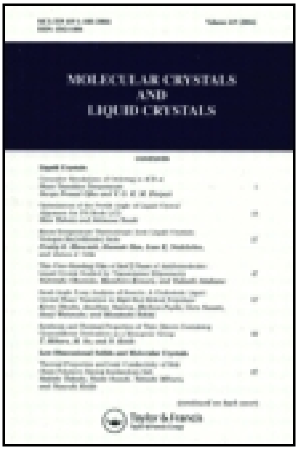

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Study of Dynamic and Nonlinear Optical Properties of Polyaniline-Fullerene-Liquid Crystal Structures

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Study of Dynamic and Nonlinear Optical Properties of Polyaniline–Fullerene–Liquid Crystal Structures

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In the present article, the characteristics of the polyaniline (PANI)-fullerene-nematic liquid crystal (NLC) have been studied. It has been noticed that dealing with nanostructured medium based on fullerene-doped PANI sufficiently accelerates transitional processes in a dispersed LC structure, causing the mesophase reorientation in shorter times.

A quasi-transition from the nematic phase to the smectic one has been observed. The registered switching times of the fullerene-containing NLC-systems are in the range of tens of microseconds, which is not peculiar to the substance in the nematic phase, and have been observed earlier in the smectic phase only. In addition, the nonlinear absorption of laser radiation has been established at a wavelength of 805 nm in the systems studied. These structures could be applied in human eye and optical device protecting systems.

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Keywords: fullerenes; laser-matter interaction; liquid crystal; nanotubes; nonlinear transmission; optical limiting; polyaniline; switching

1. INTRODUCTION

Electrooptical materials, such as liquid crystals (LCs), have been studied last two decades, because these compounds have been widely used in biology and medicine and intensively applied in optoelectronics, laser physics, telecommunication systems, and display technology. The area of problems, which has been successfully solved with the aid of LCs, is very broad. For example, these materials are used for the correction of phase aberrations, in light-controlled mirrors, in optical data storage systems, in LC displays of a new generation, etc. LC structures and spatial light modulators based on them are constantly modified and developed. Among the main LC element characteristics, the speed of an LC structure (switching time) is a very important characteristic which determines the working performance of organic LC elements for the displays and light modulators used in optical data processing systems. The strong requirement for the switching time is its minimum value. The problems connected with the optimization of the temporal characteristics of LC devices have been extensively studied by many research groups (see, e.g., [1–6]). It is clear that the optimum response cannot be achieved by only selecting the parameters of the system design. Solving this task requires the consideration of physical mechanisms related to the intermolecular interactions in complex multicomponent organic materials. A promising direction of research is related to the use of C_{60} or C_{70} fullerenes and nanotubes for accelerating the process of LC switching between the states with maximum and minimum birefringence [6–8]. From the physical point of view, the mechanism of the influence of a fullerene on the dynamic properties of organic nanocomposites is related to a change in the local specific polarizability of a medium and in the macroscopic polarization of the whole system [8] in the presence of fullerene molecules which are capable to accelerate the reorientation of anisotropic molecules under the external optical or electrical action. From the chemical point of view, the role of fullerenes is related to their ability for a reversible modification under the action of light, with the transition from neutral C_{60} and C_{70} molecules to their radical-ion forms [9]. From structural point of view, the nanoobjects adding provokes a change in the order parameters of a nematic LC. As the results, the quasi-smectic transition has been observed with less phase transition temperature [10]. Concerning the nanotubes, these nanoobjects can accelerate the properties of matrix materials due to an additional absorption of odd electrons from the top and from the body of nanotubes [11].

In the present article, the switching and the nonlinear optical properties of liquid crystal systems based on the polyaniline-fullerene complex have been investigated.

2. EXPERIMENTAL

The experiments were performed with LC cells of the S-type with an initial planar orientation. The electrooptical layer was based on standard NLC systems from the cyanobiphenyl group with positive values of the optical and dielectric anisotropy. In this study, NLC was modified by introducing donor–acceptor complexes, where the donor was represented by PANI and the acceptor by fullerene C_{60}. After mixing the components and their dispersion, a homogeneous blend has been obtained, in which the refractive index of NLC for the ordinary wave was matched with the refractive index of the photosensitive component. The drops of the photosensitive component dispersed in the NLC matrix had diameters within 30–100 nm. The cell thickness was about 10 µm. The fullerene content relative to the dry PANI weight was varied within 0.1–15 wt%. The sensitization was performed in order to shift the absorption spectrum of PANI toward the wavelength of a laser used in this study. To confirm the fact of complex formation, we studied the optical and mass spectra of the PANI–fullerene system. The mass spectrum of this system was considered in [6]. The LC cells were obtained using capillary forces which pulled the NLC into a gap with the width controlled by insulating spacers made of mica, teflon, or polyethylene. The orientation of the NLC layer was provided by different methods, for example, by the rubbing technique, by holographic way, and by the treatment of a surface electromagnetic wave [12]. The last way leads to a decrease of the applied voltage retaining switching parameters. The temporal (switching) and modulation characteristics were studied by measuring changes in the transmission of the radiation of a He–Ne laser ($\lambda = 633$ nm) through a cell placed between crossed polarizers. The electrooptical response has been registered at the first transmission oscillation and detected a transition to the neighboring extremum of the S-curve, which corresponded to a change in the phase shift by π. The cell has been treated by rectangular pulses with the amplitude $A = 10$–50 V, duration $\tau_{\text{sup}} = 1$–30 ms, and repetition rate $1/T = 0.5$–200 Hz.

To study the nonlinear optical transmission, the femtosecond pulsed irradiation of a quasi-CW Ti-sapphire laser at a wavelength of 805 nm (with a pulse width of 30 fs, a repetition frequency of

82 MHz, and a power of 150 mW) was used. The sport diameter of the laser beam was 2 mm. Calibrated filters were used to vary the input power intensity.

3. RESULTS AND DISCUSSION

The basic results of this study are shown in Figures 1–4. A general views of the films obtained based on the materials treated are presented in Figure 1. To reveal the quasi-smectic structures, the different fullerene contents have been used. Figure 2 illustrates the schematic diagram showing the PANI–C_{60} charge–transfer complex responsible for the possible transition of a nematic LC into a quasi-smectic one. Figure 3 presents the plots of the temporal characteristics of the system versus the supply voltage amplitude. It should be mentioned that the other monomer and nanocrystalline structures of the organic compound–fullerene–liquid crystal type were characterized by close values of the switching times (see, e.g., [6,8]).

In the system without fullerenes, the donor-acceptor complex responsible for the reorientation of LC molecules is absent. As a result, non-sensitized LC–PANI structures exhibited the disordering upon the application of electric pulses. Apparently, the formation of a donor–acceptor complex (and the related structure possessing a large dipole moment and a higher polarizability [8]) favors a more regular and homogeneous distribution (dissolution) of the photosensitive component in the LC volume. We suggest the following interpretation of the acceleration of dynamic processes in the LC–PANI–fullerene system.

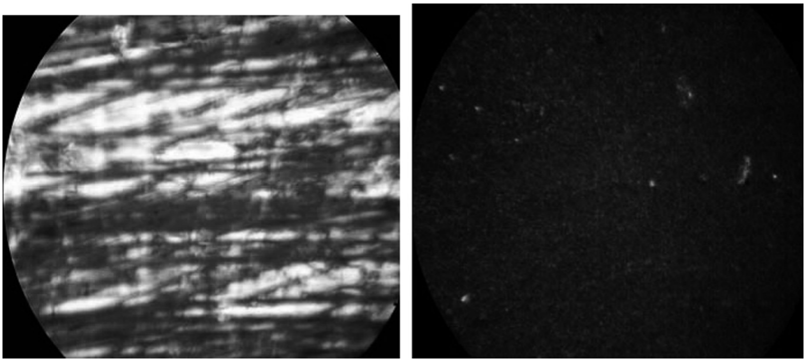

FIGURE 1 A microphotograph showing the structure of the NLC–PANI–C_{60} system (the size along the X axis is $\sim$220 μm). The fullerene content was 6 wt% (left photo) and 15 wt% (right photo). The last image has been obtained at cross polarizers.

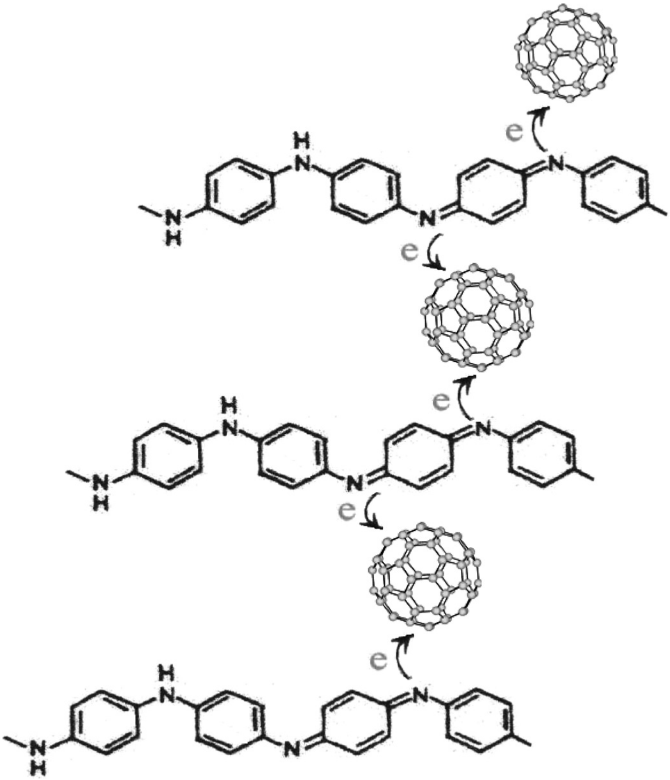

FIGURE 2 Schematic diagram showing the PANI–C_{60} charge–transfer complex responsible for the possible transition of a nematic LC into a quasi-smectic one.

The introduction of an organic (donor)–fullerene (acceptor) complex, representing a charge-transfer complex with an additional dipole moment and increased local polarizability (per unit volume of the sensitized medium), can accelerate the process of reorientation (switching) of molecules in the system. The creation of this additional dipole moment is probably favored by the effective charge generation in the structures (e.g., containing PANI) under the action of light which enhances the effective charge separation between the donor (PANI) and fullerene, thus increasing the polarization of the whole system. Thus, the orientation of the LC proceeds under the conditions when an additional distributed donor–acceptor (PANI-fullerene) complex can be included, which leads to a significant acceleration of the system response and enhances the speed of the LC cell. This fact was confirmed by the results of investigations of the dependence of

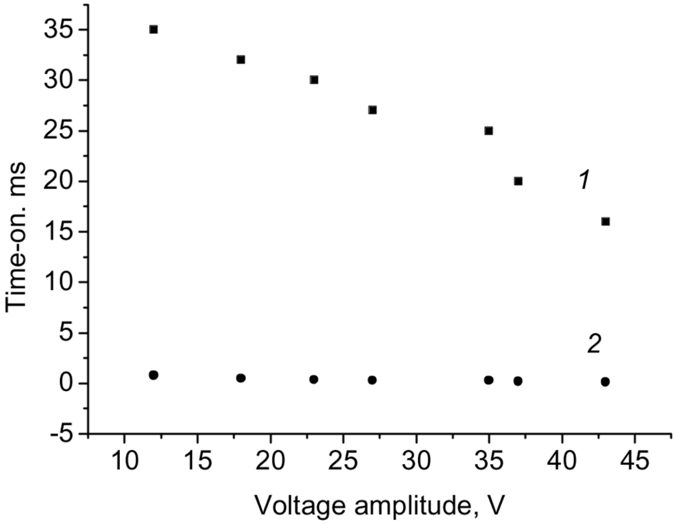

FIGURE 3 Dependence of the time-on on the amplitude of a supply voltage pulse for the LC-systems with the complexes based on PANI–C_{60}. The initial characteristics (1) and the ones after the self-arrangement (2).

the response switch-on and -off time on the amount of the introduced fullerene. It was found that an increase in the content of fullerene (at least within 0.5–6 wt.% relative to the content of PANI) leads to a decrease in the switching time, which is probably related to an increase in the number of charge-transfer complexes involved in the reorientation of LC dipoles. Moreover, the introduction of donor-acceptor complexes leads in some time to the NLC separation into quasi-smectic layers, that is, to a self-organization of the system stimulated by the intermolecular complex formation.

This effect has been checked for some polymer and monomer materials (see, e.g., [6,8]) featuring intramolecular donor–acceptor interactions in the matrix. An analogous separation of the NLC structure into domains was observed upon the introduction of the PANI–fullerene complex (see Fig. 1). It should be mentioned that the fullerene doping with a large content decreases the contrast of the systems studied. Thus, the compromise between switching and contrast should be carefully checked. The data confirmed this evidence are presented in Table 1. It should be mentioned that the appropriate characteristics have been observed at a fullerene concentration close to 0.5 wt.%. Above the fullerene concentration of 0.5 wt.%, the contrast ratio of the system decreases drastically. However, as can be seen from these

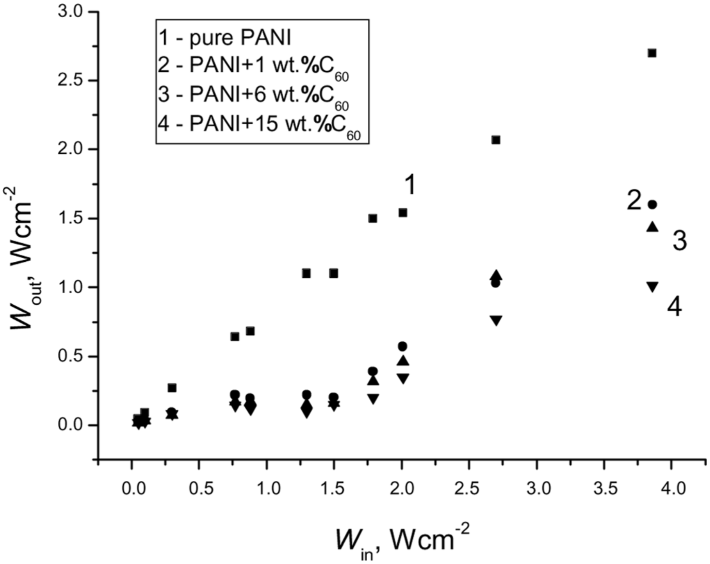

FIGURE 4 Dependence of the output power density (W_{out}) on the input one (W_{in}) for the films based on NLC-PANI-C_{60} systems with fullerene contents: 0 wt.% (1); 1 wt.% (2); 6 wt.% (3); 15 wt.% (4). The wavelength was 805 nm, and the laser pulse duration was 30 fs. The laser sport diameter was 2 mm.

experimental data, the temporal characteristics of the NLC are significantly improved by the introduction of photosensitive charge-transfer complexes which more strongly influence the rate of NLC switching after the additional self-organization. It should be noted that the switching times of the cells based on the self-organized structures were two orders of magnitude less than those in the analogous fullerene-free cells studied previously (see Fig. 3). Thus, the use of fullerenes ensures the transition from the milli- to microsecond range of

TABLE 1 Switching Time vs. Contrast Ratio (in Crossed Polarizers) at Different Fullerene Concentrations in the Nematic LC Cell Based on PANI-C_{60} Complex

Structure	Fullerene content, wt.%	Time-on, μs	Time-off, μs	Contrast ratio
LC-PANI-C_{60}	0.1	250	420	87
	0.5	200	380	79
	1	170	300	59
	6	165	280	55

TABLE 2 The Speed of Modified NLC

Modified LC compound	Thickness of the layer, μm	Laser wavelength, nm	Supply voltage	t_{on}/t_{off}, ms	Ref.
NLC + orange dye	30	514.5		20	[13]
NLC (LC drops of diameter 100 nm in polymer matrix)	12–16			Theoretical prognosis to optimize the response	[1]
NLC + dipentaerythrol hydroxypenta acrylate (DPHPA) + stabilizer	13–16	632.8	Positive pulse 1/T = 100 Hz	0.5/0.7	[3]
NLC + PMMA + azodye	36	Ar + -record, 633-readout	A = 100 V, 1/T = 100 Hz	5/5	[14]
NLC + dye (DRed-1)	32	532 and 670		74	[4]
NLC + rhodamine 6 G; LC-polymers; separated systems of photolayer-LC	15	532	cw 10 V	10/100	[15]
Photolayer-NLC, sensitization with a fullerene mixture $C_{60} + C_{70}$	5–10	532	30–50 V, 30–300 ms 1/T = 0.2–7 Hz	5–10	[16]
COANP + C_{60} + NLC + plasticizer	10–12	633	25–50 V,30–60 ms, 1/T = 50 Hz	6–2.5/15–10	[17]
COANP + C_{70} + NLC	10–12	532		Possible model to re-orient LC dipole	[18]
NLC + COANP + C_{70} and NLC + polyaniline + C_{60} (after self-organization)	10–12	633	25–50 V, 3–30 ms, 1/T = 25–2000 Hz	0.05/0.2	[6,8]
NLC + C_{60} + Me-part and CN-group in PVK-phenyl derivative chromophores	10–12	633	10–50 V, 1–30 ms, 1/T = 25–100 Hz	0.07/0.2	[19]

switching parameters, which is characteristic of smectic LCs. It should be mentioned that the commercial NLCs used by different companies to develop new display elements reveal the switching parameters in the range of 4–16 ms at an element thickness of 1–3 μm. The switching results presented by different research groups are shown in Table 2. Subsequently, we are planning to study the change in the order parameter in the NLC-PANI-C_{60} system using NMR techniques. Previously, this method provided the data on an increase in the order parameter in the LC system based on a charge-transfer complex between 2-cyclooctylamine-5-nitropyridine (COANP) monomer and fullerene [10].

It should be mentioned that an additional absorption of light due to the complex formation has been found in the optical limiting experiment. To study the nonlinear transmission, the dependence of the output energy density (W_{out}) on the input one (W_{in}) for the films based on NLC–PANI–C_{60} systems with different fullerene contents has been measured. It should be remembered that the wavelength was 805 nm and the laser pulse duration was 30 fs. Moreover, it should be mentioned that, for pure fullerene structures, the transition of 1.6 eV ($\sim$805 nm) is forbidden. Analyzing the results showed in this nonlinear optical study, one can say that it is a promising way to develop a new optical attenuator in the near infrared spectral range using NLC–PANI–C_{60} compounds. The level of the attenuation and the value of the output energy density provoke the future investigation of the optical limiting effect to protect human eyes and technical devices from a high-intensity laser irradiation.

4. CONCLUSIONS

Firstly, we have studied the influence of fullerene-containing charge-transfer complexes between PANI and C_{60} on the switching time of NLC cells. The switching times on a microsecond level are obtained, and the structural changes in the LC mesophase sensitized by the fullerene-containing donor–acceptor complexes are demonstrated.

Secondly, the nonlinear transmission has been observed in the near infrared range at a wavelength of 805 nm. The obtained nonlinear transmission characteristics of the new organic materials are significantly superior to those of the traditional matrix components, which makes the fullerene- or nanotubes-doped compositions compatible with silicon-based ones, which are widely used in nonlinear optics, solar power engineering, absorption spectroscopy, medicine, and photonics.

The direction of research is of interest both from the standpoint of practical applications of novel nanomaterials and due to the possibility of a deeper insight into the basic processes in sensitized LC media interacting with light (in particular, with laser radiation), with a surface (under the condition of the presence or absence of aligning agents), and with various organic and inorganic inclusions into the mesophase, including biological objects.

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