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Diffraction efficiency enhancement caused by employing liquid crystal phthalonitrile derivative in nematic liquid crystals

O. Köysal [a,*], M. Okutan [a], S.E. San [a], M. Durmuş [b], F.N. Ecevit [a], V. Ahsen [b]

[a] *Department of Physics, Gebze Institute of Technology, P.O. Box 141, Gebze 41400, Kocaeli, Turkey*
[b] *Department of Chemistry, Gebze Institute of Technology, P.O. Box 141, Gebze 41400, Kocaeli, Turkey*

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Abstract

The change of refractive index, originated by photoinduced molecular reorientation, brings about a significant diffraction capability in E7 coded nematic liquid crystal system doped by 2,3-dicyano-1,4-di[3,4,5-tri(dodecyloxy)phenylcarbonyloxy]benzene (DCDPB) which is called as liquid crystal phthalonitrile derivative. Results of a grating diffraction experiment are reported for the constructed sample. The accessible diffraction efficiency, η, is roughly of the order of 10% under the optimum conditions and analysed results propose this novel system to be appropriate and promising for the excitation wavelength of a 632.8 nm He–Ne laser.

Keywords: Nematic liquid crystal; Phthalonitrile derivative; Grating diffraction

1. Introduction

Intensive research continues in the development of holographic and diffractive optical devices for integrated optics, displays and optical data storage. Holography is a promising candidate for storage of high density information as well as recording of three dimensional objects. Recently, numerous reports have concentrated on the development of materials with high diffraction efficiency, resolution and sensitivity [1–4]. Due to their large and broadband birefringence, liquid crystals (LCs) are excellent materials for use in these optical devices. The difference in refractive indices, for fields polarized along, and perpendicular to, the director axis brings about a large birefringence property, which is an advantage for various applications [5]. Director axis reorientation based effects causing a change of refractive index and showing several interesting dynamic and storage wave-mixing effects have been extensively studied [5–11]. Compared with others, LC based systems require lower characteristic voltages to be applied for the realization of molecular gratings and relatively lower light power for efficient modulation of refractive index. It is experimentally proven that doping a small amount of agent decreases the required threshold of molecular reorientation further in LC materials [12–14]. This phenomenon has potential applications such as holographic data storage. Because of the large broadband birefringence of nematic liquid crystals, it is obvious that these highly sensitive films could be applied in a variety of image processing systems operating with low optical power.

Phthalonitrile derivatives are known precursors to phthalocyanines, an important class of molecules with various application possibilities in sensors, catalysis, non-linear optics, optical data storage, photodynamic cancer therapy and nanotechnology [15,16]. On the other hand, liquid crystalline phthalonitrile derivatives, having a large negative dielectric anisotropy value, are being used for liquid crystal displays [17–20]. Phthalonitrile polymers also demonstrate potential as high-temperature polymers for use in a wide variety of

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* Corresponding author. Tel.: +90 262 6538497; fax: +90 262 6538490.
E-mail address: oguzkoysal@gyte.edu.tr (O. Köysal).

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the applications such as composite matrices, adhesives and electrical conductors [21–25].

In this work, we have investigated the optical behaviour of 2,3-dicyano-1,4-di[3,4,5-tri(dodecyloxy)phenylcarbonyloxy] benzene (DCDPB) in E7 nematic liquid crystal as well as their contribution to reorientation efficiency. We have performed the two-wave-mixing experiment where the diffraction efficiency was measured as a function of applied DC voltage. Accessible diffraction efficiency η is found to be ~10% by using He–Ne lasers for nematic–discotic mixture while it is only 3% for pure nematic LC.

2. Experimental

2.1. Materials

3,4,5-Tri(dodecyloxy)-1-benzenecarbonyl chloride (1) was prepared according to literature procedure [26]. 2,3-Dicyanohydroquinone and all other reagents and solvents were reagent-grade quality and were obtained from commercial suppliers and were dried as described in Perrin and Armarego before use [27]. Elemental analyses were obtained from Carlo Erba 1106 instrument. Infrared spectra in KBr pellets were recorded on a Bio-Rad FTS 175C FT-IR spectrophotometer. The mass spectra were acquired on an LCQ-ion trap (Thermofinnigan, San Jose, CA, USA), equipped with an electrospray source. Electrospray full scan spectra, in the range of *m/z* 50–2000 amu or *m/z* 2000–3000 amu, were obtained by infusion through fused silica tubing at 2–10 μL min^{-1}. The solutions were analysed in positive mode. The LCQ calibration (*m/z* 50–2000 amu) was achieved according to the standard calibration procedure from the manufacturer (mixture of caffeine, MRFA and Ultramark 1621). An ES-Tuning Mix solution (Agilent) was used to calibrate the spectrometer between 2000 and 3000 amu. The temperature of the heated capillary of the LCQ was set to the range of 180–200 °C, the ion spray voltage was in the range of 1–7 kV with an injection time of 5–200 ms. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions on a Bruker 500 MHz spectrometer using TMS as an internal reference.

2.2. Synthesis of 2,3-dicyano-1,4-di[3,4,5-tri(dodecyloxy)phenylcarbonyloxy]benzene

Steps of phthalonitrile derivative synthesis are sketched in Fig. 1. To a stirring mixture of 3,4,5-tri(dodecyloxy)-1-benzenecarbonyl chloride (1) (2.98 g, 4.3 mmol) in 10 ml of dry THF and triethylamine (1.74 g, 17 mmol) was added dropwise a solution of 2,3-dicyanohydroquinone in 10 ml of dry THF. This mixture was stirred at room temperature for 12 h. The THF was completely evaporated under reduced pressure. The white solid residue was dissolved in CH_2Cl_2 (100 ml) and the residue was removed by filtration. CH_2Cl_2 solution was extracted with water, dried with Na_2SO_4 and filtered. CH_2Cl_2 was removed. The crude white product was recrystallized from CH_2Cl_2/*n*-heptane (1:10). The crystals were filtered, washed with *n*-heptane and dried. Yield: 1.92 g (67%). M.p.: 74 °C. IR: $\nu_{\max}$ cm^{-1} (KBr pellet); 3124 (Ar CH), 2924 and 2854 (CH_2), 2230 (C≡N), 1743 (C=O), 1592 (C=C), 1464, 1339, 1247, 1181 (C–O–C), 742 (N–O). ^{1}H NMR ($CDCl_3$) δ ppm: 0.89 (t, 18H, CH_3), 1.29 (m, 84H, CH_2), 1.50 (m, 12H, OC–CH_2–CH_2), 1.77 (m, 12H OC–CH_2), 4.07 (t, 12H, OCH_2), 7.44 (d, 4H, Ar H), 7.85 (d, 4H, Ar H); ^{13}C NMR ($CDCl_3$) δ ppm: 14.13 (CH_3), 22.70 (CH_2), 26.08 (CH_2), 29.26–30.35 (CH_2), 31.95 (CH_2), 69.32 (OCH_2), 73.71 (OCH_2–CHO), 108.92 (Ar CH), 110.66 (Ar C), 111.70 (C≡N), 121.45 (Ar C), 128.63 (Ar CH), 144.10 (Ar C), 150.74 (Ar C), 153.17 (Ar C), 163.20 (Ar CO). MS (ES-MS), *m/z* (%): 1474 $[M+H]^{+}$.

2.3. Sample preparation and experiment

Before the construction of the cells, indium tin oxide (ITO) covered glass substrates were spin coated with polyamide layers (~100 nm) and then unidirectional rubbing was performed with a soft cloth in order to obtain alignment of LC molecules. The ultimate form of the constructed cell is

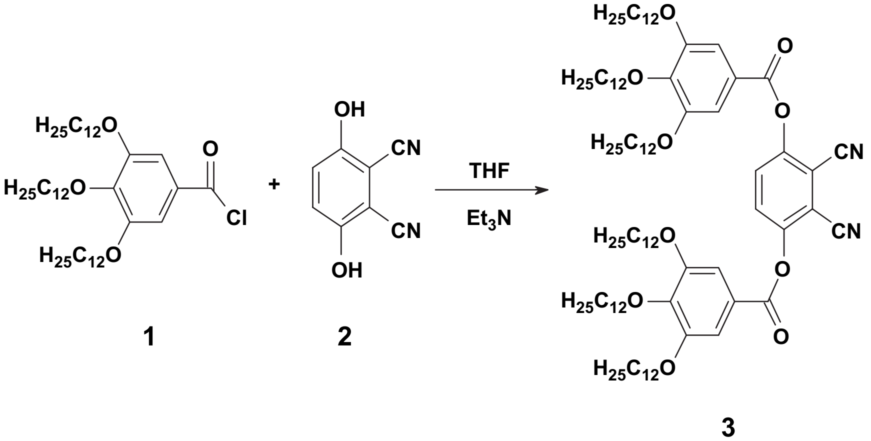

Fig. 1. Synthesis of phthalonitrile derivative.

planar with roughly ~2° rubbing tilt. Measurement cells were made up of two glass slides separated by Mylar sheets having ~6.2 μm thickness. These cells were filled in capillary action with the samples mixed in ultrasonic water bath for 30 min and chemical formulas of used E7 nematic host and dopant DCDPB are depicted in Fig. 2a and b, respectively. Two samples were prepared; one of them contains pure E7 which was purchased from Merck, the other one was filled with E7 + DCDPB 1% (w/w). The optical texture image of DCDPB (Fig. 3a) and E7 + DCDPB mixture (Fig. 3b) is obtained by using a polarized microscope at room temperature. The optical texture image of pure DCDPB reveals that it is discotic phase whereas the E7 + DCDPB mixture is nematic phase under the same conditions. Therefore, this mixture can be regarded as nematic LC. As the absorbance spectra of pure and mixture samples show the same characteristic, only absorbance spectra of the mixture is given in Fig. 3c. The experimental set up for grating diffraction study is shown in Fig. 4. It consists of a pumping source He–Ne laser (632.8 nm), which is divided into two components having approximately equal power by a beam splitter. Polarization of laser is arranged to be parallel to preliminary orientation of LC molecules. The intersection angle of two beams 2θ ~3° is used with corresponding grating constant $\Lambda \sim 24$ μm for He–Ne. Since $\Lambda^2 \gg \lambda d$, diffraction can be considered in the Raman–Nath regime.

3. Results and conclusion

In this work, low power He–Ne laser induced dynamic phase grating formation has been studied on 1% DCDPB doped in nematic liquid crystal E7 under applied DC voltage. The speciality of the examined LC system is mainly the doping a discotic LC agent in nematic LC. This approach is used in this application for the first time as far as author's knowledge.

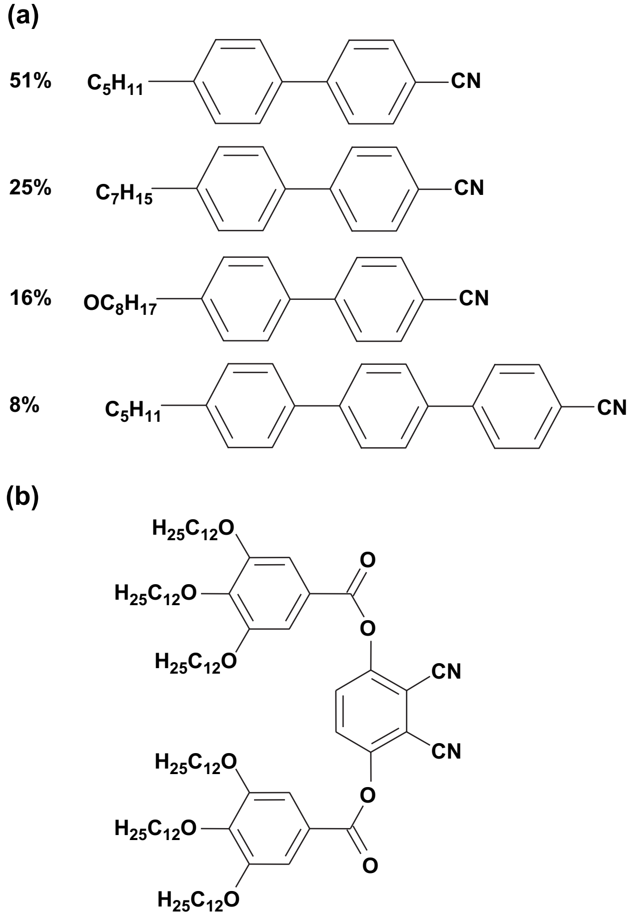

Fig. 2. Chemical formulas of: (a) nematic host, E7; (b) liquid crystal phthalonitrile derivative (DCDPB).

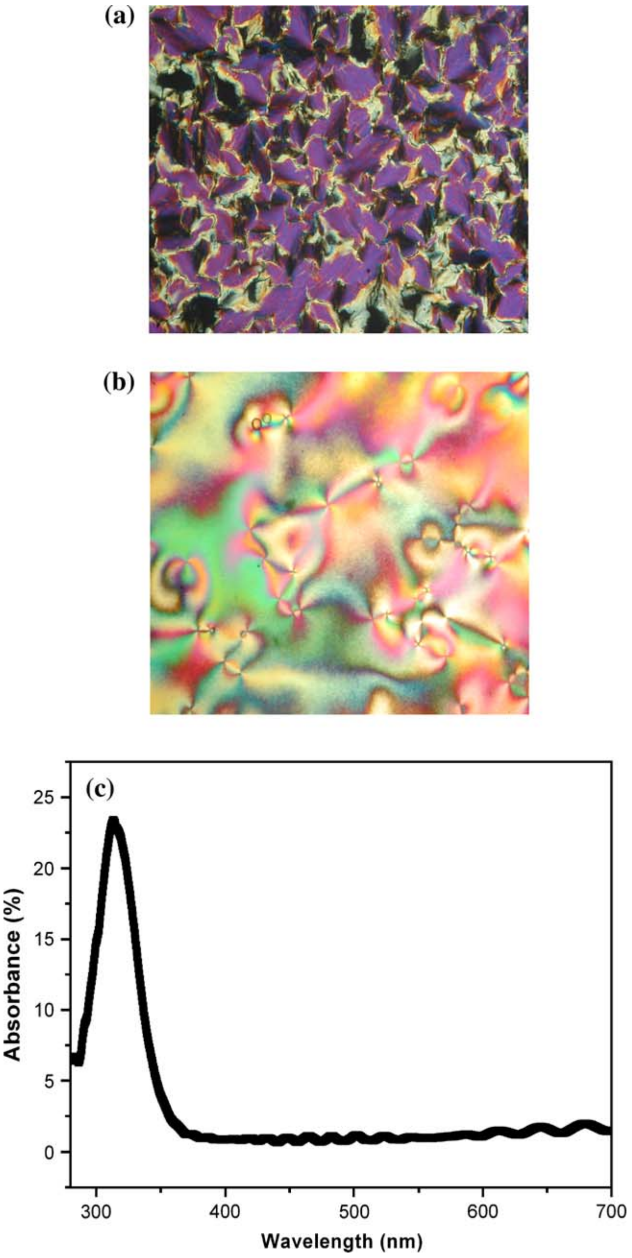

Fig. 3. Optical texture, using polarizing microscope at room temperature, of (a) pure liquid crystal phthalonitrile derivative (DCDPB) and (b) phthalonitrile derivative (DCDPB) 1% (w/w) doped in host E7 mixed sample. (c) Absorbance spectra of the mixed sample (E7 + DCDPB).

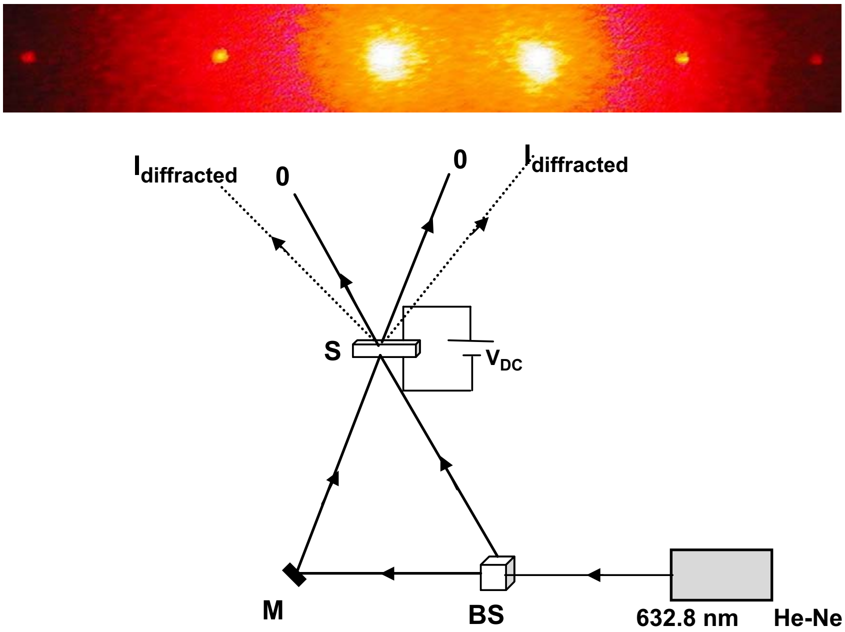

Fig. 4. Schematic diagram for two-wave-mixing set up (inset: photographs of self-diffraction spots). BS: beam splitter, M: mirror, S: sample.

Grating diffraction experiments are the basis for performance evaluation of holographic applications. Therefore, the character of the systems was investigated in terms of the diffraction signals depending on applied DC voltage. The origin of diffraction is the molecular reorientation taking place in bright regions and grating is formed with bright–dark periodicity reinforced by interference pattern. Self-diffraction spots were considered in experiments and diffraction efficiency η was calculated as the intensity ratio of the first-order diffraction beam to the incident beam in the absence of one side of the two beams. For the constructed system, diffraction efficiency is ~10% (±1%) under optimum circumstances when the intersection angle of beams $2\theta = 3°$, $V_{DC} = 4.5$ V for beam power ~10 mW (±0.1 mW). Fig. 5 demonstrates the dependency of diffraction signals on the applied DC voltage. As it can be seen, diffraction efficiency is significantly enhanced in the DCDPB doped sample. Since the diffraction efficiency depends on optical anisotropy in Raman–Nath regime, the high diffraction efficiency occurred in mixed sample.

Possible reorientation mechanisms are not considered in detail in the scope of this work, while the change of optical anisotropy that is one of the most obvious properties of LCs is considered as the dominant factor of reorientation enhancement according to our experimental observation and from the absorbance spectra of the mixture. Addition of DCDPB increased effectively the absolute value of optical anisotropy. In this system, phthalonitrile derivatives DCDPB play important role in evaluating the holographic grating and the diffraction efficiency η enhancement as various dye doped LCs did in previous works [8,12].

The obtained results and the performance evaluation of the system reveal the promising and compatible character of this doping in similar applications.

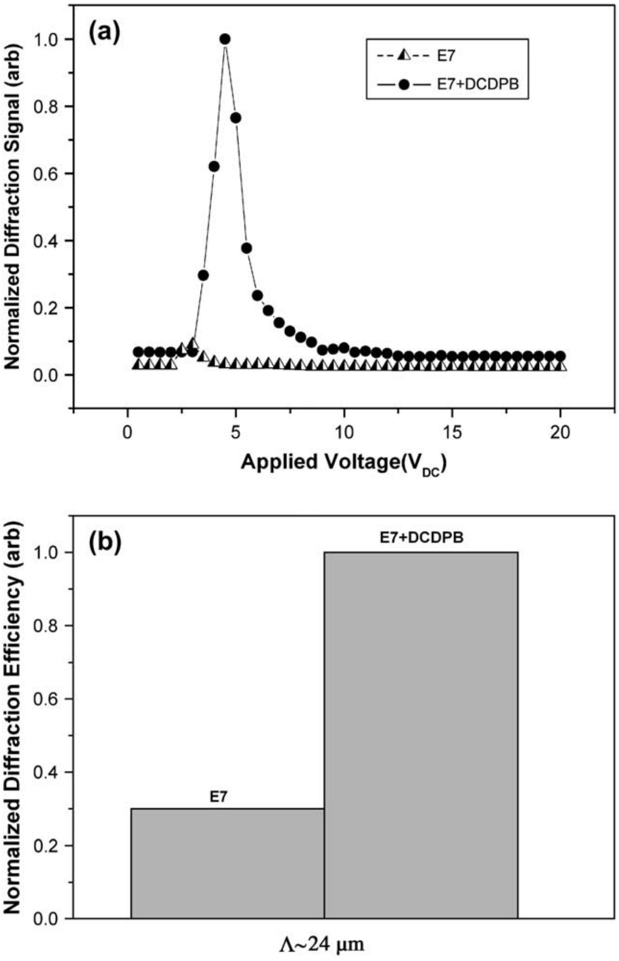

Fig. 5. (a) Normalized diffraction signals versus applied DC voltage with He–Ne laser. Experimental conditions: $2\theta \sim 3°$, pumping beams, $I_0 = 10$ mW;s (b) relative values of obtained diffraction efficiencies.

Acknowledgment

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