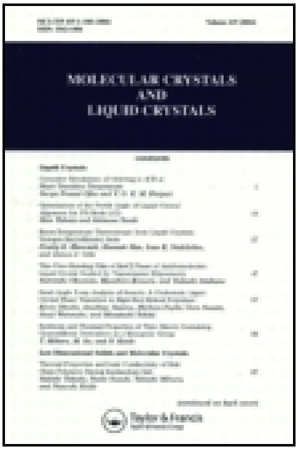

Molecular Crystals and Liquid Crystals

Performance of UV-stable STN Mixtures for PL-LCDs

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PERFORMANCE OF UV-STABLE STN MIXTURES FOR PL-LCDS

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In general commercial STN mixtures are based on materials, which absorb UV light and are degraded by it. In order to generate long lifetimes for Photoluminescent Liquid Crystal Displays (PL-LCDs) it is necessary to develop STN mixtures that are transparent and, therefore, stable when operating with UV light. We have formulated STN nematic mixtures by adding UV-transparent chiral dopants into an UV-stable nematic mixture. Comparisons of the results of life tests and absorption spectra of these mixtures with analogous mixtures with conventional UV-unstable LCs, which contain conjugated phenyl rings and/or cyano-groups, show that such groups absorb in the UV and consequently lower the UV stability of the mixtures. The physical properties of the mixtures have been evaluated to assess the likely device performance of the resulting PL-LCD. In order to assess its multiplexability the sharpness of its electro-optic response was determined using single pixels with twists of 180°, 240° and 270°. We found that 240° twist gives the best multiplexing as 270° showed hysteresis.

Keywords: liquid crystals; PL-LCD; STN mixture; UV-stability

INTRODUCTION

Owing to their unique electro-optical properties, the potential applications of liquid crystals have been extended into many new areas. In addition to working in the visible spectral region, they are also required to operate in the infrared, e.g., in telecommunication devices (operating wavelength

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1550 nm) [1], as well as the near UV region, e.g., in Photoluminescent Liquid Crystal Displays (PL-LCDs) [2]. PL-LCDs use the nematic phase as a shutter to modulate the incidence and intensity of narrow-band excitation light (usually in the near UV) on a flat screen covered with a regular pattern of photoluminescent phosphors, which in turn emit visible light, i.e., red, green and blue light, due to the Stoke's shift. Using a monochromatic collimated beam of light with a very narrow band-width for orthogonal incidence removes the angle dependency and dispersion effects of the light output from the LCD part of the PL-LCD. This allows major improvements in the electro-optic performance (e.g. multiplexability and contrast) of the LCD. The phosphor screen then converts this modulated beam of monochromatic UV into bright visible light with a Lambertian distribution, i.e., without any angle dependence. Thus, the PL-LCD essentially combines the exceptional light output from a CRT with the lightness and flat, thin shape of an LCD. The greatly improved characteristics and electro-optic efficiency of PL-LCDs should make possible radically new emissive display panels for the important emerging markets in desktop computer monitors, video screens and large area displays.

Present PL-LCDs use fluorescent tubes to obtain 390 nm light by activating a suitable phosphor with a low-pressure mercury discharge. But even the best available phosphors only give bandwidths of about 20 nm FWHM. High-pressure mercury lamps give lines around 365 nm having a much narrower effective bandwidth, i.e., $\sim$3 nm FWHM. Therefore, use of UV light with a wavelength of 365 nm, rather than 390 nm, should give rise to a much improved performance for PL-LCDs. However, the nematic liquid crystal mixtures used in conventional LCDs absorb UV light and, therefore, suffer from photochemical degraded under UV exposure (particularly for $<$390 nm) within a short period of time. Therefore, the development of UV-stable nematic liquid crystals, which can reliably function over a prolonged period at least at 390 nm or even below, is a important issue for the optimisation of the device performance, especially life-time, of PL-LCDs with high light output.

With the above aim in mind, we have formulated UV-stable nematic mixtures for use in PL-LCDs with an STN-LCD as the beam modulator, that are transparent above 300 nm and last for longer than $>$30,000 hours at 390 nm or $>$8000 hours at 365 nm. The physical properties of the mixtures have been evaluated in order to assess the performance of the resulting PL-LCD. The electro-optic responses of single pixels with various degrees of twist have also been measured in order to assess the device multiplexability. Several commercially available nematic mixtures from E. Merck, designed for other applications, with a low UV-absorption and other suitable physical properties, have been modified as described below to function in prototype PL-LCDs incorporating an STN-LCD.

EXPERIMENTAL

Suitable nematic host mixtures were initially selected according to their UV absorption spectra. The candidates chosen as host LC mixtures for use in a modified form in STN-LCDs were ZLI-2222-000 and MLC-9000-000, both of which possess positive dielectric anisotropy (E. Merck). In order to avoid the UV absorption of conventional glass substrates, the test cells were made using quartz plates with a 6 µm cell gap.

The UV spectra, obtained using a UV/Vis Spectrometer (Unicam, UV4), are shown in Figure 1.

The UV spectrum of ZLI-2222–000 exhibits an absorption peak, the tail of which extends beyond 300 nm. However, MLC-9000-000 is almost completely transparent above 300 nm. This means that the latter would be expected to be more UV-stable. Therefore, MLC-9000-000 was chosen as a suitable nematic host mixture for modification for use in STN-LCDs. Two chiral dopants (JC-16 and JC-17) were prepared. A small amount of these chiral dopants were added to MLC-9000-000 (1.14% of JC 16, and 1.68% of JC 17) to produce the chiral nematic mixtures MJ16 and MJ17, respectively, with the desired magnitude of twist for use in STN-LCDs.

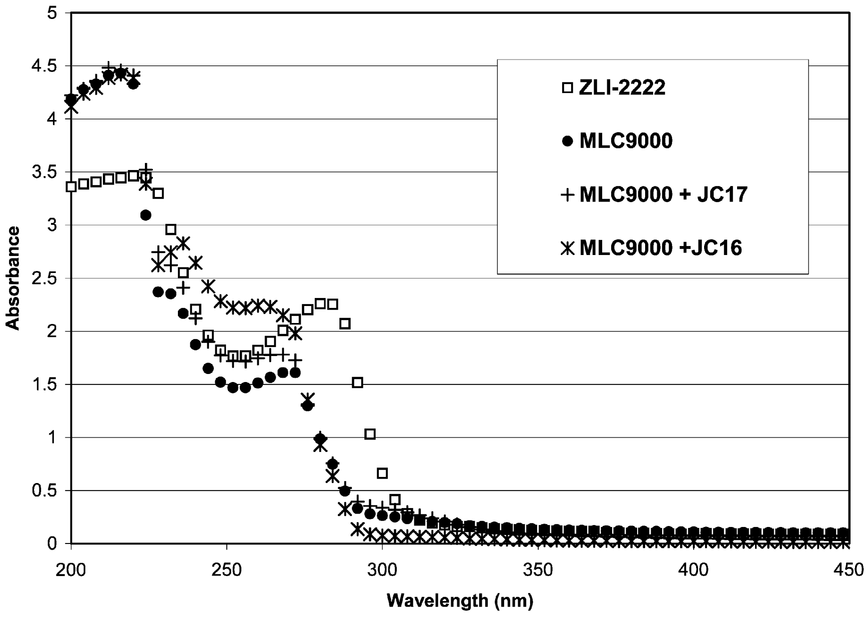


FIGURE 1 UV absorption spectra for ZLI-2222, MLC-9000/000, MLC-9000/000 + JC16 (1.14%) and MLC-9000/000 + JC17(1.68%) in quartz cells.

The life-time tests were carried out by filling the nematic mixtures into glass cells with a 6 μm gap, which were then exposed to 365 nm light in a UV life-test unit. This is an accelerated test for operation at 390 nm, since the life-time of nematic mixtures at 390 nm has been shown to be approximately four times that determined for the same mixture illuminated at 365 nm. In the UV life-test set-up, a 365 nm nominal, unfiltered, low-pressure fluorescent lamp was used. The spectrum is essentially narrow band (about 18 nm FWHM) at 365 nm. However some spectral lines from the mercury discharge are also observed as a visible glow from the lamp. The main wavelengths are at 405 nm, 436 nm, 546 nm and 615 nm. The intensity of the emission at 365 nm was monitored and the radiant flux maintained at 3 mWcm^{-2} at the test samples by adjusting the position of the lamp during the tests as the intensity decreased over time. The lamps were replaced when this level could no longer be achieved. The cabinet was maintained at 40℃. The resistance and capacitance of the test cells were measured periodically using a Hewlett Packard Multifrequency LCR meter (Model 4274A). The quality of the alignment was also checked visually by rotating the samples between crossed polarisers. The test cells were monitored about once every week.

In order to assess the performance of the doped chiral nematic mixtures in an STN-LCD, relevant physical properties, such as dielectric anisotropy, birefringence dispersion (in a range of 340 nm to 850 nm), the splay-to-bend elastic constant ratio (k_{33}/k_{11}), helical twisting power and the electro-optic response of single pixels, were measured. The equipment for measuring dielectric properties of liquid crystals included a Schlumberger (SI 1260) Impedance/Gain-phase Analyser, a Chelsea Dielectric Interface and a programmable Mettler Temperature Controller (FP82) with a Central Processor (FP 80). This allows elastic constants to be determined when fitting a set of dielectric permittivity measurements to the variation of applied ac field for both the homeotropic and planar aligned liquid crystal cells. Birefringence values in a wide wavelength range (from UV to the infrared) were obtained by determining the phase differences occurring when monochromatic polarised light propagates through a medium with an anisotropic refractive index [3] using an optical spectrum analyser (Rees Instruments). The helical twisting powers of the two chiral dopants were measured by using the Grandjean-Cano method [4] for wedge-shaped cells filled with the "guest-host" chiral nematic mixtures by using a travelling microscope (DECK 45115). Finally, the electro-optical transmission as a function of applied voltages for different pixels with various twist angles was measured using a range of computer controlled equipment including a Functional Generator (WAVETEK MODEL 275), Autocal Digital Multimeter (1065, DATRON Electronics Ltd.), remote-controllable Oscilloscope (LeCroy 9420 DUAL 350 MHz) and Lock-in Amplifier (EG&G Instruments 7260 DSP).

RESULTS AND DISCUSSIONS

1. UV-Stability:Dependence on Chemical Structures of LCs

Liquid crystals often decompose steadily upon exposure to high intensity light, which they absorb. In other words, the photo-stability of liquid crystals is largely related to their absorption spectra. The latter is determined by the electronic transitions between energy levels. It is well known that the transition from excited σ-bonds (e.g. -CH_2-CH_2-) gives rise to absorption at the shortest wavelengths (120–200 nm). The n-π^* and π-π^* transitions (including -CH_2O-, C=O, C=C, etc.) have absorptions at longer wavelengths than 200 nm. Moreover, absorption may shift towards even longer wavelengths with increased conjugation. In principal, to modulate light in the UV, especially for $\lambda < 390$ nm, liquid crystals ought to possess as many saturated chemical bonds and as few conjugated double bonds, especially those in conjugated aromatic rings, as possible.

The nematic mixture ZLI-2585 is a UV-stable material [5], since it is primarily composed of CCH homologes, which contain two saturated cyclohexane rings with no carbon-carbon double bonds. Consequently, such CCH derivatives exhibit almost no absorption at wavelengths >250 nm. However, although demonstrating satisfactory UV stability is possible using nematic mixtures based on liquid crystals incorporating CCH molecular cores, the nematic mixture ZLI-2585 is not suitable for STN-LCD applications, because it is of negative dielectric anisotropy. The nematic mixture MLC-9000-000 is intended for use in TN-LCDs with active matrix addressing. Therefore, it is primarily composed of poly-fluorinated components of positive dielectric anisotropy. Although, for proprietary reasons, the detailed composition of this mixture is not known to us, fluorinated compounds with low conductivity used in mixtures for active matrix LCDs are usually are less prone to ionic accumulation from the substrates than analogous nitrile-containing materials. This is illustrated by comparing the nematic mixture ZLI-2222-000, described as a 'high threshold sharpness mixture for high duty ratio and second minimum TN displays', with MLC-9000-000. The UV spectrum of ZLI-2222-000 (shown in Fig. 1) exhibits absorption peaks for longer wavelengths (>300 nm) than that of MLC-9000-000. This is probably due to the presence of benzonitrile derivatives used to induce a positive dielectric anisotropy in the mixture. This indicates that it is probably less photo-stable than MLC-9000-000. However ZLI-2585 and ZLI-2222-000 were used as reference materials to compare measurements for both UV absorption and UV life-time tests.

The two chiral dopants, JC16 and JC17, used to induce the desired amount of twist in the host nematic mixtures do not contain a phenyl ring bonded to another aromatic ring or a non-saturated group, such as a nitrile function. Therefore, the absorption spectra of these two compounds show no absorption at wavelengths above 300 nm. Due to their stable chemical features and the fact that very little absorption occurs above 300 nm, the dopants are expected to be fairly stable under UV and thus not to affect the photo-stability of the corresponding STN mixtures.

2. UV-Stability: Nematic Mixtures

UV life-time tests were carried out for the host nematic mixtures MLC-9000-000, ZLI-2222-000, ZLI-2585 as well as the corresponding doped nematic mixtures MJ16 and MJ17. Because the test is very time consuming, some of the tests started in 1997 as soon as the LCs tested were purchased.

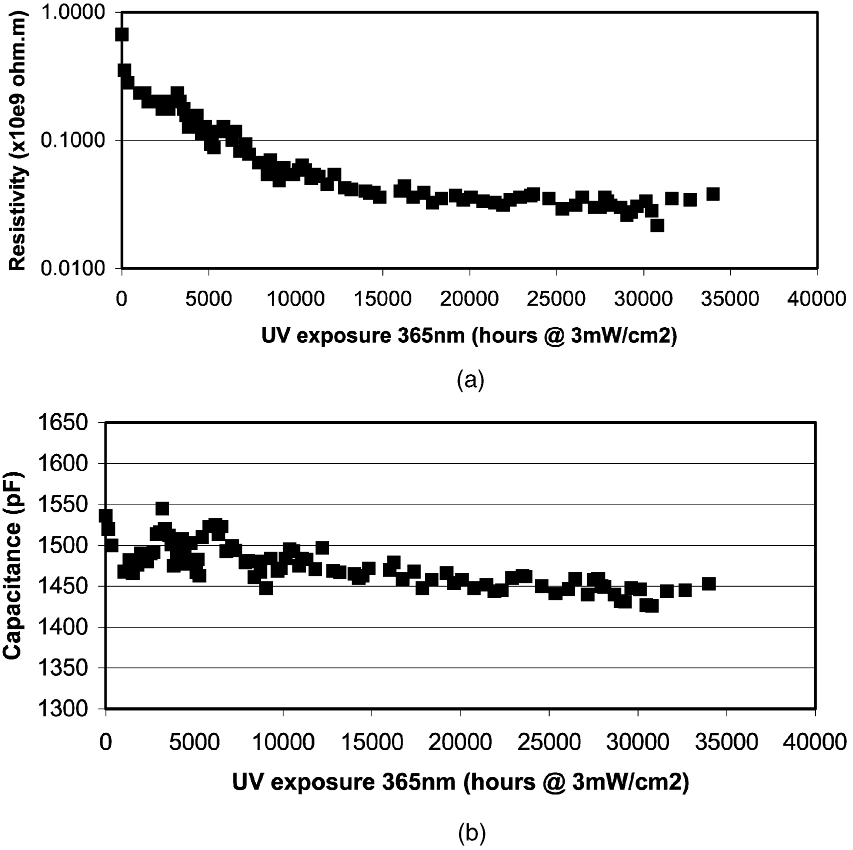
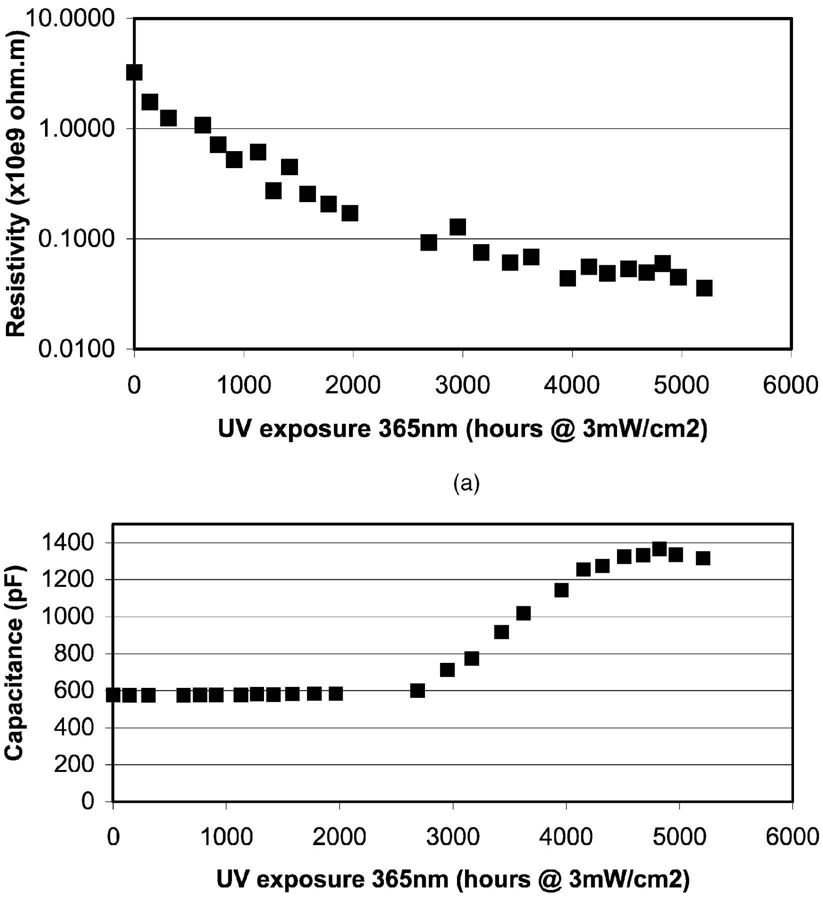


FIGURE 2a–b UV life-time results of ZLI-2585. **a** (top) resistivity vs time; **b** (bottom) capacitance vas time.

The results of the life-time test for resistivity and capacitance against time exposure to 365 nm UV rays for ZLI-2585, ZLI-2222-000 and MLC-9000-000 are shown in Figures 2–4, respectively.

From the results for ZLI-2585 in Figure 2a–b, it can be seen that, with time, its resistivity drops initially and then becomes stable, while the capacitance stays almost unchanged. Furthermore, regular observation of the alignment through crossed polarisers shows that the planar cell alignment remains unchanged. All of these facts confirm that, after life-testing for longer than 4 years, the material is still usable. The excellent



(a)

(b)

FIGURE 3a–b UV life-time results of ZLI-2222. **a** (top) resistivity vs time; **b** (bottom) capacitance vas time.

UV-stability can be clearly attributed to the absence of conjugated carbon-carbon double bonds in the liquid crystalline components of this mixture.

The life-test results for ZLI-2222 are shown in Figure 3a–b. As for ZLI-2585, its resistivity decreases steadily with time. However its capacitance started increasing after being stable for about 2500 hours and finally stayed at a higher level. Between crossed polarisers it was found that the originally homogeneous alignment of the test cell gradually changed into homeotropic after the turning point in capacitance. This behaviour was found to be very reproducible with duplicate cells. We conclude that the continuous decrease in resisitivity reflects ionic accumulation in the molecular system under

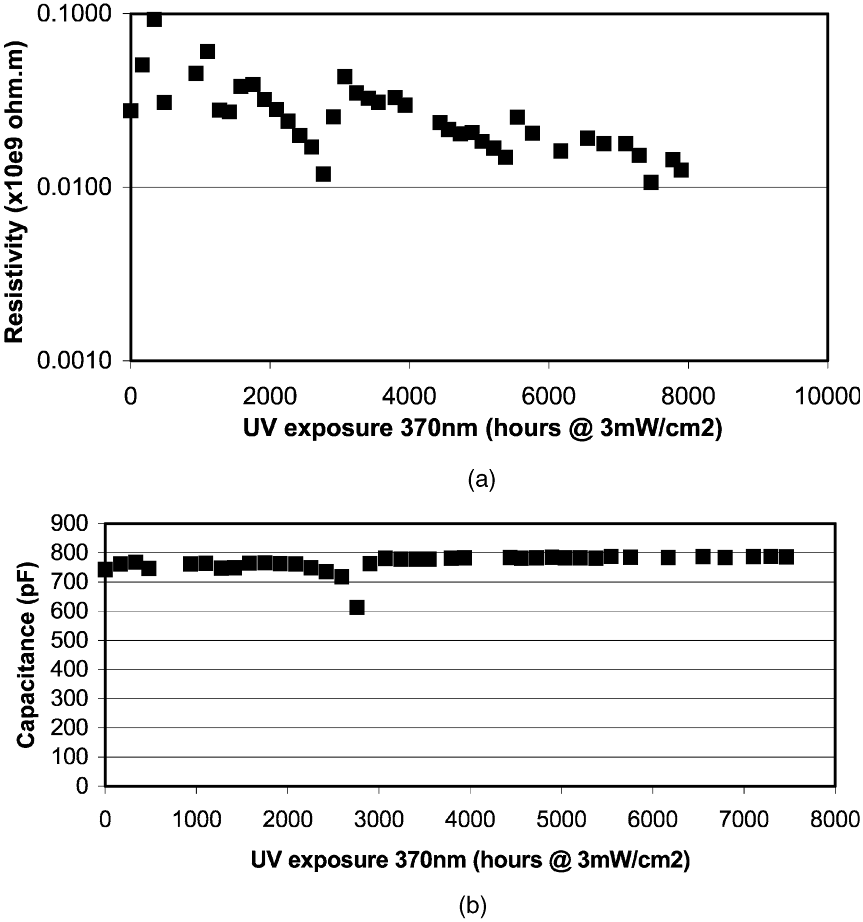
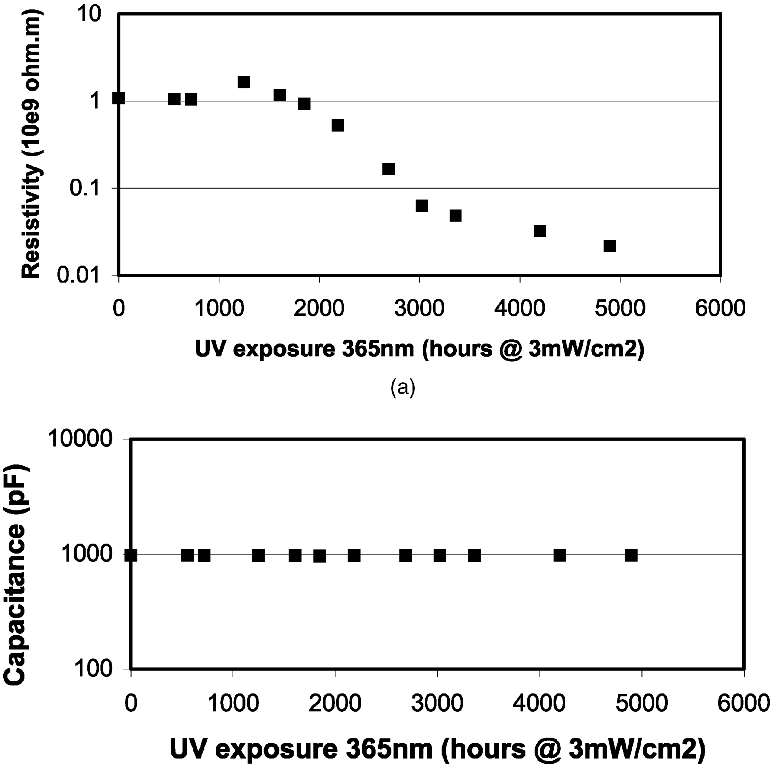


FIGURE 4a–b UV life-time results of MLC-9000/000. **a** (top) resistivity vs time; **b** (bottom) capacitance vas time.

exposure to UV. Consequently, the accumulated ions on the surfaces of the ITO coated glass substrates changed the alignment from planar to homeotropic. This gives rise to an increase in cell capacitance. Although the nature of the UV-generated ions remains unclear, the observed photo-instability is probably related to conjugated phenyl rings present in the BCH and CBC components as well as the conjugated cyano group in the BCH component.

So far as we know, MLC-9000-000 is a mixture of fluorinated compounds. As indicated in Figure 4a–b, its life-test results show similar behaviour to that of ZLI-2585. However, after about 8000 hours, the test cells began to form a gas and bubbles appeared in the cells. However no changes in capacitance or the cell alignment could be determined. Gassing occurred not only for MLC-9000-000 but also for other mixtures, even in some of the cells containing ZLI-2585.



(a)

(b)

FIGURE 5a–b UV life-time results of MLC-9000/000 + JC16 (1.14%). **a** (top) resistivity vas time; **b** (bottom) capacitance vas time.

There are two possible explanations for this problem: a) chemical decomposition of LC molecules or impurities in the cells; b) cell leakage due to the failure of the sealing glue. Our investigation is still in progress for clarifying this point. But the consistency of the results for many samples suggests that the former is likely to be the case for MLC-9000-000. For ZLI-2585, since some cells did not gas it seems likely that b) applies to the cells that did. The phenomenon of gassing was also found for the corresponding doped nematic mixtures MJ16 and MJ17 (the relevant results are shown in Figs. 5–6), after about 5000 hours for MJ16 at 365 nm light (20000 hours

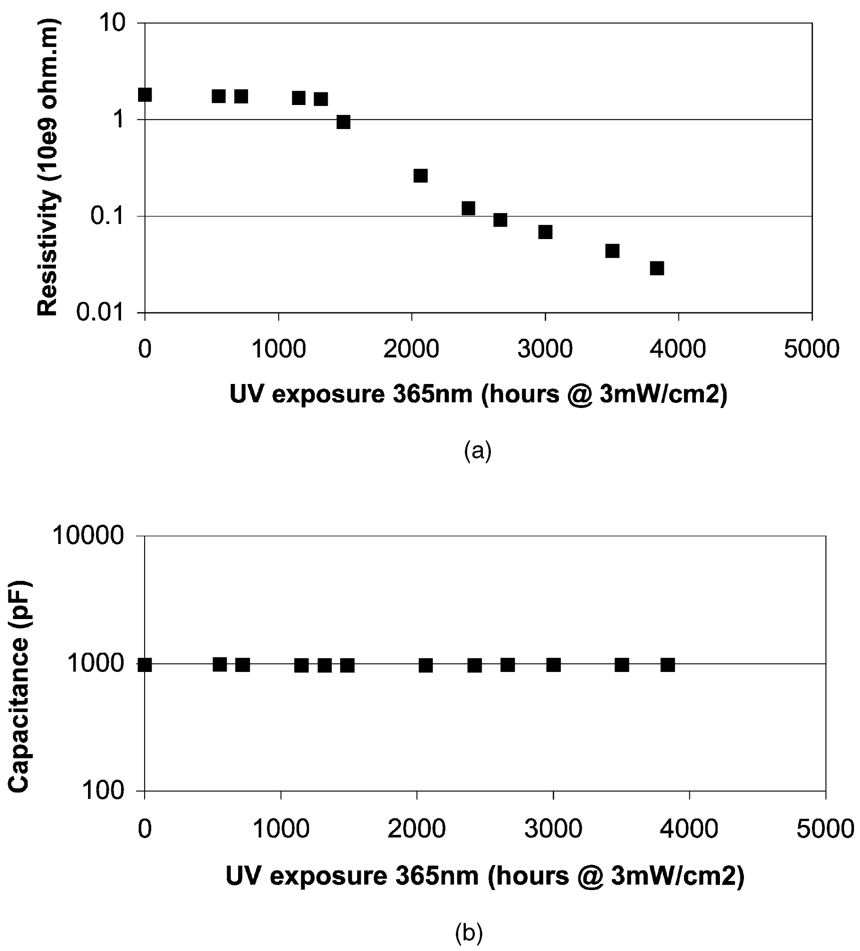


FIGURE 6a–b UV life-time results of MLC-9000/000 + JC17 (1.68%). **a** (top) resistivity vas time; **b** (bottom) capacitance vas time.

at 390 nm light), and 4000 hours for MJ17 at 365 nm light (16000 hours at 390 nm light).

3. Physical Properties and Multiplexability of the STN Mixtures

The UV-stable host MLC-9000-000 is a nematic mixture designed for use in TN-LCDs with TFT active matrix addressing. It has a fairly large dielectric anisotropy and modest values for the elastic constants. Consequently, it has a fairly low threshold voltage. The results of the evaluation of its physical properties with regard to the operating wavelengths of 365 nm and 390 nm, are given in Table I. The helical twisting power of two chiral compounds JC16 and JC17 was also measured and found to be $8.8\,\mu m^{-1}$ and $6.1\,\mu m^{-1}$, respectively.

In order to evaluate the multiplexability when using the STN mixtures, the sharpness of the electro-optic responses of single pixels with various degrees of twist, i.e., 180°, 240° and 270°, were determined. The transmission as a function of applied voltage (square wave, 1000 Hz) for the two mixtures under illumination with 365 nm light is shown in Figure 7a–b.

It can be seen from Figure 7a–b that for both mixtures the pixels with 240° twist exhibit maximum sharpness. Hysteresis loops were found from the E-O responses for 270° twist cells. Accordingly, 240° twist will give rise to maximum multiplexability when used for analogue switching. Using the relevant data obtained from the electro-optic measurements, the calculated multiplexability for the two mixtures according to the Multiple-Row-Addressing Method [6] is found to be 227 for MJ16 and 198 for MJ17.

TABLE I Evaluated Data of MLC-9000-000

Clearing point (°C)	88
S-N transition (°C)	-40
Elastic constants (20°C)	$\kappa_{11} = 11.05 \times 10^{-12}$ $\kappa_{33} = 18.56 \times 10^{-12}$ $\kappa_{33}/\kappa_{11} = 1.68$
Dielectric anisotropy (20°C)	$\Delta\varepsilon = 8.36$ $\varepsilon_{\parallel} = 12.62$ $\varepsilon_{\perp} = 4.26$
Optical anisotropy (20°C)	0.094 (365 nm) 0.091 (390 nm)
Threshold voltage (V) (10,0,20)	1.4

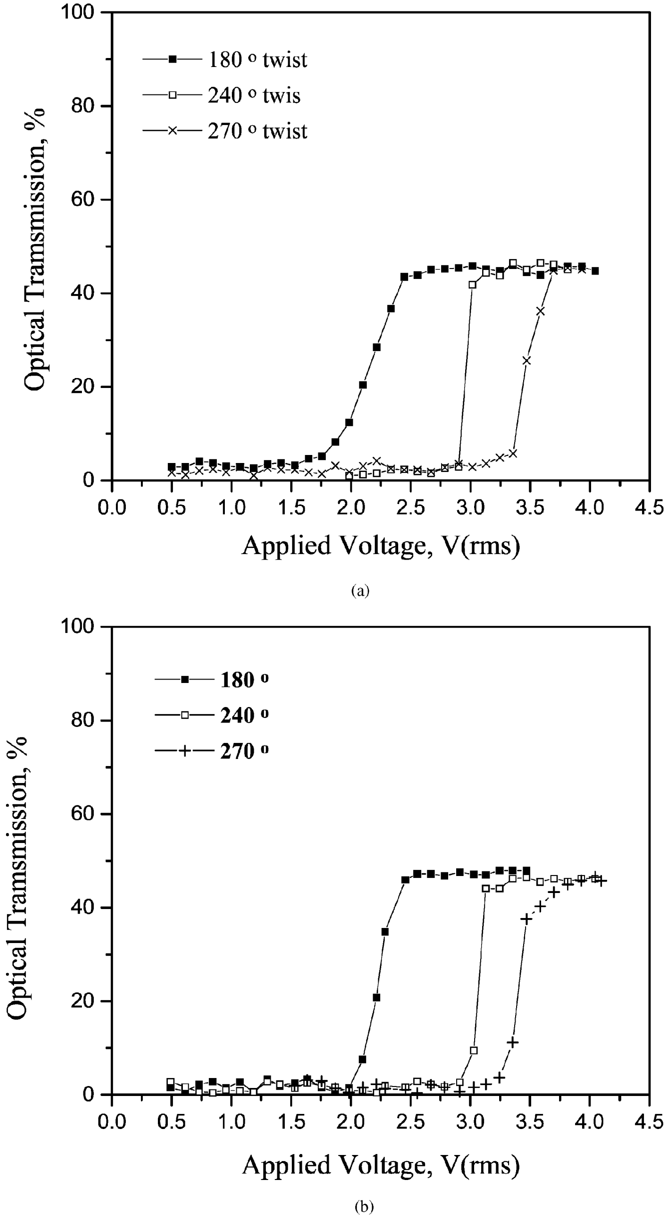


FIGURE 7a–b E-O response of STN mixtures based on MLC-9000-000 + JC16 (1.14%) in single pixels with twisting angles of 180°, 240° and 270° under 365 nm light at room temperature. **a** (top) MLC-9000-000 + JC16 (1.14%); **b** (bottom) MLC-9000-000 + JC17 (1.68%).

CONCLUSIONS

Two UV-stable nematic mixtures for use in STN-LCDs were formulated by doping the nematic mixture MLC-9000-000 designed for use in TN-LCDs with a chiral dopant. The life-time of the host MLC-9000-000 is about 8000 hours for 365 nm and 32000 hours for 390 nm. The resulting mixtures have been found to have life-times longer than 4000 hours for 365 nm and 16000 hours for 390 nm. Gassing occurred in many of the test cells after thousands hours of exposure to UV light. However the capacitance values of the relevant cells remained unchanged. Investigations into this problem are ongoing. In order to assess the likely performance of future PL-LCDs, the sharpness of the electro-optic responses of single pixels (filled with the STN mixtures) with different degrees of twisting of 180°, 240° and 270° were measured. It was found that the 240° twist cell gives rise to the sharpest response. The multiplexability of the mixtures in 240° twist cells was then determined to be 277 for mixture of MJ16 and 198 for MJ17.

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