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Nano-, pico- and femtosecond study of fullerene-doped polymer-dispersed liquid crystals: holographic recording and optical limiting effect

N. Kamanina*, S. Putilin, D. Stasel'ko

Vavilov State Optical Institute, 12 Birzhevaya Line, 199034 St. Petersburg, Russia

Abstract

In the fullerene-doped polymer-dispersed liquid crystals (PDLCs) the holographic recording and optical limiting (OL) effect have been established to be intermediate between those for fullerene-doped liquid crystals and for fullerene-doped polymers. It has been shown that fullerene-doped PDLCs could be applied for OL at the incident laser power of 0.3–0.4 J cm^{-2}. They can be used as effective diffractive optical elements. © 2002 Published by Elsevier Science B.V.

Keywords: Organic materials; Polymer-dispersed liquid crystals; Fullerenes; Optical limiting

1. Introduction

At present, a study of polymer-dispersed liquid crystals (PDLCs) holds the great promise because they combine the properties of a polymer matrix and electro-optical parameters of an LC mesophase [1]. In high-performance PDLC refractive index of LC ordinary wave n_o should be close to refractive index of polymer n_p, while refractive index of LC extraordinary wave n_e should satisfy the relation $n_e > n_o, n_p$. If there are no external fields, a random orientation of the LC molecule director causes gradient of refractive index at the interface of an LC drop–polymer, resulting in high light scattering in the composite. On application of an external electric field or under a light irradiation normal to the sample surface, transmission augmentation is observed because of an LC molecule director alignments along the field.

Recently, fullerenes have been introduced to control the transmission both of LC [2,3] and polymers [4–8]. Fullerene introduction in PDLC structure has been made in the papers [9–13]. Investigations of fullerene-doped PDLC have shown that they could be applied in LC display technique, for recording holograms and they have been also used as laser optical limiting (OL) devices. Ono et al. [9–11] studied the orientational photorefractive grating generated in LC-poly-(vinyl alcohol) composites doped with C_{60}. They also observed the grating formation in the PDLC based on C_{60}-doped poly(methyl methacrylate). Reverse saturable absorption in liquid crystal composites based on polyimides and polyvinyl alcohol with added fullerenes has been investigated by Kamanina and Kaporskii [12]. It was established that laser radiation was attenuated tenfold in these structures. The first holographic recording experiment with PDLC structure based on fullerene-doped 2-cyclooctylamino-5-nitropyridine (COANP) has been done in the paper [13].

In this paper, holographic grating and OL have been studied in fullerene-doped PDLCs based on polyimide 6B (PI6B), COANP and *N*-(4-nitrophenyl)-(L)-prolinol (NPP) compounds.

2. Experiment

With stirring, the initial mixture of polymer PI6B and nematic liquid crystal (NLC) was prepared in the ratio of 3 polymer to 2 NLC. 3 and 6.5% solutions of PI6B in 1,1,2,2-tetrachloroethane (TClE) were used. A finely divided powder of fullerenes (0.2 wt.% of a C_{60} and C_{70} mixture) was introduced either in NLC or in the polymer solution.

PDLCs based on COANP and NPP structures were made in the ratio of 1 photosensitive component to 2 NLC. A 2.5% solution of nonphotosensitive polyimide 81A in TClE 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_{70} and C_{60} concentration in COANP and NPP materials was 5 and 1 wt.%, respectively. It should be noticed that fullerene-free COANP

* Corresponding author. Tel.: +7-812-328-0231; fax: +7-812-247-1017.
E-mail address: kamanin@ffm.ioffe.rssi.ru (N. Kamanina).

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and NPP compounds are effective π-conjugated systems, which peculiarities were discussed in the papers [14–17] in detail. The spectral and nonlinear-optical properties of fullerene-doped NPP and COANP compounds were first investigated in the paper [18,19].

The emulsion was poured over a substrate with calibrated spacers followed by drying to remove the solvent. A thickness of the samples was 10 μm. A size of NLC drops in the photosensitive matrix was 2–3 μm. ZhK999, ZK1282, and E7(BDH) were used.

A second harmonic (532 nm) of the pulsed Nd-laser was applied to investigate the nonlinear transmission of the films in the nano-second region and to study the holographic grating formation in the pico-second one. A pulsewidth was 15 ns and 400 ps, respectively. A laser spot diameter on the sample surface was 3–3.5 mm for OL experiment and 4 mm for holographic one. A set of light filters was used to vary the incident beam energy. As an alternative technique the spectroscopic measurement was carried out using a Perkin-Elmer Lambda 9 instrument in the wavelength range 200–3000 nm.

3. Results and discussion

Dependence of an output energy E_{out} on an input energy E_{in} is shown in Fig. 1 for the samples based on ZhK999 and PI6B without (curve 1) and with (curves 2 and 3) fullerenes. An attenuation of the laser energy was found in the fullerene-doped samples by factor 8–10.

Generally, the OL effect in the visible spectral region and in the nanopulse regime was associated with a formation of the fullerene molecule in triplet state, that was caused by absorption of a quantum at $\lambda = 532$ nm [20,21]. Since a pulsewidth τ_p is 15 ns and characteristic time of singlet–triplet interaction of 1.2 ns, i.e. $\tau_p > \tau_{S1 \rightarrow T1}$, the triplet state accumulates the excited molecules. The triplet state molecule is characterized by an absorption cross-section, which is several times more than that of the unexcited molecule. We have recently estimated the possibility of the complex formation in the fullerene–polyimide systems and have shown that at $\lambda = 530$ nm the absorption cross-section of donor–acceptor complex of fullerene with triphenylamine is about 300 times more than the one of intramolecular polyimide complex between the acceptor diimide fragment and the donor triphenylamine fragment [22].

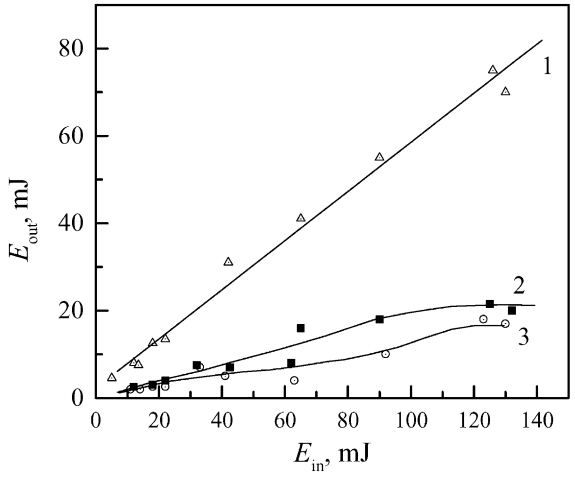

Fig. 1. Output energy vs. input energy: fullerene-free sample of 3% PI6B and ZhK999 (curve 1); fullerene-doped samples of ZhK999 and 6.5% (curve 2) and 3% (curve 3) PI6B.

In additional, because the overlapping band existing between the fluorescence spectrum of PI6B and the absorption spectrum of fullerenes dissolved in polyimide coincides with irradiation wavelength, the Förster resonance conditions [7,23] are met in our case. Therefore, the energy transfer in accordance with the Förster mechanism can be included in the OL consideration for PDLC based on fullerene-doped PI6B.

It should be noted that the threshold value of E_{in}, at which the saturation of E_{out} begins, is more for the sample with the polyimide concentration of 6.5% ($\sim$0.7 J cm^{-2}) than that with the polyimide concentration of 3% (0.3–0.4 J cm^{-2}). These samples are shown in Fig. 1 by curves 2 and 3, respectively. The effect is associated with an influence of the interfaces between the NLC drop and polyimide, which is more at a more polyimide concentration. As the results, both reorientation effect reported in paper [24] for NLC doped with fullerenes and laser-induced scattering can contribute in this case. A small increase in transmission at $E_{in} > 120$ mJ (Fig. 1, curve 3) is caused by the transition of NLC to isotropic phase on its heating.

Dependence of E_{out} on E_{in} is shown in Fig. 2 for the samples based on E7(BDH) and both COANP and NPP compounds. Twice attenuation of the laser power is found in the fullerene-doped structures that is close to the OL level for pure C_{60} film. The difference in the nonlinear transmission in 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. Moreover, a little enhancement of absorption at the wavelength of laser irradiation ($\lambda = 532$ nm) has been observed on doping NPP materials with fullerenes C_{60} because the resonance line for C_{60} fullerene (565 nm) is close to the experimental irradiation wavelength.

It should be noticed that, besides the reverse saturable absorption mechanism included for explanation of OL, in the COANP and NPP compounds effect is caused by a complex formation between a donor fragment of the COANP or NPP molecule and fullerene as well. Really, electron affinity of fullerene is 2.65 eV, that is more than the one for acceptor fragments of most organic molecules. Specifically, the acceptor fragment of the COANP and NPP molecule is a NO_2 group, which is bound to the donor fragment by the benzene ring. For a separate NO_2 molecule or radical, electron affinity is 2.3 eV, while the NO_2 group bound to the benzene ring has electron affinity of only

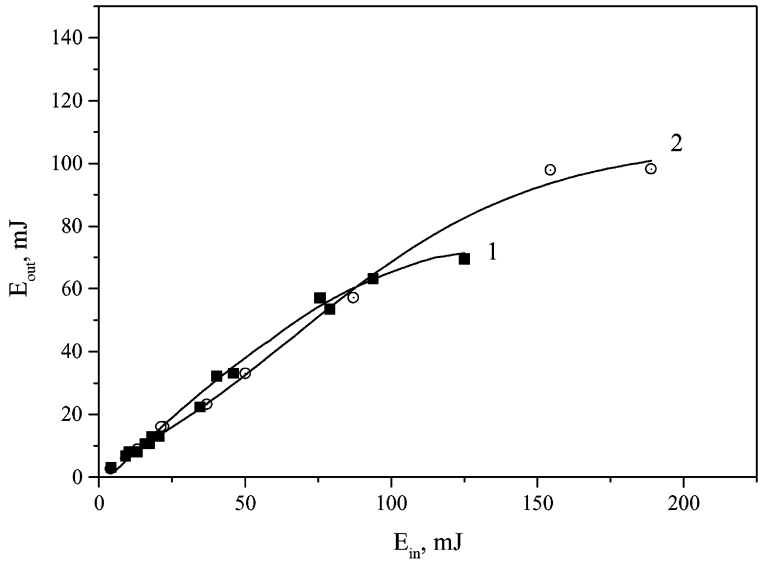

Fig. 2. Output energy vs. input energy: 5 wt.% C_{70}-doped sample of COANP and E7(BDH) (curve 1); 1 wt.% C_{60}-doped sample of NPP and E7(BDH) (curve 2).

0.54 eV [25], that is, it is smaller than the one of fullerene by a factor of 4. Therefore, fullerenes are more effective acceptors and hence they are likely to dominate over intramolecular acceptor fragment of COANP and NPP.

Moreover, the carriers become free after the charge transfer to the fullerene molecule, where the surface charge is delocalized [26]. Therefore, due to the free-carrier absorption the reinforcement of donor–acceptor interaction in the structures influence the OL effect in fullerene-doped compounds.

The first OL experiments have been carried out for PDLC based on COANP-C_{70} and E7 under femtosecond pulsed irradiation of a quasi-CW Ti-sapphire laser ($\lambda = 805$ nm). The pulses were of the pulsewidth of 70 fs, the repetition frequency of 80 MHz, the power of 150 mW. The spot diameter at the film surface was 0.2 mm. Taking into account the saturation effects in quasi-CW mode, the tenfold attenuation of the laser beam has been detected. It should be mentioned that the additional absorption band in the range 800–820 nm was preliminary found in the COANP compound sensitized by fullerene C_{70}.

The experiment allowed dynamics of photo-induced processes to be investigated at upper excitation levels, which were characterized by the transition times of 1 fs, and the

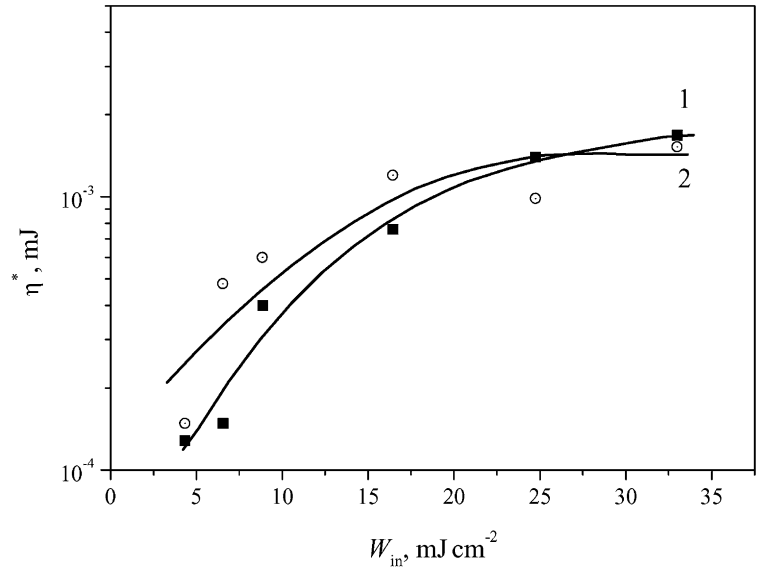

Fig. 3. The dependence of the first diffraction order response (η^*) on the input laser energy density (W_{in}) for PDLC based on COANP with 5 wt.% C_{70} (curve 1) and NPP with 1 wt.% C_{60} (curve 2). Spatial frequency was 100 mm^{-1}.

reverse saturable absorption to be revealed in the fullerene-doped organic structures based on COANP, that did not contradict the results of paper [27]. 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 laser beam.

Under the Raman–Nath diffraction conditions the thin phase holograms in the PDLC cell based on the fullerene-doped COANP and NPP compounds have been recorded. The corresponding curves are presented in Fig. 3. The concentration of fullerene C_{70} in COANP was 5 wt.% and that of C_{60} in NPP was 1 wt.%. Note that, 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. Some increase in the absorption of the NPP system after the addition of fullerene C_{60} is previously demonstrated in Ref. [13]. To eliminate the thermal nonlinearities, we have estimated the laser-induced refractive index using second harmonic of the pulsed Nd-laser (532 nm) in the pico-second range. Twice increase in it has been observed as the laser energy density increased in 10 times. The value of laser-induced Δn for PDLC cell based on fullerene-doped COANP is 0.75×10^{-3} at the laser energy density of 33 mJ cm^{-2} that is in five times more than the one observed by Khoo [24] in LC doped with dyes (only 0.16×10^{-3}). The laser-induced refractive index change was estimated using the relationship between diffraction efficiency and Δn from paper [28]. The large laser-induced change in refractive index influences the OL effect in PDLCs based on above mentioned photosensitive molecules, predicts the large increase in nonlinear coefficient n_2 and therefore gives an opportunity to apply these systems for conversion of laser radiation. It should be noticed that the change in refractive index can increase by an electrical control.

4. Conclusion

OL and holographic recording peculiarities in the π-conjugated organic fullerene-doped PDLC systems based on the PI6B, COANP, and NPP have been investigated in the nano-, pico-, and femtosecond regions. It has been established that fullerene-doped PDLC systems could be applied for OL at the incident laser energy density of more than 0.3–0.4 J cm^{-2}. It has been mentioned that the reverse saturable absorption mechanism, free-carrier absorption, LC reorientation effect, and scattering have been discussed to explain the OL in the fullerene-doped PDLC structures. Moreover, the spectral features, the reinforcement of donor–acceptor interaction, as well as the Förster mechanism should be included in this consideration.

It has been established that fullerene-doped PDLC structures can be used for hologram recording. The laser-induced refractive index has been estimated in the systems studied. The large laser-induced change in refractive index influences the OL effect in PDLCs based on these systems and predicts the large increase in nonlinear coefficient n_2. Therefore, it gives an opportunity to apply these systems for conversion of laser radiation.

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