Formation of microstructures on the surface of a carbazole-containing azopolymer by the action of laser beams

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Abstract. The formation of microstructures on the surface of a carbazole azopolymer occurred with a Gaussian beam of a linearly polarized laser with wavelengths of 405, 485, and 532 nm. Power density was changing. Images of the formed microprotrusions and their parameters were obtained depending on the power density and wavelength. The effect of the wavelength and susceptibility of the azopolymer to laser radiation at various wavelengths is shown.

1. Introduction
Beams with inhomogeneous polarization are used to create highly focused beams [1], nanostructuring materials [2], micromanipulation [3], encoding and transmission of information in free space [4]. The use of such beams gives an advantage due to the special distribution of the vector electromagnetic field. Obtaining vector beams with inhomogeneous polarization is possible due to the use of polarizing sector plates or sector half-wave plates [5], using the used a 'pile-of-plates' polarizer (Stoletov's pile) [6], sub-wave reflective or transmissive diffractive optical elements (DOE) [7-8], using anisotropic crystals [9]. Due to the special organization of the polarization distribution in the zone of the beam impact, it is possible to change the distribution of forces acting on the object.

The study of the effect of these forces on objects or materials, the modeling and prediction of the force acting on an object, the dynamics of the formation of the height of the relief or mass transfer is very important for technology. Biological objects [10], metals [11], azopolymers [12], or chalcogenide glassy semiconductors [13–14] are widespread in impact objects. There is a wide variety of types of azopolymers that can have different physicochemical properties, due to the possibility of varying the combination of the structure of the main polymer chain and azo dye. Azo-containing materials have the effect of light-induced birefringence and dichroism, like birefringent crystals [15], which allows them to be used as a dynamically changing material that controls the redistribution of the components of the electric field of beams with polarization features. The combination of these properties of beams and materials may allow the creation of completely new optical devices based on them, such as rewritable optical memory based on azopolymers [16], a holographic microscope [17], optical systems with optically controlled elements [18-19].
In this regard, depending on the requirements, there is a need to search for and study the properties of new types of azopolymers, as well as the preparation modes for various applications, to search for the optimal concentration of azo dye. In the works [20-21], previously, we studied the properties of a carbazole-based azopolymer and investigated nonlinear effects under the action of high-intensity light [22]. In this work, the properties of this azopolymer will be experimentally studied, and the results of the formation of nanostructures will be presented with the help of a focused Gaussian beam with different wavelengths.

2. Materials and methods

For the experiment, azopolymer was deposited on a K8 glass substrate by centrifuging. The azopolymer was prepared by the method described in [20-21]. Starting materials 340 mg of poly-N-epoxypropylcarbazole with 34 mg of 4- (4-nitrophenylazo) -aniline were copolymerized in boiling toluene (2 ml) for 3 hours. To obtain the latter, the chromophore dispersed orange DO-3 (Sigma-Aldrich) with 90% of the dye was used. The resulting solution, containing 30% mass fraction of azo dye, was filtered and deposited on a substrate. Sample thicknesses after drying of the polymer were measured by a profilometer (P16 +, KLA Tencor). The absorption spectra of the film with a thickness of 1600 nm in the ultraviolet and visible regions, obtained by a spectrometer (MS7504, Solar TII), are shown in figure 1.

As can be seen from the graph, the high absorption obtained azopolymer has in the spectral region from purple to green.

The optical setup shown in figure 2 was used as an experimental setup.

In experimental studies, single-mode linearly polarized lasers with wavelengths of 532 nm, 485 nm, and 405 nm were used. As can be seen from figure 1, 485 nm, the wavelength corresponds approximately to the absorption peak of the azo dye. 405 nm is to the left in the absorption spectrum of the azo-solvent, 532 nm, respectively, to the right. The laser power directed to the azopolymer surface was monitored by a Thorlabs PM100A power meter. Laser radiation passing through the diaphragm (D), expanded with a collimator consisting of two lenses (L) and pinhole (PH). A quarter wave plate (\(\lambda/4\)) was used to control the state of polarization of the beam. The unpolarized beam divider and high-speed camera were used to control the position of the laser spot focused on the sample. The lens in front of the sample was characterized by a numerical aperture value of 0.1.
With the help of the setup described, individual irregularities were recorded by the action of laser beams with linear polarization. The beam power was varied in the range of 50–3180 W / cm². The recording time of each structure was 180 s.

After recording, the formed microrelief was measured using a Solver Pro-M, NT-MDT scanning probe microscope.

Images of the surface microrelief formed as a result of the action of focused Gaussian beams with linear polarization at a wavelength of 532 nm are shown in figure 3.

Figure 3a – d show that with an increase in the power density of laser radiation, the height of the nanostructures formed increases. Nanostructures have an asymmetrical appearance and correspond to the structures previously studied by us in [21]. The surface microrelief is an elevation with a long base along one axis of symmetry. Along the orthogonal symmetry axis, the base of the elevation is strongly compressed due to the formation of local depressions at the base. An increase in the power density leads to an increase in the height of the microstructure, an expansion in the size of the regions of local depressions and their depth. Given that the height of the nanostructure in figure 3, d is greater than the initial resist thickness, it is obvious that the growth occurred due to mass transfer not only near the focal spot, but also beyond it. Given the high power density near the impact zone, the azopolymer was in a mobile state at a fairly considerable distance around. This led to the fact that a high needle was formed from an azopolymer and its almost complete absence in a certain zone around it. With increasing power density, the complexity of the microrelief structure is also seen.

When the wavelength is changed to 485 nm, corresponding to the absorption peak of the azo dye of the synthesized azopolymer, anisotropic nanostructures are also formed (figure 4), have a characteristic appearance and form a relief of considerable height even at minimum power. With increasing power density, the elevation of the relief increases.

The surface microstructure shown in figure 5 was obtained by irradiating the surface of an azopolymer with radiation with a wavelength of 405 nm. As can be seen, as the radiation power density increases, the height of the central microprotrusion increases. The relief obtained in Figure 5 is very similar to the relief formed at a wavelength of 532 nm (figures 3 d). This asymmetry of the azopolymer material was previously mentioned in [23–24]. The structure shown in figures 3c–d was obtained at high power densities up to 3000 W/cm² and has a more complex shape. At elevation, the formation of two additional elevations at the initial stage, which are similar to the corresponding microstructures in [25], is observed.

It is impossible to speak unequivocally about the dependence of the height of the microstructure on the power density due to the formation of microstructures of various shapes, but this can be traced at all wavelengths of 405-532 nm. This behavior can be explained by the same optical gradient forces manifested when irradiated by polarized laser radiation near the absorption peak of azo dyes of azopolymer molecules. Earlier, in [21], we presented the symmetric structures of the azopolymer...
obtained by irradiation with circularly polarized light. It can also be noted (figures 3, 4, 5) that when irradiated with light corresponding to the absorption peak of azo dyes, the formed microrelief most strongly responds to the incident radiation. When irradiated with light with a wavelength of 405 nm, the carbazole base may be involved in the absorption and, as shown in figure 5d a deep crater forms in the irradiated area at high light intensity without forming a central protrusion, unlike the microrelief shown in figures 3, d.

![Figure 4. Surface relief of a polymer film after laser irradiation with linearly polarized state: at intensity: a) 56 W / cm², b) 120 W / cm².](image)

![Figure 5. A polymer film with linearly polarized state: at intensity: a) 28 W / cm², b) 56 W / cm², c) 120 W / cm², d) 200 W / cm².](image)

3. Conclusion
The article presents the new results of the study of azopolymer based on poly-N-epoxypropylcarbazole and 4- (4-nitrophenylazo) aniline chromophore under the action of a Gaussian beam with linear polarization at different wavelengths. During experiments with it, surface microstructures were obtained under the influence of a focused polarized Gaussian laser beam with different power densities. The effect of wavelength on the microrelief formed on the surface is shown. Also, it is likely that both the azo dye groups and the base polymer molecules are involved in the microrelief nourishment process. New results can help the creation of a physico-mathematical model of mass transfer under the influence of optical forces of a different nature. This can give a significant impetus to the development of such areas as holographic optical memory, holographic polarization microscopy, etc., where fully optically controlled polymer materials can be used.

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Acknowledgments
This work was financially supported by the H2020-TWINN-2015 HOLO project (nr. 687328), Russian Foundation for Basic Research (grants 16-29-11698-ofi_m, 18-29-20045/18-mk, 18-07-01470-a, 18-07-00613) and by the Ministry of Science and Higher Education of Russia (agreement No. 007-GZ/C3363/26).