Fabrication of active fluorescent microstructures with given parameters is an important task of integrated optics. One of the most efficient methods of fabrication of such microstructures is two-photon laser lithography. However, most polymers used in this technology have a relatively low quantum yield of fluorescence. In this work, the properties of microcavity structures obtained by the indicated method from hybrid polymers with addition of various dyes have been studied. The possibility of formation of high-quality microstructures from activated polymers, conservation of their luminescent properties after polymerization under intense laser irradiation, and reduction of the exposure of two-photon laser lithography by two orders of magnitude in the presence of Coumarin-1 dye has been demonstrated. The nonlinear optical microscopy study has shown that the spatial distribution of scattered fluorescence in microcavity structures based on the polymer with the dye corresponds to the excitation of cavity modes or whispering gallery modes.

Fabrication of active fluorescent microstructures with given parameters is important for rapidly developing research fields such as integrated optics and biophotonics [1–4]. Two-photon laser lithography (TPLL) is one of the methods of formation of such structures and performs well in fabrication of microcavities, optical microelements (microprisms and microlenses), waveguides, etc. [5–10]. The main advantage of this method is the pronounced locality of the action area compared to other kinds of optical lithography, which ensures the resolution better than 50 nm when using near infrared laser radiation as pump radiation [11]. Active development of TPLL led to the appearance of methods that make it possible to more accurately control the quality of the surface and the shape of the resulting microstructure, which is particularly important for microcavities of whispering gallery modes [12].

One of the main restrictions of the TPLL technology for the formation of active photonic microstructures, i.e., structures where effects of interest occur at frequencies different from the pump radiation frequency, is a low quantum yield of fluorescence of the initial polymer. This problem can obviously be solved by adding dyes or fluorescent nanoparticles (e.g., quantum dots) to the polymer that serve as active elements in the microstructure. A hollow cylinder from the acrylate polymer with Rhodamine B dye [13] and other structures [5, 14] have already been fabricated with this approach.

A similar method was used to fabricate active microstructures based on the OrmoComp polymer [15], which belongs to hybrid (organic–inorganic) polymers and is one of the most promising candidates for TPLL [16]. Lithography with this polymer activated by the Pyrromethene 597 dye has already provided disk microcavities with a diameter of about 50 μm and a Q-factor of more than 10^6 [17], which is a high value for cavities of such size. In this work, using two-photon laser lithography with OrmoComp polymer, we fabricate a number of microstructures of various shapes and characteristic sizes up to 25 μm with Coumarin-1 dye, mixture of Rhodamine-640 and Rhodamine-590 dyes (below, microstructures with Rhodamine) in equal mass concentrations, reveal features of two-photon lithography for polymer activated by various dyes, and demonstrate nonlinear luminescent properties of these structures.

Radiation of an Avesta Tif-DP femtosecond Ti:sapphire laser with direct diode pump, a wavelength of 780 nm, a pulse repetition frequency of 80 MHz, and a pulse duration of 60 fs was used as pump radiation for TPLL. Pump radiation was guided by mirrors through a telescope with a magnification factor of 0.5 to an acousto-optical modulator. Then, the diffracted beam passed through the telescope with a magnification factor of 5 joined with a spatial filter and reached
an $X-Y$ galvanoscanner located at the focus of the 4F system with a magnification factor of 2. The input lens of a Nikon Plan APO 60x immersion objective with a numerical aperture of 1.4, which was fixed on a piezoelectric translator with a displacement range of 40 μm, was placed at the second focus of this system. The 4F system was placed vertically, and the optical system ensured the total magnification factor that allowed one to match the beam diameter and the size of the input aperture of the objective. A three-coordinate table, which was displaced by means of stepper motors and on which Thorlabs CG15CH cover glass with liquid polymer drop or film was located for printing of microstructures, was placed above the objective. The region of sharp printing by means of the galvanoscanner had dimensions of $100 \times 100 \times 40$ μm; the diameter and height of the voxel were 0.4 and 1 μm, respectively.

To mix dye with OrmoComp polymer, we used OrmoDev developer, which is a mixture of two solvents, isopropanol and methyl isobutyl ketone, in which dyes used in this work were well dissolved. The solution of OrmoDev with dye was mixed with OrmoComp in a mass ratio of 1 : 2. The cover glass was preliminarily kept for 30 min in piranha solution for cleaning, was then placed on the table of a centrifuge, and was dried by centrifuging in an inert atmosphere. Then, OrmoPrime08 adhesion promoter (primer) was deposited on the surface of the dry substrate rotating at a speed of 3000 rpm. The primer had dimensions of $100 \times 100 \times 40$ μm and the diameter and height of the voxel were 0.4 and 1 μm, respectively.

Films with mass concentrations of 0.04 and 0.083 of Rhodamine and Coumarin-1 dyes, respectively, in OrmoComp polymer were prepared. The radiation fluences for the high-quality polymerization of microstructures in the process of two-photon laser lithography were determined to be $4 \times 10^{-5}$, $4 \times 10^{-5}$, and $5 \times 10^{-7}$ J/voxel for pure OrmoComp, with Rhodamine dye, and with Coumarin-1 dye, respectively. Printing was performed at a pump power of 0.7–10 mW in the waist, the printing rate was 50–1000 μm/s depending on the type of dye, and the print step in the lateral plane was 0.2–0.4 μm and between layers was 0.2–0.5 μm.

It is noteworthy that the addition of Coumarin-1 dye to OrmoComp polymer reduces approximately by two orders of magnitude the exposure time required for two-photon polymerization under TPLL compared to the polymer without dye, which can be used to increase the rate of printing structures. This effect was not observed in the presence of other studied dyes (Rhodamine and Coumarin-30). This is presumably due to an increase in the absorption of OrmoComp polymer activated with Coumarin-1 dye, whose absorption band almost coincides with the absorption band of the photoinitiator of the main polymer [18, 19]. In this case, optical excitation can be efficiently transferred from dye to the photoinitiator, which reduces the radiation fluence necessary for TPLL. This property is promising for the development of high-speed two-photon laser lithography.

To study the linear and nonlinear optical properties of the prepared microstructures, we used a setup similar to that described in [20]. The tunable signal radiation of an Avesta TOPOL-1050-C optical parametric oscillator at wavelengths of 800 and 700 nm with a pulse duration of 150 fs and a pulse repetition frequency of 70 MHz or the 405-nm radiation of the diode laser was used as pump radiation, which ensured the possibility of two-photon and single-photon excitation of photoluminescence, respectively. Probe radiation was focused by a Mitutoyo Plan Apo 100× objective with a numerical aperture of 0.7 into a region with a diameter of about 1 μm on the microstructure. The same objective was used to collect fluorescence from the structure under study. Radiation was detected either integrally by a photomultiplier tube or spectrally resolved by a spectrometer. When the diode laser was used for pumping and single-photon fluorescence was excited in the structure, a focusing lens and an aperture were additionally placed in front of the detector in order to collect the signal from the region on the sample with a diameter of about 1 μm. Studies were performed in the transmission scheme at the focusing of probe radiation on the upper surface (far from the substrate and close to the pump beam) of the structure.

Figure 1 shows the two-photon fluorescence spectrum of microstructures consisting of polymer with...
Rhodamine under pumping by 800-nm laser radiation. The spectral maximum corresponds to a wavelength of 600 nm. Similar results are observed for single-photon fluorescence.

Figure 2 shows maps of the two-photon fluorescence intensity in the (a) microdisk and (b) micropentagon, which indicate that the distribution of dye in the structure is uniform. It is seen that objects are geometrically regular and correspond to the initial model. The shape of the fabricated structures implies that various cavity modes such as whispering gallery modes, the so-called bow-tie modes, or analogs can be excited in them.

One of the methods of detecting such modes is the analysis of the distribution of scattered fluorescence [21]. Such a distribution for these structures was obtained with a CCD camera in the transmission scheme. It is seen in Figs. 3a and 3b that the fluorescence signal is enhanced near the edge of the microcylinder, which is expected and typical for whispering gallery modes. Both an increase in the fluorescence intensity near the edges of the micropentagon and the existence of a more complex internal signal distribution closer to its center are remarkable (Fig. 3b). We note that fluorescence maps shown in Fig. 3b were obtained under the excitation of the center of microstructures; a change in the geometry of optical excitation results in insignificant differences between fluorescence intensity maps in the micropentagon.

Figures 3c and 3d show the calculated distribution of the magnitude of the electric field at the pump frequency in structures with parameters corresponding to experimental ones. Two most typical calculated distributions are presented because the experimental photograph of the pentagon exhibits the superposition of excited cavity modes because of the absence of the spectral selectivity of the CCD camera. It is noteworthy that two main types of cavity modes are observed for the micropentagon: (i) whispering gallery modes propagating over the perimeter of the structure and (ii) bow-tie modes associated with the circulation of radiation inside the structure under reflection from some lateral faces of the pentagon. The simultaneous excitation of these modes determines the form of scattered fluorescence.

Similar studies were performed for microstructures made from OrmoComp polymer with Coumarin-1 dye; in this case, two-photon processes were studied under pumping by 700-nm radiation, for which the absorption coefficient at the double frequency is large.

![Fig. 2.](image-url) (Color online) Maps of the two-photon fluorescence intensity in the (a) microdisk and (b) micropentagon made of Ormo-Comp polymer with Rhodamine as obtained by nonlinear optical microscopy at a pump wavelength of 800 nm.

![Fig. 3.](image-url) (Color online) (a, b) Maps of the fluorescence intensity scattered in the (a) cylinder (excitation point is at the edge of the cylinder) and (b) micropentagon (excitation point is in the center) made of OrmoComp polymer with Rhodamine and (c, d) calculated spatial distributions of the electric field in the micropentagon.
The corresponding spectrum of two-photon fluorescence is shown in Fig. 4. It is seen that the intensity is maximal near a wavelength of 450 nm; the results for single-photon fluorescence are similar.

Microstructures of various shapes—hollow hexagons and cylinders, pentagons, and disks—were fabricated from this mixture of polymer and dye. The maps of the two-photon fluorescence intensity (Fig. 5) demonstrate that the distribution of dye in the polymerized structure is uniform and the resulting geometric parameters correspond to those specified in the 3D model. The spatial distributions of scattered single-photon fluorescence in microdisks and micropentagon also indirectly confirm the excitation of cavity modes (Fig. 6).

One of the features of structures based on dyes is their photobleaching, i.e., a decrease in the efficiency of fluorescence under intense irradiation, which restricts the possibility of application of corresponding materials in photonics [22]. To study single- and two-photon photobleaching, we examined the kinetics of fluorescence of fabricated microstructures based on polymers with various dyes. Measurements were performed for three wavelengths: 405 nm for single-pho-
Two-photon photobleaching, 700 or 800 nm for two-photon photobleaching for achieving more efficient absorption at the double frequency of each of the dyes. Typical curves are presented in Fig. 7. Experimental data were approximated by the two-exponential function

\[ I(t) = B + \sum_{i=1,2} A_i e^{-\gamma_i t}, \]  

where \( \gamma_i \) are the photobleaching rates.

The coefficients obtained from the approximations for Rhodamine and Coumarin-1 are summarized in Tables 1 and 2, respectively.

These approximations demonstrate a lower photodegradation rate for Rhodamine compared to Coumarin-1 and a much higher quantum yield after the same exposure time (at similar mass concentrations of dyes).

Thus, it has been demonstrated experimentally that active microstructures based on OrmoComp polymer with Coumarin-1 dye and the mixture of Rhodamine-640 and Rhodamine-590 dyes can be formed by two-photon laser lithography. It has been shown experimentally that the addition of Coumarin-1 dye to the main OrmoComp polymer reduces the exposure time necessary for using OrmoComp polymer without additions in TPLL by almost two orders of magnitude. The implementation of the method that makes it pos-

**Fig. 6.** (Color online) Map of the fluorescence intensity scattered in the micropentagon (excitation point is in the center) made of OrmoComp polymer with Coumarin-1.

**Fig. 7.** (Color online) Single-photon photobleaching curves measured for OrmoComp polymer with (a) Rhodamine and (b) Coumarin and their two-exponential approximations.

### Table 1. Parameters of photobleaching for OrmoComp polymer with Rhodamine

| \( \lambda_{\text{pump}} \) | 405 nm | 700 nm | 800 nm |
|---|---|---|---|
| \( B \), arb. units | 3.54 | 1.70 | 3.06 |
| \( A_1 \), arb. units | 7.55 | 1.57 | 3.83 |
| \( \gamma_1 \), s\(^{-1} \) | 0.31 | 0.26 | 0.23 |
| \( A_2 \), arb. units | 7.50 | 1.58 | 3.60 |
| \( \gamma_2 \), s\(^{-1} \) | 0.04 | 0.033 | 0.027 |

### Table 2. Parameters of photobleaching for OrmoComp polymer with Coumarin-1

| \( \lambda_{\text{pump}} \) | 405 nm | 700 nm | 800 nm |
|---|---|---|---|
| \( B \), arb. units | 0.4 | 0.5 | 1.44 |
| \( A_1 \), arb. units | 3.12 | 0.44 | 2.85 |
| \( \gamma_1 \), s\(^{-1} \) | 0.47 | 0.23 | 0.29 |
| \( A_2 \), arb. units | 1.79 | 0.9 | 3.46 |
| \( \gamma_2 \), s\(^{-1} \) | 0.055 | 0.026 | 0.034 |
sible to fabricate microcavity structures in which cavity modes can be excited owing to single- or two-photon fluorescence of dye introduced in polymer has been described.

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CONFLICT OF INTEREST
The authors declare that they have no conflicts of interest.

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