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Dielectric anisotropy, memory state and diffraction efficiency properties of the spiropyranylazobenzoate AP-SPAB7 doped nematic liquid crystal

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Abstract

Dielectric anisotropy, memory state and diffraction efficiency properties of E7 liquid crystal and AP-SPAB7 doped liquid crystal composite are investigated by dielectric and electrical conductivity properties. The liquid crystals exhibit dielectrically controlled positive dielectric anisotropy (p-type $\Delta\varepsilon$) with the critical frequency transition to negative dielectric anisotropy (n-type $\Delta\varepsilon$) behavior. The AP-SPAB7 doping does not change the memory state properties of LC, while the doping changes dependency of dielectric anisotropy on applied voltage. The diffraction efficiency is significantly enhanced in the AP-SPAB7 doped LC. The refractive index modulation values of the E7 and E7/AP-SPAB7 were found to be $\Delta n = 3.9 \times 10^{-3}$ and $\Delta n = 9.7 \times 10^{-3}$, respectively. The AP-SPAB7 doping increases the refractive index modulation of E7 LC.

Keywords: Liquid crystal; AP-SPAB7; Dielectric anisotropy; Memory state

1. Introduction

Organic materials have extensively been investigated because of large optical and dielectric anisotropy properties and fundamental success of molecular engineering in creating a new class of materials with appropriate physical and optical properties. Particularly, liquid crystals (LCs) have become recently extremely important in several key areas of flat panel displays and fiber-optic communications [1]. Dielectric spectroscopy is a powerful method for the investigation of liquid crystals [2–4]. This method contributes significantly to the overall characterization of liquid crystals and the dielectric anisotropy properties can be determined by this method. 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 (LCDs), 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 (LCDs) is strongly dependent on the dielectric anisotropy of the LC. The fact that a new class of materials with appropriate physical and optical properties is created is very important for development of LCs.

The aim of this study is to investigate dielectric anisotropy, memory state and diffraction efficiency properties of the spiropyranylazobenzoate AP-SPAB7 doped nematic liquid crystal to determine physical parameters.

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2. Experimental

2.1. Synthesis of AP-SPAB7

The spiropyranylazobenzoate (AP-SPAB7) was synthesized by the condensation of [1′,3′,3′-trimethylspiro(2*H*-1-benzopyran-2,2′-indoline)-6-yl] azo-benzoic acid (SPAB) with 4-heptyloxyphenol, in the presence of dicyclohexylcarbodiimide (DCC) and 4-*N*,*N*-dimethylaminopyridine (DMAP). SPAB was obtained from condensation reaction of Fischer's base with 4-(3′-formyl-4′-hydroxyphenylazo) benzoic acid, adapting to the known method [7].

2.1.1. [1′,3′,3′-Trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl] azo-(4′-heptyloxyphenyl) benzoate, AP-SPAB7

Yield 79%; mp 124–125 °C (125 °C); IR (cm^{-1}) 3358 (m), 2930 (s), 2851 (s), 1735 (s), 1633 (s), 1273 (s), 1210 (s), 1022 (m), 961 (s), 722 (m); ^1H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, 3H), 1.20 (s, 3H), 1.34 (s, 3H), 1.29–1.49 (m, 8H), 1.81 (m, 2H), 2.77 (s, 3H), 3.99 (t, 2H), 5.82 (d, $J = 10.2$ Hz, 1H), 6.56 (d, 1H), 6.86 (d, $J = 8.7$ Hz, 1H), 6.88 (t, 1H), 6.94 (d, $J = 8.7$ Hz, 2H), 6.97 (d, 1H), 7.10 (d, 1H), 7.15 (d, 2H), 7.21 (t, 1H), 7.75 (s, 1H), 7.83 (d, 1H), 7.95 (d, $J = 8.4$ Hz, 2H), 8.33 (d, 2H).

2.2. Preparation of liquid crystal cells

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

AP-SPAB7 was dissolved in toluene and the toluene fraction was evaporated to eliminate AP-SPAB7 powders, which later mixed to nematic host E7 1% (w/w) under the reinforcement of ultrasonic effect. Pure E7 and AP-SPAB7 doped liquid crystal was injected into sample cells by capillary action with room temperature. Chemical formulas of AP-SPAB7 and nematic host are depicted in Fig. 1. Experimental set up is shown in Fig. 2. Hp4194 impedance analyzer was used in the measurements which are performed at room temperature with a high accuracy (0.17% typical).

3. Results and discussion

3.1. Dielectric anisotropy properties of E7 and E7/AP-SPAB7 LCs

Fig. 3 shows the dielectric constant as a function of the applied voltage at various frequencies. The voltage applied to LC causes the reorientation of LC molecules. Initially, the dielectric constant increases slowly with voltage up to a certain voltage and then increases drastically and reaches a saturation. This behavior is so-called Frederiks threshold. The increase in the dielectric constant is probably due to molecular reorientation, i.e., the dielectric constant is dependent on external effects due to the anisotropic nature of LC. An example of anisotropic parameter of liquid crystals is the dielectric constant. There are two types of structures regarding dielectric constant which are positive ($\Delta\varepsilon > 0$ is called positive type, its molecules align with the director parallel to the electric field) and negative (in the negative type AP-SPAB7 with $\Delta\varepsilon < 0$, they align perpendicular to the field) dielectric anisotropies [8,9]. When a liquid crystal (LC) is brought in a sufficiently strong electric field, the director tends to align parallel or perpendicular to the electric field. Thus, LC shows a dielectric anisotropy property. The dielectric anisotropy for the LC is defined as [10],

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

where $\varepsilon_{\parallel}$ is the parallel and $\varepsilon_{\perp}$ is the perpendicular part of the dielectric constant. The dielectric anisotropy values were measured and are given in Table 1. At low frequencies, E7 and E7/AP-SPAB7 LCs exhibit positive dielectric anisotropy which changes into negative at higher frequencies. When an electric field with direction *E* is applied to E7 and E7/AP-SPAB7 LCs, a torque acts on the molecule due to the dielectric anisotropy.

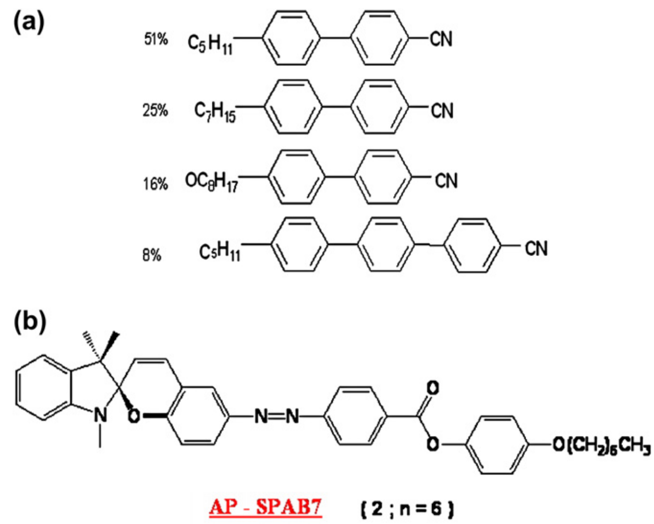

Fig. 1. Chemical formulas of: (a) nematic host, E7 and (b) AP-SPAB7.

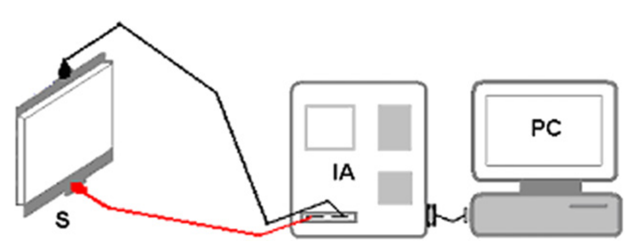

Fig. 2. Experimental set up for electrical measurements. S: sample and IA: impedance analyzer.

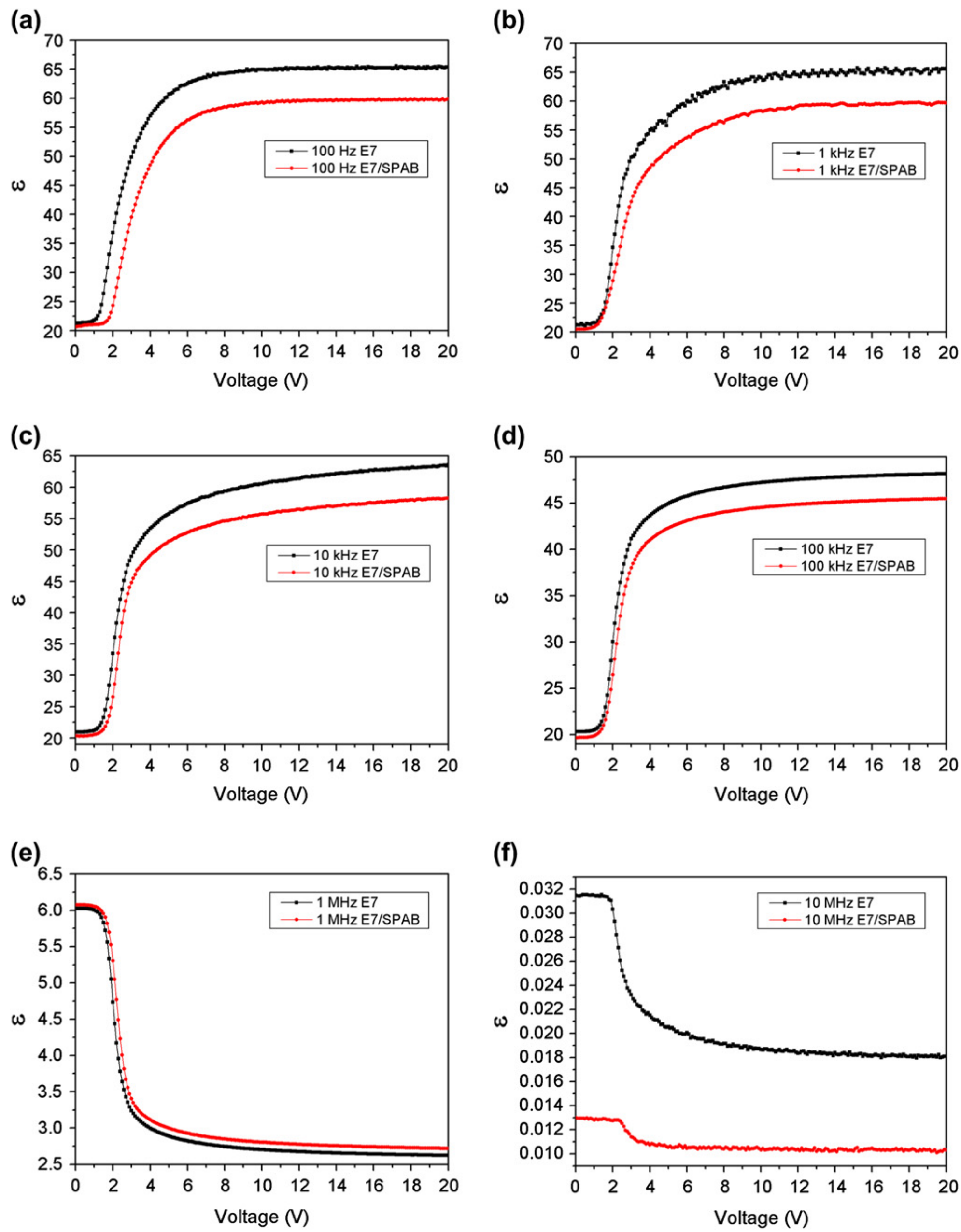

Fig. 3. The plots of dielectric constant vs applied voltage at various frequencies.

The torque tends to align the molecule parallel to the field. When the field is strong enough, the molecule will be almost parallel to the field. Thus, E7/AP-SPAB7 shows a p-type dielectric anisotropy. As seen in Table 1, the dielectric anisotropy values of E7 are higher than that of E7/AP-SPAB7. This suggests that the AP-SPAB7 content has a decreased effect on the dielectric anisotropy values of E7.

3.2. Memory effect of E7 and E7/AP-SPAB7 LCs

Fig. 4 shows the electrical conductivity properties of E7 and E7/AP-SPAB7 liquid crystal at various voltages. The electrical conductivity increases with the increase in frequency and reaches a saturation. The E7 and E7/AP-SPAB7 liquid crystals continue to show higher electrical conductivity after voltage application (memory state) than those in their initial off-state. At higher voltages, the memory start-state of doped LC starts the earlier time. The memory start-state of E7 and

Table 1
The dielectric anisotropy values of the E7 and E7/SPAB cells

f	$\Delta\varepsilon$ for E7	$\Delta\varepsilon$ for E7/AP-SPAB7
100 Hz	43.58	38.13
1 kHz	42.68	37.42
10 kHz	39.44	34.84
100 kHz	26.78	24.42
1 MHz	−3.31	−3.249
10 MHz	−0.013	−0.0025

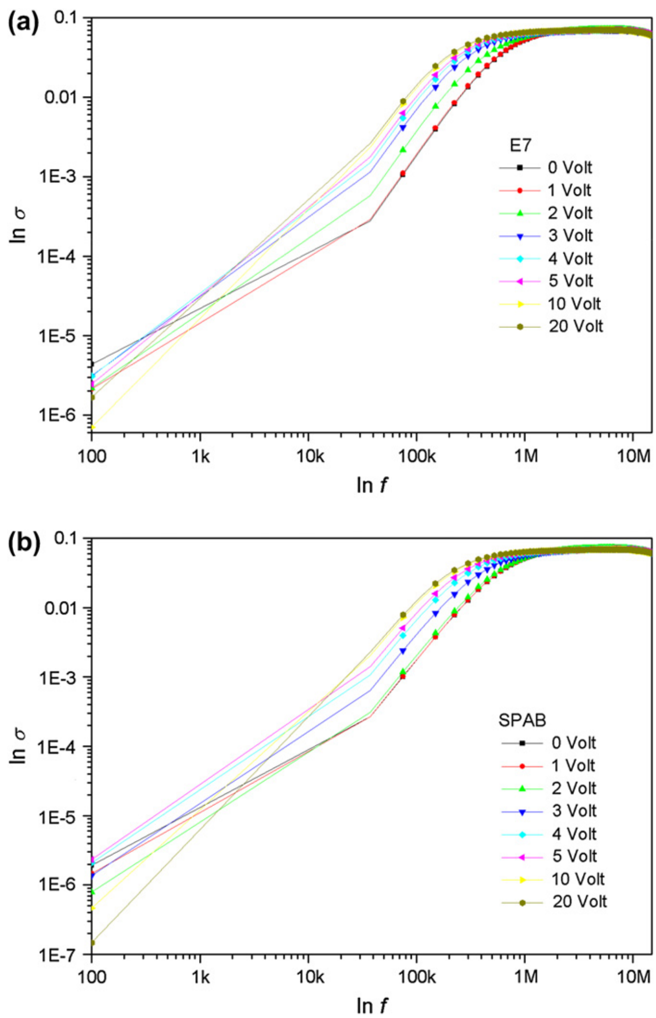

Fig. 4. The conductivity vs frequency plots of LCs: (a) nematic host, E7 and (b) AP-SPAB7 doped LC nematic host.

E7/AP-SPAB7 liquid crystals is almost the same. This suggests that doped AP-SPAB7 quantity does not change the memory state.

3.3. Diffraction efficiency of E7/AP-SPAB7

An experimental arrangement for the two-wave mixing is schematically shown in Fig. 5. It consists of a He–Ne ($\lambda = 632.8$ nm) pumping source and this source is split 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. Pumping beams, having 12 mW power, were intersected on the sample with $\theta \simeq 1.5°$ that makes grating constant Λ to be $\sim$24 μm and since $\Lambda^2 \gg \lambda d$, diffraction is considered to be in the Raman–Nath regime [11].

Fig. 6 demonstrates the dependency of diffraction signals on the applied DC voltage for pure E7 and E7/AP-SPAB7. 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. For the studied system, diffraction efficiency is $\sim$9% ($\pm$1%) under optimum circumstances when the intersection angle of beams $2\theta = 3°$, $V_{DC} = 2.5$ V for pumping beam powers $\sim$12 mW ($\pm$0.01 mW), while pure E7 have just 1.5% diffraction efficiency around the same voltage value. Fig. 7 demonstrates the normalized diffraction efficiency. The diffraction efficiency is defined by the percentage of the diffracted light intensity over the incoming light intensity.

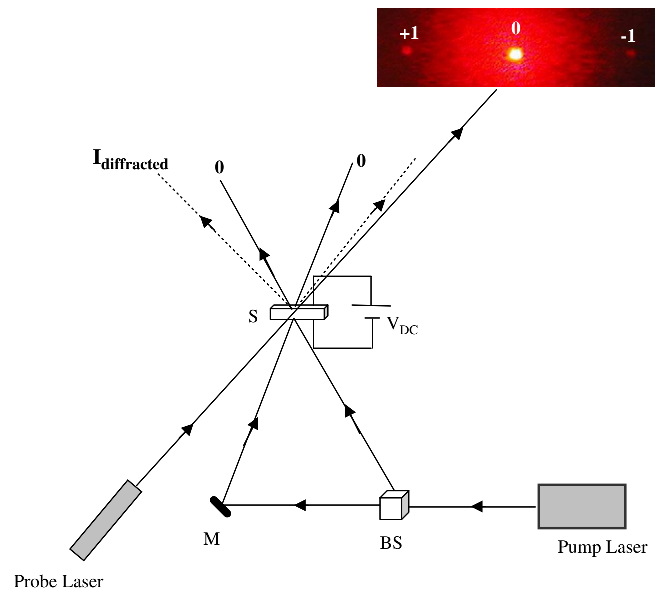

Fig. 5. The experimental set up for diffraction efficiency measurements.

As seen in Fig. 6, a peak is observed in curves. The peak position of E7 shifts to lower voltage values with AP-SPAB7 doping. The diffraction efficiency significantly increases in the AP-SPAB7 doped LC. Also, using the $\eta = (\pi \Delta n d/\lambda)^2$ formula, we estimated refractive index modulation $\Delta n = 3.9 \times 10^{-3}$ and $\Delta n = 9.7 \times 10^{-3}$ for E7 and E7/AP-SPAB7,

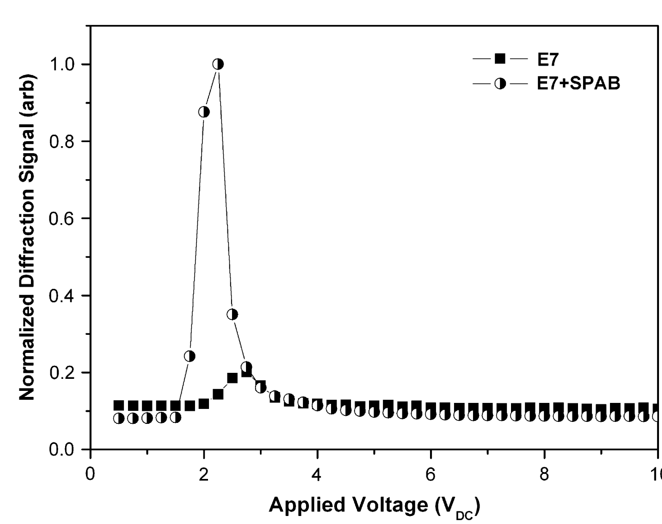

Fig. 6. Dependency of normalized diffraction signals on the applied DC voltage.

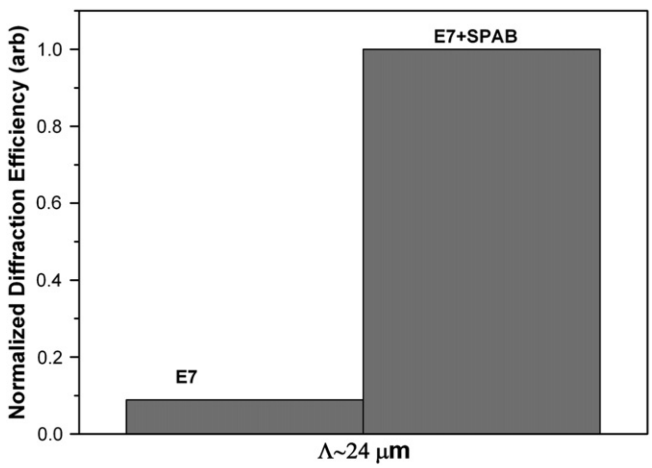

Fig. 7. Normalized diffraction efficiency of the investigated LCs.

respectively, using the following parameters: $d = 6.2$ μm, $\lambda = 0.632$. It is noteworthy to consider the fact that refractive index modulation was an increasing tendency in the AP-SPAB7 doped LC during the measurements.

4. Conclusions

Dielectric anisotropy property, memory state and diffraction efficiency of E7 LC and E7/AP-SPAB7 doped liquid crystal composite are investigated by concerning the frequency dependent dielectric and electrical conductivity properties. A transition in the dielectric constant takes place due to the liquid crystal director reorientation. The increase in frequency alters the structure type from positive to negative. The behavior called Frederiks threshold is observed in the LCs. The AP-SPAB7 doping does not change the memory state, while the doping changes the dependency of dielectric anisotropy on applied voltage.

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