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Liquid crystalline blue phase in mixtures of fluorinated compounds with positive and negative dielectric anisotropy and its electro-optic performance

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Dependence of a blue phase temperature range on a chiral dopant and cyano compound addition as well as character of nematic base mixture was investigated. Base nematic mixtures of fluorinated compounds, one with positive and the other one with negative dielectric anisotropy, were chosen. Various fluoro compounds, chiral compounds and cyano compound were added in order to evaluate the relationship between blue phase stability and molecular structure of components. The stability of a blue phase in selected mixtures has been extended by polymer network formation. Fundamental electro-optic properties such as Kerr constant, operating time and switching voltage of a polymer-stabilised blue phase with positive and negative dielectric anisotropy are given, too. It has been confirmed that blue phase temperature range and its electro-optic performance strongly depends on molecular structure of mixture components as well as chiral dopants and their helical twisting power. Specifically, it was found that the cyano compound addition causes destabilisation of blue phase in mixtures consisted of fluorinated compounds.

Keywords: liquid crystal blue phase; Kerr effect; polymer network

1. Introduction

Today's commercial devices operate very close to the physical limits of the nematic liquid crystals on which they are based, consequently research on new liquid crystalline materials is necessary. Blue phase (BP) exhibits several revolutionary features in comparison to conventional nematic materials. First, it does not require any alignment layer, such as polyimide, which simplifies the manufacturing processes and reduces the cost. Second, the electro-optic response times, rise as well as decay time, are lower than 1 ms [1,2]. The magnitude of response time is proportional to the rotational viscosity γ_1, square of the helical pitch p and inversely proportional to the elastic constant k [3], which can be presented by Equation (1). The response time is independent of the cell gap in contrast to the other liquid crystal devices. This feature is attractive especially for fabricating large-screen displays and devices working in longer areas of electromagnetic radiation (infra red, terahertz and gigahertz frequency range), wherein the liquid crystal gap is larger.

$$\tau \approx \frac{\gamma_1 p^2}{\mathrm{k}(2\pi)^2} \tag{1}$$

The dark state of a BP liquid crystal display is optically isotropic. Anisotropy appears when an external electric field is applied, which results in splitting the light beam passing through the sample at an angle varying from the direction of an electric charge flow. This phenomenon is called the electro-optic Kerr effect and is affected by operating voltage. The higher is the Kerr constant K, the smaller on-state voltage V_{on} is required. In order to extend this parameter the host liquid crystal material should preferably have high birefringence Δn, large dielectric anisotropy $\Delta\varepsilon$, long pitch length p and small elastic constant k [3], which is expressed by Equation (2):

$$\mathrm{K} \sim \frac{\Delta n_{\mathrm{ind}}}{\lambda E^2} \approx \Delta n \cdot \Delta\varepsilon \frac{\varepsilon_0 p^2}{\mathrm{k}\lambda(2\pi)^2} \tag{2}$$

There are, however, a few remaining challenges that need to be met, like hysteresis, narrow temperature range and high operating voltage. Fast response time at relatively low voltages cannot be obtained by the helical pitch variation, because the response time is proportional to the helical pitch and on-state voltage is inversely proportional to its value [see Equations (1)–(2)]. It is possible to reduce high operating voltage by inventing new device structures [4,5] or developing new materials with high birefringence and high dielectric anisotropy.

According to the literature data it is not clear what chemical structures are preferred for induction of BP with optimal properties. Investigated systems are based on commercial mixture of fluorinated compounds diluted 4-cyano-4′-pentylbiphenyl (5CB) [6,7],

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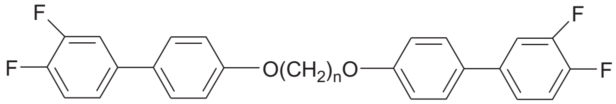


Figure 1. Chemical structure of material exhibiting blue phase over wide temperature range.

cyanoesters were also mentioned [8]. Another known system was published by Coles et al. [9]. He reported a BP with temperature range larger than 44 K in mixture consisted of liquid crystalline dimmers with large flexoelecricity, see Figure 1.

To induce BP a chiral compound is added to the nematic medium. Usually used chiral dopants have helical twisting power (HTP) higher than 70 μm^{-1} and expanded spatial structure [10]. The disadvantage of these compounds is their low solubility caused by large enthalpy and temperature of melting point. What is more, very often small photostability causes the loss of chiral properties. There are several methods to extend temperature range of BP: adding nanoparticles [11], bent-shaped molecules [12], T-shaped molecules [13], by polymer network creation [14] and combined [15].

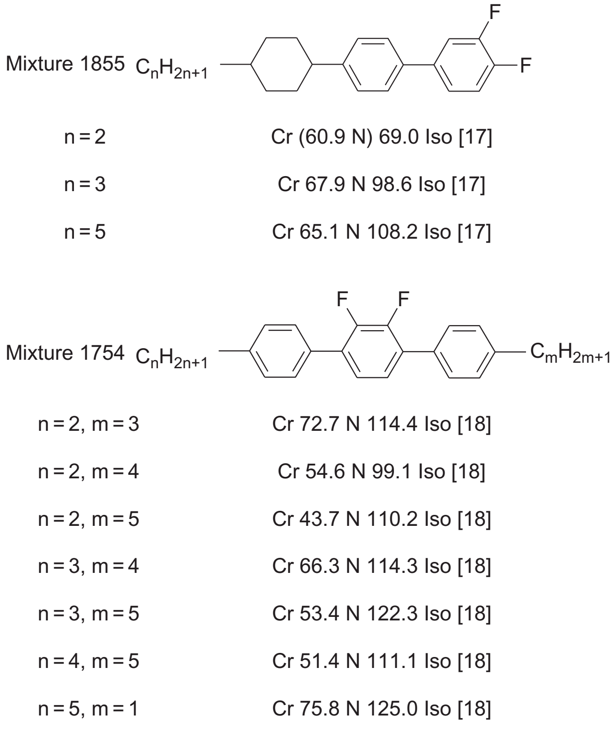
We started a systematic study on liquid crystal compounds and chiral dopants for BP induction with optimal properties [16]. In presented article, the BP temperature range and its electro-optic performance have been measured for modifications of two types of materials, given in Figure 2. These host mixtures are based on fluorinated compounds because they exhibit necessary high resistivity, high photochemical stability and low viscosity. Dielectrically positive mixture 1855, composed of 3,4-difluoro-4′-(4-alkylcyclohexyl)biphenyls [17] and the second material, dielectrically negative mixture 1754, consisting of 2′,3′-difluoro-4,4″-dialkyl-[1,1′;4′,1′]terphenyls, were chosen.

The ability for induction of the BP in host mixtures was tested by doping them with chiral compounds with different rigid core structure and HTP. Base nematic mixtures were modified with various other two, three and four rings aromatic fluorinated compounds in order to evaluate the relationship between BP stability and molecular structure of mixture components. Electro-optic measurements were performed for polymer-stabilised BP in selected systems.

2. Results and discussion

2.1 Influence of chiral compound

Two base nematic mixtures were prepared in our laboratory. Dielectrically positive mixture 1855 ($\Delta\varepsilon$ = 7.06 measured at 1 KHz and 20°C), consisted of fluorinated alkylcyclohexylbiphenyls from Yantai Valiant Fine Chemicals (Yantai, Shandong, China), has following nematic range $T_{\text{N–Iso}} = 94.1°\text{C}$, $T_{\text{m}} = 15.0°\text{C}$, birefringence $\Delta n = 0.1481$ for sodium line D, bulk viscosity $\eta = 24.93$ mPa s, both measured at 20°C. Second host with negative dielectric anisotropy is mixture 1754 ($\Delta\varepsilon = -1.82$ measured at 1 KHz and 20°C), containing fluorinated terphenyls, synthesised in our laboratory [18]. Temperatures of phase transitions are the following: $T_{\text{m}} = 16.7°\text{C}$, $T_{\text{N-Iso}} = 114.2°\text{C}$, optical anisotropy is $\Delta n = 0.2528$ measured at 20°C for sodium line D.



n = 2	Cr (60.9 N) 69.0 Iso [17]
n = 3	Cr 67.9 N 98.6 Iso [17]
n = 5	Cr 65.1 N 108.2 Iso [17]

n = 2, m = 3	Cr 72.7 N 114.4 Iso [18]
n = 2, m = 4	Cr 54.6 N 99.1 Iso [18]
n = 2, m = 5	Cr 43.7 N 110.2 Iso [18]
n = 3, m = 4	Cr 66.3 N 114.3 Iso [18]
n = 3, m = 5	Cr 53.4 N 122.3 Iso [18]
n = 4, m = 5	Cr 51.4 N 111.1 Iso [18]
n = 5, m = 1	Cr 75.8 N 125.0 Iso [18]

Figure 2. General formula of nematic base mixtures.

To induce BP in base nematic mixtures, three chiral diesters were used, synthesised by Kula [19], see Figure 3. They have two asymmetric carbon atoms in terminal chains and different rigid cores. The solubility and miscibility of these chiral agents are very good as a result of low meting enthalpies and low melting points. What is worth to notice, compound 1 is a liquid at room temperature, its solubility is theoretically unlimited [20]. Base nematic mixtures were doped with 0.1 mole fraction of chiral dopants.

In host mixture 1855 BP was observed in all modifications, see Figure 4. The widest temperature range of BP (2.6°C) was observed in system containing chiral dopant 1 with biphenyl rigid core. In other two mixtures, BP temperature range was 1.1°C in mixture doped with fluorosubstituted terphenyl 2 and 0.9°C in mixture containing unsubstituted terphenyl 2.

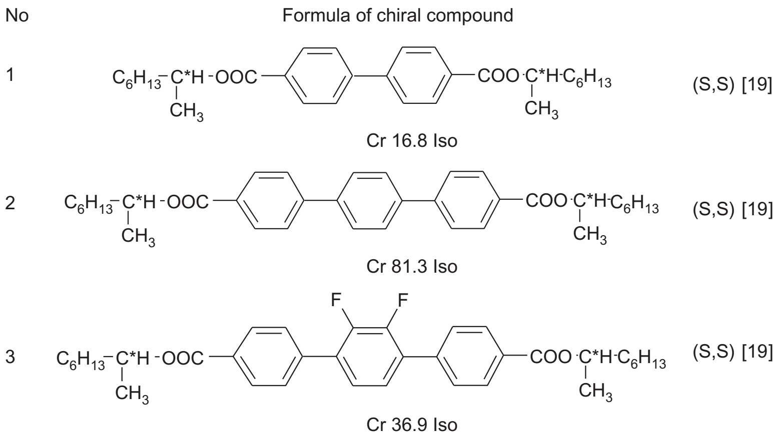


Figure 3. Formulas of investigated chiral compounds.

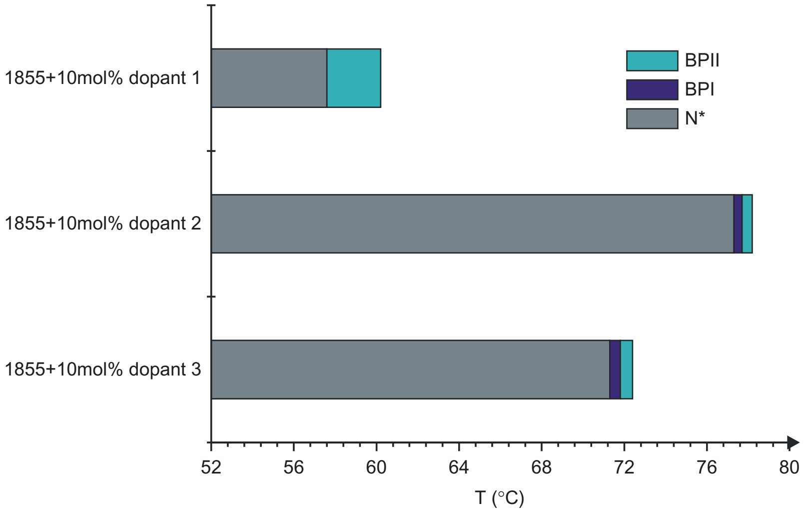


Figure 4. (colour online) Temperatures of phase transitions of dielectrically positive mixture 1855 doped with various chiral compounds (measured in heating cycle).

Among systems based on mixture 1754 (Figure 5), BP was not observed in system with dopant 1, in contrast to modifications of mixture 1855. The widest temperature range was noticed in mixture containing compound 3 with fluorinated terphenyl rigid core (1.9°C). In system doped with unsubstituted terphenyl 2 the BPI was observed over 1.3°C.

The phase type in mixtures with only one BP was established by miscibility method. Nematic hosts were doped with two chiral agents, where mixture with one of them has known phase sequences. The concentration of chiral dopants was 0.1 mole fraction together. The molar ratio of two chiral compounds was changed from 1:0 to 0:1. In Figure 6, the phase sequences and temperatures of phase transitions of mixtures 1855 doped with unsubstituted terphenyl (compound 2) and biphenyl (compound 1) are shown. The temperature range of BPI is constant and the range of BPII increases with concentration of the biphenyl 1. The BPI was observed over only 0.2°C in mixture containing terphenyl 2 and biphenyl 1 in molar ratio 9:1, and completely vanished in mixture doped with pure biphenyl. In the same way, the type of BP has been determined in systems based on the host 1754.

In order to find the effect of HTP on the BP induction and its temperature range, the values of HTP of the chiral agents in host mixtures were measured. The temperature dependencies of HTP for mentioned compounds are shown in Figures 7 and 8, measured from 20°C to 50°C. The highest values of the HTP were observed for laterally difluoro substituted terphenyl (compound 3) measured in both nematic hosts. Very small temperature dependence was noticed for this compound. The HTP values measured at 20°C are 33 μm^{-1} in host 1855 and 31 μm^{-1} in host 1754. Despite the fact that compound 3 has the highest value of HTP, it does not induce the widest range of BP

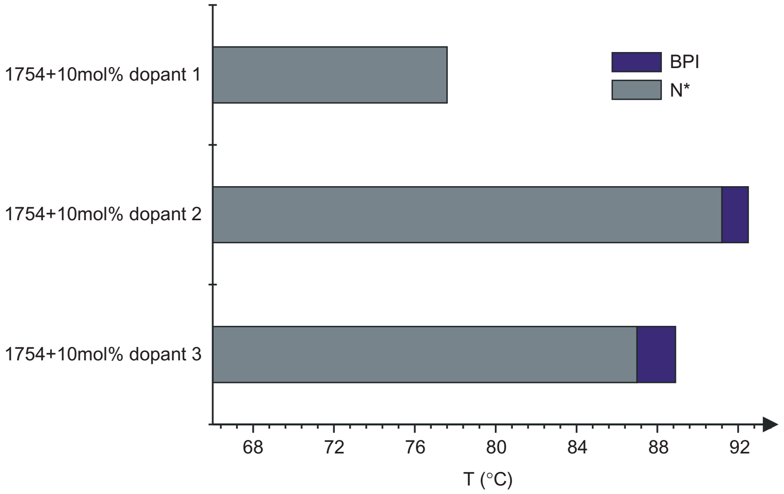


Figure 5. (colour online) Temperatures of phase transitions of dielectrically negative mixture 1754 doped with various chiral compounds (measured in heating cycle).

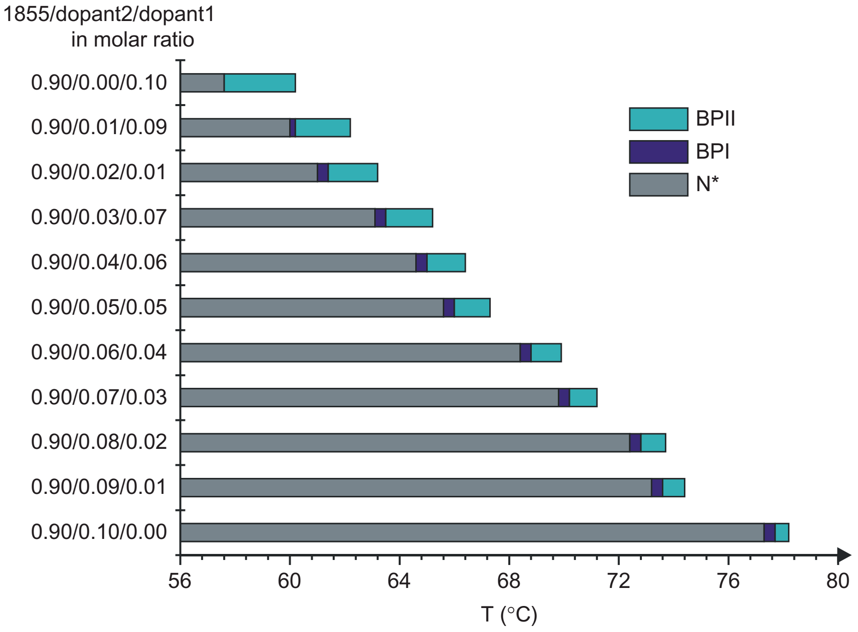


Figure 6. (colour online) Phase sequences and temperatures of phase transitions of mixtures 1855 doped with chiral compounds 1 and 2 (measured in heating cycle).

in mixture 1855. The widest range of BP in mixture 1855 was observed for the two ring compound 1, with medium value of HTP, while in mixture 1754 chiral agent 1 does not induce BP at all. The temperature dependencies in Figures 7 and 8 are excellent examples of HTP behaviour of chiral agents in liquid crystalline medium: it can be increasing, decreasing or constant.

2.2 *Effect of the structure of the nematic base components and cyano dopant addition*

To estimate the best composition of nematic hosts for BP stability, various fluorinated compounds synthesised in our laboratory [21–23] given in Figure 9, were doped to the base mixtures.

The systems based on 1855 were doped with 0.18 mole fraction of fluorinated compounds 4–7 and 0.1 mole fraction of chiral compound 1. The chiral agent 1 was chosen, because it causes the widest temperature range of BP (2.6°C) among systems comprising different chiral compounds. The results show that BP was not observed in mixtures containing compounds with cyclohexyl rings in rigid core (compounds 4 and 7), while in mixture 1855 containing only chiral agent 1 the BP was observed over 2.6°C, see Figure 5. The range of BP is slightly larger in systems with

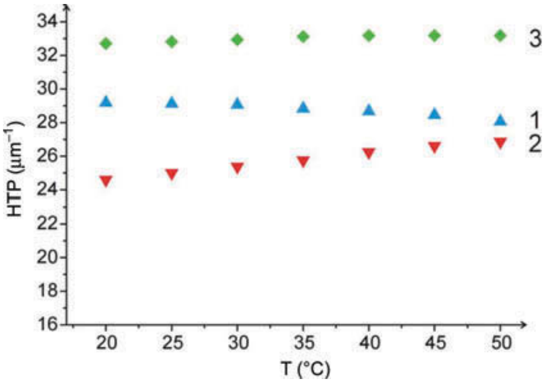


Figure 7. (colour online) Temperature dependence of HTP of chiral compounds in nematic host 1855 ($\Delta\varepsilon > 0$).

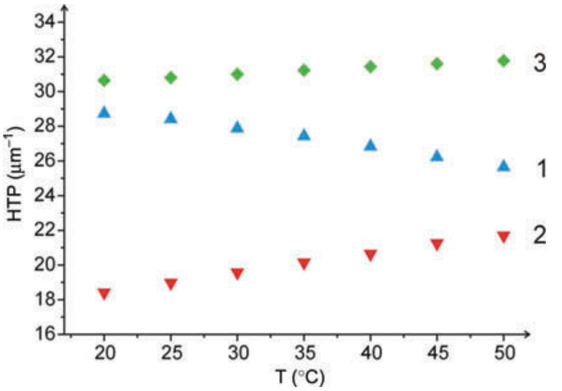
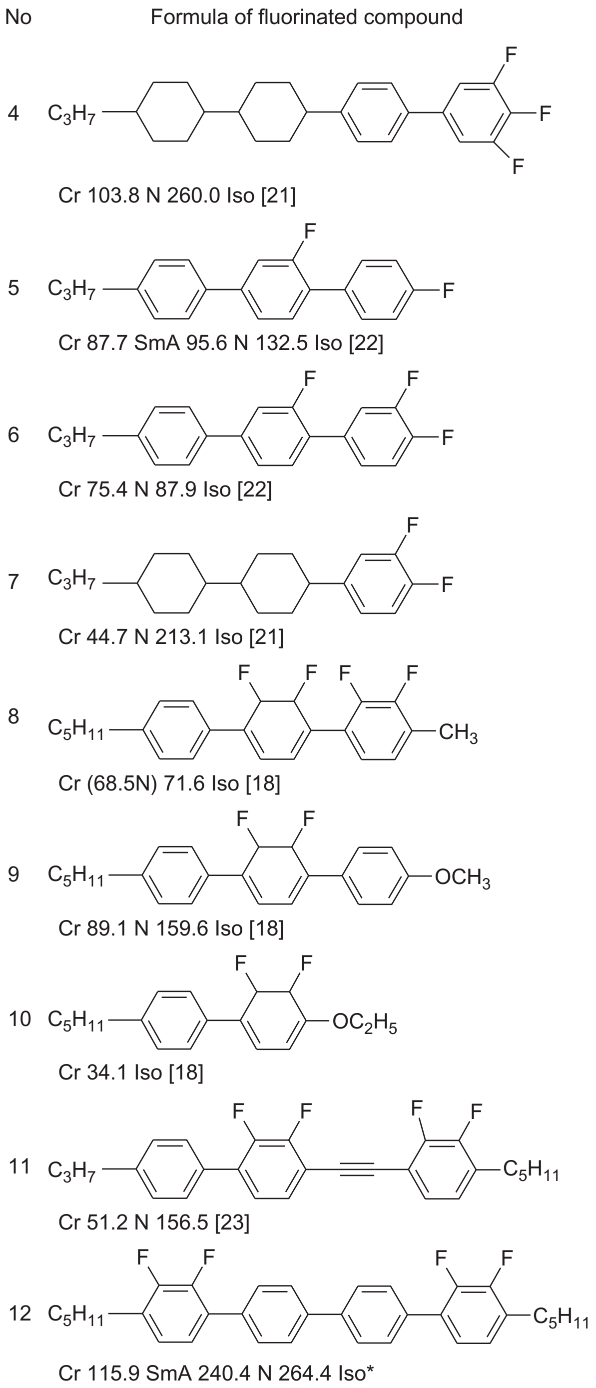


Figure 8. (colour online) Temperature dependence of HTP of chiral compounds in nematic host 1754 ($\Delta\varepsilon < 0$).

compounds 5 and 6 than without them. The aromatic rings are preferred in systems with chiral agent 1.

The second group of mixtures, based on host 1754, were doped with 0.1 mole fraction of fluorinated compounds 8–10 and then 0.1 mole fraction of chiral agent 2, (unsubstituted terphenyl), since only this compound causes BP appearance in host mixture. As a result the molar ratio of base mixture 1754, fluorinated dopant and chiral agent was 81/9/10. In all cases, we have observed exactly the same temperature range of BP (1.7°C), slightly larger than in mixture 1754 doped with only chiral compound 2.

According to the literature data the most of reported systems are diluted by cyano compounds. In this study, we examined if the presence of cyano compounds reduces BP stability or whether BP may be observed without them. This fact has practical aspects, because in the systems addressed by active matrices mainly fluorinated compounds are used. They exhibit necessary high resistivity, high photochemical stability and also low viscosity. For this purpose the 5CB, synthesised in our laboratory, was chosen and doped to various mixtures containing fluorinated compounds, mentioned before. The phase transition temperatures of the host mixtures 1855 and 1754 modifications diluted with 0.18 mole fraction of 5CB are shown in Table 1. The temperature range of BP in mixture 1855 doped with difluoro substituted compound 5 and 5CB is 0.5°C narrower in comparison to the



Cr 103.8 N 260.0 Iso [21]

Cr 87.7 SmA 95.6 N 132.5 Iso [22]

Cr 75.4 N 87.9 Iso [22]

Cr 44.7 N 213.1 Iso [21]

Cr (68.5N) 71.6 Iso [18]

Cr 89.1 N 159.6 Iso [18]

Cr 34.1 Iso [18]

Cr 51.2 N 156.5 [23]

Cr 115.9 SmA 240.4 N 264.4 Iso*

Figure 9. Formulas of investigated fluorinated compounds.
Note: reported the first time in this article.

Table 1. Phase transition and BP range in the chiral modifications of base nematic mixtures 1855 and 1754 doped with various fluorinated compounds (4–10) at a heating rate of 1 K/min.

		Transition temperature/°C		
LC mixture	Molar ratio	N*-BP	BP-Iso	ΔT_{BP}
1855/1	90/10	57.6	60.2	2.6
1855/4/1	72/18/10		90.6^a	–
1855/5/1	72/18/10	62.5	65.3	2.8
1855/6/1	72/18/10	51.9	54.6	2.7
1855/7/1	72/18/10	–	71.5^a	–
1855/4/5CB/1	58/14/18/10	–	76.6^a	–
1855/5/5CB/1	58/14/18/10	51.4	53.7	2.3
1855/6/5CB/1	58/14/18/10	42.1	44.8	2.7
1855/7/5CB/1	58/14/18/10	–	59.7^a	–
1754/2	90/10	91.2	92.5	1.3
1754/8/2	81/9/10	87.1	88.8	1.7
1754/9/2	81/9/10	94.8	96.4	1.7
1754/10/2	81/9/10	82.4	84.0	1.6
1754/8/5CB/2	65/7/18/10	80.1	81.4	1.3
1754/9/5CB/2	65/7/18/10	88.0	89.3	1.3
1754/10/5CB/2	65/7/18/10	76.7	78.0	1.3

Note: ^{a}The temperature of N*-Iso phase transition.

mixture without cyano compound. Addition of 5CB to the mixtures containing fluorinated compounds with bicyclohexyl rigid core (compound 4 and 7) does not cause BP induction. Among modifications of dielectrically negative host 1754 doped with 5CB, the BP was observed over 0.4°C or 0.3°C narrower than in mixtures with no 5CB. In all examined systems based on dielectrically positive mixture 1855 and dielectrically negative host 1754, the 5CB addition has entailed the reducing of BP temperature range.

Comprehensive study of the influence of 5CB on BP stabilisation by polymer network in host mixture 1855 is given in [16]. It has been demonstrated that the presence of 5CB is not necessary for polymer stabilisation, because it decreases the clearing point (as a result the BP range in polymer-stabilised material is narrower than without 5CB) and complicates the stabilisation process. In early stages of polymerisation, the temperatures of phase transition are likely to shift, so it is required to use material with as wide BP temperature range as possible. However, for certain applications that require large dielectric anisotropy value, the cyanobiphenyls and cyanoesters should be used in order to increase the anisotropy.

2.3 *Electro-optical performance*

The electro-optical properties have been measured for selected systems in polymer stabilised BP (PSBP). Pure base mixture 1855 and its modifications containing 0.2 mole fraction of compounds 4, 5, 6 and 7 were doped with 0.1 mole fraction of chiral compound 2 with unsubstituted terphenyl rigid core and prepared according to the description in Section 4.3. The obtained polymer-stabilised composites have been marked as PSBP1855, PSBP1855A, PSBP1855B, PSBP1855C and PSBP1855D. The same process was conducted with dielectrically negative host 1754 and its version containing 0.1 mole fraction of compounds 11 and 12. Resulting materials have been named as PSBP1754, PSBP1754E and PSBP1754F.

First the voltage-dependent transmittance (VT) curves were measured. Results are shown in Figures 10 and 11. In the plot, the transmittance is normalised to the maximum value from the two parallel polarisers. The light leakage in the voltage-off state is because the reflection bands of the samples are in the visible region and reflection would change the polarisation state. Among modifications of mixture 1855 the lowest driving voltage was measured for composite PSBP1855C (purple line on the graph), comprising of compound 6, which is trifluoro substituted terphenyl. The driving voltage for T_{100} (100% normalised transmittance) was 87 V. The second lowest voltage for T_{100} was 90 V, observed in systems 1855A (red line) and 1855D (light blue line) containing compounds 4 and 7, respectively. These compounds have cyclohexyl rings in their structure. Very similar value was 91 V observed in composite based on only host mixture 1855 (dark blue). The highest driving voltage was observed in system 1855B (green line), comprising of compound 5, with two fluorine atoms substituted in middle and terminal aromatic rings. The most interesting feature is the driving voltage 70 V causing 50% of transmittance for all measured systems except system containing compound 5, with separated fluorine atoms.

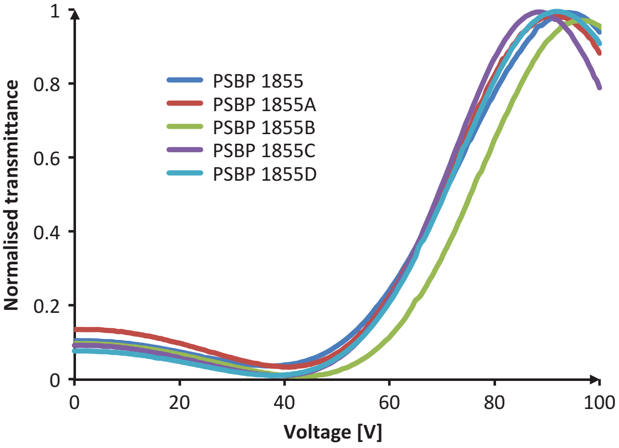


Figure 10. (colour online) Voltage dependent normalised transmittance of the PSBP modifications of the nematic host 1855 ($\Delta\varepsilon > 0$) at 23°C and $\lambda = 633$ nm, crossed polarisers.

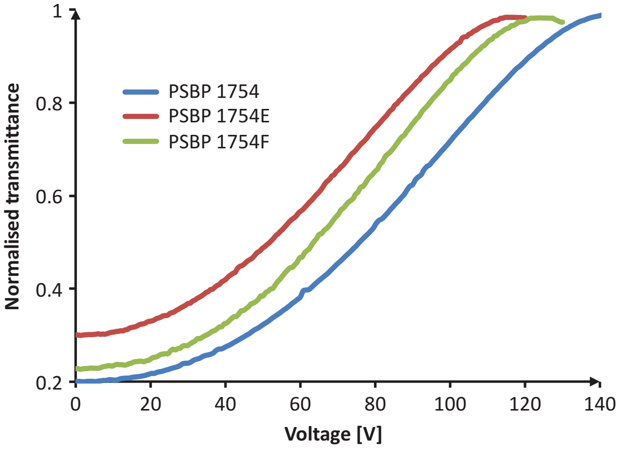


Figure 11. (colour online) Voltage dependent normalised transmittance of the PSBP modifications of the nematic host 1754 ($\Delta\varepsilon < 0$) at 23°C and $\lambda = 633$ nm, crossed polarisers.

Higher values of driving voltage and more meaningful differences have been observed in composites based on mixture 1754. In Figure 11, the blue VT curve for composite PSBP1754 shows T_{100} for 140 V. After doping fluorine substituted quaterphenyl 12, the value of driving voltage for 100% transmittance decreases to 121 V (green line represents composite PSBP1754F). The lowest voltage was noticed for the system 1754E, see red line on the plot. Addition of fluoro substituted tolane 11 results decreasing driving voltage to 112 V. To obtain lower operating voltage, the compounds forming mixtures should have structure elements providing π electrons and groups facilitating electron transfer.

In both types of formation an addition of compound with high polarisability results in significant increasing of Kerr constant value. The Kerr constants calculated by fitting the experimental data as adjustable parameters are given in Tables 2 and 3, with response times. Among dielectrically positive systems all calculated values are in range 0.38–0.49 nm/V^2, see Table 2. The medium containing compound 6, with three laterally trifluoro substituted aromatic rings has the highest Kerr constant. Lower values or Kerr constant has been observed in composites based on mixture 1754 ($\Delta\varepsilon > 0$), about 0.10 nm/V^2 to 0.13 nm/V^2, measured for composite with tolane 12.

Table 2. Electro-optic properties of PSBP modifications of the nematic host 1855 at 23°C, $\lambda = 633$ nm and cell gap $d = 10$ µm.

Mixture $\Delta\varepsilon > 0$	Kerr constant [nm/V^2]	Rise time [ms]	Decay time [ms]
PSBP 1855	0.447	0.336	0.214
PSBP1855A	0.480	0.316	0.128
PSBP1855B	0.376	0.212	0.103
PSBP1855C	**0.494**	0.189	**0.099**
PSBP1855D	0.408	**0.164**	0.167

Table 3. Electro-optic properties of PSBP modifications of the nematic host 1754 at 23°C, $\lambda = 633$ nm and cell gap $d = 10$ µm.

Mixture $\Delta\varepsilon < 0$	Kerr constant [nm/V^2]	Rise time [ms]	Decay time [ms]
PSBP 1754	0.100	**0.086**	0.192
PSBP 1754E	**0.134**	0.139	0.629
PSBP 1754F	0.129	0.115	**0.189**

Response times have been measured by applying voltage corresponding to the maximum transmittance, showed on VT curves. Listed rise time is a time from 10% to 90% of the peak signal and fall time is a time from 90% to 10% peak signal. Total response time is within the range from 550 µs in system of unmodified base mixture 1855 to 290 µs is system 1855C containing terphenyl 6. In the group of systems with negative dielectric anisotropy the total response time is the shortest for composite prepared from undoped mixture 1754 and its value is only 280 µs. The longest total response time was measured in system containing compound 12, the same one which increases Kerr constant and decreasing driving voltage.

3. Conclusions

In conclusion, we have demonstrated the influence of components structure on BP temperature range and electro-optic properties of obtained materials. Significant influence of chiral dopant as well as base nematic mixture on BP induction has been observed. Addition of fluorinated compounds with high density of π electrons in their structure results in wider BP temperature range and improves the electro-optic performance. Proposed PSBP materials have very fast total response time (even 280 µs) and Kerr constant about 0.13 nm/V^2 in dielectrically negative systems and 0.49 nm/V^2 in dielectrically positive systems. We have demonstrated that cyano derivative addition is not necessary to obtain stable BP material. All offered materials are comprised of only fluorinated compounds. They exhibit necessary high resistivity, high photochemical stability and also low viscosity. This fact has practical aspects, because mainly fluorinated compounds can be used in devices addressed by active matrices.

4. Experimental

4.1 Phase identification

Phase identification has been performed by an optical method. An Olympus BX51 (Tokyo, Japan) polarising optical microscope equipped with a Linkam THMS-600 (Tadworth, UK) heating stage and temperature controller TMS93 were used to identify and determine phase transition temperatures. The liquid crystal specimen was placed between two microscopic glass plates without any alignment layers or spacers for thickness control. Textures were observed during heating and cooling cycles with a temperature rate 0.5 K/min and accuracy ±0.1 K. The phase sequences and types were established by an observation of characteristic microscopic patterns and miscibility method.

4.2 HTP measurements

The HTP has been measured by means of selective light reflection method [24] and evaluated according to the equation $\mathrm{HTP} = (px_{\mathrm{e}})^{-1}$ [25], where x_{e} is the mole fraction of chiral compound and p is helical pitch. The helical pitch is linear function of selectively reflected light wavelength $\lambda_{\max}$ and is defined by the relationship $\lambda_{\max} = p_{\bar{n}}$, where $\bar{n} = (2n_{\mathrm{o}} + n_{\mathrm{e}})/3$ is the average refractive index. Prepared samples have been put between two glass plates without any surface treatment. To provide the planar alignment of molecules, the liquid crystal sample was heated to isotropic phase on a single glass plate, then cooled down, and after the transition to cholesteric phase started, the second plate was put onto the top. The cell has been placed into UV−VIS-NIR spectrophotometer Shimadzu UV−3600 (Kyoto, Japan) inside a Peltier cell equipped with a temperature controller. The measurements were conducted with 5 K step upon the cooling cycle.

4.3 PSBP preparation

To prepare the composites by forming amorphous polymer network in the liquid crystal BP, monofunctional monomer (dodecyl acrylate, from Sigma Aldrich; St. Louis, MO, USA), bifunctional monomer (1,4-bis-[4-(3-acryloyloxypropoxy) benzoyloxy]-2-methylbenzene) (from Chemos GmbH; Regenstauf, Germany) and photoinitiator (2-hydroxy-2-methyl-1-phenyl-1-propanone) were added to the mixtures with BP in concentration 4.5%, 5.5%, 0.5%, respectively. The homogenous mixture composed of liquid crystals, monomers and photoinitiator were prepared by stirring in isotropic phase. Then mixture in isotropic phase was filled into glass cell with controlled cell gap (10 µm) and indium thin oxide (ITO) coating on inner sides. Afterwards the cell was cooled down to the temperature 0.2 K below the N*-BPI transition (measured in heating). Then, the cell was irradiated in a supercooled state for 30 min with UV light, the density power was 2 mW/cm^2 measured at 365 nm (the light source was metal halide lamp Hamamatsu Photonics LC6; Hamamatsu, Japan). After polymerisation, the cell was cooled with the rate of temperature change 1 K/min.

4.4 Electro-optical measurements

The measurements have been conducted in a vertical field switching (VFS) mode [26]. In a VFS cell, the electric field direction is perpendicular to the ITO-coated glass plates and the optical axis of the induced refractive index ellipsoid is along the electric field direction, hence only the incident light at an oblique angle can experience phase retardation effect. In presented experiment the long axis of the cell was at an angle 70° to the incident laser light. Light is normally incident to the polariser and analyser. The absorption axis of polariser is at 45° and that of analyser is at –45° to the incident plane. The cell was immersed in a transparent container filled with glycerol in order to increase the angle of light passing through the sample. Without glycerol liquid, the incident angle would be greatly reduced due to Snell's refraction law. Figure 12 shows the experimental set-up for measurements in VFS mode. The cells gap was 10 µm, with ITO-coated glass substrates and without polyimide layer. All measurements were performed at about 23°C.

The measured transmittance can be converted to phase retardation ϕ by

$$\mathrm{T} = \sin^2\left(\frac{\phi}{2}\right) \tag{3}$$

The phase retardation in Equation (3) is related to the incident angle θ and applied electric field E as

$$\phi(\mathrm{E}) = \frac{2\pi}{\lambda} n_o(\mathrm{E})\mathrm{d}\left[\sqrt{1 - \frac{n_{\mathrm{g}}^2 \sin^2\theta}{n_{\mathrm{e}}^2(\mathrm{E})}} - \sqrt{1 - \frac{n_{\mathrm{g}}^2 \sin^2\theta}{n_{\mathrm{o}}^2(\mathrm{E})}}\right] \tag{4}$$

where λ is the laser wavelength, n_{g} is the refractive index of glycerol liquid ($n_{\mathrm{g}} = 1.47$) and θ is the incident angle in the glycerol. In the experiment, $\theta = 70°$, $n_{\mathrm{o}}(\mathrm{E})$ and $n_{\mathrm{e}}(\mathrm{E})$ are electric field dependent ordinary and extraordinary refractive indices of the PSBP composite [27], which can be described as

$$n_{\mathrm{o}}(\mathrm{E}) = n_{\mathrm{i}} - \frac{\Delta n_{\mathrm{ind}}(\mathrm{E})}{3} \tag{5}$$

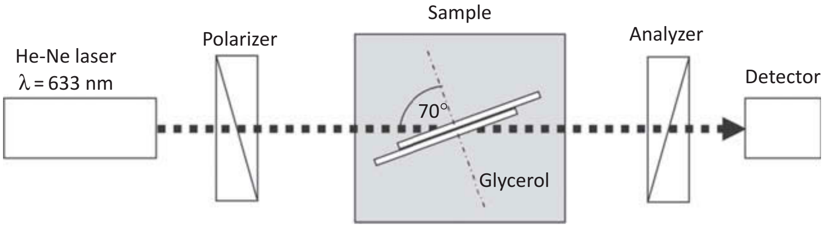


Figure 12. Experimental set-up for electro-optic measurements.

$$n_e(\mathrm{E}) = n_i + \frac{2\Delta n_{\mathrm{ind}}(\mathrm{E})}{3} \qquad (6)$$

In Equations (5) and (6), n_i represents the refractive index of the PSBP composite in the voltage-off state. The induced birefringence $\boldsymbol{\Delta} n_{\mathrm{ind}}$ is expressed by Equation (7), proposed by Yan [28], where $\boldsymbol{\Delta} n_{\mathrm{sat}}$ stands for the saturated birefringence and E^{s} represents the saturation field.

$$\Delta n_{\mathrm{ind}} = \Delta n_{\mathrm{sat}} \left(1 - \exp\left[-\left(\frac{\mathrm{E}}{\mathrm{E}_s}\right)^2\right]\right) \qquad (7)$$

Combining Equations (3)–(7), we are able to fit the experimental data leaving $\boldsymbol{\Delta} n_{\mathrm{sat}}$ and E_s as adjustable parameters. After obtaining the two parameters, Kerr constant K can be calculated by Equation (8) [26], since Equation (7) can be expanded and reduced to Kerr effect under small field approximation:

$$\mathrm{K} = \frac{\Delta n_{\mathrm{sat}}}{\lambda \mathrm{E}_s^2} \qquad (8)$$

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