spectrum of the irradiated PMMA depending on the pressure P at 323K: 1a – 0,1 MPa, 2a – 100 MPa, 3a – 300 MPa, and annealing time at 353 K: 1b – 10 min., 2b – 40 min., 3b – 70 min.

We recorded the kinetics of the change in the intensity of extreme lines (indicated with arrows in fig.1) of the initial 9-component spectrum, since the lines of the secondary lines formed within the burning do not overlap with the extreme lines of the initial spectrum. The obtained kinetic data quite reliably relate to the loss process of end macroradicals, since they do not overlap with the lines of secondary radicals formed during annealing and the kinetic data quite reliably relate to the loss of end macroradicals. The radical loss is well described by the kinetic equation for the second-order reactions at conversion rates up to 80% and pressure up to 300MPa. These results indicate that the radical loss occurs by the recombination reaction. The reaction rate constants did not depend on which of the lines of the spectrum indicated by arrows in fig.1b were subjected to kinetic analysis.

The dependence of chemical reaction rate constant on the pressure is expressed by the following equation [6-8];

$$k=k^1\left(-\frac{PV^*}{RT}\right) \quad (1)$$

Here: $k^1=k_0\left(-\frac{E}{RT}\right)$ – the value of the reaction rate constant at $P \rightarrow 0$, V^* – activation volume, E – activation energy. According to the theory of absolute rates of the reaction V^* , there is a change in molal volume within the formation of the activated complex. The value of V^* is positive, if the volume of the activated complex exceeds the sum of the volumes of the reacting molecules; if the formation of the activated complex is accompanied by a decrease in volume, then V^* is negative. Thus, the analysis of the activation volume makes it possible to determine the value and sign of volume change within the formation of the activated complex.

Experiments on carrying out the chemical reactions at high pressures allow us to determine the activation parameters of the reactions V^* , E_p and E_v . For example, the activation energy of the reaction at constant volume

$$E_v = -R[\partial \ln k / \partial (1/T)]_v \quad (2)$$

and the activation energy of the reaction at constant pressure

$$E_p = -R[\partial \ln k / \partial (1/T)]_p \quad (3)$$

According to the known thermodynamic relations

$$E_p = \Delta H^* = \Delta U^* + P\Delta V^* \quad (4)$$

Where ΔH^* – the enthalpy of activation, ΔU^* – the internal activation energy
The expression for the activation energy at constant volume is given by:

$$\Delta E_v = \Delta H^* - P_T\Delta V^* = \Delta U^* - P_B\Delta V^* \quad (5)$$

Here: $P_T = T(\partial P / \partial T)_v$ is "thermal pressure", $P_B = P_T - P$ - "internal pressure".
From equations (4) and (5) it follows that

$$E_p = E_v + P_T\Delta V^* \quad (6)$$

Since $P_T = T(\partial P / \partial T)_v = \alpha K$, then

$$E_p = E_v + T\alpha K\Delta V^* \quad (7)$$

Where $\alpha = \frac{1}{V} \left(\frac{\partial P}{\partial T}\right)_p$ is the coefficient of thermal expansion.

The first term on the right side of equations (6) and (7) is the energy barrier of the process, and the second is the work of formation of the activation volume of the ΔV^* process.

Thus, the use of high pressure technique in kinetic studies makes it possible to determine the activation parameters, which is necessary for detailed analysis of the mechanism of the process, in this case of reaction.

Figure 2 shows the experimental data of the dependencies of recombination rate constants of radicals on pressure in γ -irradiated PMMA. From these data, two main features of pressure dependencies can be mentioned. First, the rate constants sharply decrease with pressure. Secondly,

the pressure dependences of the rate constants are not linear - they become weaker with the increase of pressure.

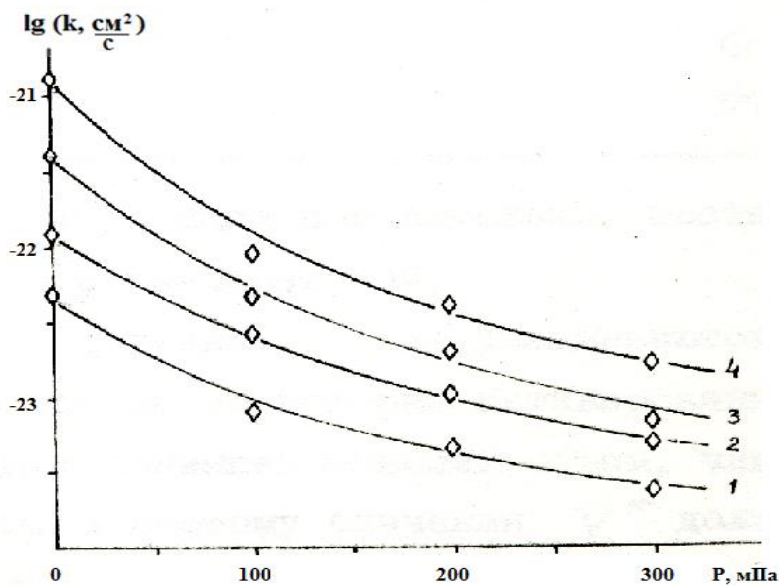


Fig. 2. The pressure dependences of the rate constants of macro-radical loss in γ -irradiated PMMA at temperatures of 323 (1), 333 (2), 343 (3), and 345K (4).

Let's consider both results in more detail. According to equation (1), from the angle of inclination of dependences $\lg k = f(P)$, we can determine the activation volume of V^* reaction. The values of V^* (for $P \rightarrow 0$) at different temperatures were shown in Table 1.

Table 1. Volume of activation of V^* reaction of radical loss in γ -irradiated PMMA ($P \rightarrow 0$)

T, K	$V^* \pm 5 \text{ cm}^3/\text{mol}$
323	45
333	52
343	65
353	77

The activation volume of the reaction is positive, constitutes 40-80 cm^3/mol and increases with temperature growth.

The obtained values of V^* are not appropriate to existing concepts, according to which activated complex in the bimolecular reaction occupies a smaller volume than the total volume of the original molecules, and therefore the values of V^* must be negative, i.e. the reaction must be accelerated by pressure. This corollary of the theory is confirmed by the results of numerous studies of the kinetics of bimolecular reactions in the liquid phase [4-6]. So, the activation volume is approximately 30 cm^3 / mol for the dimerization of cyclopentadiene in the liquid phase. The value of V^* for the reaction of hydrogen atom abstraction of diphenyl picrylhydrazyl (DPPH) radicals from thioalcohol is from 13 to 29 cm^3 / mol .

What do the high positive values of V^* associated with for the recombination of radicals in

PMMA and other polymers?

Unlike liquid media, the polymer matrix is characterized by significantly higher relaxation periods of molecular motion. Molecular mobility in polymers controls the kinetics of chemical reactions, limiting the frequency of encounter of active centers. The observed decrease in the rate of the recombination reaction is most likely associated with a decrease in the intensity of molecular motions with increasing hydrostatic pressure. Let us compare the value of the obtained activation volumes with activation volumes V^* for the main types of molecular motions. The value of V^* is in the range of 150-500 cm^3/mol for α -relaxation due to the motion of segments of macromolecules, and 20-40 cm^3/mol for β -relaxation (motion of smaller kinetic elements of the chain) [3,4]. From the data in Table 1, it follows that the values of V^* for the recombination of radicals are close to the activation volume V^* for the β -relaxation process. Thus, activation volumes, obtained in high-pressure experiments, characterize the minimum value of the fluctuation free volume, required for small-scale molecular motion.

Let us consider the reasons for the deviation from the linearity of the pressure dependences of the rate constant for reaction k (Fig. 2). It is known that the pressure dependences of the diffusion coefficients of low-molecular particles in polymers are described by the equation (6):

$$D = D' \exp\left(-\frac{B \cdot P}{K}\right) \quad (8)$$

Where the quantities D' and B do not depend on the pressure. The reason for the nonlinearity of the diffusion coefficients of low molecular particles in polymers was a change in the bulk modulus K with pressure. In addition, the dependence of the diffusion coefficients on the pressure is also linear in the coordinate $\lg D - P/K$.

In the same coordinates, the pressure dependence of the radical recombination rate constant is also linear (Fig. 3).

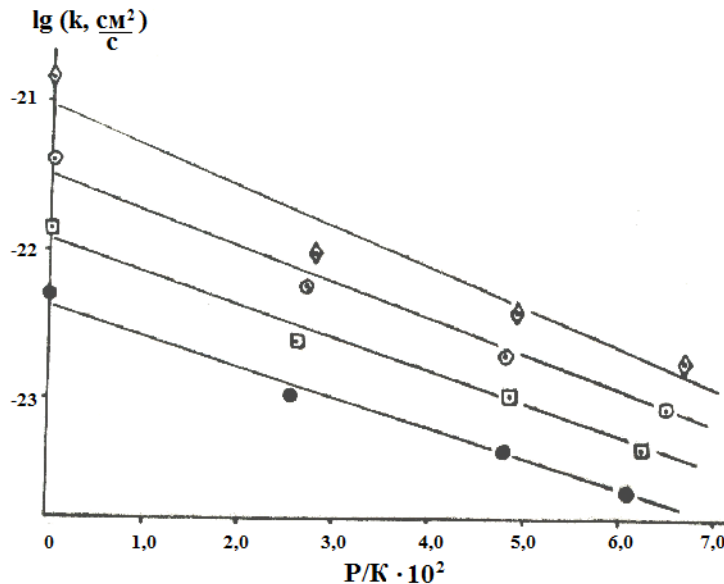


Fig. 3. Dependence of $\lg k$ on P/K for the reaction of macroradical loss in γ -irradiated PMMA.

The temperatures, corresponding to the curves, are indicated in the caption in Fig.2

Consequently, the changes with the pressure of the rate constant of reaction K subject to the same laws as the diffusion coefficients, and the expression for the rate constant is described by an equation similar to (6):

$$k=k'\exp\left(-\frac{B \cdot P}{K}\right) \quad (9)$$

Another confirmation of the relationship between the kinetics of reactions with molecular dynamics and the macroscopic characteristics of polymer is the nonlinearity of the pressure dependences of $\lg k=f(P)$, which indicates a decrease in the volume of activation with pressure (Fig. 3). The same deviations from linearity are also characteristic for pressure dependence of the frequencies of molecular motion. When analyzing data on spin probes, the reason for the nonlinearity of the pressure dependences of molecular mobility is a decrease in the compressibility of the polymer β (or an increase in the bulk modulus). The relationship between the volume of activation and the compressibility coefficient is manifested in an increase of β with temperature and a decrease with pressure (Fig. 3). The same dependences become linear in the $1/V^*$ coordinates from P . In addition, at high pressures, the influence of γ -radiation on PMMA, forming radicals, plays an important role in destructive processes.

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О МЕХАНИЗМЕ ГИБЕЛИ РАДИКАЛОВ В γ - ОБЛУЧЕННОМ ПОЛИМЕТИЛМЕТАКРИЛАТЕ В УСЛОВИЯХ ГИДРОСТАТИЧЕСКОГО ДАВЛЕНИЯ

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Резюме: Показано, что γ -облученные до доз 10Мрад пленки ПММА дают 9-и компонентный спектр

ЭПР и в зависимости от давления P константы скорости рекомбинации радикалов уменьшается не линейно. Объем активации V^* гибели радикалов положительны в γ -облученном ПММА и составляет 40-80 см³/моль.

Высказано мнение и некоторой степени по данным метода спиного зонда установлено, что причиной нелинейности барических зависимостей молекулярной подвижности является уменьшение с давлением сжимаемости β полимера. Показано, что эти же зависимости становятся линейными в координатах $1/V^*$ от p . При высоких давлениях воздействие γ -излучения на ПММА в деструкционных процессах играют важной роли.

Ключевые слова: полиметилметакрилат, гидростатическое давление, поляризация, макрорадикал.

γ -ŞÜALARLA ŞÜALANDIRILMIŞ POLİMETAKRİLATIN HİDROSTATİK TƏZYİQ ALTINDA RADİKALLARIN MƏHV OLUNMA MEXANİZMİ HAQQINDA

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Xülasə: Göstərilmişdir ki, PMMA təbəqəsini 10 Mrad dozaya qədər γ -şüaları ilə şüalandırdıqda EPR-spektrində 9-u komponent yaranır və P təzyiqinin təsirindən radikalların rekombinasiya sürətinin sabiti qeyri-xətti azalır. Şüalandırılmış PMMA-da aktivləşmə həcmi radikalların məhvi müsbətdir və 40-80 sm³/mol təşkil edir.

Müəyyən edilmişdir ki, molekulyar hərəkətliliyin təzyiqdən asılılığı polimerin β sıxılma təzyiqinin azalmasına səbəb olur. Göstərilmişdir ki, bu asılılıq $1/V^*$ - p kordinantında xəttidir. Yüksək təzyiqlərdə PMMA γ -şüalanma ilə təsir etdikdə burada destruksiya prosesi vacib rol oynayır.

Açaq sözl r: polimetakrilat, hidrostatik t zyiq, polyarla ma, üalanma, makroradikal.