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Features of fluorescence enhancement in fluorophore-saturated polymer foams

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The results of experimental studies of the fluorescence response of polylactide foams saturated with rhodamine 6G and composites used for their preparation in the region of transition from spontaneous fluorescence to stochastic laser generation are presented. A small increase in the threshold of stochastic laser generation in foamed composites compared to the expected one is interpreted as a result of the contribution of the waveguide mode of fluorescence propagation in the polymer matrix..

Keywords: polylactide foam, spontaneous fluorescence, stochastic laser generation, waveguide mode.

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High-porosity matrices based on bioresorbable polymers are currently used in regenerative medicine as a material platform for the fabrication of substrates (or, in technical language, scaffolds) that facilitate proliferation of regenerating tissue structures [1]. The technique of foaming of polymers plasticized in an atmosphere of supercritical carbon dioxide is one of the known approaches to their synthesis [2–4]. Foaming is performed by reducing the pressure in a reactor (with the initial polymer introduced into it) in accordance with a certain predefined procedure. The specifics of this procedure define the structural characteristics of the synthesized matrix (mean size and form factor of pores, the degree of their connectivity, the volume fraction of polymer in the matrix [5,6]).

Note that although considerable progress has been made in supercritical fluid (SCF) synthesis of such structures, the approaches to examination of their characteristics are based on traditional materials science techniques (scanning electron microscopy, X-ray microtomography, etc. [5,6]). The development of novel optical diagnostics methods for porous polymer structures is of interest both in practical terms and for fundamental research into the specifics of light propagation within such systems. One of the feasible approaches here is fluorescence diagnostics that utilizes the effect of enhancement of fluorescence of a medium with an increase in intensity of external laser pumping. The concurrent narrowing of the fluorescence spectrum is interpreted as a transition from spontaneous fluorescence to stochastic lasing in a medium (see, e.g., [7]).

In the present study, we report on the examination of the effect of transformation of fluorescence spectra in D, L-polylactide foams, which are saturated with rhodamine 6G (R6G), and in the initial materials for their synthesis that is induced by an increase in the laser pumping intensity in the vicinity of the absorption maximum of R6G ($\lambda_p = 532$ nm). In addition to their diagnostics applications, these studies are relevant to further progress in research into the specifics of radiation transfer within foam-like systems.

The used technique for SCF foaming of D, L-polylactide has been detailed earlier in [8]. The initial samples were a mixture of polylactide granules (PURASORB DL 04, product # 26680-10-4 Corbion Purac, $6.0 \cdot 10^{-5}$ kg), anatase nanoparticles (product No. 637254, Sigma Aldrich, United States, $1.0 \cdot 10^{-5}$ kg), and a solution of R6G in ethanol ($60\,\mu$l, $3.4 \cdot 10^{-3}$ M). Anatase nanoparticles were introduced as a component with a high efficiency of scattering in synthesized matrices that facilitates the transition from spontaneous fluorescence to stochastic lasing. The samples were kept in cylindrical containers 11 mm in diameter and 1 mm in height on glass substrates and were homogenized in preparation to the experiments by heating them to 333 K within 600 s and stirring gently. Homogenized samples were introduced into a high-pressure SCF reactor [8] and plasticized in an atmosphere of supercritical CO_2 (pressure: 8.2 ± 0.1 MPa, temperature: 318 ± 1 K) within 1800 s. The pressure in the reactor was then reduced to approximately 1 MPa at a rate of ~ 0.02 MPa/s; after that, the CO_2 pressure was reduced further to the atmospheric one at a rate ~ 0.0015 MPa/s (Fig. 1, a). The results of preliminary experiments revealed that foam expansion factor $Y = V_f/V_c$ achieved in this procedure is roughly equal to 5–6 (V_f is the synthesized foam volume and V_c is the homogenized composite volume). According to the optical microscopy data, the mean size of pores in foam was $600 \pm 300\,\mu$m.

The schematic diagram of experiments on laser pumping of polylactide foams and the initial composites is presented in Fig. 1, b. Pulse-periodic pumping was performed using a LOTIS TII 2134 laser ($\lambda_p = 532$ nm, beam diameter: 5.0 ± 0.2 mm, pulse duration: 10 ns, pulse repetition rate: 10 Hz, pulse energy: 0.3–100 mJ). Thus, pumping intensity

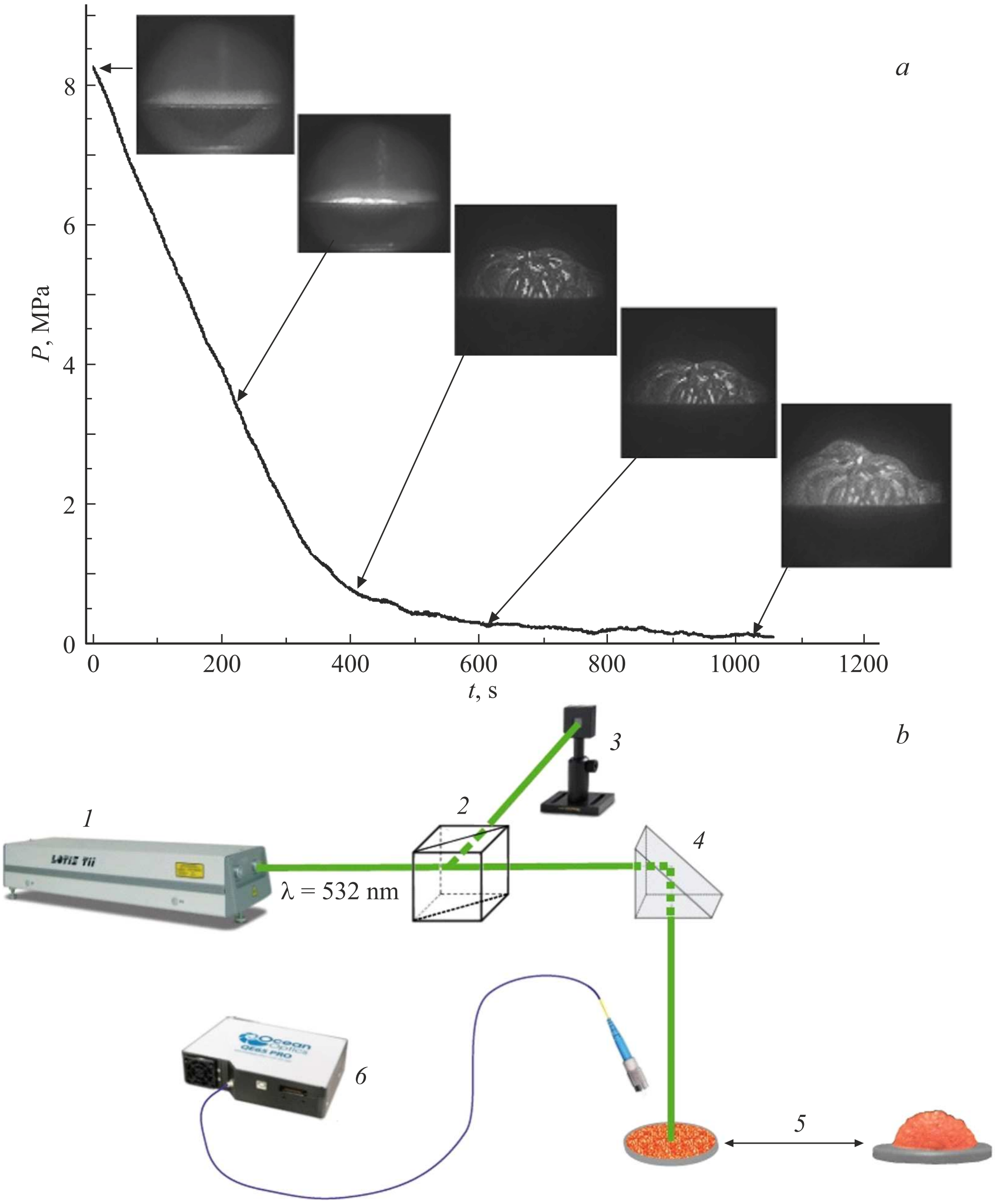

Figure 1. *a* — Procedure of pressure reduction in an SCF reactor in foaming of polylactide foams. The evolution of foam in the process of pressure reduction is shown in the insets. *b* — Diagram of the setup for examining the fluorescence response of samples of foam and the initial composites: *1* — laser, *2* — beam splitting cube, *3* — energy and power meter (Gentec Maestro), *4* — rotary prism, *5* — studied samples, *6* — spectrometer.

I_p on the sample surface within a pulse varied from $1.5 \cdot 10^5$ to $5.2 \cdot 10^7$ W/cm^2. Fluorescence spectra of samples were recorded with an Ocean Optics QE65000 spectrometer. As the pumping intensity increases, normalized fluorescence spectra $\tilde{I}_f(\lambda, I_p) = I_f(\lambda, I_p)/\int\limits_0^\infty I_f(\lambda, I_p)d\lambda$ of the polylactide/R6G/nanoparticles composite and the synthesized polylactide foam (Fig. 2, *a*) undergo a typical transition from the mode of spontaneous emission to stochastic lasing. This transition is attributable to the enhancement of the induced component of the fluorescence response of a pumped medium. The dependences of normalized response $\Psi = \int\limits_{\lambda_{\max}-\Delta\lambda/2}^{\lambda_{\max}+\Delta\lambda/2} I_f(\lambda)d\lambda/\int\limits_0^\infty I_f(\lambda)d\lambda$ of the studied systems in the stochastic lasing band of R6G on the pumping intensity ($\lambda_{\max} \approx 573.8$ nm and $\Delta\lambda \approx 4.4$ nm correspond to the maximum and the limit FWHM of the R6G fluorescence spectrum in the studied systems at high pumping intensities) are shown in the inset of Fig. 2, *a*. The growth of $\Psi(I_p)$ with a trend to saturation is reflective of the enhancement of the induced component of the fluorescence response

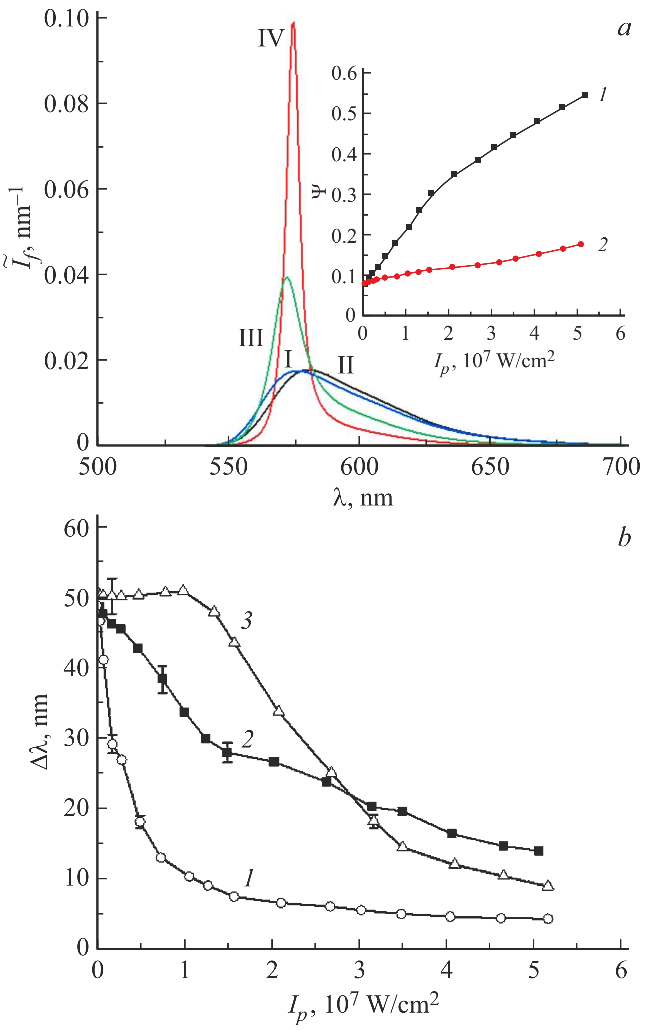

Figure 2. *a* — Normalized fluorescence spectra of the synthesized polylactide foam (I — $1.47 \cdot 10^5$ W/cm^2, III — $4.7 \cdot 10^7$ W/cm^2) and the initial polylactide/R6G/nanoparticles composite (II — $1.47 \cdot 10^5$ W/cm^2, IV — $2.7 \cdot 10^7$ W/cm^2). The dependences of parameter Ψ on the pumping intensity for the initial composite (*1*) and the synthesized foam (*2*) are shown in the inset. *b* — Typical dependences $\Delta\lambda(I_p)$ for homogenized composites (*1, 3*) and the synthesized foam (*2*). The indicated intervals correspond to a confidence level of 0.9 and were determined for groups of five samples.

in transition. Figure 2, *b* illustrates the phenomenon of narrowing of the fluorescence response spectra of the studied samples at higher I_p values. Dependence $\Delta\lambda(I_p)$ for sample No. 3 presented in this figure corresponds to the polylactide/R6G/nanoparticles composite with the amount of added dye reduced by a factor of 5. The dye concentration in this sample is approximately equal to the mean R6G concentration in the synthesized foam (sample No. 2). The pumping levels corresponding to the onset of a pronounced spectrum narrowing for sample No. 3 are significantly higher than those for samples Nos. 1 and 2. At the same time, sample No. 2 differs from samples Nos. 1 and 3 in that it features a more „diffuse" transition to the mode of stochastic lasing with higher values of $\Delta\lambda$ and a lack of saturation of the spectrum FWHM at high pumping intensities. The enhancement of the induced component of the fluorescence response of the studied samples may be characterized by rate $\Gamma = \Delta\lambda/\Delta I_p$ of reduction of the spectrum FWHM at low pumping intensities (the initial sections of dependences $\Delta\lambda(I_p)$). Specifically, Γ is the highest ($\sim 1.07 \cdot 10^{-5}$ nm/(W/cm^2)) for the initial composite (sample No. 1), assumes an intermediate value $\Gamma \approx 3.37 \cdot 10^{-6}$ nm/(W/cm^2) for the synthesized foam (sample No. 2), and is roughly equal to zero for the composite with the R6G concentration reduced five-fold (sample No. 3).

The observed behavior of the fluorescence response of the synthesized foam may be interpreted qualitatively by analyzing, on the one hand, the effect of enhancement of the induced fluorescence component in randomly inhomogeneous media and, on the other hand, the specifics of radiation propagation in foamed media. The enhancement effect is characterized by the ratio of mean fluorescence radiation propagation length $\langle s\rangle$ in the pumped medium to characteristic scale l_{st} of propagation of partial components of the fluorescence field between successive induced emission events: $K = \langle s\rangle/l_{st}$ [9]. It is to be expected that $\Psi \approx 0$ at $K \ll 1$ and $\Psi \to 1$ at $K \gg 1$. Characteristic scale l_{st} may be presented as $l_{st} \approx (\sigma_{st} n_0 \langle f\rangle)^{-1}$, where σ_{st} is the cross section of induced emission of fluorophore molecules, n_0 is their concentration in the pumped volume, and $\langle f\rangle$ is the relative population of the excited state of fluorophore molecules averaged over the pumped medium volume. Thus, the spectrum narrowing may be associated both with an increase in $\langle s\rangle$ and an l_{st} reduction. When the pumping intensity increases, l_{st} decreases due to the growth of $\langle f\rangle$. It is evident that the limit value of l_{st} cannot be lower than $l_{st} \approx (\sigma_{st} n_0)^{-1}$; in actual pumped systems, it turns out to be higher than the indicated value due to the restriction imposed on the maximum population of the excited state of fluorophore molecules ($\langle f\rangle_{\max} < 1$).

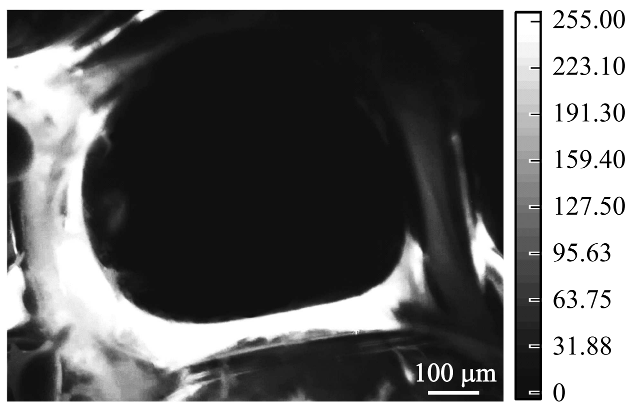

Figure 3. Grayscale (0–255) visualization of the fluorescence response ($540 \leqslant \lambda \leqslant 800$ nm) of a region of the synthesized foam surface. The pumping wavelength is 532 nm.

The photon channeling effect [10], which largely confines the propagation of both pumping and fluorescence radiation to pore walls and the regions of their intersection (Plateau–Gibbs channels), has already been noted as a distinctive feature of radiation propagation in foamed media. On the one hand, owing to channeling, the mean lifetime of fluorescence photons in the pumped medium increases relative to the one in the initial composites (and $\langle s \rangle$ also increases accordingly). On the other hand, the channeling of pumping radiation presumably contributes to an increase in the pumped medium volume, a reduction in the mean pumping field energy density in the medium, and, consequently, a reduction in $\langle f \rangle$ at high pumping intensities (relative to the corresponding values in the initial composites). The values of $\langle s \rangle$ and l_{st} increase simultaneously in the process of transformation of the initial composite material into a foamed structure and act as competing factors. In our view, this competition is the actual driver of the observed features (Fig. 2, *b*) of $\Delta\lambda(I_p)$ behavior for sample No. 2 (a relatively high value of Γ coupled with a „diffuse" transition from purely spontaneous fluorescence to fluorescence with a significant induced component). A detailed qualitative examination of this model is beyond the scope of this paper and will be performed in future studies. Figure 3 illustrates the manifestation of fluorescence channeling in the synthesized foam (or, in other words, the waveguide effect). The region of contact of three neighboring pores (Plateau–Gibbs channel) glows brightly due to the „bleeding" of a fraction of partial fluorescence field components with an unfulfilled condition of total internal reflection at the channel walls.

Conflict of interest

The authors declare that they have no conflict of interest.

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