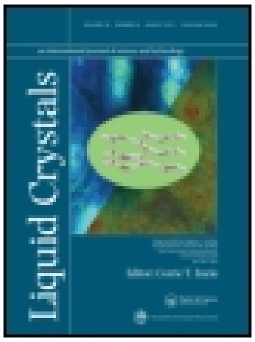

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Fast-switching effect using viscous chiral-nematic materials

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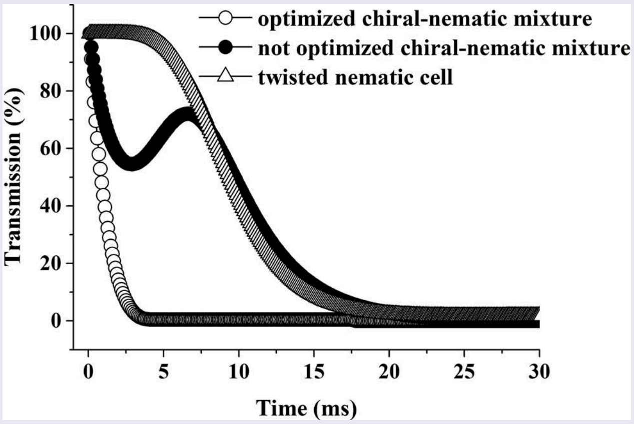
ABSTRACT

We report on chiral-nematic mixtures containing viscous chiral dopants, composed of rigid rod-like chiral molecules, in order to solve the problem of backflow in the middle layers of the liquid crystal cells. During the study, the viscoelastic properties of the liquid crystal compositions have been optimised, as well as the helical twisting power of the chiral compounds, the anchoring energy and the pre-tilt angle of alignment materials, the ratio between the cell gap and the helical pitch (d/P_0). After optimisation, we prepared test cells with low operating voltage – from 1.5 till 5.0 V, fast response time (τ_{on} + τ_{off}) – less than 1 ms, wide operating temperature range from −40°C till +100°C, and good thermal stability. It should be noted that the response time of the new electro-optical mode does not strongly depend on the cell gap, which is in contrast to other known operating modes. We have achieved rather linear than quadratic dependence of the response time when changing the thickness of the cell.



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Chiral-nematic mixtures; fast switching effect; viscosity; backflow

1. Introduction

Today, passive matrix liquid crystal displays (PM-LCDs) are still used especially in low-information content devices like digital watches, light shutters, etc. For simple low-information content displays, the twisted nematic (TN) effect was and remains the best electro-optic effect, which provides high brightness, fast response and, at the same time, requires a minimum uniformity of the cell gap and other technologically defined parameters during the production process.[1] Unfortunately, the steepness of the transmission–voltage curve of TN displays is insufficient and cannot be greatly increased by changing the liquid crystal (LC) material parameters in order to provide acceptable contrast ratio and field of view in high-information content displays. It was found that the steepness of the transmission–voltage curve depends strongly on the twist angle of the LC layer and could be dramatically increased by simply increasing the twist angle up to 180–270°.[2] At a twist angle of 270°, the central portion of the transmission–voltage curve attains an infinite slope. For twist angles >270°, the curve becomes double valued, indicating a region of bistability and hysteresis, which makes greyscale difficult to achieve.[3] To obtain twist angle >90°, an optically active dopant with an intrinsically twisted structure should be added to the nematic LC mixture. The amount of such dopants is determined by the desired twist angle and the thickness of the cell. The main advantage of this supertwisted nematic (STN) effect

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compared with the active-matrix displays is the simplicity of their design and low-cost production technology. On the other hand, STN displays have a number of drawbacks. First is the coloured appearance for the off-state, second is the slow response.[4] In this regard, the main efforts of the developers of the passive matrix displays were directed towards the improvement of the optical parameters and reduction of response time of STN displays.

To achieve lower response times is not enough to reduce the viscosity of the LC material since any reduction in the viscosity of the mixture leads to a sharp decrease in the image contrast.[5] Response time, besides viscosity, depends on many other factors: on the particular optical effect that is being used, on electrode structure, material flow in the cell, etc.[6,7] In spite of these manifold factors, there is a general tendency: the smaller the LC layer thickness, the shorter the response time. Optical mode interference (OMI) was proposed as an alternative to the highly coloured and slow STN-LCD.[8] Compared with STN, OMI exhibits a number of advantages such as better viewing angle, improved response times and less coloration. Moreover, its optical performance is much less sensitive to variations in the cell gap. The major difference between the OMI and STN-LCDs is that the optical path difference Δnd of OMI (Δn is the birefringence; d is the thickness of the cell) is much lower. However, reducing the thickness leads to a decrease of the phase delay compared to the conventional STN effect. Direct reduction of phase delay greatly reduces the brightness of the display, which is highly undesirable for portable applications, as it leads to increased power consumption.

Because the optical properties of highly TN structures depend not only on the characteristics of LC materials, but also on those of the surrounding layers (phase plates, polarisers), the task becomes so multiparametric that many research groups have stopped working on the optimisation of these devices, meaning they lost hope to find a mutually acceptable solution.

Thereby, until now the production of effective fast-switching LC devices is limited because of the low speed of reorientation of nematic LC material (the time of the reorientation is not less than 7 ms). To solve this problem, a comprehensive study of physical–chemical and electro-optical properties of chiral materials with different helical twisting power and different viscoelastic properties is required.

2. Materials and methods

At first, we assumed that viscous chiral dopants, composed of rigid rod-like chiral molecules of a defined length, with long helical pitch, low melting point and a broad temperature range of the chiral smectic C (SmC*) phase, could solve the problem of backflow in the middle layers of the cells with chiral-nematic mixtures.[9] The delay time when switching off will be equal to zero in that case (see Figure 1). To confirm our idea, 2–4-ring chiral compounds of Formula (1) have been synthesised and investigated:

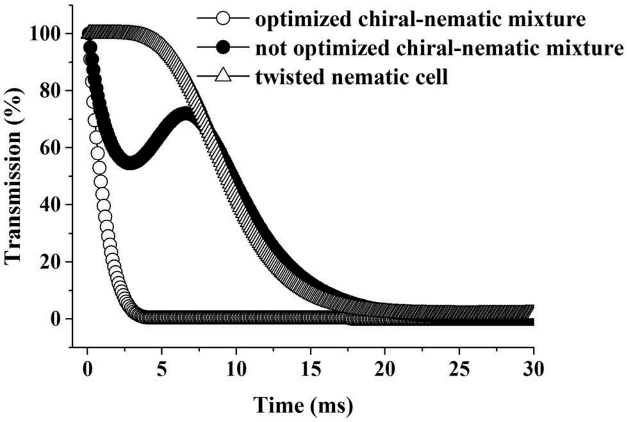
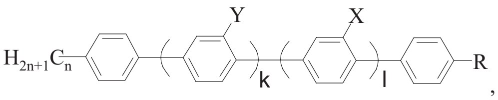


Figure 1. Transmission versus time for different liquid crystal cells.



, (1)

where $n = 4–10$; $k = 0–1$; $l = 0–1$; Y, X = Cl, F, CH_3; R = chiral fragment. New cholesteric mixtures were prepared by blending 10–30% of the compounds of Formula (1) with known commercial mixtures (Merck) ZLI-4792 (K_{11} = 13.2, K_{33} = 18.2), MLC-6657-100, ZLI-3201-100 and self-prepared mixtures M-1, M-2 on the basis of cyano-derivatives and M-3, M-4 on the basis of isothiocyanates.

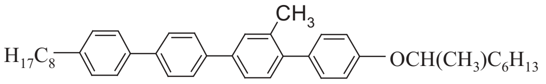
In order to study in more detail the switching behaviour of chiral mixtures, planar cells with antiparallel rubbing and 90° twist cells with different thicknesses (2–10 μm) were prepared. Commercial polyamides, nylon and other polymer materials with different pretilt angles were used as alignment layers.

The quality of LC alignment and the sample morphology were controlled using polarising optical microscope (Meiji Techno ML9400) interfaced with CCD camera at 20× in the transmission mode under crossed polariser's using white light source. Electro-optical parameters were measured using the set-up consisting of a He–Ne laser (λ = 632.8 nm), rotating table, Linkam LTS 350 hot stage coupled with the temperature controller Linkam CI 94 (with an accuracy ±0.1°C), function generator HP

33120A and the digital oscilloscope HP Infinium. The frequency of the square-wave electric field was 1 kHz for all electro-optical measurements. The light transmittance was detected by a photomultiplier and recorded using a digital oscilloscope. The rise and decay times were defined as times for optical transmittance change from 10% to 90% and vice versa.

3. Results and discussion

The first experiments showed that under use of 2- and 3-ring chiral compounds similar to Formula (1) it is impossible to obtain an ideal electro-optical response without delay time and without backflow. On the other hand, the first results with mixtures based on 4-ring chiral dopant confirmed the correctness of our reasoning:



, (2)

HTP – 1.4 μ^{-1}

Figure 1 shows electro-optical response measured for different test cells. For typical nematic mixture in 90° twist cells, we received a slow response, where the delay time is a few milliseconds and decay time is 8.8 ms. In planar cells under use of chiral-nematic mixture on the base of 3-ring chiral compounds similar to Formula (1), we obtained the electro-optical response with high delay time due to backflow. And only in the case of chiral-nematic mixture based on a 4-ring chiral compound (concentration in mixture 15 wt%) of Formula (2) in planar cells we obtained the electro-optical response without delay and with fast decay time (2.0 ms).

For further verification of our idea, we conducted a series of experiments with commercial mixtures from Merck in 90° twist cells and Merck mixtures with our dopants in planar cells. The weight concentration of our chiral dopants in the mixtures is 15%. The results presented in Table 1 show that the response time (t_{rise} + t_{decay}) is decreased 10–15 times for compositions containing our chiral dopant for cells with the same gap 4.2 μm and operating voltages 5 and 10 V.

Then, we investigated the compositions (commercial mixtures from Merck in 90° twist cells and Merck mixtures with our dopants in planar cells) under variation of the thickness, while the other cell parameters remained unchanged.

As we can see, the response time for our mode does not depend strongly on the cell thickness in comparison with the known modes. We have achieved rather linear than quadratic dependence of the response time on the thickness of the cell.

Table 1. Electro-optical parameters of Merck mixtures MLC-6657-100 and ZLI-3201-100 and described chiral-nematic mixtures.

					5 V		10 V	
Mixture	P_0 (μm)	d (μm)	V_{10} (V)	V_{90} (V)	t_{rise} (ms)	t_{decay} (ms)	t_{rise} (ms)	t_{decay} (ms)
MLC-6657-100	–	4.2	1.85	2.71	5.3	12.8	3.1	13.6
MLC-6657-100 + 15% of our dopant	4.9	4.2	2.2	2.5	2.2	0.6	0.5	0.6
ZLI-3201-100	–	4.2	2.13	3.03	9.7	18.2	5.8	19.7
ZLI-3201-100 + 15% of our dopant	4.4	4.2	2.75	3.12	4.3	1.3	0.9	1.3
ZLI-4792	–	4.1	2.13	3.07	7.1	16.2	2.8	15.7
ZLI-4792 + 15% of our dopant	4.7	4.15	2.4	3.1	1.8	0.84	0.58	0.82
M-1	5.0	4	1.5	2.1	0.9	0.9	0.4	0.9
M-2	5.1	4	1.5	2.0	0.9	0.8	0.4	0.8
M-3	5.3	4	2.0	2.1	0.4	0.7	0.2	0.7
M-4	5.5	4	1.7	1.9	0.5	0.6	0.2	0.6

As is well known, very slow decay time (several seconds) at temperatures below −20°C is one of the main problems for practical application of nematic LCs. Study of decay time at low temperatures for our chiral-nematic showed rather weak temperature dependence (see Figure 2). At a temperature of −40°C, the decay time is several hundred milliseconds in contrast to 8–10 s for a well-known nematic composition.

The next step in our experiments was to find an optimal thickness to pitch ratio d/P_0. All measurements were performed in planar cells with the same cell gap.

We found that when $0.6 < d/P_0 < 1.0$ is satisfied it is possible to realise a high-quality LCD device with fastest decay times (see Figure 3).

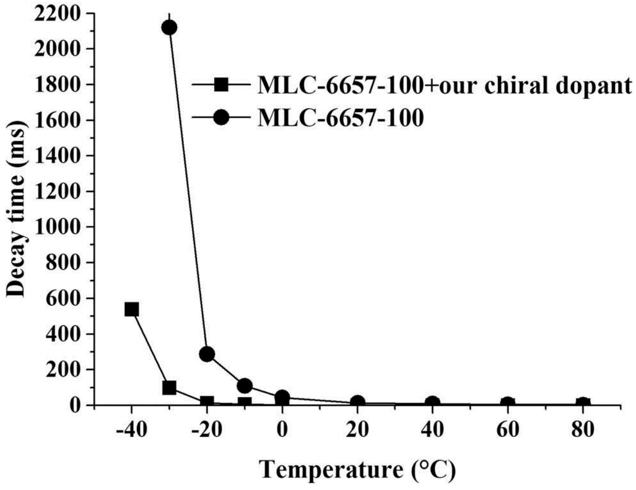


Figure 2. Decay time versus temperature.

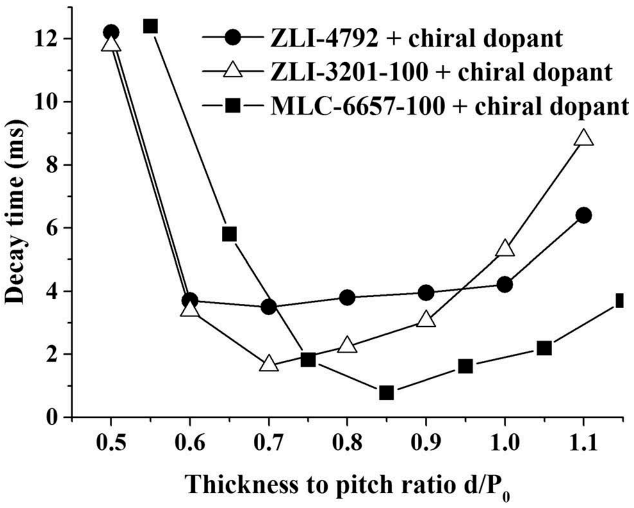


Figure 3. Decay time of the chiral-nematic mixtures versus thickness to pitch ratio d/P_0.

The results obtained allowed us to understand the key conditions for fast decay time at all cell thicknesses and at temperatures below zero. It is clear that the rise time depends primarily on the magnitude of the applied driving voltage, while a relaxation from the ON state to a twisted field state is driven by elastic torques, which depends upon the elastic constants of the material and appropriate alignment conditions. Apparently, in our case, the addition of viscous and elastic 4-ring chiral compounds causes distortion in twist-nematic LC composition and imparts a spontaneous helical twist of LC molecules with a pitch of the helical axis inversely proportional to the concentration of optically active dopants. Spontaneous helical twist of the LC molecules in combination with strong anchoring condition enhances the elastic restoring torque, tending to return the molecules to their original state. This in turn improves the decay time (Table 2).

Of course, one can obtain such optimal conditions only after optimisation of the other cell parameters (tilt angle, twist angle) and the material parameters (the helical twisting power of chiral compounds and the elastic constants of the nematic matrix).

At the final stage of our research, compositions M-1 to M-4 were designed and prepared (see Table 3).

The results presented in the Table 1 show the correctness of our estimations as for all mixtures the total switching time is about 1 ms. The best total response time is 0.8 ms. But we are sure this is not the limit. We think that with a certain selection of compounds it is possible to develop compositions with a total switching time less than 0.5 ms.

Table 2. Dependence of the response time of the nematic and chiral-nematic mixtures from the cell gap.

	MLC-6657-100					MLC-6657-100 + 15% of our dopant				
d (µm)	3.5	4.2	5.2	6.2	7.2	3.5	4.2	5.2	6.2	7.2
t_{rise} (ms)	2.3	3.1	4.8	7.0	9.9	0.47	0.5	0.57	0.66	0.78
t_{decay} (ms)	10.4	13.6	16.8	24.8	33.8	0.58	0.6	0.8	0.9	1.0

As a result, the above parameters have been optimised for planar cells:

- For alignment materials with pre-tilt angle >1°, rubbing direction on two substrates must be performed in different directions.
- Chiral-nematic LC composition contains at least one or two compounds with chiral centre.
- When $0.6 < d/P_0 < 1.0$ is satisfied, it is possible to realise a high-quality LCD device with fastest decay time <2 ms (see Figure 3).

The LC composition used for the LCD based on this effect should have the following characteristics:

- The elastic constants K_{11}, K_{33} should be higher in order to achieve fast decay time, e.g. for Merck mixture ZLI-4792 the value of elastic constants are $K_{11} = 13.2 \cdot 10^{-12}$ N, $K_{33} = 18.2 \cdot 10^{-12}$ N; meanwhile, for this mixture doped with our chiral dopant (ZLI-4792+chiral dopant): $K_{11} = 16.5 \cdot 10^{-12}$ N, $K_{33} = 21.7 \cdot 10^{-12}$ N. For mixture M-4 on the basis of isothiocyanates, $K_{11} = 15.6 \cdot 10^{-12}$ N, $K_{33} = 20.1 \cdot 10^{-12}$ N.
  Δnd should be within $0.5 < \Delta nd < 0.7$ in order to achieve high contrast and a wide viewing angle.
- The dielectric anisotropy ($\Delta\varepsilon$) has no effect and can be different.
- It should be chemically stable.

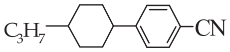
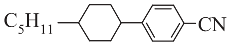
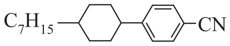
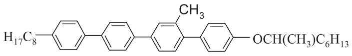
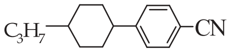
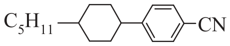
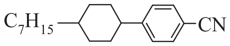
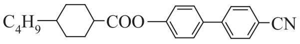
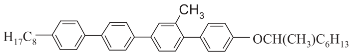
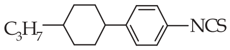
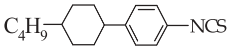
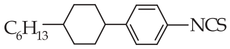
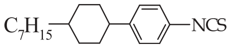
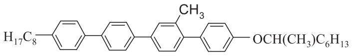
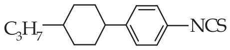
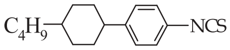
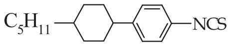
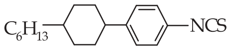
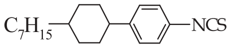
A chiral dopant used for an LC composition should have the following characteristics:

- Chemical structure should be without bridge fragments in order to attain low K_2 for chiral-nematic composition.
- Helical twisting power should be lower as 5 μ^{-1} in order to attain eutectic mixture with needed d/P_0.
- The birefringence (Δn) should be within $0.1< \Delta n < 0.25$ to attain eutectic mixture with needed Δnd.
- It should be characterised by good solubility with different classes of nematic compounds.

An alignment material should have the following characteristics:

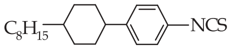
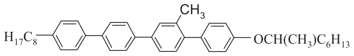
- Pre-tilt angle should be lower than 7°.
- An anchoring energy – strong anchoring (10^{-2} -10^{-3} J/m^2).

Table 3. Chemical composition of optimised mixtures.

Mixture	Formula	Concentration (wt%)
M-1		32.8
		36.2
		16.0
		15.0
M-2		27.8
		31.2
		13.0
		13.0
		15.0
M-3		32.8
		13.1
		32.0
		7.1
		15.0
M-4		29.6
		13.0
		1.6
		28.6
		5.6

(*Continued*)

Table 3. (Continued).

Mixture	Formula	Concentration (wt%)
		6.6
		15.0

```
                 current         mean          std dev         min            max
  Rise time(2)     Edge?    -------------- -------------- -------------- --------------
  Fall time(2)  766.4 µs      776.07 µs      10.70 µs       763.1 µs       797.4 µs
```

Figure 4. (colour online) Picture from oscilloscope: decay time for optimised chiral-nematic mixture.

4. Conclusions

The viscoelastic properties of the LC compositions as the helical twisting power of chiral compounds, the anchoring energy and pre-tilt angle of alignment materials, the twist angle Ψ and the ratio between the cell gap and the helical pitch (d/P_0) were optimised. After optimisation of all conditions, we prepared cells with low operating voltage – from 1.5 till 5.0 V, fast response time ($t_{\text{rise}} + t_{\text{decay}}$) – less than 1 ms, wide operating temperature range from −40°C till +100°C and good thermal stability. It should be noted that the response times of new electro-optical mode does not depend strongly on the cell gap in comparison with the well-known modes (Figure 4).

On the basis of the presented experimental data, we could establish a picture for the reorientation of molecules inside the cell, depending on the nature of chiral molecules and their helical twisting power, their anchoring energy and pre-tilt angle of the alignment materials.

Disclosure statement

No potential conflict of interest was reported by the authors.

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