Particularities of photonic and structural transformations in the polystyrene film during pulsed infrared laser irradiation

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Abstract. Two new kinds of the structural in-homogeneities in the polystyrene films were created by the irradiation of the film with nanosecond pulses of the infrared laser with 1064 nm wavelength. At the beginning of the irradiation dark micro-inclusions having unusual close to rectangular geometries appeared. After about 30 seconds of the irradiation one more kind structural distortions appeared having the geometries of the systems of the concentric micro-rings. Simultaneously with the creation of these concentric micro-rings the film started to emit bright blue luminescence all over its area and significant focusing of the laser beam during its propagation through the film was observed resulting in the generation of the bright white flashes at the screen installed behind the film. The creation of the dark rectangular spots as well as of the concentric micro-rings are ascribed to the non-linear interactions between the laser radiation and the structural distortions produced in the film due to photo-thermal processes excited in the film.

1. Introduction
This paper concerns the development of new techniques for creation of regular microscopic and nanoscopic superstructures in organic polymers by laser treatment. This topic is actual either from practical or fundamental considerations. Organic polymers like polystyrene and many others are highly prospective materials for new kinds of electronic and optoelectronic devices. In comparison with traditional semiconducting materials organic polymers possess a wide set of advantages [1-4]. Their production is cost-effective, the materials have low weight, mechanical flexibility, chemical resistivity, etc. The morphologies, chemical compositions and technical parameters of polymer products can be modified rather easily. On the other hand, the understanding of the nature of optical and electron phenomena in organic polymers as well as techniques of governing of their properties is important for applications in various optical and electronic devices. But it is far from completion in comparison with inorganic materials. For example, the science and technology of creation of periodical micro- and nano-structures from inorganic materials by means of self-organization is rather well investigated [5 – 7], providing an effective basement for modern cost-effective technologies. On the other hand, studies of self-organization processes in organic polymers have not achieved the inorganic level yet [8]. This is explained by essentially younger of synthetic polymer history on the one hand and significantly more complicated structures of these substances on the other hand. It is worth to emphasize that modification of microscopic and nanoscopic morphologies of polymer surfaces...
by especially regulated laser irradiation is rather well developed [9 – 12]. But this development concerns preparations of ripple – like structure from parallel lines by means of interference of two or more laser beams. The preparation of more sophisticated morphologies inside the volume of polymer materials is problematic up to now. In the studies described in this paper we have found that irradiation of polystyrene films by infrared laser nanosecond pulses being applied with proper parameters produces inside the volume of the material periodical microstructures from concentric rings possessing interesting optical properties for practical applications. Besides self-organization of the circular structure and its influence on the interaction of laser beam with the irradiated material the originality of the results presented here is connected with the creation of the modifications of the internal structure of the polystyrene by the flow of photons with the energies several times lower than the energy necessary for direct excitation of polystyrene interatomic bonds. Our studies of the nature of the self-organized structural transformations induced in the polystyrene films by nanosecond infrared radiation showed that the main reason of these processes is connected with the positive non-linear feedback between the local structural transformations of the material and the redistributions of the laser beam intensity.

2. Methods of experiments
The polystyrene films were prepared by solidification of the solution of polystyrene in benzene poured onto optically polished glass slides (usually applied in optical microscopes). Mean thickness of the films was about 500 micrometers. The luminescence ability of polystyrene was activated with molecules of 2.5 - diphenyloxazole (PPO) and 2,2- p-phenylene-bis(5-phenyloxazole) (POPOP) [13]. The film was irradiated with pulsed infrared laser (wavelength 1.064 µm, pulse duration about 20 ns, mean energy in the pulse 0.03 Joule). Irradiation could be arranged by single pulses or in periodical regime with the frequency from 6 to 30 pulses per second. The process of laser treatment of the films was recorded by video-camera registering the spatial and spectral characteristics of the luminescence. The modifications of the film structures were analyzed by optical and scanning electron microscopes. The laser irradiation of the films has been made at open air and in liquid nitrogen.

3. Experimental results and discussion
Irradiation of the films of polystyrene, activated with PPO and POPOP, with 20 ns pulses of 1.064 µm laser described above resulted in the generation of the light flux in violet and blue spectral regions (Figs. 1 and 2). It should be emphasized that at the beginning of the laser irradiation the violet luminescence is observed only, whereas after 20 – 30 seconds of the irradiation the blue luminescence appears. The spatial distributions of these two kinds of the luminescence are quite different. The violet emission inside the film is induced in the region where the film is crossed by the laser beam. Its angular distribution does not have noticeable anisotropy (Fig. 1a, left). On the other hand, the blue luminescence is seen across the whole film area (Fig.1b, right).

On the other hand, the blue luminescence is seen across the whole film area (Fig. 1b). It is important to emphasize that simultaneously with the generation of the blue luminescence the bright white emission appears at the screen installed behind the film/ a at the distance about 4 cm. The reasons of these transformations of the luminescence of the film will be discussed lower in correlation with the transformations if the film morphology. In addition, it should be noted that the dependencies of the violet and blue light emissions on the intensity of the laser pulses demonstrate distinct super-linear character with the sharp threshold of the intensity. The luminescence is not observed when the intensity of the laser irradiation becomes lower than this threshold.

We analyzed the transformations of the morphology of the film at each stage of the spectral and spatial distributions of the luminescence described above. At the first stage when the
Figure 1. (a) (left) and 1b(right). Fig. 1a presents the violet emission of the polystyrene film excited by the infrared laser pulses (the right edge of the photo) and the moderate white emission at the screen (the left edge of the photo). (b) presents blue luminescence all over the same polystyrene film and simultaneously excited bright flame at the screen

violet luminescence is observed small dark spots (with dimensions of several µm) appear in the irradiated region (Fig. 2).

It is worth to emphasize that these dark spots in the regions of the films with any structural in-homogeneities demonstrate the anisotropy of their geometry. Say, some polystyrene films acquired the superstructure of parallel straight lines during their solidification at the glass slides, revealed clearly with the optical microscopy (Fig. 3).

It turned out that in the regions where this superstructure prevails the dark spots demonstrate the rectangular geometry close to squares with the sides of these squares being parallel to the lines of the super-structure. On the other hand, when the blue light emission of the films appears the new regular super-structures inside the films are observed (Fig.4).

These super-structures have the geometry of the concentric rings. The distances between the neighbor rings revealed by the optical microscopy are about several tens of micrometers. It is worth to note that the internal appearances of the systems of the concentric rings created in the different regions of the films look like each other. This means that the concentric rings produced in different regions of the same film are characterized by the analogous internal morphologies of the rings concerning the microscopic scale.

We suppose that either the rectangular dark spots formed at the initial stage of the laser irradiation or the concentric rings formed at the next stage appeared as the result of the mutual interactions with the positive feedback between the laser radiation propagating through the film and the structural in-homogeneities created inside the film by this radiation. This means that the fluctuations of the spatial distribution in the films morphology (and the local optical parameters correspondingly) and the corresponding distortions of the spatial distribution in the laser radiation flow enhance mutually each other. And these mutual enhancements result in the creation of the two rather unusual kinds of the in-homogeneities of the films: the rectangular dark spots and the concentric systems of the rings. Concerning the creation of the dark spots
Figure 2. Two new kinds of the self-organized structural distortions in the polystyrene film produced by irradiation of nanosecond pulses of 1.064 μm infrared laser (rectangular dark spots and concentric rings)

Figure 3. Self-organized linear structure of the polystyrene film solidified from the solution
Figure 4. The systems of concentric rings produced by nanosecond laser irradiation of the polystyrene film. The horizontal dimension of the left photo is 500 µm, of the right photo 120 µm

we suppose that when the laser beam passes through the polystyrene in the vicinity of one of the linear in-homogeneities its trajectory is distorted due to the gradient of the refractive index induced by this structural in-homogeneity. Due to the local bending of the light flow the distribution of its intensity will be varied. This variation will induce the further structural and refraction variations enhancing the bending of the trajectories of the beams, etc. In the local regions of the increase of the light intensity the refraction index will be changed due to the optical non-linearity of the substance inducing the further local enhancement of the intensity. Hence the fluctuations of the local structure of the film will induce the local enhancement of the absorption of the light energy. Due to the increased energy absorption the enhanced local chemical decomposition of the polystyrene will start with the subsequent creating of the dark spot (e.g. its darkness can result from the local carbonization of polystyrene induced by the combined actions of light and local heating [14]). The local increase of the refraction index will induce the attraction of the light flow to the place of this increase. Hence the light flow will be redistributed in the direction parallel to the initial linear superstructure creating the rectangular dark spots with limited dimensions along and perpendicular to the initial linear super-structure. The detailed quantitative analysis of these processes will be published later.

The systems of the concentric rings created by the laser irradiation of polystyrene films with 20 nanoseconds light pulses and observed in the transmission light manifest the corresponding local modifications of the refractive index as well. The positive feedback between local disturbances of the refractive index and the light flow redistribution will be able to produce the essential enhancement of the light intensity at the screen behind the film with corresponding generation of the bright flame. In this case the self-generated structural and refraction in-homogeneities will work as the local Fresnel focusing phase lattice. On the other hand, the part of the incident laser flow will be deviated by this phase lattice in the directions along the film exciting the blue luminescence across the whole film area. The quantitative analysis of these processes which we plan to finish soon will take into consideration the instabilities of the morphology, chemical composition and corresponding optical parameters of the film combined with the spatial redistributions of the delivered and absorbed light beam energy. The mutual positive influence of these factors is capable to create new interesting kinds of the combined waves of the transformed
Figure 5. Scanning electron microscopy of the blisters produced in the polystyrene film by nanosecond pulses of the infrared laser photon flows and structural defects (see, for example, the theoretical papers of the team of Prof. V. Emelyanov [15,16]).

The scanning electron microscopy of the films at the stage of the concentric rings revealed blisters with the micrometer diameters (Fig. 5).

Some of these blisters had anisotropic crack-like holes in their centers and manifest severe local over-heating. We suppose that these blisters work as the sources of the initial scattering of the laser light inside the film resulting in the self-organizing creation of the concentric rings as well as of the excitation of the blue luminescence all over the film. Generally speaking, the both new super-structural components found in our experiments (the rectangular dark micro-spots and the circular systems of the concentric rings) were formed due to essentially non-linear behaviors of the absorption and refraction of the polystyrene films as functions of the light intensity. The analytical estimations of their creation which we are going to make later will consider the inhomogeneities of the local temperature and of the intermolecular and interatomic bonds as well as the redistributions of the energy supply by the laser beam and the outflow of the energy by means of the convection and thermal conductivity. Our experiments on the laser irradiation of the same films immersed in liquid nitrogen showed that the balance between the inflow and outflow of the energy is one of the main factors of regulation of these super-structures. It turned out that the behavior of the films immersed into liquid nitrogen has changed radically in comparison with the open air. We have not observed in this case either the creation of the dark spots or the formation of the concentric rings. Correspondingly the excitation of the blue luminescence all over the film was not observed as well. We ascribe these changes to the severe enhancement of the energy introduced into the film by the laser via liquid nitrogen, so the photo-thermal destruction of the polystyrene structure induced by the laser beam at the room temperature could not start. On the other hand, the thermo-elastic stresses induced by the local thermal expansion of the polymer at the point of the strong multiphoton absorption created tensile stresses around this point. Due to the decrease of the plasticity of the polymer these tensile stresses could not relax by the deformation mass-transfer and created the star-like system of the radial cracks.
Figure 6. Optical microscopy of the polystyrene film irradiated by nanosecond laser pulses in liquid nitrogen

Conclusions

We found two new kinds of self-organized super-structures produced in the polystyrene films by the multiphoton absorption of the infrared 1.064 µm laser nanosecond pulses: the non-transparent micro-inclusions with unusual rectangular geometry and the systems of coaxial micro-rings. The appearances of both of these in-homogeneities are ascribed to the active interactions between the embryo of the structural distortions and the redistributions of the laser light flow induced by these distortions resulting to their mutual enhancement.

The systems of the coaxial micro-rings created generate severe redistributions of the laser flow propagating through the polystyrene film: the effective focusing of the light flow behind the film inducing the laser avalanche and the precise partial scattering of the laser flow inside the film resulting in its overall blue luminescence.

The creation of the rectangular and the coaxial structural distortions produced in the polystyrene films by infrared laser pulses are ascribed to the effective mutual interactions with the positive feedback between the emerging structural in-homogeneities and redistributions of the laser flow induced by these in-homogeneities.

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