

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

The electro-optic properties of colloidal silica filled nematics

N. J. Diorio Jr; M. R. Fisch; J. W. West

Online publication date: 11 November 2010

To cite this Article Diorio Jr, N. J. , Fisch, M. R. and West, J. W.(2002) 'The electro-optic properties of colloidal silica filled nematics', *Liquid Crystals*, 29: 4, 589 – 596

To link to this Article: DOI: 10.1080/02678290110114891

URL: <http://dx.doi.org/10.1080/02678290110114891>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The electro-optic properties of colloidal silica filled nematics

N. J. DIORIO JR., M. R. FISCH* and J. W. WEST

Liquid Crystal Institute, Kent State University Kent, Ohio 44242-0001, USA

(Received 1 February 2001; in final form 20 October 2001; accepted 29 October 2001)

The optical and electro-optical properties of filled nematic liquid crystals, nematic systems with added colloidal silica nanoparticles ($\leq 6\%$), have been studied. The macroscopic near IR birefringence of cells constructed from these materials was measured for wavelengths between 2 and $5\mu\text{m}$, and a wavelength independent value of 0.16 was obtained. The visible optical behaviour of cells formed with untreated ITO substrates using both filled nematic, and filled nematic and dichroic dyes was similar to those observed in polymer dispersed liquid crystals. At an electric field of $1\text{--}2\text{ V }\mu\text{m}^{-1}$, the cells were highly transmitting while at low fields they were highly scattering. The effects of colloidal silica nanoparticle concentration, cell thickness, electric field and substrate preparation (rubbed polyimide versus no surface treatment) on the electro-optical behaviour of these cells were studied.

1. Introduction

Over the past decade there has been considerable interest in liquid crystal dispersions such as polymer dispersed liquid crystals (PDLCs) [1] and 'filled' nematics, nematic liquid crystals that contain a small percentage (typically 1–5%) of small (<10 nanometer diameter) dispersed particles [2–5]. These mixed materials allow the material near the dispersed particles to be structured differently than the bulk. These systems are of continuing theoretical and experimental interest [6–10], and are of interest in displays. In one common version of a filled nematic display, fumed silica (aerosil), which is manufactured by flame hydrolysis of SiCl_4 , is added to the liquid crystal. These particles generate defects in the liquid crystal which scatter light making the filled liquid crystal medium appear cloudy. The application of an electric field to this medium causes reorientation of the liquid crystal and transformation of the defects so that a clear, weakly scattering state results. The behaviour of the medium after removal of the field is somewhat more complex, and depends on the chemical composition of both the liquid crystal and the silicon dioxide aerosil surface. Two behaviours have been observed. The first is characterized by the system relaxing back to a scattering state; while in the second the clear state remains—the system exhibits a memory effect.

Several potential applications exist for these materials. For example, if the filled particles are small enough, then scattering may be small. Such filled nematics may have applications as near IR devices. In the higher scatter-

ing situations, these devices are similar to PDLCs. In this mode of operation, filled nematics may be easier to fabricate than standard PDLCs. Moreover, because of their high liquid crystal content, dichroic dyes that are soluble in the liquid crystal may be added to produce coloured devices. The switching speeds of such devices are also important. Filled nematics may provide both long optical path length and fast switching times.

This paper describes experiments that study the optical properties of filled nematics constructed with colloidal silica nanoparticles. These materials exhibit switching behaviour but no memory effect for drive frequencies of 60 Hz and 1 kHz. When appropriate concentrations of silica are added, the optical behaviour is similar to that of PDLCs. These materials are largely liquid crystal, containing less than 6% silica; for this reason they may be doped with birefringent dyes and coloured cells made. Both dye-containing and dye-free cells have been constructed. A wide range of colloid sizes and concentrations in pure liquid crystals and liquid crystal mixtures of the cyanobiphenyl type have been examined. Millisecond ON switching times and 10–15 millisecond OFF times are routinely obtained in ITO coated cells that are $47\mu\text{m}$ thick. Switching voltages of approximately 0.5 to $1\text{ V }\mu\text{m}^{-1}$ are needed to switch the cell from the scattering state to the clear state. A small bias voltage of approximately 0.1 to $0.2\text{ V }\mu\text{m}^{-1}$ is used to improve the speed and performance of some of the cells. The response of the cell, both as a pure scattering device and between crossed polarizers, as a function of colloidal silica concentration, cell thickness and applied voltage are presented in this paper.

* Author for correspondence; e-mail: mfisch@lci.kent.edu

2. Materials and sample preparation

The colloidal silica was obtained from Nissan Chemical, Tokyo, Japan. It is supplied in a liquid dispersing agent (the dispersing agents in the present study were methanol and water) and contains negatively charged particles of amorphous silica. In the unaggregated state the particles are essentially spherical and have a narrow (± 10 – 15%) distribution of sizes. The properties of the colloids studied are outlined in the table.

The liquid crystals were Merck cyanobiphenyl compounds E7 and K15 (5CB). E7 is eutectic mixture while K15 is a pure compound. These materials can form hydrogen bonds with the silica as discussed in refs [4] and [6].

The mixtures were prepared with concentrations (c) between 0.2 and 6 wt %. Here, $c = m_s A / (m_{LC} + m_s A)$, where m_s is the concentration of silica and dispersant, A is the weight fraction of silica in the mixture of silica and dispersant, and m_{LC} is the mass of liquid crystal. Typical sample preparation consisted of adding the silica sols to the liquid crystal and mixing well. The mixture was then heated slowly to evaporate the dispersing liquid. This was done with occasional mixing at a temperature approximately 10°C above the nematic to isotropic transition temperature.

The test cells were constructed from rectangular glass substrates coated with transparent ITO (indium tin oxide) electrodes. The glass was cleaned with organic solvents and heated to evaporate all residual solvent prior to assembly. The cells were assembled with spacers (spin-coated or sprayed onto one substrate) of diameter 16 and $47\ \mu\text{m}$, and glued on two parallel edges. The cells were capillary filled with the nematic–silica mixture at temperatures well into the isotropic temperature of the mixture. We independently showed that for the concentrations studied the variation in nematic to isotropic transition temperature was less than 0.1°C from that of the silica-free liquid crystal.

Table. Characteristics of colloids used in this study.

Type (Nissan)	SiO ₂ /wt %	Dispersant	Size/nm
MT-ST	30	Methanol	12–14
MA-ST-S	30	Methanol	8–10
MA-ST-UP	15	Methanol	Elongated ^b
ST-ZL	40	Water	70–100
AMT-130S	40 ^a	Methanol	?

^a This is a high refractive index ($n = 1.67$) colloid of antimony pentoxide.

^b This is an aggregated form of silica in which the silica spheres aggregate into elongated, string-like objects with a width of approximately 10 nm and lengths in the range 40 to 300 nm.

The resulting cells were characterized under a polarizing microscope and through their optical response. The polarizing microscope showed textures that strongly depolarized light. The size of the structures varied, and the structures were quite close together. They varied from as small as could be determined, approximately $1\ \mu\text{m}$, to larger than $20\ \mu\text{m}$.

3. Investigations

The motivation for each investigation, the experiments performed, and the results of the study are presented in this section. Because of the rather limited literature on colloidal silica filled nematics, and the desire to avoid several short reports, this paper presents the results of a number of different experiments.

3.1. Filled nematic birefringence in the near IR

3.1.1. Motivation

Filled nematics with particles of diameter less than about one twentieth of the wavelength of light in the material are expected to be weakly scattering, yet still have the potential to be of use in new optical devices. In the absence of aggregation, for particles of diameter 10 to 30 nm the factor of twenty corresponds to visible wavelengths. If the particles aggregate, then the weak scattering condition will be satisfied in the near IR. Optical microscopy indicated that a range of sizes existed in these mixtures and that structures larger than 30 nm were in the liquid crystal–nanoparticle mixture. Furthermore, there is continuing interest in IR applications of liquid crystals to telecommunications, military and other uses. With these ideas in mind, we investigate the birefringence of these mixtures in the near IR.

3.1.2. Experimental

The magnitude of the optical birefringence (Δn) of liquid crystals is essential to a number of electro-optic applications. The technique of Wu *et al.* [11] was used to obtain the optical birefringence. This technique utilizes polarized IR measurements on aligned samples to determine the birefringence. The present measurements were performed using a Nicolet FFT IR spectrometer and IR polarizers on samples at room temperature. This technique has the advantage of being simple, and measuring the average birefringence over a large macroscopic area, approximately 1 cm in diameter. The wavelength region studied was limited by the absorption of the glass substrates at high wavelengths and the range of the spectrometer at low wavelengths. The 20°C data supplied by Merck was fit to the ‘single-band’ model discussed in Khoo and Wu [12]. A fit that matches the birefringence in the visible to ± 0.001 and obtains a birefringence of 0.185 in the region of the IR studied ($\Delta n = 0.186$ and

$\Delta n = 0.184$ at 2 to 5 μm respectively) is obtained. The fitting parameters obtained from the present fit are essentially identical to those in ref. [12].

3.1.3. Results and discussion

The results of the present study are shown in figure 1. Four observations may be made. First, there are characteristic resonances visible near 3.5 and 4.5 μm ; these resonances are also visible in the E7 data in [12]. Second, the background birefringence is essentially wavelength independent in the region of study (wavelengths not too close to the resonances) for both pure E7 and E7–colloidal silica nanoparticle mixtures. This agrees with the above results for pure E7, and more importantly indicates that for nanoparticle concentrations less than 6%, and in the presence of strong alignment layers, the silica nanoparticles do not destroy the large-scale optical birefringence. Thirdly, the birefringence is independent of concentration of added silica. This is important because it allows these filled nematics to be used in applications where the birefringence is essential to device operation. Lastly, the birefringence determined in the present experiment is somewhat smaller (by about 0.025) than that predicted by the above model. This may be because the samples were not oriented precisely in the spectrometer.

3.2. Static optical properties of filled nematics in the visible

3.2.1. Motivation

Devices that utilize the change in transmitted light between the voltage ON, low scattering state, and the low bias voltage, high scattering state can be constructed from these materials. The simplest such device is filled

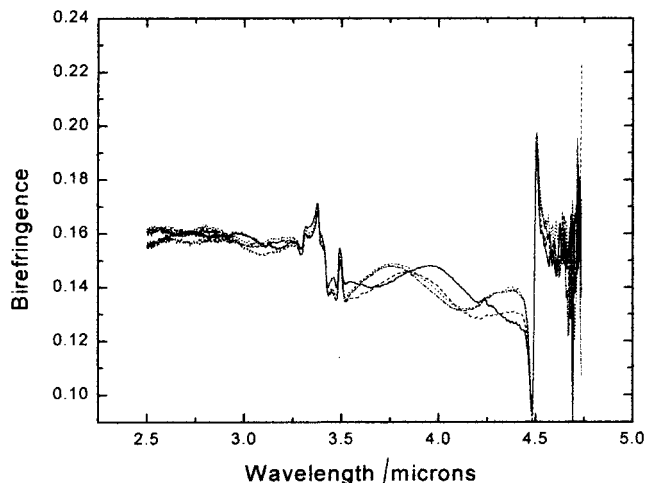


Figure 1. Birefringence of E7 and E7–ST-ZL silica mixtures vs. wavelength in the near IR. (— pure E7, ---- 1.3% ST-ZL, ···· 3.8% ST-ZL, ····· 6% ST-ZL).

nematic between optically transparent electrodes. Such a device is reminiscent of PDLCs, and when operated in this model these devices have many of the same advantages as PDLCs. In particular, they are very insensitive to incident light polarization, insensitive to variations in filled nematic thickness, optically efficient in the transmitting state, and can be made quite large. Except for 4–5% reflection losses at the air–glass interfaces, nearly all of the incident light can be transmitted through such devices.

3.2.2. Experimental

The static (steady state) behaviour of these devices must be investigated with care. Drzaic [1] stresses the importance of the collection optics in describing the static electro-optic response of scattering devices. This is because the contrast ratio [transmission in the low scattering state]/[transmission in the high scattering state] of such devices depends on the $f/\#$ of the detector. By adjusting the $f/\#$ of the detector the contrast can be varied by several orders of magnitude. For $f/0$ optics, a PDLC typically achieves a contrast ratio of less than two.

This series of experiments was performed at room temperature, over visible wavelengths with a Perkin-Elmer™ 19 spectrophotometer equipped with an integrating sphere detector. The devices were placed in contact with the entrance hole of the integrating sphere. This means the detector has an $f/\#$ near $f/0$. Thus, we measured the combination of the directly transmitted and the diffusely transmitted light using $f/0$ optics.

3.2.3. Results and discussion

The amount of visible light transmitted through two different filled nematics is shown in figure 2. The transmission is not spectrally flat. However, the maximum variation in transmission throughout the visible is less than 10%. In addition, the amount of light transmitted through the sample using $f/0$ optics changes very little, only a few %, between the scattering and unscattering states. This is despite the great difference in resolution of the images viewed through the devices in these two states—a sign across the room could not be read in the scattering state, yet could be read in the transmitting state.

A large number of different types and concentrations of colloids were tested. The elongated shape was not very effective. However, good optical performances were obtained with both the small (MA-ST-S) and the larger size colloids (ST-ZL and AMT-130S). These cells also exhibit a dependence of the scattering on nanoparticle concentration. The amount of light scattered increased with the concentration of silica, reached a maximum and then decreased. The maximum scattering occurred at a

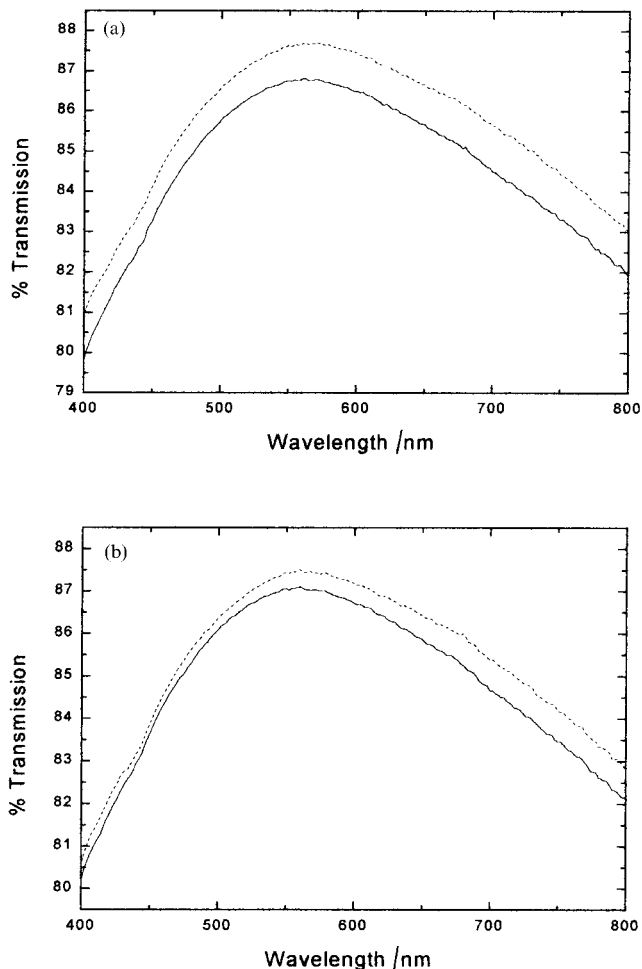


Figure 2. (a) Light transmitted through $47\ \mu\text{m}$ cell versus wavelength with $f/0$ collection optics for 1.3% ST-ZL colloid in E7. Top curve: 47 V applied to sample; bottom curve: 0 V applied. (b) As (a) except 1% AMT-130S in E7, and top curve corresponds to 48 V.

concentration of approximately 1–2%. Such behaviour has also been observed in protein solutions [13] and has the following explanation. The initial increase in scattering is due to an increase in the number of scattering centres. At high concentrations, the scattering decreases due to correlations in the positions of the scattering centres. Thus for example, perfect crystals with well correlated molecular positions scatter very little light. Hence, at some intermediate concentration a peak in scattering is expected.

These filled nematics have the property of scattering somewhat more light (about 15%) when a small ($0.1\text{--}0.2\ \text{V}\ \mu\text{m}^{-1}$) voltage is applied than when no voltage is applied. This was generally observed and suggested that a scattering state voltage not equal to zero is optimal; this is verified by experiment. At present, we have no theory to explain this phenomenon; we speculate

that the liquid crystal may become somewhat ordered by the nanoparticles, and this helps ‘index match’ the silica to the liquid crystal. The small electric field then changes this orientation so that there is a greater index mismatch and more scattering.

Lastly, the data illustrate that these filled nematics scatter very strongly in the forward direction. A $47\ \mu\text{m}$ sample in the scattering state is not completely opaque; rather it scatters sufficiently strongly that detail such as written words or faces cannot be discerned. However, colours can be discerned.

3.3. Static optical properties of dye-containing filled nematics in the visible

3.3.1. Motivation

PDLCs have found applications as electrically controlled shutters. Because they are scattering devices that contain roughly 50% liquid crystal, they scatter strongly in the voltage OFF state and appear white. In the voltage ON state, these devices are clear. There are applications where a colour other than white in the scattering state and no colour (or relatively much less colour) is desired in the non-scattering state. Because filled nematics are largely liquid crystal, adding dyes is expected to change the colour of the material. This series of experiments explored this possibility.

3.3.2. Experimental

The same mixtures as used in all the experiments discussed in this paper were the starting points. To some mixtures small amounts of dichroic dyes manufactured for liquid crystal displays were added. Typically, a concentration of 1% or less of the dye in the liquid crystal led to cells that exhibited the desired properties. These properties are a strong scattering and well coloured voltage OFF state (or low voltage state), and a weakly scattering, weakly coloured voltage ON state. Two dichroic dyes were used in this study: the blue coloured cells contained Nippon Chemical G-256 dye, while the orange coloured cells contained Nippon Chemical G-206. The transmission versus wavelength of these devices (at room temperature) was performed with a Perkin-Elmer 19 spectrophotometer in the same geometry as used for the static measurements in undyed devices.

3.3.3. Results and discussion

These cells exhibit a combination of both scattering and absorption. The amount of transmitted light for cells that appeared to be blue and orange to the naked eye is shown in figure 3. There is still some residual absorption even in the voltage ON state; to the eye, this is less serious than appears from the graphs. A white

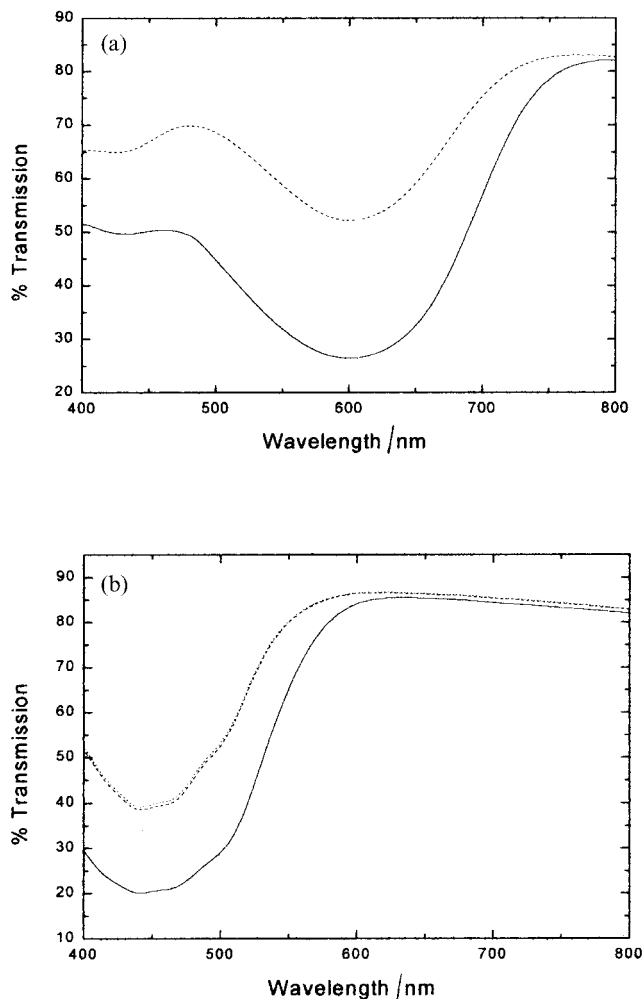


Figure 3. (a) Light transmitted through a $47\ \mu\text{m}$ sample consisting of 1.2% AMT-130S and 0.3% G-256 in E7 versus wavelength. Top curve: 47 V applied; bottom curve: 0 V applied. (b) Light transmitted through a $47\ \mu\text{m}$ sample consisting of 1.5% AMT-130S and 0.4% G-206 in E7 versus wavelength. Top curves: 47 and 95 V applied, respectively; bottom curve: 0 V applied.

wall takes on a slight blue or orange colour when viewed through these devices in the voltage ON state. In the OFF state, the samples are highly scattering and well coloured. Also, the response is essentially complete when the applied voltage is $1\ \text{V}\ \mu\text{m}^{-1}$. Changing the applied potential to $2\ \text{V}\ \mu\text{m}^{-1}$ (as shown in the bottom panel of figure 3) results in no change in the wavelength response of the cell, see figure 3(b).

While the change in colour appeared to be reasonably large, it was quantified by using an electro-optics measurement system that was designed and built in-house. This instrument includes a spectrometer that can be used to determine the chromaticity of displays. By referencing the spectra to the CIE 1931 chromaticity diagram, the (x, y) coordinates of the blue cell are (0.243, 0.213) in the

scattering state and (0.273, 0.245) in the non-scattering state. The corresponding coordinates for the orange dye cell are (0.345, 0.377) and (0.312, 0.363). While neither device is pure white in the transmitting state, the colour changes a noticeable amount when the field is applied.

3.4. Switching times

3.4.1. Motivation

In many applications, a liquid crystal light valve is switched between two states characterized by differences in transmitted light intensity. This is in fact a simple description of a (TN) device. It is well known that most displays are designed as a compromise between fast switching times and good optical performance [14]. The optical performance of a display is best at large cell gaps, while the switching times are fastest at small cell gaps. The goal of this series of experiments was to investigate the ability the silica nanoparticles to break up the liquid crystal so that the switching times were similar to those of a thin cell, while maintaining large cell gap optical performance.

3.4.2. Experimental

The optical switching characterization of these cells was performed using the electro-optics measurement system developed in house. Briefly, this instrument used a white light source (Oriel Model 77501 Fibre Optic Illuminator) connected to a large diameter fibre. The output of the fibre was supported in a standard holder. A sheet polarizer in a rotation stage followed next in the optical train; this polarizer was generally oriented so that the light passing through it was polarized either vertically, horizontally, or at 45° from the horizontal. The filled nematic cell followed next in the optical train. Another sheet polarizer on a rotation stage followed when measurements between crossed polarizers were performed. A Tektronics J6523 1° Narrow Band Luminance Probe was the detector. The frequency of the square-wave electric field applied to the cell could be varied; however, the measurements performed with this instrument were limited to 992 Hz. Visual observation and optical polarizing microscopy was also performed using 60 Hz a.c. Even at 60 Hz, no memory effects, where the state of the nematic did not change on removal of the voltage, were observed.

Three variants of the filled nematic cells were tested. The first simply placed filled nematic between untreated ITO coated glass slides. The second variant consisted of filled nematic between antiparallel rubbed polyimide (Du Pont PI2555) ITO coated glass slides. This type of cell might be of use as a phase shifter or similar device. The third type of cell was the standard TN cell with the same rubbed polyimide alignment layers.

3.4.3. Results and discussion (untreated substrates)

Several general observations may be made about this type of cell. First, the rise and fall times are independent of colloid concentration and type. For example, at room temperature the optimal fall time in non-surface treated $16\ \mu\text{m}$ spaced cells was between 12 and 15 ms for MA-ST-S, ST-ZL, and ATM-130S colloids in the concentration range 0.4–6%. Over the same concentration range the rise times varied from 0.5 to 2.5 milliseconds. The corresponding times for similarly prepared $47\ \mu\text{m}$ spaced samples are 12–16 ms for the fall time and 1.5–3 ms for the rise time. In all cases, there are the 90% to 10% fall times and 10% to 90% rise times. The above are all ‘optimal’ times—the scattering state voltage (bias voltage) was adjusted to give no more than about 5% bounce in the intensity when switching from the transmitting to the scattering state.

The data illustrate another important point: the fall time is independent of cell thickness. There is sufficient filler that the decay time is dependent only weakly and erratically upon colloid concentration. The rise time depends on the potential difference applied across the cell. A systematic study of a 2% MT-ST-S sample showed the rise time is proportional to $1/V^2$ where V is the potential applied to the cell in the transmitting state. The above characteristic times correspond to an applied potential of $1\ \text{V}\ \mu\text{m}^{-1}$. The fall times obtained from the same sample show no systematic variation with the cell potential, showing a value of approximately 18 ms for potentials between 0.5 and $2\ \text{V}\ \mu\text{m}^{-1}$.

A typical device response is illustrated in figure 4, where data obtained from a $47\ \mu\text{m}$ thick sample of 1% MT-ST-S in E7 are shown. This is a graph of the normalized response of the cell to turning it on and turning off with two different bias voltages. The bottom

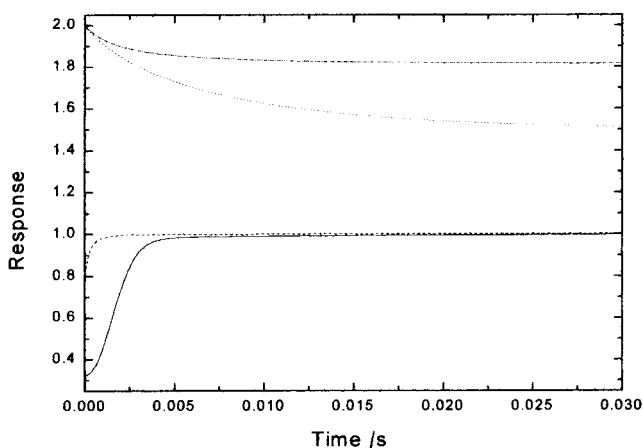


Figure 4. Normalized temporal response of a $47\ \mu\text{m}$ thick sample of 1% MT-ST-S in E7. The top two curves have been displaced by 1 so they vary from 2 to 1 rather than 1 to 0. (— 0 to 47 V, ---- 15 to 47 V, 47 to 0 V, ····· 47 to 15 V).

two curves show the turn-on behaviour and the top two curves the turn-off behaviour. The turn-on curves are normalized to 1 at long times, while the turn-off curves are normalized to 1 at time = 0. Upon turning the cell on, a faster response is obtained when the bias voltage is 15 V rather than 0 V. However, this comes at the cost of lower contrast. In this case, the OFF state voltage is 80% of the ON state voltage. In the case of $V_{\text{bias}} = 0\ \text{V}$, the OFF state detector signal is 30% of the ON state signal. This is also reflected in the turn-off response where a faster decay time is evident for the higher bias voltage.

The effects of sample thickness and bias voltage on the response of 2.4% ST-ZL colloid in E7 samples are shown in figure 5. Figure 5 is a graph of the normalized temporal response (in the same manner as in figure 4) of 16 and $47\ \mu\text{m}$ thick samples, when the maximum voltage applied to the cell is $1\ \text{V}\ \mu\text{m}^{-1}$. The bottom two curves show the turn-on behaviour of these cells. Although they have different bias voltages (4.7 V for the $47\ \mu\text{m}$ cell and 3 V for the $16\ \mu\text{m}$ cell), the rise time of these two cells are essentially identical. The normalized turn-off response is shown, displaced by one unit, at the top of the figure. The fall time of the $16\ \mu\text{m}$ cell is slightly faster than that of the $47\ \mu\text{m}$ cell. The curve that attains a minimum and then rises corresponds to a bias voltage of zero V. This response is typical of these cells when the bias voltage is zero. The bias voltage is the minimum voltage that ‘flattens’ this curve, and is empirically determined. It is usually $0.1\text{--}0.2\ \text{V}\ \mu\text{m}^{-1}$, and tends towards the higher value in the $16\ \mu\text{m}$ cells.

3.4.4. Results and discussion (rubbed substrates)

The behaviour when filled and unfilled nematics are placed between rubbed antiparallel glass plates is more

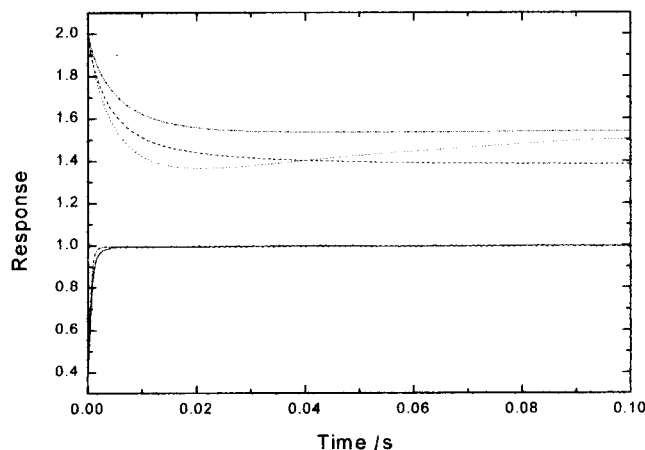


Figure 5. The normalized temporal response for 16 and $47\ \mu\text{m}$ samples of 2.4% ST-ZL samples in E7. The top curves have been displaced upwards by one unit. (— $16\ \mu\text{m}$, 3 to 16 V, ····· $47\ \mu\text{m}$, 5 to 47 V, $16\ \mu\text{m}$, 16 to 0 V, ---- $16\ \mu\text{m}$, 16 to 0 V, ······ $47\ \mu\text{m}$, 47 to 5 V).

complex than that seen with samples between untreated glass slides. Normalized responses for this type of cell are shown in figure 6. The data summarized in this figure was obtained with the incident white light polarized at 45° to the rubbing direction, and the analyser perpendicular to the polarizer. With the polarizers in this orientation, one expects a signal when no (or little) voltage is applied to the rubbed cells and no signal when a high potential is applied across the cell. Interestingly, this behaviour was not wholly verified. The ON voltage state was less transmitting than the OFF state. However, the ON state did not give zero transmission. In all of the curves, the data is normalized so that the maximum signal is one; the top two curves are displaced by one unit. In all cases, there are significant switching transients. In the rubbed cells where transients persist approximately 10 ms after the voltage is applied, while in the filled cell without alignment layers the transient lasts less

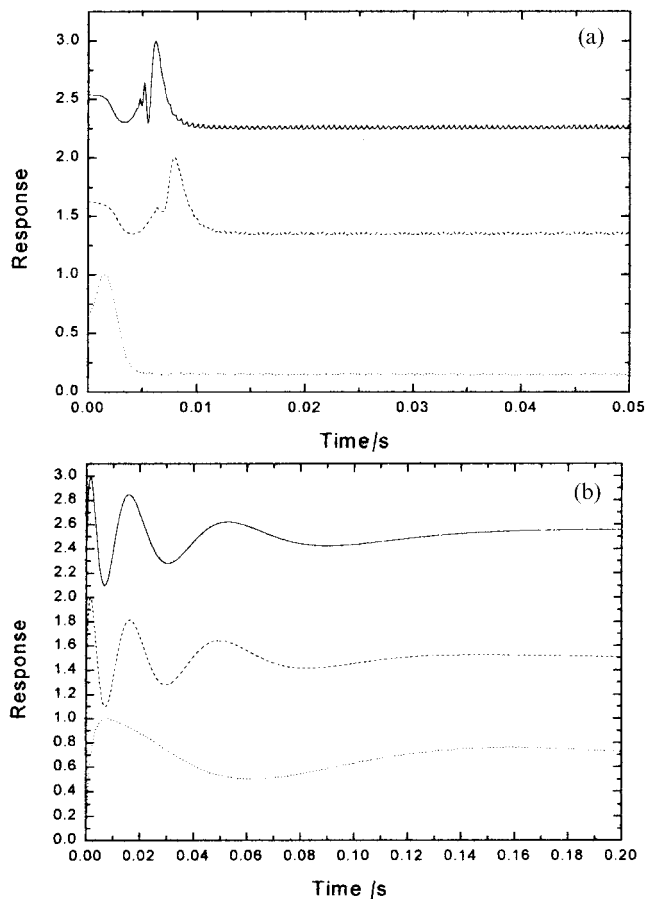


Figure 6. Comparison of normalized temporal response of $47\ \mu\text{m}$ samples in rubbed antiparallel cells and untreated cell between crossed polarizers. (a) Switching from 0 to 47 V; (b) switching from 47 to 0 V (— pure E7 rubbed cell, ---- 1% MA-ST-S rubbed cell, 1% MA-ST-S untreated cell).

than 5 ms, see figure 6(a). The situation upon removing the voltage is similar, if not worse; the rubbed cells take approximately 150 ms to relax, while the untreated cell relaxes in about 50 ms, see figure 6(b).

Colloidal silica filled nematics were also tested in twisted nematic cells. The slow response times associated with 'thick' TN cells containing single frequency addressing LCs are well known and these experiments demonstrated these problems once more. Typical data are presented in figure 7. They were obtained with the twisted nematic cell between crossed polarizers with the incident polarization parallel to the incident face rubbing direction. In this configuration, the optical system transmits maximum intensity when no potential is applied to the cell and minimum intensity when a potential is applied to the cell. The normalized response as a function of time for turn-on conditions is shown at the top of the graph. The corresponding time scale is along the top of the graph. The rise time in both filled and unfilled nematics is close to 400 ms. The normalized turn-off response is shown at the bottom of the graph with a much smaller time scale. The fall time is of order 10 ms for both filled and unfilled nematics. The filled nematic cell has a faster fall time and a slower rise time than the corresponding unfilled nematic. However, the product of these two times is roughly constant and equal to $2.5 \times 10^{-3}\ \text{s}^2$. These numbers should be compared with the same material in an unrubbed cell, as shown in figure 6. In an unrubbed cell, the contrast is lower, but the rise and fall times are significantly faster. Note also that all normalization in this report is by the peak transmission; it is *not* defined so that the minimum transmission is

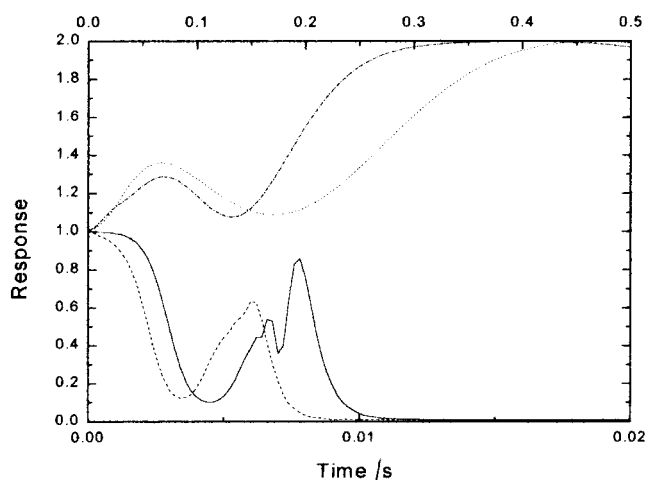


Figure 7. Normalized temporal response of $47\ \mu\text{m}$ twisted nematic cells. The top two curves refer to the top time axis and the bottom two curves to the bottom time axis. The top curves have been displaced by 1. (..... E7, 47 to 0 V; ---- 1% MA-ST-S in E7, 47 to 0 V; — E7, 0 to 47 V; ---- 1% MA-ST-S in E7, 0 to 47 V).

is zero and the maximum transmission is one. In conclusion, the present devices do not provide an advantage over pure liquid crystal when used in cells that include alignment layers.

4. Summary

The optical and temporal properties of colloidal silica filled nematic light valves in a number of different configurations have been investigated. The addition of colloidal silica particles to the liquid crystal changes the switching characteristics of the cells. With no voltage applied, the cell is in a highly scattering state. By applying a voltage between 0.5 and 1 V μm^{-1} , the cell can be switched to a weakly scattering state. The speed and performance of the switch can be enhanced by providing a bias voltage of 0.1 to 0.2 V μm^{-1} in the scattering state, rather than using zero voltage. Several different types and concentrations of colloidal particles were studied, and the best results were obtained with larger size particles in concentrations between 0.5 and 2% by weight. Under these conditions, the switching time between scattering and non-scattering states is essentially independent of cell thickness and concentration of colloid. When used without polarizers, these cells may be useful for beam steering and adaptive optic applications where their high polarization independence, rapid change in refractive index, and high transmission under applied voltages fulfil a standing need.

This work was supported by the National Science Foundation Advanced Liquid Crystal and Optic Materials science and technology centre under Grant No. DMR-8920147. The authors thank Dr Phil Bos for the use of optical test equipment. We also thank

Dr Matsumara of Nissan Chemical for supplying the colloidal silica and suggesting some of the silica types and sizes that were investigated; also Dr Jon Ruth for helpful comments.

References

- [1] See for instance, DRZAIC, P. S., 1995, *Liquid Crystal Dispersions* (New Jersey: World Scientific).
- [2] EIDENSCHINK, R., and DE JEU, W. H., 1991, *Electron. Lett.*, **27**, 1195.
- [3] KREUZER, M., TSCHUDI, T., and EIDENSCHINK, R., 1992, *Mol. Cryst. liq. Cryst.*, **223**, 219.
- [4] KREUZER, M., TSCHUDI, T., DE JEU, W. H., and EIDENSCHINK, R., 1993, *Appl. Phys. Lett.*, **62**, 1712.
- [5] KREUZER, M., and EIDENSCHINK, R., 1996, *Liquid Crystals in Complex Geometries*, edited by G. P. Crawford and S. Zumer (London: Taylor and Francis), pp. 307–324.
- [6] GLUSHCHENKO, A., KRESSE, H., RESHETNYAK, V., REZNIKOV, YU., and YAROSHCHUK, O., 1997, *Liq. Cryst.*, **23**, 241.
- [7] GUBA, G., REZNIKOV, YU., LOPUKHOVICH, N., OGENKO, V., RESHETNYAK, V., and YAROSHCHUK, O., 1994, *Mol. Cryst. liq. Cryst.*, **251**, 303.
- [8] RUHWANDL, R. H., and THERENTJEV, E. M., 1997, *Phys. Rev. E*, **55**, 2958.
- [9] BELLINI, T., CLARK, N. A., DEGIORGIO, V., MANTEGAZZA, F., and NATALE, G., 1998, *Phys. Rev. E*, **57**, 2996.
- [10] LEE, S., and PARK, C., 1999, *Mol. Cryst. liq. Cryst.*, **333**, 123.
- [11] WU, S.-T., EFRON, U., and HESS, L. D., 1984, *Appl. Opt.*, **21**, 3911.
- [12] KHOO, I.-C., and WU, S.-T., 1993, *Optics and Nonlinear Optics of Liquid Crystals* (New Jersey: World Scientific), p. 90.
- [13] SIEZEN, R. J., FISCH, M. R., SLINGSBY, C., and BENEDEK, G. B., 1985, *Proc. natl. Acad. Sci. USA*, **82**, 1701.
- [14] YE, P., and GU, C., 1999, *Optics of Liquid Crystal Displays* (New York: John Wiley).