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Dielectric anisotropy, and diffraction efficiency properties of a doped nematic liquid crystal

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Abstract

The dielectric anisotropy and diffraction efficiency properties of E7 liquid crystal and SPCI-C7 doped liquid crystal composite have been investigated. The dielectric constant components ($\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$) in the nematic phase of E7 were measured as a function of frequency. The liquid crystals exhibited dielectrically-controlled positive dielectric anisotropy (p-type $\Delta\varepsilon$) with transition to negative dielectric anisotropy (n-type $\Delta\varepsilon$). SPCI-C7 doping lowered dielectric anisotropy and increased the diffraction efficiency of E7. The refractive index modulation values of E7 and E7/SPCI-C7 were $\Delta n = 3.9 \times 10^{-3}$ and $\Delta n = 6.95 \times 10^{-3}$, respectively, and this parameter was increased by doping.

Keywords: Liquid crystal; SPCI-C7; Dielectric anisotropy

1. Introduction

Liquid crystals (LCs) have become extremely important in several key areas of flat panel displays and fiber-optic communication [1]. Dielectric spectroscopy is a powerful method for the investigation of liquid crystals [2–4] and enables the dielectric anisotropy properties of such compounds to be determined. Dielectric anisotropy ($\Delta\varepsilon$) is one of the most important physical properties of liquid crystalline compounds, which in essence determines the lower threshold voltages of liquid crystal displays (LCDs) [5].

With the development of multimedia liquid crystal displays, a strong demand has been created for new liquid crystalline materials with clearing temperature, high dielectric anisotropy and low viscosity [6]. Liquid crystal mixtures with a positive dielectric anisotropy are used for most active matrix displays and the image quality of liquid crystal displays is strongly dependent on the dielectric anisotropy of the LC. The fact that a new class of material with appropriate physical and optical properties is created is very important for the development of LCs.

The aim of this study was to investigate the dielectric anisotropy, memory state and diffraction efficiency properties of SPCI-C7 doped nematic liquid crystal.

2. Experimental

2.1. Synthesis of SPCI-C7

4″-(4‴-Heptyloxyphenylimino)phenyl-1′,3′,3′-trimethylspiro [2*H*-1-benzopyran-2,2′-indoline]-6-yl carboxylate (*SPCI-C7*) was synthesized by condensation of 6-carboxy-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (*SP-COOH*) with 4-(4′-heptyloxyphenylimino)phenol (*HOPIP*) in methylene chloride, in the presence of dicyclohexylcarbodiimide (DCC) and 4-*N*,

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N-dimethylaminopyridine (DMAP). SP-COOH and HOPIP were prepared by known procedures [7,8].

2.1.1. 4″-(4‴-Heptyloxyphenylimino)phenyl-1′, 3′,3′-trimethylspiro[2H-1-benzopyran-2, 2′-indoline]-6-yl carboxylate, SPCI-C7

Yield 25%; M.P. 125 °C [7]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 3H), δ 1.20 (s, 3H), δ 1.33 (s, 3H), δ 1.34−1.59 (m, 8H), δ 1.82 (m, 2H), δ 2.76 (s, 3H), δ 4.03 (t, 2H), δ 5.79 (d, 1H), δ 6.57 (d, 1H), δ 6.81 (d, 1H), δ 6.88 (t, 1H), δ 6.95 (d, 1H), δ 6.98 (d, 2H), δ 7.10 (d, 1H), δ 7.19 (t, 1H), δ 7.19 (d, 2H), δ 7.25 (d, 2H), δ 7.84 (d, 2H), δ 7.95 (s, 1H), δ 7.98 (d, 1H), δ 8.40 (s, 1H). High-resolution MS: calculated for $C_{40}H_{42}N_2O_4$ 614.3145; found 614.3168.

2.2. The preparation of liquid crystal cells

The measurement cells comprised two glass slides separated by Mylar sheets of 6.2 μm thickness. Before construction of the cells, indium tin oxide (ITO) coated glass substrates were spin coated with polyvinyl alcohol at 2000 rpm and cured at 50 °C for 2 h. The thickness of the coating was 100 nm and the coated layers were exposed to unidirectional rubbing with velvet in order to obtain preliminary molecular orientation. The ultimate form of the constructed cell was planar with a 2° rubbing tilt.

SPCI-C7 was dissolved in toluene and the toluene fraction was then evaporated to secure SPCI-C7 powder, which later was mixed with the nematic host E7 (1%) using ultrasound. Pure E7 and SPCI-C7 doped liquid crystal was injected into the sample cells by capillary action at room temperature. The formula of SPCI-C7 and the nematic host is depicted in Fig. 1. The experimental set-up is shown in Fig. 2. An HP 4194 Impedance Analyzer was used and measurements were performed at room temperature with high accuracy (0.17% typ.) [9].

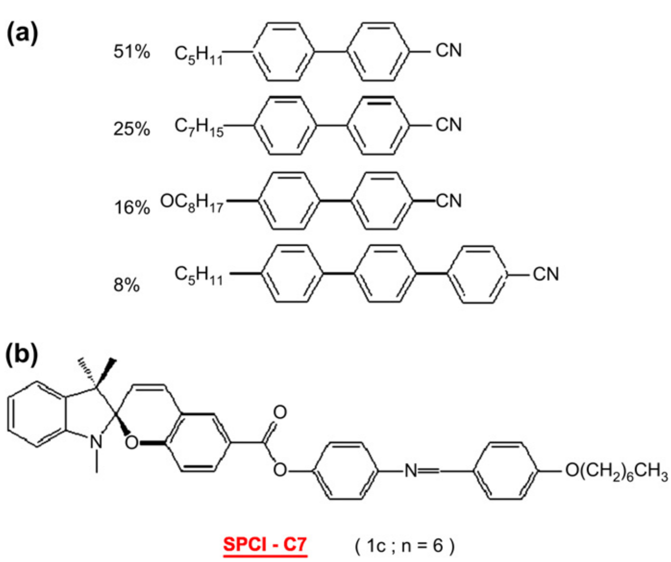

Fig. 1. Chemical formula of: (a) Nematic host, E7 and (b) SPCI-C7.

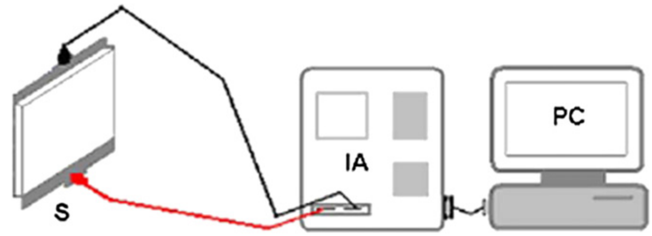

Fig. 2. Experimental set-up for electrical measurements. S: sample; IA: impedance analyzer.

3. Results and discussion

3.1. Dielectric anisotropy properties of E7 and E7/SPCI-C7 LCs

The dielectric constant dependence of the applied voltage at various frequencies is shown in Fig. 3. The voltage applied to the LC reoriented the LC molecules. Initially, the dielectric constant increased slowly with increasing voltage up to a certain voltage and then increased drastically and finally reached a constant value. This behavior is the so-called Frederiks threshold. The increase in dielectric constant is probably due to molecular reorientation as the dielectric constant depends on external effects due to the anisotropic nature of the LC. There are two types of dielectric anisotropy in LCs:

- positive or p-type, when $\Delta\varepsilon > 0$ in which the molecules align parallel to the applied electric field;
- negative or n-type, when $\Delta\varepsilon < 0$, in which the molecules align perpendicular to the applied field [10,11].

The dielectric anisotropy for the LC is expressed by the following relationship [12]:

$$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} \tag{1}$$

where $\varepsilon_{\parallel}$ is the parallel and $\varepsilon_{\perp}$ is the perpendicular part of the dielectric constant. In order to obtain the dielectric anisotropy value of the LC studied, the capacitance of the liquid crystal cell was measured as a function of applied voltage. Because of the energetic requirements of supporting elastic deformations, below a particular voltage, the liquid crystal will not deform. The point at which the cost of creating elastic distortion equals the energy of the applied field is referred to as the Frederiks transition, V_{th}. At applied voltages lower than V_{th}, the capacitance measured is $C_{\perp}$ (since the director is perpendicular to the electric field) and gives $\varepsilon_{\perp}$ ($C_{\perp} = \varepsilon_0 \varepsilon_{\perp} A/d$). At applied voltages much higher than the Frederiks transition ($V > 3V_{th}$), the capacitance can be plotted as a function of V_{th}/V. By linearly fitting the data, the intercept $V_{th}/V = 0$ gives the capacitance $C_{\parallel}$ (i.e., the director is parallel to the electric field) which yields $\varepsilon_{\parallel}$ [11,13−16]. In order to calculate the $\varepsilon_{\perp}$ and $\varepsilon_{\parallel}$ values of the LC studied, plots of ε as a function of voltage at various spot frequencies were constructed (Fig. 3). The dielectric anisotropy $\Delta\varepsilon$ values were determined from these figures and are given in Table 1.

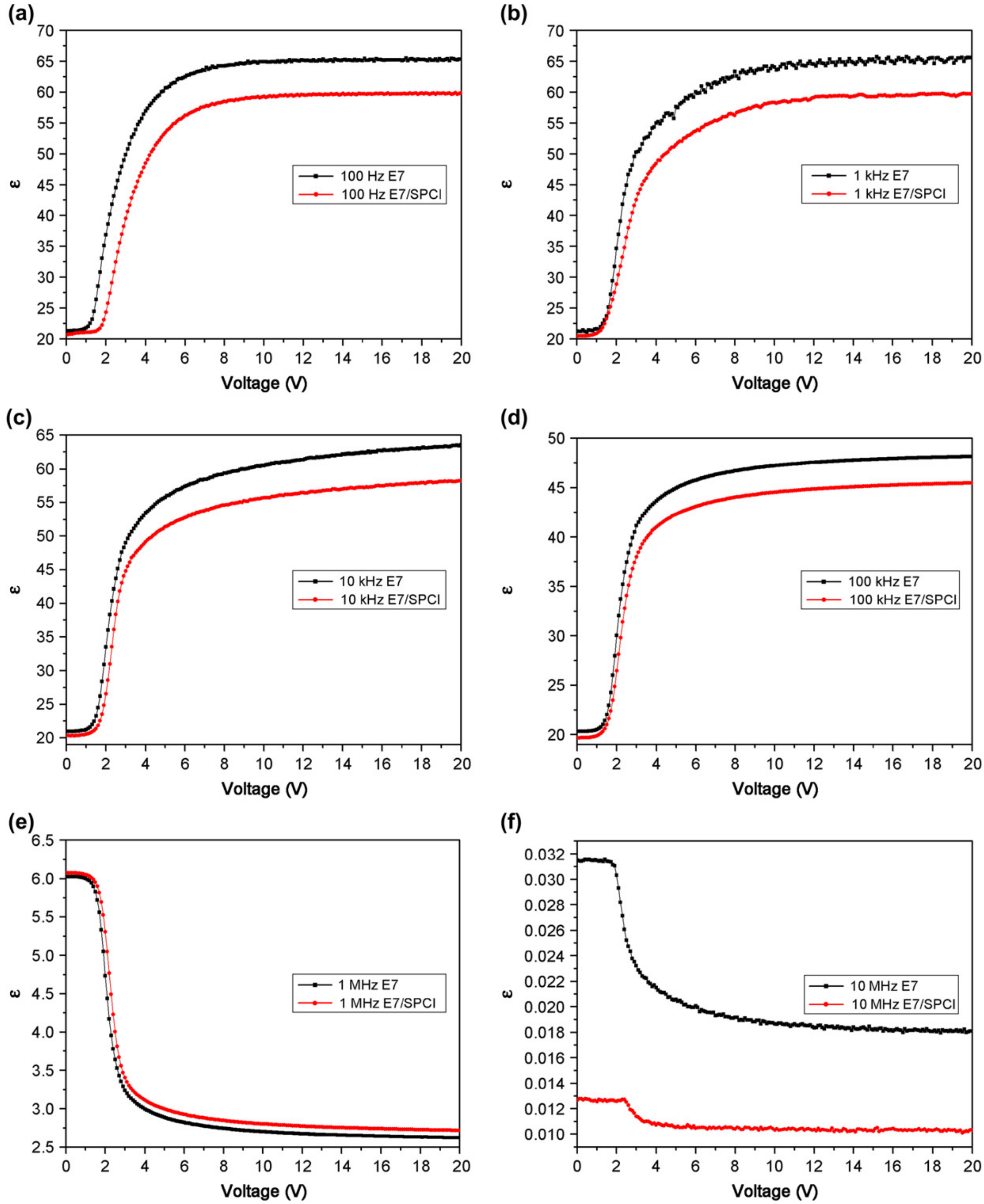

Fig. 3. The plots of dielectric constant vs applied voltage at various frequencies.

The E7 and E7/SPCI-C7 liquid crystals exhibited positive dielectric anisotropy up to 1 MHz and, above 1 MHz, the LC's displayed negative dielectric anisotropy. When an electric field of direction E is applied to E7 and E7/SPCI-C7 LCs, a torque effect acts on the molecules due to the LCs dielectric anisotropy; the torque tends to align the molecule parallel to the applied field. When the field is strong enough, the molecules will be aligned almost parallel to the field. Thus, E7/SPCI-C7 shows p-type dielectric anisotropy. The dielectric anisotropy values of E7 are higher than that of E7/SPCI-C7 and so the SPCI-C7 doping lowers the dielectric anisotropy values of E7.

3.2. Memory effect of E7 and E7/SPCI-C7 LCs

The variation of the conductivity of E7 and E7/SPCI-C7 liquid crystals at various voltages is shown in Fig. 4. On the

Table 1
The dielectric anisotropy values of the E7 and E7/SPCI-C7 cells

f	$\Delta\varepsilon$ for E7	$\Delta\varepsilon$ for E7/SPCI-C7
100 Hz	43.58	38.35
1 kHz	42.68	37.17
10 kHz	39.44	34.98
100 kHz	26.78	24.23
1 MHz	−3.31	−3.250
10 MHz	−0.013	−0.0023

logarithmic scale, electrical conductivity increased with increasing frequency and reached a plateau which showed that both the E7 and E7/SPCI-C7 liquid crystals have a memory. This memory start time varied according to applied voltage; as the start state of both the E7 and E7/SPCI-C7 liquid crystals was almost the same, it appears that doping with SPCI-C7 does not influence the memory state of the LC.

3.3. The diffraction efficiency of the E7/SPCI-C7

Fig. 5 shows the experimental arrangement used for two-wave mixing and comprised an He–Ne ($\lambda = 632.8$ nm)

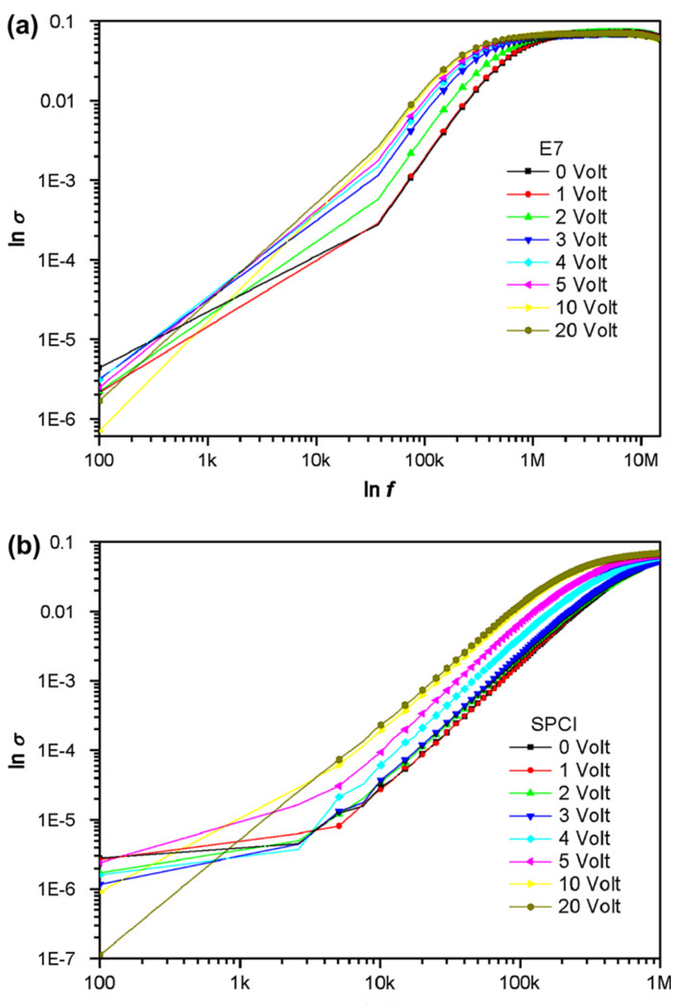

Fig. 4. The conductivity vs frequency plots of LCs (a) nematic host, E7 and (b) SPCI-C7 doped LC nematic host.

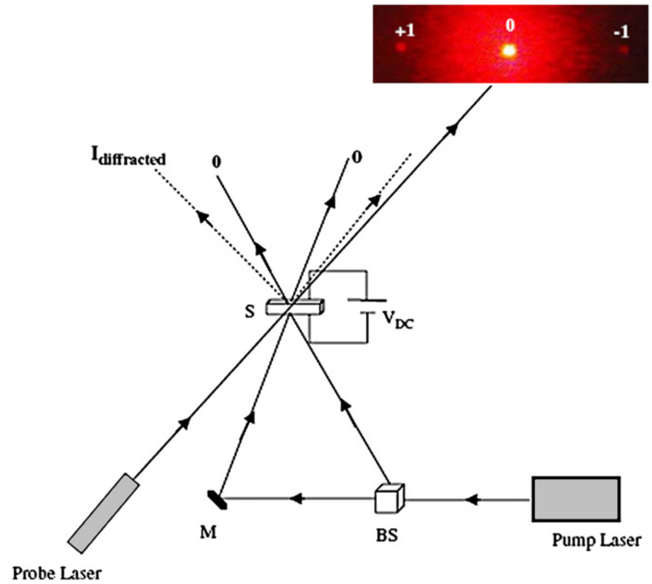

Fig. 5. The experimental set-up for diffraction efficiency measurements.

pumping source that was split into two approximately equal components by a beam splitter. Polarization of the laser was parallel to the preliminary orientation of the LC molecules. Pumping beams (12 mW) intersected the sample with $\theta = \sim 1.5°$ so that the grating constant Λ was ~ 24 μm and since $\Lambda^2 \gg \lambda d$, diffraction is considered to be in the Raman–Nath regime [17].

The diffraction signal's dependency on applied DC voltage for both E7 and E7/SPCI-C7 is shown in Fig. 6. Probe diffraction of 2 mW He–Ne laser was considered in the analysis of the diffraction efficiency. Diffraction efficiency η was calculated as the intensity ratio of the first-order diffraction beam to the incident beam. In the case of E7/SPCI-C7, the diffraction efficiency was $\sim 7\%$ ($\pm 1\%$) under optimum conditions (intersection beam angle $2\theta = 3°$, $V_{DC} = 2.9\ V$ for a pumping beam power of ~ 12 mW (± 0.01 mW)) whilst E7 had just 1.5% diffraction efficiency for the same voltage. Fig. 7 shows the normalized diffraction efficiency which is defined by the

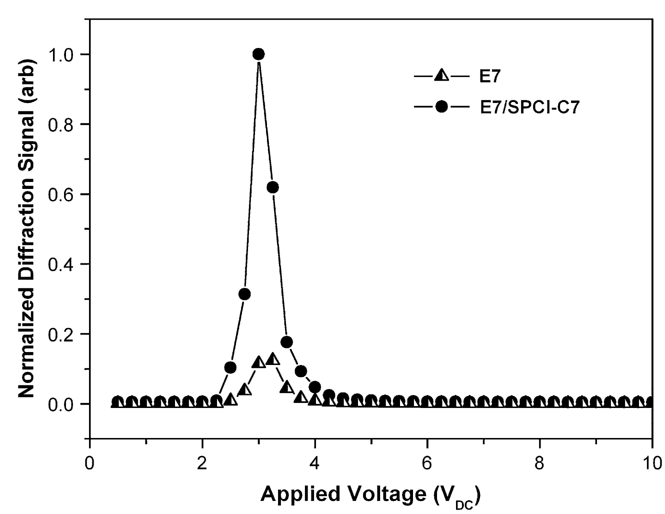

Fig. 6. Dependency of normalized diffraction signals on the applied DC voltage.

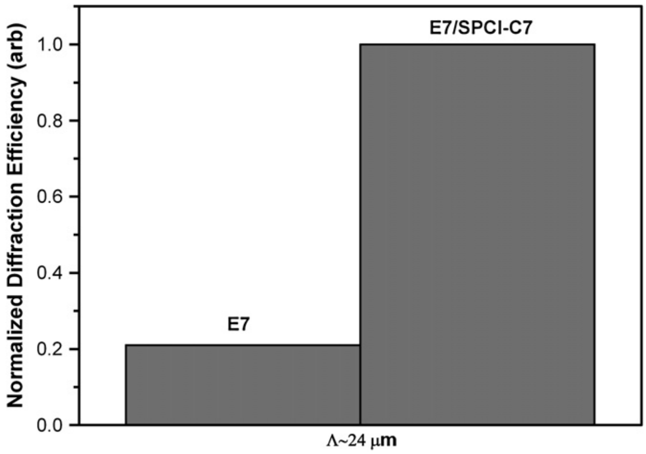

Fig. 7. Normalized diffraction efficiency of the investigated LCs.

percentage of the diffracted light intensity over the incoming light intensity. The peak in the curve for E7 shifted to lower voltage as a result of doping with SPCI-C7. The diffraction efficiency increased markedly with doping. The refractive index modulation for the LCs are given as

$$\eta = \left(\frac{\pi \Delta n d}{\lambda}\right)^2 \tag{2}$$

where $d = 6.2$ μm; $\lambda = 0.632$ μm. Δn values for E7 and E7/SPCI-C7 LCs were found to be 3.9×10^{-3} and 6.95×10^{-3}, respectively. The Δn value of the SPCI-C7 doped LC is higher than that of E7.

4. Conclusions

The dielectric anisotropy of E7 and E7/SPCI-C7 liquid crystals exhibited dielectrically-controlled positive dielectric anisotropy (p-type $\Delta\varepsilon$) with transition to negative dielectric anisotropy (n-type $\Delta\varepsilon$) behaviour. SPCI-C7 doping reduced dielectric anisotropy values. The diffraction efficiency of E7 increased with SPCI-C7 doping. The refractive index modulation value of E7 ($\Delta n = 3.9 \times 10^{-3}$) was lower than that of E7/SPCI-C7 ($\Delta n = 6.95 \times 10^{-3}$). Hence, doping with SPCI-C7 changes the dielectric anisotropy and diffraction efficiency properties of E7.

Acknowledgements

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