Optical Properties of a New Photorecording Polymer Based on 2,2-Difluoro-4-(9-Anthracyl)-6-Methyl-1,3,2-Dioxaborine


Abstract—The optical properties of a new photorecording polymer based on 2,2-difluoro-4-(9-anthracyl)-6-methyl-1,3,2-dioxaborine have been investigated. This material is found to change its absorption coefficient and refractive index in the visible range under illumination with a wavelength \( \lambda = 405.9 \) nm. This circumstance makes it possible to record static holograms with a spatial frequency up to 2500 lines/mm, a diffraction efficiency above 60%, and a lifetime more than 6 months. A dynamic change in the effective refractive index of this material under 405.9-nm irradiation is found, due to which one can form control optical elements of the light–light type with a modulation frequency up to 50 Hz in it.

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One of the main problems of photonics is the study of the optical properties of new materials and search for photorecording media to design sensitive elements of optical sensors, holographic deflective elements, and elements of integrated optical circuits. The most promising materials include photosensitive polymers, in which light induces photorecording processes leading to the formation of photoproducts with optical properties differing from those of the initial complex. Light can penetrate polymer recording media at a significant depth, due to which multilayered and bulk optical elements can be formed. In most cases, these media do not need postexposure treatment, a circumstance that greatly simplifies the technology, from the fabrication of optical elements to their application, and allows one to monitor the quality of the structures that are formed during recording. Photochemical reactions for some polymers are reversible; hence, erasable data storage devices can be designed based on these media. Promising compounds for developing photorecording materials on the polymer basis are \( \beta \)-diketonates of boron difluoride [1–5], which exhibit strongly pronounced nonlinear optical properties [6] and intense luminescence in solutions, crystals, and polymer compositions. They are used as laser dyes and active components of solar collectors, organic LEDs, and photosensitive materials for electrography [2–5]. Some compounds of \( \beta \)-diketonates of boron difluoride have already revealed effects of molecular photoaggregation, in particular, with a reversible change in luminescence [7, 8]. Among these compounds, anthracene-containing chelates, which are characterized by a strongly pronounced photocycloaddition reaction [9], are of special interest. However, these media belong to a relatively new class of quasi-aromatic compounds and their photochemical and optical properties have not been thoroughly analyzed yet. Hence, the purpose of this study is to investigate the optical properties of a new photoactive polymer, which is based on polymethylmethacrylate (PMMA) and contains boron chelate (BC)-2,2-difluoro-4-(9-anthracyl)-6-methyl-1,3,2-dioxaborine.

To prepare polymer samples for analysis, boron chelate (0.06 g) [9] was mixed with benzoyl peroxide (0.005 g), after which the mixture was dissolved in 8 ml prepolymer PMMA [10]. The solution was filtered, degassed, and heated at 60°C for 20 h. The polymer obtained due to these operations was kept at a temperature of 40°C for 4 h.

Figure 1a (curve 1) shows the absorption spectrum of the thus-prepared photoactive polymer (PAP), which was recorded on a Varian Cary 5000i spectrophotometer. It can be seen that the light absorption is maximum in the wavelength range of 350–420 nm. To perform photomodification of PAP, we chose radiation of a cw solid-state laser with the wavelength \( \lambda_M = 405.9 \) nm, which lies in the aforementioned spectral range [11]. It was found that an increase in the PAP exposure \( (E) \) to this radiation (which will be referred to as modifying below) leads to a gradual decrease in the absorption coefficient of the material at the wavelength \( \lambda_M \), which is illustrated by the dependence in Fig. 1b (curve 1). One can see that the slope of this dependence is steepest at \( E < 400 \) J/cm²; however, the slope decreases with a further increase in...
The absorption coefficient stops changing when the exposure exceeds $5 \times 10^4$ J/cm$^2$. The portion of curve 1 for exposures from $1.6 \times 10^3$ to $5 \times 10^4$ J/cm$^2$ is not shown in Fig. 1b to save room. However, we should note that $\alpha$ continues to decrease monotonically from $18 \text{ cm}^{-1}$ at $E = 1.6 \times 10^3$ J/cm$^2$ to the minimum value $\alpha_{\text{min}} = 14 \text{ cm}^{-1}$ at $E = 5 \times 10^4$ J/cm$^2$ in this portion.

A decrease in $\alpha(\lambda_M)$ leads to an increase in the penetration depth ($l_{\text{M}}$) of modifying radiation in the material exposed. The measured dependence of $l_{\text{M}}$ on the PAP exposure is shown in Fig. 1c. These data suggest that the effective thickness of the optical elements recorded in the material under study can be controlled.

The change in the PAP absorption coefficient in a wide spectral range under modifying radiation is illustrated by a dependence in Fig. 1a (curve 2). A comparison of this curve with curve 1 in Fig. 1a shows that the absorption of the exposed PAP in the range of 350–470 nm decreases by one to two orders of magnitude in comparison with the unexposed material. Therefore, amplitude diffraction elements can be recorded in this spectral range. It can also be seen that, when passing on the range of 530–650 nm, the difference in the absorption coefficients of the exposed and unexposed samples is insignificant; hence, it is not reasonable to record amplitude diffraction elements in this wavelength range. Nevertheless, we found that the refractive index $n$ of the material studied changes in this range, due to which phase holographic gratings can be recorded in it. Figure 1b (curve 2) presents a characteristic experimental curve, which demonstrates the change in $n$ at the wavelength $\lambda = 589.3$ nm, depending on the exposure of the material to modifying radiation.

To study the features of the material under consideration when recording phase holographic gratings, we used the system schematically shown in Fig. 2a. The radiation of a cw laser $I$ with a wavelength $\lambda_M$ is split into two beams, $B_1$ and $B_2$, which then converge at an angle $\theta_0$ in a PAP sample with a thickness $d \sim 1$ mm. A holographic grating is recorded in the sample under the interference field of these beams. The experimental setup makes it possible to vary the convergence angle of the beams $B_1$ and $B_2$ in a wide range and thus vary the spatial frequency of the recorded holographic gratings. The recorded grating is read using the radiation of a Ne–Ne laser 2. According to Fig. 1a, both exposed and unexposed PAP samples are characterized by relatively small absorption coefficients at this radiation wavelength.

When recording holographic gratings, the intensity $I_0$ of the beams $B_1$ and $B_2$ did not exceed 6 W/cm$^2$; this limitation excluded beam-induced destruction (melting) of the material under study. The average stability time of the interference field of the recording beams (which was provided by isolating the system from fluctuations of temperature and other environmental factors) was $\tau_0 \sim 4$ min. In accordance with the aforementioned conditions, the exposure $E_0 = \tau_0 I_0 \sim 1.4 \times 10^3$ J/cm$^2$ was chosen to be a reference level, providing reproducible properties of recorded holographic gratings with a diffraction efficiency (DE) sufficient to be detected by the existing photodetectors.

Figure 3a (curve 1) shows the measured dependence of the DE in the first diffraction maximum on the spatial frequency of the recorded gratings. The increase in DE at $\Omega > 90$ lines/mm is explained by the transition from the Raman–Nath diffraction (Fig. 2, inset I) to the Bragg diffraction (Fig. 2, inset II). The decrease in DE for the gratings with spatial frequencies $\Omega > 1000$ lines/mm is related to the limiting resolution of the material studied. The data in Fig. 3a indicate that holograms with a spatial frequency of no