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MULTIPULSE LUMINESCENCE DETECTION OF THE SPATIAL DISTRIBUTION OF REAGENTS AND THE DIFFUSION FLOW OF O_2 MOLECULES INTO POLYMER LAYER

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Abstract. *The problem of monitoring processes involving molecular oxygen in porous media still remains relevant due to the development of technologies based on the use of nanostructured systems. It is becoming important to study the characteristics of the reactions in nano cells with different morphologies and connectivity. The specifics of the localization and transport of reagents, which determine the yield of the product during transformations, provide valuable information for analyzing the process and optimizing its flow conditions. In this regard, it is necessary to improve the methodology for measuring photoinduced signals of oxygen-containing systems in non-stationary modes with time resolution to determine the current concentrations of reactant molecules. The kinetics of oxidative photoreactions in a colored polymer film was studied with multiple pulse activation of the system taking into account the layer-by-layer diffusion replenishment of the concentration of oxygen consumed in the reaction from the atmosphere. The process of chemical binding of oxygen molecules with immobilized anthracene molecules in an oxygen-permeable polymer film of polyvinyl butyral containing molecules of an organic dye (erythrosine) as a photosensitizer was recorded. A mathematical model is proposed that describes the kinetics of oxygen-dependent photoreactions in the film and the formation of luminescent response signals during its multi-pulse laser activation taking into account the diffusion replenishment of oxygen molecules in the intervals between the activating pulses. Based on a comparative analysis of the experimental and calculated luminescence signals, the nature of the non-uniform spatial distribution of the photosensitizer and the oxidized reagent in the polymer film is assessed.*

Keywords: Singlet oxygen, chemical traps, delayed fluorescence quenching, sensitized activation.

1. Introduction

Oxygen transport in tissues, its interaction with target biological molecules, the degree of tissue oxygenation, the role of active oxygen species in biological processes are the subject of close study in the field of biochemistry, physiology and medicine [1-8]. Oxygen permeability is an important characteristic in the design of biosimilar materials [2-3]. At the same time, the complexity of biological systems and their multi-level organization make many physical and chemical research methods directly inapplicable due to the possible disruption of the protein structure of tissues. One of the exceptions in terms of non-invasiveness are optical methods. Thus, in works [6-7] a luminescent microsensor introduced into tissues is considered, which allows determining local tissue saturation with oxygen, which is important in the treatment of ischemic diseases of the extremities.

In addition, the problem of monitoring processes involving molecular oxygen in porous nanostructured media remains relevant due to the development of a large number of different technologies based on the use of percolation systems with different morphology and connectivity of nanocells. It is becoming important to study the characteristics of the reactions in nanocells of such systems as reaction chambers. The specifics of the localization and transport of reagents, which determine the yield of the product during transformations, provide valuable information for analyzing the process and optimizing its flow conditions. In this regard, it is necessary to improve the methodology for measuring photoinduced signals of oxygen-containing systems in non-stationary modes with time resolution to determine the current concentrations of reactant molecules.

An alternative way to study the reaction mechanisms and diffusion processes of oxygen molecules is to use model systems where the polymer matrix is oxygen-permeable and is responsible only for its transport, and the binding of oxygen molecules is provided by an additional reagent, for example, as in this work – anthracene [9-10].

The excited singlet state of the oxygen molecule $^1\Delta_g(O_2)$ has the highest reactivity due to its specific orbital electron structure. The relatively high mobility of O_2 molecules in liquid and porous media, as well as the long lifetime of the state $^1\Delta_g(O_2)$, ensure effective transfer of electron excitation energy over fairly large, on a molecular scale, distances. Singlet oxygen is capable of destroying the native state of biological macromolecules, both through oxidative mechanisms - chemically binding to them, and by transferring excess energy to the macromolecule, which leads to disruption of its secondary and tertiary structure. Photogeneration of high concentrations of active oxygen in living cells leads to the death of the latter, which is the basis for photodynamic therapy of malignant tumors [11-18]. In studying the influence of singlet oxygen on biological systems, various experimental methods are used, based on measuring the characteristics of the intrinsic luminescence of O_2 in the infrared region of the spectrum, recording the influence of singlet oxygen on the signals of delayed fluorescence of dyes, and using chemical traps to immobilize excited O_2 molecules. In this paper, a variant of the combined use of the last two methods is proposed to determine the features of the spatial distribution of reagent molecules in an oxygen-permeable polymer layer and to record the diffusion flow of O_2 molecules from the air atmosphere into this layer. In order to adequately decipher the time-resolved signals recorded, a special mathematical model of the processes has been developed, on the basis of which their course in oxygen-permeable polymer films will be analyzed during pulsed laser activation of the system with different gating frequencies.

2. Experimental procedure

The experiments used an oxygen-permeable polymer film of polyvinyl butyral, into which molecules of an organic dye (erythrosine) and an aromatic hydrocarbon (anthracene) were embedded. Erythrosine acted as a photosensitizer, which upon activation ensured the transformation of oxygen molecules from the triplet to the singlet form. At the same time, it also acted as a luminescent probe, the signal of delayed fluorescence of which was used to estimate the concentration of oxygen in the system. This technique is original and was developed by the authors in a number of their previous works [19-23]. In this work, unlike in [21-22], anthracene molecules played the role of chemical traps for singlet oxygen molecules, effectively reducing its local concentration in the film. Anthracene molecules acted as chemical traps for singlet oxygen molecules, effectively reducing its local concentration in the film [19-23]. Experimental samples were prepared from alcohol solutions of polyvinyl butyral, anthracene and erythrosine by casting onto a glass substrate (Fig. 1), and after drying they were polymer films about 2 μm thick with a constant dye concentration (5 mM) and different anthracene concentrations (0, 0.5, 1.0, 2.5 and 5 mM).

24x24 mm cover glasses, a 3% ethanol solution of polyvinyl butyral and 0.1 mM alcoholic solutions of erythrosine and anthracene were used as substrates. Since the concentration and volume of the polymer solution were the same for all samples, the thickness of the films was also the same. For each concentration of anthracene, 4 film samples were produced, and their absorption and luminescence spectra were recorded to control the optical characteristics of the obtained samples. Thus, for samples from the same series, the differences in the spectra did not exceed 2-3%.

The films were then irradiated with a series of laser pulses with an energy of 1-2 mJ each and a duration of 10-12 ns at a wavelength of 532 nm (in the absorption band of erythrosine) with a delay between pulses of 0.1-0.2 s. Upon completion of each pumping pulse, a delayed fluorescence (DF) signal was recorded at a wavelength of 585 nm with a time resolution of 50 ns.

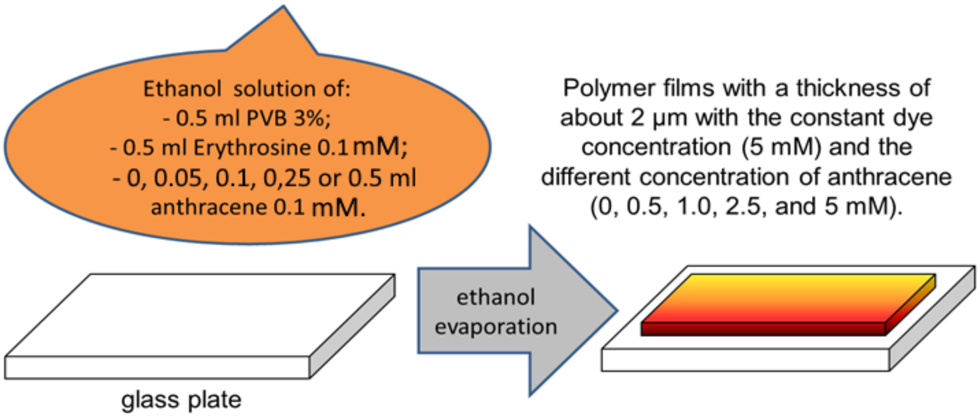


Fig.1. Sample preparation scheme.

To separate the DF signal from the "fast" fluorescence of the dye during laser pumping, the sensitivity of the PMT was modulated by applying an electric pulse of negative polarity to its first dynode ("locking" the PMT). The experimental design is shown in Fig. 2.

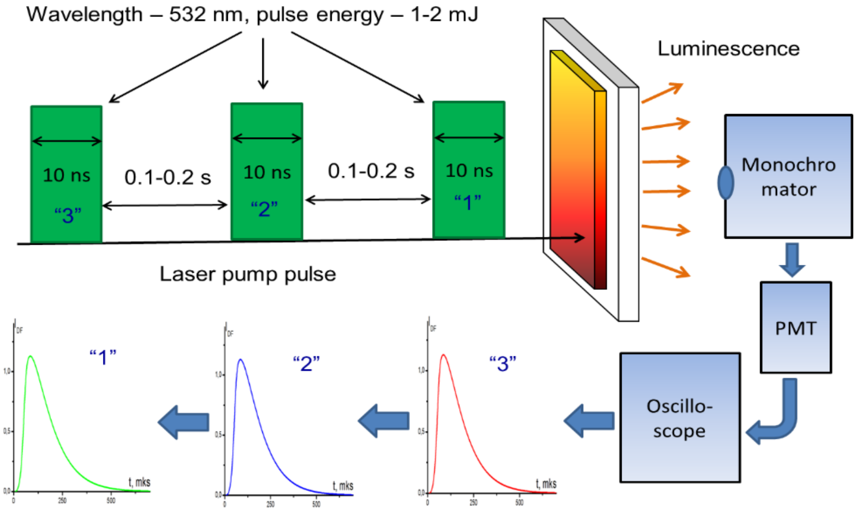


Fig.2. Experimental design.

3. Results and discussion of the experiment

In an oxygen-free environment, the decay time of the delayed fluorescence signal of erythrosine is about 800 μs, and in the presence of oxygen in the system under normal conditions for films without anthracene, the luminescence signal has a duration of about 50 μs, which is due to the active quenching of the triplet states of the dye by oxygen. In this case, the shape and duration of the signal do not change depending on the number of pump pulses, which indicates the absence of irreversible photochemical processes in the film. In samples containing anthracene molecules, the DF curve undergoes changes with each subsequent pump pulse: the signal amplitude decreases and its duration increases. From Fig. 3 it is clear that a smaller delay between pump pulses corresponds to a larger amplitude of the effect (about 20% for 0.1 s and 8-10% for 0.2 s).

The nature of the curves' change can be explained by a decrease in the oxygen concentration in the film when it is bound by anthracene and the subsequent comparatively slow replenishment of the O_2 molecule concentration due to their diffusion from the atmosphere. Accordingly, with a longer delay between pulses, the diffusion replenishment of oxygen in the polymer proceeds more effectively. This conclusion is also confirmed by the fact that after a pause of several seconds, the sample restores its initial parameters and, upon repeated exposure to a series of pulses, the effect of a decrease in the amplitude and an increase in the duration of the signal with an increase in the number of pumping pulses is also observed.

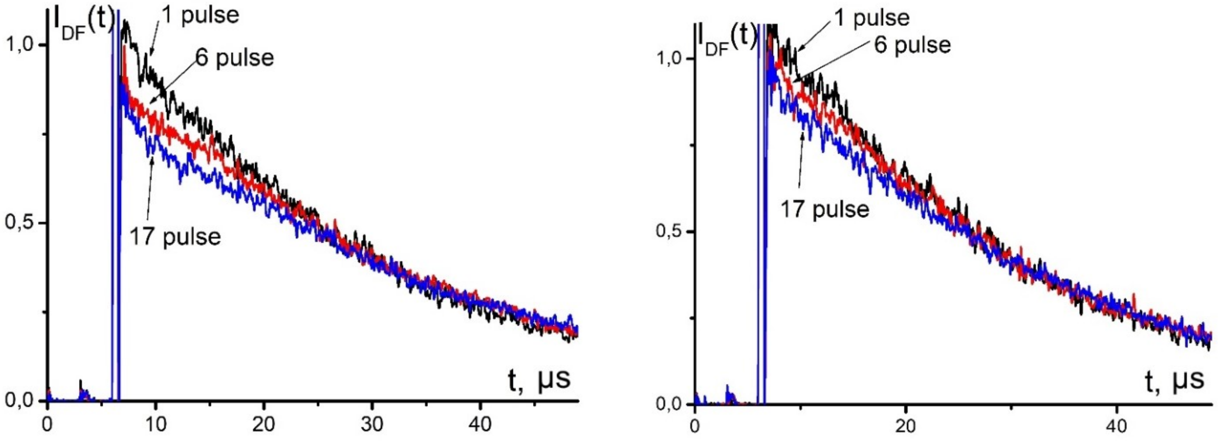


Fig.3. Kinetics of delayed fluorescence of erythrosine (C=5 mM) in a film of polyvinyl butyral with anthracene (C=0.5 mM) depending on the number of pumping pulses. Duration between pulses a) – 0.1 s, b) – 0.2 s.

Fig. 4 shows that with an increase in the anthracene concentration, the decrease in the amplitude of the delayed fluorescence signal of erythrosine is more pronounced (for a sample with the maximum anthracene concentration, this effect reaches values of 30-40%), and the duration of the glow increases, which also confirms the direct influence of anthracene molecules on the local concentration of free oxygen in the film. Fig. 5a shows the relative effect of anthracene in the system on the decrease in the maximum of delayed fluorescence signals when the sample is exposed to a series of pump pulses. It is evident from the graphs that with an increase in the anthracene concentration in the film, the magnitude of the effect increases, and the dependence $I_{DF}(N_{pulse})$ becomes nonlinear. The latter is due to the fact that with a significant decrease in the local concentration of oxygen in the film, the process of its replenishment due to diffusion from the external environment accelerates.

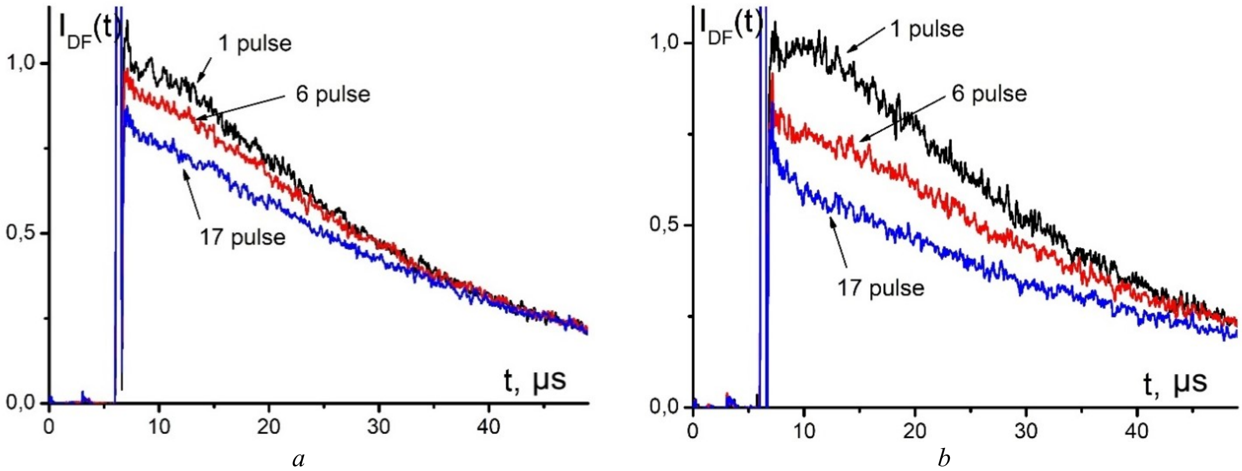
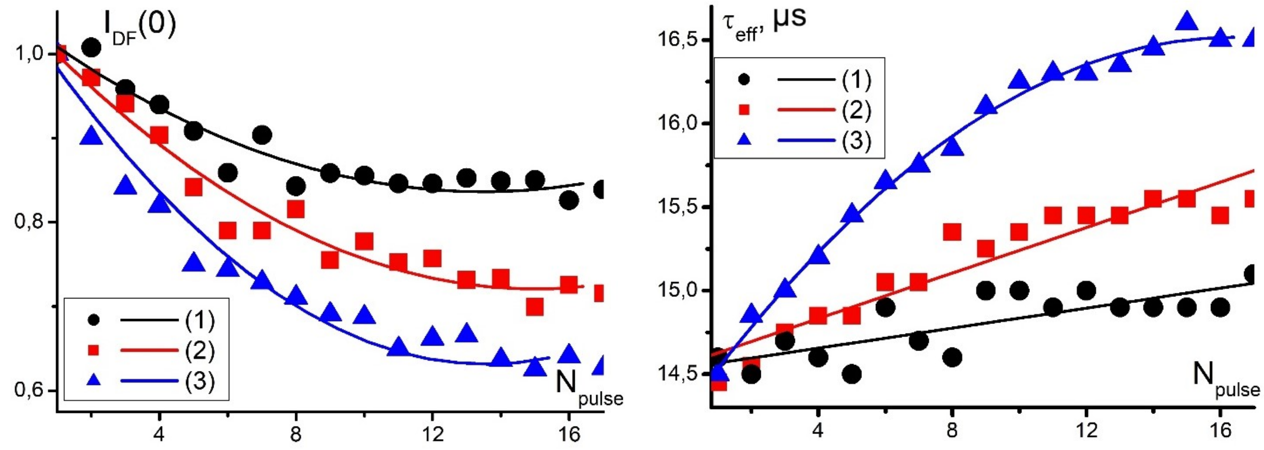


Fig.4. Kinetics of delayed fluorescence of erythrosine (C=5 mM) in a polyvinyl butyral film with anthracene with a concentration of a) – C=2.5 mM, b) – C=5.0 mM depending on the number of pump pulses (duration between pulses 0.1 s).

Since the kinetics of the delayed fluorescence signal in the presence of oxygen is non-exponential [10-12], the average duration of the delayed fluorescence signal, defined as

$$\tau_{eff} = \int t \cdot I_{DF}(t)dt \Big/ \int I_{DF}(t)dt .$$

It follows from Fig. 5b that with an increase in the total exposure, the duration of the glow signals increases, and in samples with a high concentration of anthracene, the dependence $\tau_{eff}(N_{pulse})$ becomes nonlinear. It is evident from Fig. 5b that the curve reaches a horizontal asymptote corresponding to the balance – mutual compensation of the processes of oxygen binding by anthracene in the polymer volume and its diffusion leakage from the outside.



a *b*

Fig.5. Intensity (a) and effective decay time (b) of the delayed fluorescence signal of erythrosine (C=5 mM) in a polyvinyl butyral film with different anthracene content (1) – 0.5, (2) – 2.5 and (3) – 5 mM depending on the number of pump pulses.

The obtained results allow us to estimate the proportion of oxygen molecules remaining in the system after the *k*-th pump pulse as

$$\frac{n_{Ox}(k)}{n_{Ox}(0)} \sim \frac{\tau_{eff}(0)}{\tau_{eff}(k)}.$$

Thus, in the film with the maximum anthracene content, about 3% of dissolved oxygen is bound under the action of the first pump pulse, and the maximum free oxygen deficit after 17 pulses is about 14%. These data allow us to determine the effective coefficient of oxygen diffusion into the film and the efficiency of oxygen binding by chemical traps. By analyzing the luminescence signals of samples placed in an oxygen-containing atmosphere and excited by a series of laser pulses, we can obtain information on the nature of the distribution of the oxidation product across the film thickness and estimate the value of the enrichment/depletion zone of the surface layers of the polymer film with the oxidized reagent.

4. Theoretical model

Considering the set of processes initiated by pulsed laser action in a polymer system containing immobile (bound to the matrix) photosensitizer molecules (Er - erythrosine) and oxygen molecule binding centers (chemical traps) (A - anthracene), they can be divided into separate groups according to characteristic times of occurrence. Thus, the duration of the process of interaction of sensitizer molecules with the optical pumping pulse and the formation of the resulting spatial distribution of T-centers $n_T(x)$ is tens of nanoseconds, the characteristic time of photoreactions involving O_2 molecules is tens of microseconds $t \sim \tau_T \sim \tau_\Delta$, and the diffusion influx of oxygen from the atmosphere unfolds on the scale of the T interval between adjacent laser pulses, i.e. on the order of tens to hundreds of milliseconds $t \sim T$.

Noting the short duration of the pump pulse compared to the characteristic time of photoreactions, we will omit a detailed analysis of the interaction of the light pulse with the dye molecules [16-17] here. Taking into account the high quantum yield of erythrosine in the triplet state and the incoherent saturation of absorption in the film, we will assume that the action of the pump pulse transfers all photosensitizer molecules from the ground energy state $S_0(Er)$ to a metastable one $T_1(Er)$.

In an oxygen-free environment, the decay of triplet states occurs according to an exponential law with its own lifetime τ_T. In an oxygen-permeable environment, the decisive role is played by the processes of quenching of excited triplet centers by oxygen molecules in the ground state

$$T_1(Er) + {}^3\Sigma_g^-(O_2) \rightarrow S_0(Er) + {}^1\Delta_g(O_2) \tag{1}$$

and subsequent cross-annihilation of excited oxygen molecules with triplet states of dye molecules, accompanied by the emission of a quantum of delayed fluorescence

$${}^1\Delta_g(O_2) + T_1(Er) \rightarrow {}^3\Sigma_g^-(O_2) + S_1(Er) \rightarrow S_0(Er) + h\nu_{DF}. \tag{2}$$

In the presence of anthracene molecules (chemical traps) in the system, singlet oxygen reacts with them in an oxidation reaction to form a stable compound – anthraquinone [19]

$$^{1}\Delta_g(O_2) + A \rightarrow AO_2, \tag{3}$$

which leads to a decrease in the overall concentration of oxygen molecules in the film.

First pulse. Upon completion of the action of the first initiating laser pulse, as a result of oxidation of molecules A by singlet oxygen $O_2(^{1}\Delta_g)$ on the time scale $t<<T$, a non-uniform distribution $n_{ox}(x)$ (*x*-profile) of oxygen molecules in the ground (unexcited) state will be formed.

Then, in the first-time interval T_0, up to the beginning of the action of the second pulse, as a result of the resulting gradient $n_{ox}(x)$, diffusion leakage of O_2 molecules from the atmosphere into the film begins. It occurs at times $\tau_T \sim \tau_\Delta \le t \le T_0$ and forms a new, resulting x-profile $n_{ox}(x,T)$ by the end of the time interval $T=T_0$.

To analyze the kinetics of large-scale time diffusion of oxygen inflow into a film of thickness *L*, a boundary value problem is set for the function $n(x,t)$ – the density of O_2 molecules in layer *x*

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2}, \quad 0<x<L. \quad 0<t<T_0 \tag{4}$$

$$\begin{aligned} &n(0,t) = n_{ox}^{(0)}, && 0<t<T_0 \\ &\left(\frac{\partial n}{\partial x}\right)_{x=L} = 0, && 0<t<T_0 \\ &n(x,0) = f_1(x) = n_{ox}^{(1)}(x), && 0<x<L \end{aligned} \tag{5}$$

The solution to the boundary value problem (4)-(5) upon completion of the first *j*=1 time stage $T=T_0\, j$ takes the form

$$n^{(1)}(x,T) = n_{ox}^{(0)} + \sum_{k=0}^{\infty}\left\{a_k^{(1)} - \frac{4}{\pi}\frac{n_{ox}^{(0)}}{(2k+1)}\right\}\exp\left[-\frac{(2k+1)^2\pi^2}{4L^2}D\cdot T\right]\sin\left[\frac{(2k+1)\pi}{2L}x\right], \tag{6}$$

where

$$a_k^{(j)} = \frac{2}{L}\int_0^L f_j(x')\sin\left[\frac{(2k+1)\pi}{2L}x'\right]dx'. \tag{7}$$

At the moment $t_2=T_0$ of the beginning of the second pulse, oxygen is distributed non-uniformly in the film in accordance with expression (6), which now serves as the initial distribution of O_2 molecules in the layer *x* at the second time stage *j=2*, $T_0<t<2T_0$. For the function $n^{(2)}(x,t)$ of the density of O_2 molecules at this stage, formula (6) is still valid, but with the replacement $a_k^{(1)} \rightarrow a_k^{(2)}$, where $a_k^{(2)}$ is determined by formula (7), but with $f_2(x) = n^{(1)}(x,T)$, given by formula (6), and $T=2T$. Then this procedure can be continued an arbitrary number of times - depending on the size of the series of laser pulses initiating the system. After the pulse with number *N*, we obtain the function of the density of molecules $n^N(x, NT<t<(N+1)T)$, which will determine the kinetics of photo-processes in the film, including oxidation, as well as the pulse shape and the luminescence intensity of sensitizers – phosphorescence and cross-annihilation delayed fluorescence initiated by singlet oxygen.

Note that under conditions of a uniform initial distribution of oxidizable molecules in the film and insignificant Bouguer attenuation of the light beam, the kinetics of photo-processes after the first laser pulse and after the pulses following it will differ significantly. This is due to the fact that after the first pulse, the molecules of singlet oxygen uniformly distributed over the entire thickness of the film are bound. And after the second and subsequent pulses, previously formed non-uniform profiles $n_{ox}(x,T)$ already manifest themselves in the thickness of the film. Non-uniform concentration profile $n_T(x,T+t)$ is either formed initially or, like the profile $n_\Delta(x,T+t)$, after the first laser pulse.

Within the kinetic approach, which does not take into account the features of the microdiffusion of oxygen molecules in the polymer, we introduce the bimolecular rates of the following reactions: K_Σ – triplet state quenching, K_{Δ} – cross-annihilation and K_A – anthracene oxidation, and the lifetimes of: τ_{Δ} – the excited singlet state of the oxygen molecule and τ_{Δ} – the triplet state of the photosensitizer molecule. We denote the average volume concentrations of triplet and trap centers by $n_T(t)$ and $n_A(t)$, and the concentrations of oxygen molecules in the ground and excited states by $n_{\Sigma}(t)$ and $n_{\Delta}(t)$, respectively.

Time j-stages after the first pulse. At each stage $j \cdot T_0 \le t \le (j+1)T_0$ after the end of the action of the next pulse, photo-processes unfold, the kinetics of which is determined by the following system of equations (8).

Assuming that the rate constants of quenching and cross-annihilation of T-states of the sensitizer are close in magnitude $K_{\Sigma} \approx K_{\Delta} = K$, we write the system of kinetic equations after the end of the action of the j-th laser pulse in the form *((j+1)T₀>t>jT₀)* [10-13]

$$\begin{cases} \dfrac{\partial n_T(x,t)}{\partial t} = -\left(\dfrac{1}{\tau_T} + K\left[n_{\Sigma}(x,t) + n_{\Delta}(x,t)\right]\right) n_T(x,t) \\ \dfrac{\partial n_{\Sigma}(x,t)}{\partial t} = -K\left[n_{\Sigma}(x,t) - n_{\Delta}(x,t)\right] n_T(x,t) + \dfrac{1}{\tau_{\Delta}} n_{\Delta}(x,t) \\ \dfrac{\partial n_{\Delta}(x,t)}{\partial t} = -\left(\dfrac{1}{\tau_{\Delta}} + K_A n_A(x,t) + K n_T(x,t)\right) n_{\Delta}(x,t) + K n_T(x,t) n_{\Sigma}(x,t) \\ \dfrac{\partial n_A(x,t)}{\partial t} = -K_A n_A(x,t) n_{\Delta}(x,t) \end{cases} \tag{8}$$

By integrating the last equation of the system, we obtain a quasi-stationary x-distribution of the oxidized A-reagent on the j-th time interval

$$n_A^{(j)}(x, j \cdot T_0 + 3\tau_T) = n_A^{(j)}(x, j \cdot T_0) \exp\left(-K_A \int_0^{3\tau_T} n_{\Delta}^{(j)}(x,t)dt \right) \tag{9}$$

The upper integration limit in (9) is chosen for convenience in the form $3\tau_T$, since upon its completion the population of the T-state of the sensitizer is practically empty, and the sensitization processes under consideration are completed. When implementing a specific computational procedure, the upper integration limit can tend to infinity. If the exponential expression is small enough $K_A \int_0^{3\tau_T} n_{\Delta}^{(j)}(x,t)dt << 1$, then the approximate equality holds $n_A^{(j)}(x, jT_0 + 3\tau_T) \approx n_A^{(j)}(x, jT_0)\left(1 - K_A \int_0^{3\tau_T} n_A^{(j)}(x,t)dt\right)$, or $n_{\Sigma}(x, T+t) + n_{\Delta}(x, T+t) \approx n_{ox}^{(j)}(x,T) - n_A^{(j)}(x) K_A \int_0^{\infty} n_{\Delta}^{(j)}(x,t)dt$.

In the time interval $j \cdot T_0 \le t \le j \cdot T_0 + 3\tau_T$, provided that the number of oxidized molecules $n_A^{(j)}(x) K_A \int_0^{\infty} n_{\Delta}^{(j)}(x,t)dt$ during the time $j \cdot T_0 \le t \le j \cdot T_0 + 3\tau_T$ is sufficiently small, it can be assumed that the total concentration of O$_2$ molecules does not depend on the «fast» time.

$$n_{\Sigma}(x, T+t) + n_{\Delta}(x, T+t) = n_{ox}^{(j)}(x,T) . \tag{10}$$

Then the solution to the system of equations

$$\begin{cases} \dfrac{\partial n_T(x,T+t)}{\partial t} = -\left(\dfrac{1}{\tau_T} + Kn_{ox}(x,T)\right) n_T(x,T+t) \\ \dfrac{\partial n_\Delta(x,T+t)}{\partial t} = -\left(\dfrac{1}{\tau_\Delta} + K_A n_A(x,T+t) + 2Kn_T(x,T+t)\right) n_\Delta(x,T+t) + \\ +Kn_T(x,T+t) n_{ox}(x,T) \end{cases} \tag{11}$$

at the j-th stage of laser activation, expressions for the concentrations of excited molecules in metastable states T- and $^1\Delta_g(\mathrm{O}_2)$ can be written in the following form [10]

$$n_T^{(j)}(x, j\cdot T+t) = n_0^{(j)}(T)\exp\left\{-\frac{t}{\tau_T} - Kn_{ox}(x, j\cdot T_0)\cdot t\right\}, \tag{12}$$

$$\begin{gathered} n_\Delta^{(j)}(jT_0+t \mid n_0^{(j)}, n_{ox}^{(j)}) = Kn_{ox}^{(j)}(x, j\cdot T_0)\times \\ \times\int_0^t n_T^{(j)}(x, jT_0+\tau \mid n_0^{(j)}, n_{ox}^{(j)})\exp\left[\frac{\tau-t}{\tau_\Delta} - 2K\int_0^t n_T^{(j)}(x, jT_0+\tau' \mid n_0^{(j)}, n_{ox}^{(j)})d\tau'\right]d\tau \end{gathered} \tag{13}$$

The intensities of the cross-annihilation delayed fluorescence $I_{DF}^{(N)}(t)$ and phosphorescence $I_{Ph}^{(N)}(t)$ signals of the sensitizer after a series of N laser pulses are determined by the following integrals over the thickness of the dye-containing film

$$I_{DF}^{(N)}(T+t) \sim K_\Delta \int_0^L n_T^{(N)}(x,T+t) n_\Delta^{(N)}(x,T+t)dx, \tag{14}$$

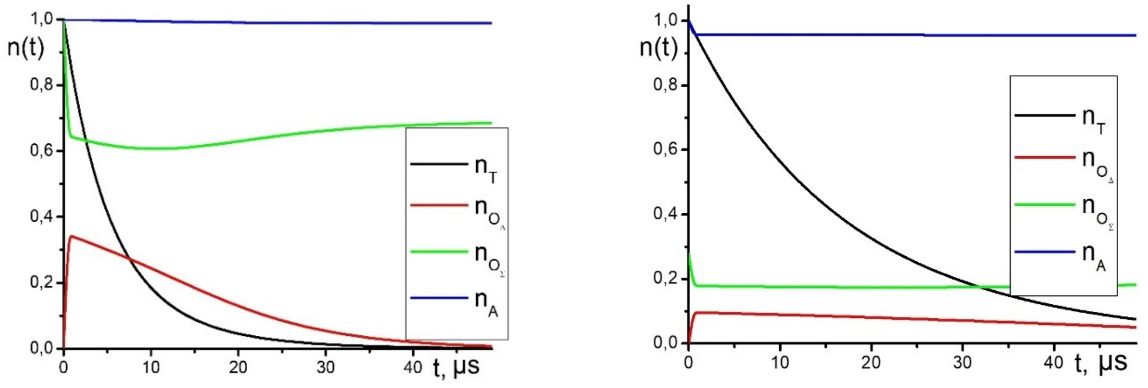
$$I_{Ph}^{(N)}(T+t) \sim \int_0^L n_T^{(N)}(x,T+t)dx. \tag{15}$$

Then, we can study the amplitude and shape of the pulse signals (14)-(15) from the number of laser pulses N in a series and compare the calculation results with the experiment. An important feature of the proposed model is that it considers the possible non-uniformity of the distribution of triplet and "trap" centers across the film thickness. Non-uniform distribution of reagents in the film can be obtained purposefully by layer-by-layer pouring of the film with solutions with the required ratio of anthracene and erythrosine. Then, in addition to the simplest case of uniform distribution, other characteristic variants of the x-distribution of reagents are of interest: a near-surface zone of the polymer layer enriched in trap or triplet centers and, accordingly, a case of a depleted near-surface zone. By analyzing the luminescence signals of samples placed in an oxygen-containing atmosphere and excited by a series of laser pulses, we can obtain information on the nature of the distribution of reagents across the film thickness and estimate the size of the enrichment/depletion zone.

Fig. 6 shows model calculations of the average volume concentrations of excited triplet centers, triplet and singlet oxygen and anthracene molecules by the first and 17-th pumping pulses. Fig. 6b shows a multiple decrease in oxygen concentrations compared to Fig. 6a, which leads to an increase in the effective lifetime of excited T-centers.

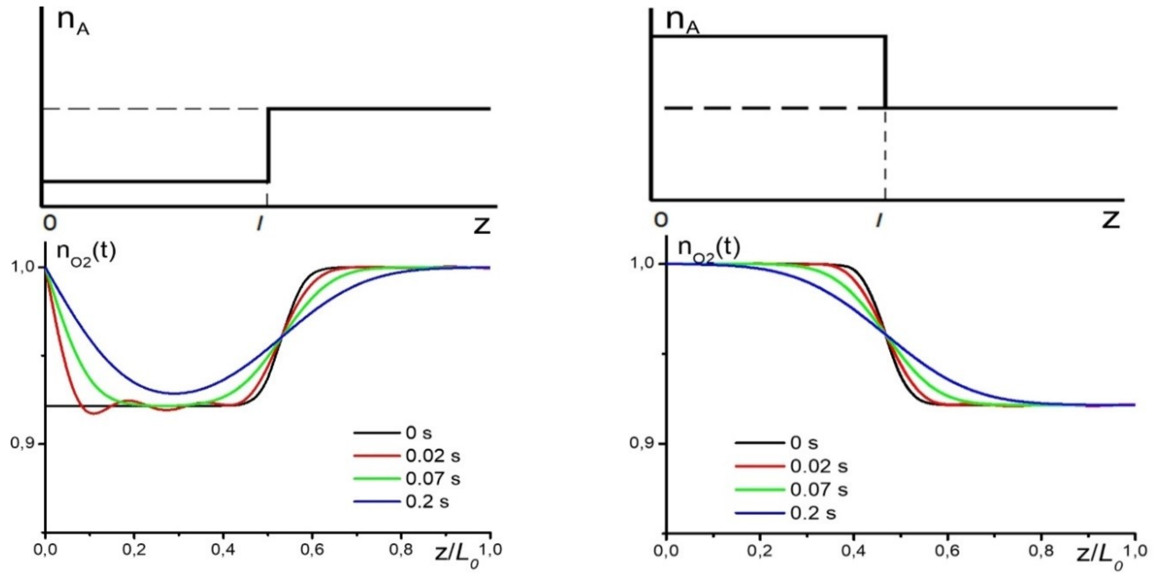
Calculations using the model show that the kinetics of photoreactions reacts weakly to the specific distribution of triplet and trap centers in the film. The diffusion of oxygen molecules in the film at the end of the next pumping pulse, on the contrary, reflects well the initial distribution of the reagents. Moreover, the enrichment of some characteristic region of the film with trapping centers or photosensitizer leads to similar results for the picture of the diffusion influx of oxygen (Fig. 7).

This is explained by the fact that it is in the enrichment region (no matter with anthracene or photosensitizer) that the oxygen binding reactions proceed most intensively and form a region with a deficiency of O_2, which is then filled by diffusion. The kinetics of luminescent signals, depending on the number of pumping pulses, also changes with a change in the nature of the distribution of reagents in the film (Fig. 8).



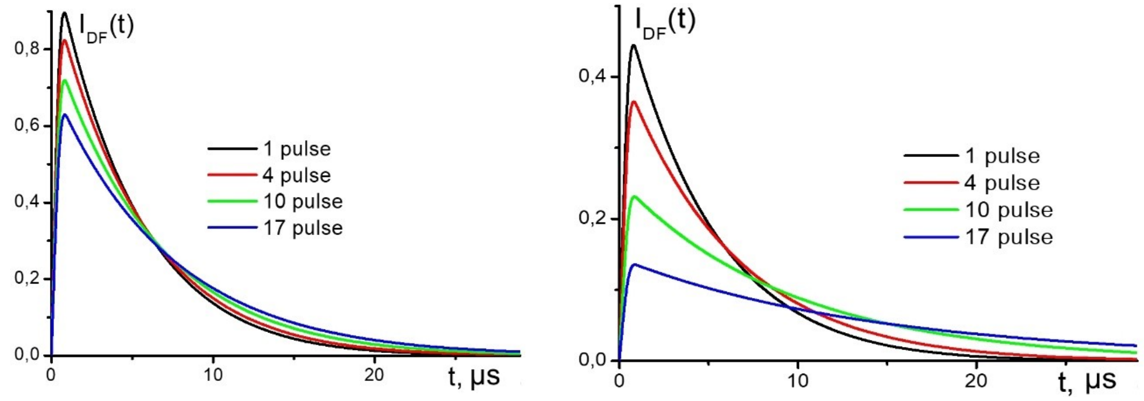
a *b*

Fig.6. Kinetics of reagent concentrations in the film upon activation by the first (a) and 17-th (b) pump pulses (uniform initial distribution of reagents).



a *b*

Fig.7. Approximation of the non-uniform distribution of sensitizer molecules by piecewise constant functions. Below: diffusion kinetics of oxygen molecules into the film after the first pump pulse is completed with enrichment of the surface layers of the film (a) and deep layers (b) by trapping centers.



a *b*

Fig.8. Calculated pulse signal of delayed fluorescence of dye in the film depending on the total number of pump pulses during enrichment of capture centers of the surface layers of the film (a) and deep layers (b).

Considering the maximum intensity (Fig. 9a) and the effective decay time (Fig. 9b) as the parameters of the change in the delayed fluorescence signals, it can be noted that with enrichment of the surface layer with T-centers or deep layers with A-centers (curves 2 and 5), the amplitude of the effect is minimal (the luminescence signal changes slightly with an increase in the number of pulses).

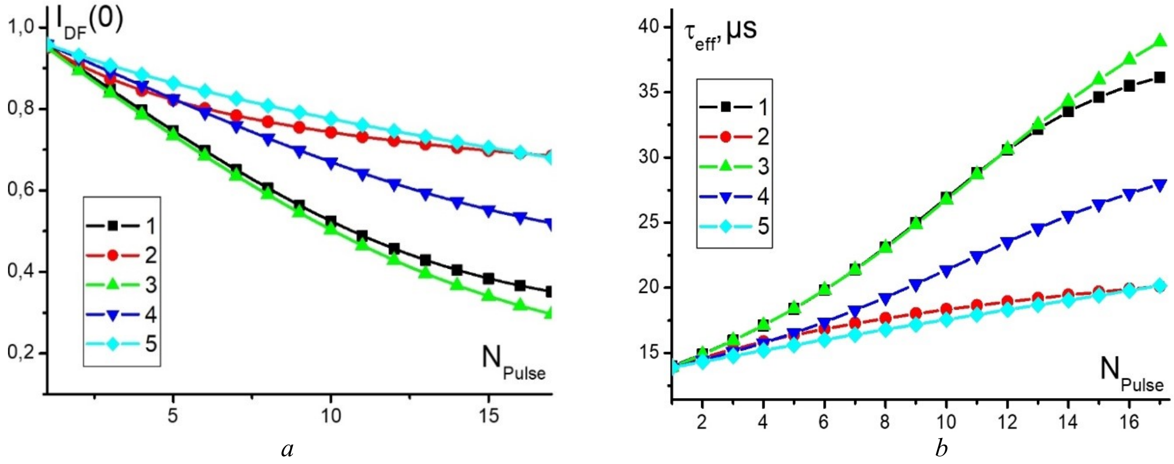


Fig.9. Intensity amplitude (a) and effective decay time (b) of the pulsed signal of delayed fluorescence of the dye in the film depending on the total number of pump pulses. (1) – uniform distribution of T- and A-centers; (2) – surface region of the film enriched in T-centers; (3) – deep region of the film enriched in T-centers; (4) – surface region of the film enriched in A-centers; (5) – deep region of the film enriched in A-centers.

The maximum change in the luminescence signals is observed with a deep distribution of T-centers. By varying the nature of the distribution of reagents over the film thickness as a model parameter, it is possible to obtain good agreement between the calculated and experimental dependences for the delayed fluorescence signals. In our case, this was achieved under the assumption of enrichment of the surface region of the film with capture centers by 35-45% of its thickness with a concentration ratio of the enriched and unenriched regions of 3:1.

4. Conclusion

The kinetics of oxidative photoreactions in a polymer film was studied with multiple pulse activation of the system considering the layer-by-layer diffusion replenishment of the concentration of oxygen consumed from the atmosphere.

To study the diffusion and reaction properties of O_2 molecules in an oxygen-permeable polyvinyl butyral film, it was proposed to use anthracene molecules, which act as "trap" centers for singlet oxygen $^1\Delta_g(O_2)$. Activation of O2 molecules in the $^1\Delta_g$-state was carried out in a sensitized manner from photoexcited erythrosine molecules accumulated in the long-lived triplet (T) state. At the same time, the photosensitizer also acted as a luminescent probe, the delayed fluorescence signal of which was used to estimate the oxygen concentration in the system at the moment of arrival of the next laser pulse.

It has been shown experimentally that an increase in the concentration of anthracene molecules in the polymer leads to a decrease in the maximum of the delayed fluorescence signal and an increase in the effective decay time of the luminescence signal with an increase in the number of pump pulses, which indicates a decrease in the local oxygen concentration in the film.

A mathematical model is proposed that describes the kinetics of oxygen-dependent photoreactions in the film and the formation of luminescent response signals during its multi-pulse laser activation, taking into account the diffusion replenishment of oxygen in the intervals between activating pulses. Based on a comparison of experimental luminescence signals and calculated curves, the nature of the placement of reagents across the film thickness is analyzed and the sizes of the enrichment/depletion region of the near-surface layers of the polymer film with the oxidizable reagent are estimated.

Conflict of interest statement
The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

CRediT author statement
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