Formation of self-trapping waveguides in bulk PMMA media doped with Phenanthrenequinone

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Abstract: Experimental and theoretical investigations of light self-trapping waveguides in a bulk polymeric medium based on polymethylmethacrylate (PMMA) with photosensitive phenanthrenequinone (PQ)-molecules are examined. Self-channeling was generated for the first time in this nonlinear bulk PQ-PMMA media with a thickness up to several millimeters and 0.1 mol. % PQ-concentration. The experimental formation of volume waveguide structures with a length of 2 - 3 cm at different laser wavelengths (405 nm, 488 nm, and 514.5 nm) was demonstrated. The calculations based on a model for the laser beam propagation in the bulk PQ-PMMA medium with competitive nonlinearities are in a good agreement with the experiments.

OCIS codes: (090.2900) Optical storage materials; (160.5320) Photorefractive materials; (160.5470) Polymers; (190.4400) Nonlinear optics, materials; (190.5940) Self-action effects.

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1. Introduction

Recently the effects of the formation of localized spatial structures due to self-interaction of light beams in nonlinear optical media, especially nonlinear photopolymeric materials, have attracted widespread attention [1–3]. Previously we have shown that thin PQ-PMMA layers, several hundreds of microns in thickness, look promising as a material for a self-trapping application with a high optical quality and thermal stability of the recorded spatial structures [3–5]. The main principle of the photochemical reaction in the PQ-containing polymeric medium is its density change caused by excitation of the dye molecules under illumination and their attachment to the polymeric matrix (Plexiglas) with the subsequent formation of a stable photoproduct [6–13].

In this work we have significantly increased the geometric dimensions of polymeric samples and used PQ-PMMA layers with a new preparation procedure. The method of the material preparation is based on the free radical bulk polymerization of a solution, consisting of a monomer (methyl methacrylate, MMA) with dye molecules (PQ) and an initiator (Azobisisobutyronitrile), placed into the mold of polished glass [13]. It is possible to form PQ-PMMA layers with a thickness up to several millimeters, whereas their shape can be determined by a glass mask (usually the size of samples is 20×30 mm^2 with a thickness of 3-5 mm). The solubility of the PQ-molecules in MMA on bulk polymerization is limited by the dye concentration up to 0.25 mol.%.

To avoid the decrease of the refractive-index modulation caused by a lower dye concentration, one can use light sources with higher spectral frequencies, switching from green to blue excitation wavelengths (from 514.5 nm to 488 nm or even to 405 nm, which corresponds to the maximum of the PQ-absorption band). This allows to generate a change of the refractive index Δn (up to 10^{-4}) required for the nonlinear self-trapping formation through the bulk PQ-PMMA sample even at concentrations of PQ as low as 0.1 mol.%.

2. Formation of self-trapping channels in bulk PQ-PMMA samples

The experimental realization of the self-trapping waveguides and investigation of their characteristics in bulk PQ-PMMA samples were performed using different laser sources. A schematic experimental setup is presented in Fig. 1. For the channel-formation process, the commonly used Ar-laser wavelengths 514.5 and 488 nm and the wavelength of a semiconductor laser of 405 nm especially suitable for the PQ-PMMA material have been examined. To focus a laser beam on the front surface of the polymeric layer, a Lomo 68216 microscope objective with a focal length of 6.2 mm and a numerical aperture of 0.65 was applied. A mechanical XYZ stage was used in order to accurately control the position of the sample and to focus the laser light more precisely. Visualization of the self-trapping effect was obtained by a CCD-camera.

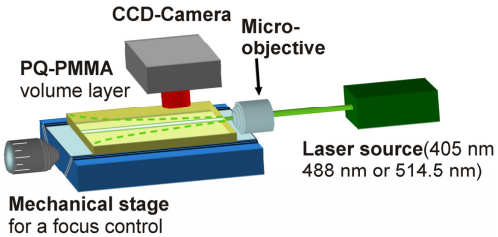

Fig. 1. Schematic setup for the formation of a self-trapped channel by different laser beams.

The laser beam propagation within a bulk PQ-PMMA layer with the use of laser sources having various wavelengths and powers is shown in Fig. 2. For comparison and with the intent to observe the light divergence, the distribution of each of the laser beams in a pure glass layer was examined [Fig. 2, top row]. The wavelength variation causes a significant change in absorption of the polymeric layer. The absorption coefficients α of PQ-PMMA

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samples were: 2 cm^{-1}, 4 cm^{-1}, and 40 cm^{-1} for the wavelengths 514.5, 488, and 405 nm, respectively. The images of the light-beam propagation through the bulk PQ-PMMA samples with a thickness of 3-4 mm are demonstrated in Figs. 2(a)–2(d).

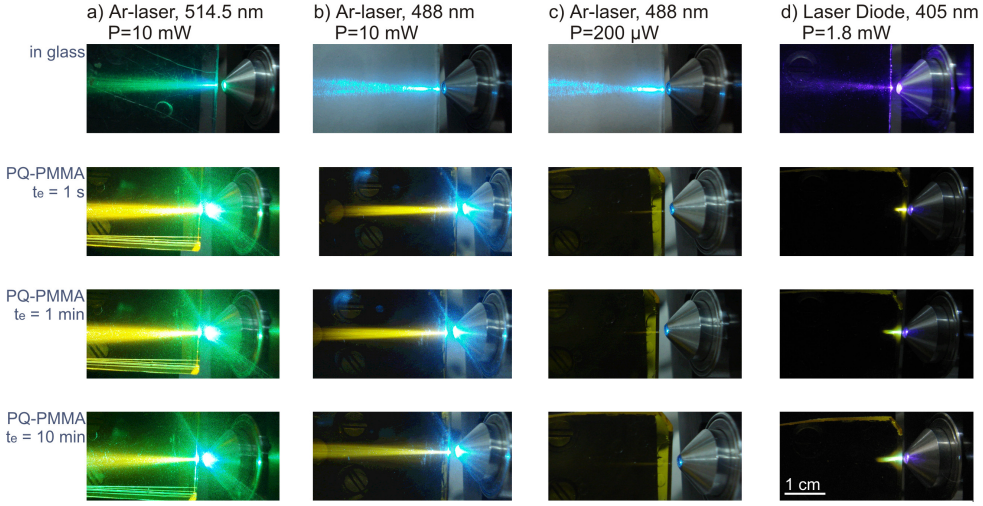

Fig. 2. Propagation of a light beam during 1s, 1 min and 10 min of the exposure time in glass [top row] and within the bulk PQ-PMMA layers [rows 2-4] using different lasers; Ar laser: (a) 514.5 nm at the power 10 mW, (b) 488 nm at 10 mW, (c) 488 nm at 200 μW; (d) laser diode illumination of 405 nm at 1.8 mW (4 mm layer thickness, 0.1 mol.% of PQ-concentration).

By applying an Ar-laser radiation at the wavelength of 514.5 nm the light beam is propagating within the PQ-PMMA sample almost over the whole length of the layer that is similar to the propagation of light in pure glass due to the low absorption coefficient on that wavelength [Fig. 2(a)]. Those, the observed behavior of the laser beam correlated well with the measured absorption coefficient of 2 cm^{-1}, for which the intensity can be reduced by two orders of magnitude at a distance of 2-3 cm in the layer. Moreover, with an increased exposure time a strong decrease of the beam cross-section at the entrance of the polymeric sample has been detected. This visual effect can be related to a decrease of absorption in the polymeric sample due to PQ-photoattachment to the macromolecules with an increase of the total intensity and of the associated reduce of the recording time of the CCD camera. Obviously, with lower exposure time, the beam at the sample entrance is visually perceived as being thinner.

By switching to a wavelength of 488 nm the absorption coefficient of the medium is doubled ($\alpha \sim 4$ cm^{-1}) resulting in a twofold decrease in length of light propagation through the polymer [Fig. 2(b)]. Within 10 min the light beam reaches the output of the photopolymeric layer. It should be noticed that, along with the increase in length of the illuminated area, its cross-section is also increasing as a result of the additional process of defocusing of the light beam due to the thermal nonlinearity effect. Comparing this broadening of the channel with broadening at 514.5 nm excitation wavelength, the formed light waveguide becomes more well established and direct. Nevertheless, the reaction of the PQ-photoattachment allows only a partial compensation of the beam divergence by switching to the wavelength of 488 nm [Figs. 2(a), 2(b), and the last row].

The behavior of light propagation changes by reducing the laser power and leads to a decrease of the thermal nonlinearity, correspondingly. As seen in Fig. 2(c), the fifty-fold intensity reduction is generating a rather narrow waveguide channel (of about 100 μm cross-section). However, this requires a longer exposure time of the laser irradiation. Controlling the width of the self-trapping waveguide by variation of the light-beam power was examined earlier in [2].

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By changing the wavelength to 405 nm, the absorption coefficient of the PQ-PMMA medium is increased by an order of magnitude (to α ~40 cm^{-1}) and, therefore, the propagation length of the light within the sample is reduced. As can be seen from Fig. 2(d), initially the light travels just about one millimeter. With increasing time a self-trapping channel starts to form, while its length is only a few millimeters even after 10 minutes of exposure time.

Thus, the analysis of the experimental results shows that the formation of a waveguide channel is significantly influenced by both parameters, the intensity and the wavelength of the exciting radiation. The wavelength of 488 nm and the power of 200 μW were chosen as optimum conditions for the beam propagation in PQ-PMMA material.

3. Theoretical model and discussion

To describe the obtained results, a theoretical model has been developed including two competing mechanisms of nonlinearity, namely the process of photoattachment of PQ-molecules with formation of a photoproduct (positive change of the refractive index Δn_{PQ}) and the negative change of the refractive index (Δn_T) by heating of the medium. A change of the refractive index during the process of photoattachment has been computed using the Lorentz-Lorenz formula [10, 12]: $\Delta n_{PQ} = (n_0^2 + 2)\left[R_N \cdot N - R_C \cdot (C_0 - C)\right]^2 / 6n_0$, where R_N and R_C are the refraction coefficients of the photoproduct and the PQ-molecules, respectively.

A change of the concentrations of PQ molecules $C(\vec{r},t)$ and of photoproducts $N(\vec{r},t) = C_0 - C(\vec{r},t)$ can be calculated with the equation:

$$\partial C/\partial t = -\varepsilon \cdot I \cdot C, \tag{1}$$

where ε is the light-sensitivity coefficient of a polymeric material and $I(\vec{r},t)$ denotes the radiation intensity distribution in a medium.

A change of the refractive index due to heating of the medium (Δn_T) may be expressed as follows: $\Delta n_T = (\partial n/\partial T)\delta T$, where $\partial n / \partial T$ is the thermo-optic coefficient of PMMA. The change of the temperature of the medium is computed using the heat-conduction equation

$$c\rho\,\partial T/\partial t = k_T \Delta T + Q, \tag{2}$$

where $\Delta = \partial^2/\partial z^2 + (1/r)(\partial/\partial r)(r\,\partial/\partial r)$, with specific heat c, material density ρ, heat-conduction coefficient k_T; $Q = \alpha(\vec{r},t) I(\vec{r},t)$ is a volume heat-release source; $\alpha(\vec{r},t) = \alpha_{mol} C(\vec{r},t)$ is an absorption coefficient of the medium and α_{mol} is a molar absorption cross-section.

The equation describing the complex light-beam amplitude with the assumption of its cylindrical symmetry has the form

$$\frac{\partial E}{\partial z} = \frac{i}{2k}\Delta_\perp E + i\frac{k\Delta n_\Sigma}{n_0}E - \frac{\alpha}{2}E, \tag{3}$$

where $\Delta_\perp = (1/r)(\partial/\partial r)(r\,\partial/\partial r)$; $k = k_0 \cdot n_0$ is a wave number; $\Delta n_\Sigma = \Delta n_{PQ} + \Delta n_T$ is the total change of the refractive index.

The solution of the coupled Eqs. (1)–(3) enables one to calculate the space-time dependences of the medium temperature, the light-induced refractive index of the medium and the light-beam intensity in the medium. The numerical calculations have been performed using the following typical parameters of the PQ-PMMA light-sensitive medium: the refractive indices of the photoproduct and the PQ-molecules R_N = 62.5 cm^3/mol, R_C = 61.5 cm^3/mol; initial concentration of PQ $C_0 = 2\cdot10^{-5}$ mol/cm^3; molar absorption cross-

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section $\alpha_{mol} = 2 \cdot 10^5$ cm/mol; refractive index $n = 1.5$; material density $\rho = 1.2$ g/cm^3; specific heat $c = 1.3$ J/(g·K); thermo-optic coefficient of PMMA $\partial n / \partial T = -10^{-4}\ K^{-1}$; light sensitivity coefficient of a polymeric layer $\varepsilon = 10^{-1}$ cm^2/J; heat conduction coefficient $k_T = 2 \cdot 10^{-3}$ W/(cm·K). The Gaussian light-beam radius at the entrance to the medium was varying within the limits of $r_0 = 50 \div 500 \mu$m; the light beam power was $P_0 \approx 200 \mu$W; the calculations have been performed for the wavelength $\lambda = 488$ nm for which the radiation self-channeling effect was observed experimentally.

The light-beam intensity distributions within the volume of a nonlinear medium at different times with the lateral size of the laser beam $r_0 = 50$ μm and the input intensity $I_0 = 3$ W/cm^2 are given in the Fig. 3(a). As can be seen, initially the dominant process is the light beam, which is defocused due to the prevailing thermal mechanism of nonlinearity. Then later, in a few fractions of a millisecond, the transverse profile shows a considerable increase (tenfold by this calculation), see Fig. 3(b). The penetration depth into the medium is decreased down to several millimeters, whereas the peak intensity is reduced by two orders.

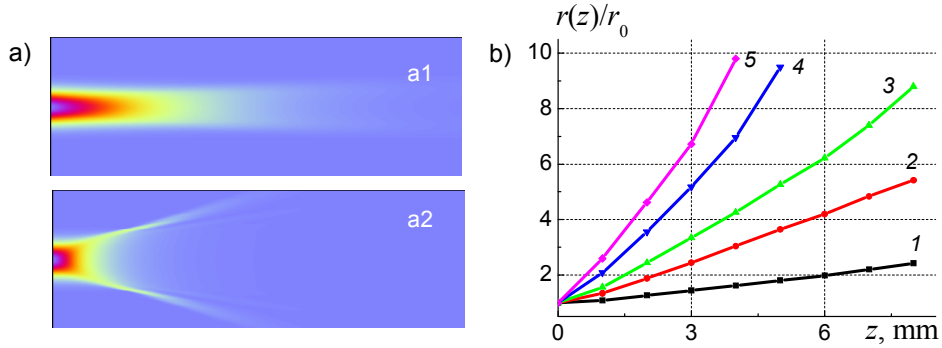

Fig. 3. (a) Light-beam intensity distribution in the volume of the medium at different times $t = 0.01$ (*a1*), 0.25 ms (*a2*); (b) the transverse profile half-width as a function of the penetration depth at different times $t = 0.01$ (1), 0.05 (2), 0.1 (3), 0.25 (4), 0.5 ms (5); size of the figure area: 8 mm x 1 mm.

Due to a significant broadening of the light beam at the starting time and a decrease of its peak intensity, the rate of nonlinear processes in a polymeric medium is considerably lowered. The further development of the dynamics of the process is observed at times on the order of tens and hundreds of seconds. To analyze the waveguide-formation processes at longer times, the effect of a sufficiently wide ($r_0 = 500$ μm) and low-intensity ($I_0 = 0.03$ W/cm^2) Gaussian light beam with the power of $P_0 = 200$ μW on a polymeric material has been considered (see Figs. 4 and 5). From the viewpoint of an equivalent intensity on retention of the power of a divergent light beam, this situation is equivalent to the above-mentioned case with a focused high-intensity beam that endured a significant defocusing in a rather short period of time (some fractions of a millisecond).

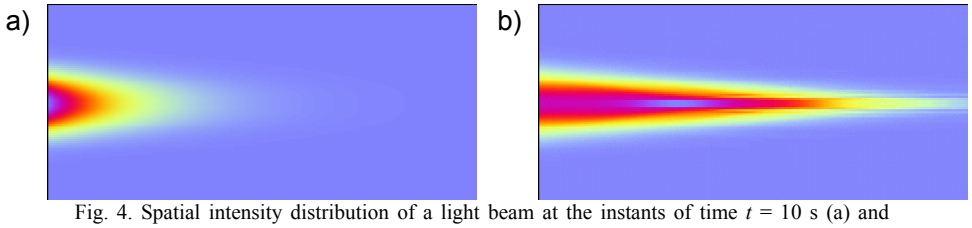

Fig. 4. Spatial intensity distribution of a light beam at the instants of time $t = 10$ s (a) and 1200 s (b); size of the figure area is 1.6 cm x 0.8 cm.

Formation of self-trapping light beam structure is naturally connected with the changes in spatial distribution of the refractive index. As follows from the performed calculations, the

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heating of the medium and the photo-attachment of PQ-molecules lead to the corresponding changes of the refractive index. Its negative thermal change, Δn_T, with time is compensated by a positive contribution to the refractive index of the photo-addition reaction Δn_{PQ}. The spatial region with the local increase of the total refractive index Δn_Σ is observed along the propagation axis z [Fig. 5(a)], and close to the axis of the light beam $r = 0$ [Fig. 5(b)].

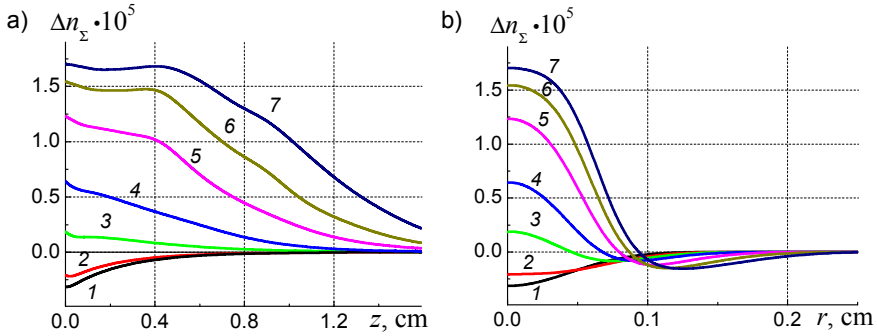

Fig. 5. Total refractive index change Δn_Σ as a function of (a) longitudinal and (b) transverse coordinates (exposure times are: t = 10(1), 50(2) 150(3), 300(4), 600(5), 900(6), 1200s (7)).

Finally, it should be noted that the spatial intensity distribution of a light beam as it propagates deeply into the polymeric material [Fig. 4(b)] correlates well with the experimental data obtained at a power of P_0 = 200 μW [Fig. 2(c)]. This applies to both viewpoints, that of the development of dynamics of the waveguide channel and its formation time.

4. Conclusions

In this paper the formation of self-trapping waveguides in bulk PMMA samples, produced by a new preparation method and with an increased thickness of up to a few millimeters, is proposed. The aim of this work was to further develop the method of generating self-trapping waveguides to expand their applications. Bulk samples with lower dye-concentrations were used and it was observed that the excitation wavelength for generating self-trapping waveguides in such materials should be optimized. With a laser beam of spectral range corresponding to a rather low absorption coefficient (α ~2 cm^{-1}) the entire sample was illuminated and it was found that the propagating light practically retains its original divergence. By this process self-trapping structures for $\alpha \geq 4$ cm^{-1} were produced. However, with the absorption coefficient of the PQ-PMMA medium close to 40 cm^{-1}, the waveguide formation process became much slower. A strong dependence of the cross-section of the waveguide channel on the light power has been observed. At a rather low laser power, when the influence of thermal effects can be neglected, the size of the self-trapping structure is determined almost totally by the size of the light beam at the entrance to the polymeric medium. An increased intensity leads to thermal defocusing of the beam already at the entrance to the PQ-PMMA layer and results in broadening of the self-trapping channel. Owing to the increased thickness of the layers, waveguiding and diffraction structures may be used more extensively for multiple self-trapping waveguide formation, optical splitters, switches, selective filters, etc.

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