Photoinduced phenomena in fullerene-doped PDLC: potentials for optoelectronic applications

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Laser-induced change in refractive index and optical limiting effect have been studied in the liquid crystal systems based on fullerene-doped 2-cyclooctylamino-5-nitropyridine, polyimide, N-(4-nitrophenyl)-(L)-prolinol compounds. Experiments have been made under nano-, pico- and femtosecond pulsed laser irradiation at the wavelength of 532 nm and 805 nm. From the results obtained, both the optical limiting level and nonlinear refractive index n2 as well as the third-order susceptibility χ(3) have been determined. Potentials of the systems studied to attenuate laser irradiation and to record thin amplitude-phase hologram over the visible and near-infrared spectral ranges have been evaluated to solve optoelectronic problems more efficiently.

Keywords: liquid crystal, fullerenes, optical limiting, laser-induced change in refractive index, optoelectronics.

1. Introduction

At present, the polymer-dispersed liquid crystals (PDLCs) are extensively being studied [1–3] for various optoelectronic applications. These systems combine film-forming capability and mechanical strength of polymers and unique electro-optical properties of liquid crystals mesophase.

Generally, PDLC is formed from liquid crystal and polymer. In this case the ordinary refractive index of the liquid crystal n0 and the refractive index of polymer n_p are close together [1]. Initially, as a result of random LC director orientation, there is a gradient of the refractive index at the interface between an LC drop and polymer that causes drastic light scattering by the composite. On application of an electrical field or under laser irradiation, the gradient becomes small, i.e., the condition n_0 ≈ n_p is met. In this case, the LC director aligns itself along the electric field or the electric vector of a light wave. As the result, the light scattering is not observed and the system clarification occurs. After switching off the electrical or light action, the composite reverts to the original state.

Until now, the different fullerene-doped photosensitive components have been used to develop PDLC structures. Poly(vinyl alcohol), poly(methyl methacrylate) [4,5], 2-cyclooctylamino-5-nitropyridine (COANP) [6,7], polyimide [8], phthalocyanine nanocrystals [9], etc. have been treated for this purpose. A fullerene introduction has been used to control PDLC systems to good advantage. The fullerene-doped systems allowed them to be applied to process optical information, to attenuate a laser irradiation and duplicate and triple the laser frequency. Moreover, these systems could be used as laser valves over visible and infrared spectral range due to good sensitisation ability of fullerenes.

In this paper the photoinduced phenomena have been investigated in the C_{70}-COANP-LC system, C_{60}-N-(4-nitrophenyl)-(L)-prolinol (NPP)-LC compound, C_{70}-polyimide-LC structure under nano- and pico-second pulsed laser irradiation over the visible spectral range. From the results obtained, the nonlinear refractive index n_2 and the third-order susceptibility χ(3) have been determined.

2. Experiment

Fullerene free COANP were thoroughly studied in Refs. 10 and 11. When COANP was doped with a dye, an additional absorption peak was found [10]. It should be noticed that the absorption edge of pure COANP lies in the range of 420–430 nm. When COANP was doped with fullerenes, the absorption edge was shifted to long wave region [12]. The PDLC cells based on fullerene-doped COANP allowed the laser irradiation to be modulated and attenuated efficiently [13]. Additional bands, which were close to 532 and 810 nm, were obtained. The absorption spectra for films of the pure COANP composite and the C_{70}-doped COANP composite, as well as pure C_{70} were presented in Ref. 14. Fullerene influence on spectral and energy ranges of the polyimide 6B [15] and NPP [16] molecules was discussed recently.

With UV stirring, the initial mixture of polymer PI6B and nematic liquid crystal (NLC) was prepared in the ratio of 3 polymer parts to 2 NLC ones. 3% solutions of PI6B in 1,1,2,2-tetrachloroethane (TCIE) were used. PDLCs based on COANP and NPP structures were made in the ratio of 1 photosensitive component to 2 NLC one. A 2.5% solution

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of non-photosensitive polyimide 81A in TCE was used as a film-forming base for COANP and NPP compounds. The relation between COANP and NPP compounds and the film-forming base was 2:1. The C\textsubscript{70} and C\textsubscript{60} concentration in COANP and NPP materials was 5 wt.% and 1 wt.%, respectively. 0.2–0.5 wt.% C\textsubscript{70} was used to dope polyimide 6B. 10 µm films were prepared from emulsion of fullerene-doped photosensitive component and LC. Two types of NLC with positive optical and dielectric anisotropy: ZhK1289 (\(\Delta n = 0.168, \Delta \varepsilon = 10\)) and E7 BDH (\(\Delta n = 0.224, \Delta \varepsilon > 0\)) were used.

A sinusoidal holographic grating was recorded by the second harmonic (\(\lambda = 532\) nm) of a pulsed Nd laser with the pulselength of both 20 ns and 400 ps. Two laser beams formed a spot of 4–5 mm in diameter on the film surface. The recording energy density was 0.5–40 mJcm\textsuperscript{-2}. The spatial frequency was 100 mm\textsuperscript{-1}. The grating was read out under the self-diffraction conditions. OL experiments were made at the wavelength of 532 nm in the nanosecond pulsed regime and using femtosecond pulsed irradiation of a quasi-CW Ti-sapphire laser at \(\lambda = 805\) nm.

### 3. Results and discussion

#### 3.1. Holographic recording study

In this part of the paper, the emphasis will be given to investigate the PDLC structure based on COANP. The dependence of the response in the first diffraction order \(\eta^*\) on the input laser energy density \(W_{in}\) is shown in Fig. 1.

It should be noticed that the response obtained under nanosecond laser irradiation (curve 1) is more than the one obtained under picosecond laser irradiation (curve 2). However, the reversible process in the picosecond range has been obtained at the higher energy density than the one observed in the nanosecond range. This effect is associated with rejection of the thermal nonlinearity and determines the potentials to irradiate the media in the picosecond range at the higher \(W_{in}\). It should be noticed that the response of the non-sensitized system was at least two orders of magnitude less than the one of the fullerene-doped system. The increase in the diffractive efficiency and hence in the induced refractive index could be explained from the spectral and thermal peculiarities of the samples, as well as in the framework of the photorefractive effect under the laser irradiation.

From the data presented in Fig. 1, the induced change in refractive index could be estimated. The first diffraction order response was changed from \(2\times10^{-4}\) to \(3.7\times10^{-3}\) mJ and from \(10^{-4}\) to \(2\times10^{-3}\) mJ as the incident energy density increased from 2.5 to 17.5 mJcm\textsuperscript{-2} (nanosecond irradiation) and from 4.2 to 35 mJcm\textsuperscript{-2} (picosecond irradiation), respectively. Therefore, using equation [17]

\[
\eta = I_1/I_0 = (\pi \Delta n_\text{d}/2\lambda)^2,
\]

the light-induced change in refractive index could be estimated to be \(7.3\times10^{-4} - 1.4\times10^{-3}\) and \(5.1\times10^{-4} - 7.2\times10^{-4}\) un-

### Table 1. Light-induced change of refractive index for materials based on COANP.

<table>
<thead>
<tr>
<th>Material</th>
<th>Impurity concentration (wt.%)</th>
<th>Wavelength (nm)</th>
<th>Light intensity (Wcm\textsuperscript{-2})</th>
<th>Incident energy density (Jcm\textsuperscript{-2})</th>
<th>Laser pulsewidth (ns)</th>
<th>Change of refractive index ((\Delta n))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>COANP + TCNQ*</td>
<td>0.1</td>
<td>676</td>
<td>2.2</td>
<td></td>
<td></td>
<td>(2\times10^{-5})</td>
<td>[10]</td>
</tr>
<tr>
<td>Pure COANP**</td>
<td>0</td>
<td>532</td>
<td>0.9</td>
<td>20</td>
<td>(\sim 10^{-5})</td>
<td>[14]</td>
<td></td>
</tr>
<tr>
<td>COANP + C\textsubscript{70}</td>
<td>5</td>
<td>532</td>
<td>0.9</td>
<td>20</td>
<td></td>
<td>(6.89\times10^{-3})</td>
<td>[14]</td>
</tr>
<tr>
<td>PDLC based on COANP + C\textsubscript{70}</td>
<td>5</td>
<td>532</td>
<td>(17.5\times10^{-3})</td>
<td>20</td>
<td></td>
<td>(1.4\times10^{-3})</td>
<td>[6]</td>
</tr>
<tr>
<td>Liquid crystal</td>
<td>0</td>
<td>514.5</td>
<td>0.2</td>
<td></td>
<td></td>
<td>(0.16\times10^{-3})</td>
<td>[18]</td>
</tr>
</tbody>
</table>

* 7,7,8,8-tetracyanoquinodimethane.
** Polyimide 81A was used to prepare the thin COANP films as a film-forming base.
der nanosecond and picosecond laser irradiation, respectively. Here \( \eta \) is the diffraction efficiency, \( \Delta n_i \) is the change in a refractive index of the medium, \( d \) is the thickness of the sample, \( \lambda \) is the wavelength, \( I_1 \) and \( I_0 \) are the light wave intensities in the first order and incident one, respectively. The values obtained was more than the thermal component typical of LCs (~10\(^{-5}\)).

The light-induced changes of refractive index for different materials based on COANP are presented in Table 1. It should be noticed that the \( \Delta n \) value obtained in the present paper for the fullerene-doped PDLC is one order of magnitude more than that for LC given in Ref. 18. Therefore, the fullerene introduction is likely strengthening the alignment of the LC molecule director. The possible reorientation mechanism of LC director using both the fast rotation ability of fullerenes and the complex formation process in conjugated organic structures has been recently discussed in Refs. 6, 7, and 9.

The investigation on the rotational behaviour of fullerenes [19,20] demonstrated that the reorientation time depended on temperature. The rotational reorientation of C\(_{60}\) and C\(_{70}\) in various solvents exhibited the following values of the reorientation time: in toluene – 7 ± 1.5 ps, decalin – 3.5 ± 1.5 ps, and in chlorobenzene – 8 ± 2 ps. Therefore, the response of fullerene on changes of the light wave is very fast. Moreover, fullerene introduction in the COANP compounds provokes the charge-transfer complex with the donor fragment of CONP molecule [14,21]. It should be noticed that fullerene has electron affinity energy of 2.65 eV that is more than the one for most organic compound acceptors. For example, for COANP compounds, NO\(_2\) group (as an acceptor fragment) has electron affinity only of 0.54 eV. Therefore fullerene dominates under acceptor fragment of COANP and creates the complex with its donor fragment. The possible scheme of donor-acceptor interaction in the fullerene-doped organic structures is shown in Fig. 2. The quantum-chemical calculation of the charge-transfer in COANP-fullerene structure has been made in the Ref. 21. To indicate this complex experimentally the mass-spectrometry and photoconductive data have been done in Ref. 22. This complex has larger dipole moment, which interacts with light wave to align LC director with good advantage.

It should be noticed that from large induced change in refractive index for PDLC based on fullerene-doped COANP it predicts more nonlinear refraction index \( n_2 \). Both \( n_2 \) and the nonlinear susceptibility \( \chi^{(3)} \) could be calculated from the following equations [23]

\[
\frac{n_2}{I} = \frac{\Delta n_i}{I}, \quad (2)
\]

\[
\chi^{(3)} = \frac{n_2 n_0 c}{16\pi^2}, \quad (3)
\]

where \( n_0 \) and \( n_2 \) are linear and nonlinear refractive indices, respectively, \( c \) is the velocity of light; and \( I \) is the intensity of the light wave. Thus, \( n_2 \) and \( \chi^{(3)} \) for PDLC based on 5 wt.% C\(_{70}\)-doped COANP are 1.6×10\(^{-9}\) cm\(^2\)W\(^{-1}\) and 4.86×10\(^{-8}\) esu, respectively, at the incident energy density of 17.5 mJcm\(^{-2}\) and \( \Delta n = 1.4\times10^{-3} \). The data obtained are close to those for silicon (10\(^{-10}\) and 10\(^{-8}\), respectively [23]), but less than the ones for pure liquid crystals. However, the nonlinear effect in the structures under present investigation could be accumulated and hence increase significantly. The nonlinear coefficients obtained demonstrate potentials of PDLC based on fullerene-doped COANP for its optoelectronic applications as efficient nonlinear optical media.

Under the Raman-Nath diffraction conditions the thin amplitude-phase holograms in the PDLC structures based on the fullerene-doped NPP compounds have been recorded for comparison. The corresponding curves are presented in Fig. 3. The concentration of fullerene C\(_{70}\) in COANP was 5 wt.% and the concentration of C\(_{60}\) in NPP was 1 wt.% Note, although the concentration of fullerene C\(_{70}\) in COANP is greater than that of C\(_{60}\) in NPP, curves 1 and 2 almost coincide. This is probably explained by the
fact that nonlinear absorption of radiation by the medium in the visible spectral range is determined not only by the reverse saturated absorption but also by a close location of the resonance line of fullerene C$_{60}$ (565 nm) with respect to the 532 nm laser wavelength.

It should be mentioned that twice increase in the laser-induced refractive index has been observed as the laser energy density increased tenfold. The large laser-induced change in refractive index influences the OL effect in PDLCs based on photosensitive molecules mentioned above (due to energy losses by diffraction), predicts the large increase in nonlinear coefficient $n_2$ and $\chi^{(3)}$ and therefore gives an opportunity to apply these systems for conversion of laser radiation. Moreover, the change in refractive index could increase by an electrical control.

3.2. Optical limiting study

The study of the OL effect allows the laser-matter interaction to be investigated and the search for the new materials for optoelectronic problems (such as the protection of human eyes and technical devices against high laser radiation) to be made.

The dependence of the output energy density ($W_{\text{out}}$) on the input one ($W_{\text{in}}$) for PDLC structures is shown in Fig. 4.

More than 10-fold attenuation of the laser beam has been obtained for the PDLC cell based on polyimide 6B at the incident energy density of 0.15–0.2 Jcm$^{-2}$. Twice attenuation of the laser energy density has been found in the fullerene-doped PDLC based on COANP and NPP compounds that is close to the OL level for 1-µm pure fullerene film. The difference in the nonlinear transmission of PDLC based on COANP structure and NPP one is associated with different matching between COANP and NLC refractive indexes as compared with that between NPP and NLC refractive indexes. Reverse saturable absorption, complex formation and laser-induced scattering could be discussed to explain OL results in the PDLC structures studied.

The first OL experiments have been carried out for PDLC based on COANP-C$_{60}$ and E7 under femtosecond pulsed irradiation of a quasi-CW Ti-sapphire laser ($\lambda = 805$ nm). Taking into account the broad absorption band in 800–820 nm associated with charge transfer in the COANP-fullerene structure [21], more than 10-fold attenuation of the laser beam has been detected. The experiment allowed dynamics of photo-induced processes to be investigated at the upper excitation levels, which were characterized by the transition times of 1 fs, and the reverse saturable absorption to be revealed in the fullerene-doped organic structures based on COANP, that did not contradict the results of Ref. 24. In that paper it was found in pure fullerene films that a photo-induced absorption increase occurred at the forbidden transition of 1.6 eV due to the electron state hybridization in the electric field of the high laser beam.

4. Conclusions

To summarize, the photo-induced change $\Delta n$ in refractive index was studied by the dynamic holographic technique in the fullerene-doped PDLC system under nano- and picosecond laser irradiation. Maximum $\Delta n$ was established to be observed in the system with 5 wt. % of C$_{60}$ in COANP, the value was $1.4\times10^{-3}$ at $W_{\text{in}}$ of $17.5\times10^{-3}$ Jcm$^{-2}$ and $7.2\times10^{-3}$ at $W_{\text{in}}$ of $25\times10^{-3}$ Jcm$^{-2}$ in nano- and picosecond pulsed wavelength region, respectively. The results obtained for different composites based on COANP and NPP were compared. The nonlinear refractive index $n_2$ and the third-order susceptibility $\chi^{(3)}$ have been determined for fullerene-doped PDLC.

The data predict optoelectronic potentials of PDLC applications for modulation and generation of the laser irradiation over the visible spectral range. The spectral peculiarities of the system studied propose to carry out the investigations over the near-infrared spectral range.

Optical limiting results have been shown for fullerene-doped PDLCs at wavelength of 532 and 805 nm. 10-fold attenuation of the laser beam has been obtained that predicts to use fullerene-doped PDLCs to protect the human eyes and technical devices against high laser irradiation.

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Fig. 4. Dependence of the output energy density ($W_{\text{out}}$) on the input one ($W_{\text{in}}$) for PDLC structures: 1 – COANP-5 wt.%C$_{70}$-LC (E7), 2 – NPP-1 wt.%C$_{60}$-LC (E7), 3 – polyimide-(0.25 wt.% C$_{60}$+C$_{70}$)-LC (ZK999), 4 – polyimide-(0.5 wt.% C$_{60}$+C$_{70}$)-LC (ZK999), $\lambda = 532$ nm.

References

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