

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>

Fabrication of pseudo- π vertical alignment mode liquid crystal devices with ultra-violet polymerisation and investigations of their electro-optical characteristics

Czung-Yu Ho^a; Jiunn-Yih Lee^a

^a Department of Polymer Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan, Republic of China

Online publication date: 16 August 2010

To cite this Article Ho, Czung-Yu and Lee, Jiunn-Yih(2010) 'Fabrication of pseudo- π vertical alignment mode liquid crystal devices with ultra-violet polymerisation and investigations of their electro-optical characteristics', *Liquid Crystals*, 37: 8, 997 – 1012

To link to this Article: DOI: 10.1080/02678291003746247

URL: <http://dx.doi.org/10.1080/02678291003746247>

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.

Fabrication of pseudo-pi vertical alignment mode liquid crystal devices with ultra-violet polymerisation and investigations of their electro-optical characteristics

Czung-Yu Ho* and Jiunn-Yih Lee

Department of Polymer Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan, Republic of China

(Received 22 January 2010; final version received 3 March 2010)

In this study, we applied the non-contact photo-polymerisation method in fabricating pseudo-polyimide (PI) liquid crystal (LC) devices with vertical alignment copolymer films, in the hope of solving the problems associated with traditional rubbing alignment processes. We mixed different photo-polymerisation-type acrylic monomers and negative dielectric anisotropy LC at proper weight percentages, and induced phase separation behaviour between the photo-polymerisation-type acrylic monomers and the LC molecules in the LC mixture solution through ultra-violet light irradiation, thereby forming copolymer films with vertical alignment effects. We further conducted preliminary characterisation of the alignment mechanism, photo-polymerisation, etc., of the LC molecules and investigated their interactions with alkyl acrylic monomers with different carbon chain lengths (the analogue of alkyl side chains in traditionally used vertical alignment-type PI) and electro-optical properties such as the transmittance, contrast ratio, and response time.

Keywords: liquid crystal; vertical alignment; negative dielectric anisotropy; phase separation

1. Introduction

The use of velvet cloth [1] in the contact mode, uni-directional rubbing of polymer films, such as polyimide (PI), is currently the most extensively employed method in the liquid crystal displays (LCDs) industry for the purpose of achieving alignment of liquid crystal (LC) molecules [1–31]. However, during the process of alignment, the use of the velvet cloth in a contact mode in rubbing the surface of the polymer film can result in uneven alignment, not to mention other shortcomings [1, 14] such as dust particle pollution, residual surface electrostatic charges and scratch marks that can damage the thin film transistor (TFT) devices and lower process yields [1]. Therefore, the development of non-contact mode LC alignment technologies has been one of the most important issues and research thrusts over the past few years. Some of the techniques employed to achieve non-contact mode LC molecules alignment include ultraviolet (UV) irradiation [10, 12, 22, 27, 29, 32–53], oblique evaporation [54–57], ion beam irradiation [22, 27, 58–61], Langmuir-Blodgett (LB) film [12, 62, 63], self-assembled monolayers (SAMs) [50, 64–70], photonic crystal [71, 72], plasma treatment [73–75] and nanoimprinting [76–81].

The phase separation composite film (PSCOF) [82] technology pioneered in 1999 by Kumar *et al.* from Kent State University has enjoyed considerable success in the development and application of layered composite structures in polymer/LC mixture over the

past 10 years [82–92]. Even before the emergence of PSCOF, there had been extensive research and development of similar applications of the photo-polymerisation technology [93–147], such as polymer disperse liquid crystal (PDLC), polymer stabilised liquid crystal (PSLC) and polymer network liquid crystal (PNLC).

Such applications of the photo-polymerisation technology are highly dependent on the structures of the different polymer types as well as the relevant process parameters and settings; variations in the photo-polymerisation type monomer structure, mix ratio of the LC and photo-polymerisation type monomer, environmental temperature, cell thickness, UV light irradiation intensity and UV light irradiation duration will all result in differences in the operation mode, electro-optical characteristics, etc., during application [84, 89, 102, 109, 113, 114, 119, 120, 126, 129]. However, with regards to the polymerisation induced phase separation (PIPS) mechanism, Kumar *et al.* have conducted extensive studies and discussions on the variations of the process parameters [84, 89]. Their experimental findings indicated that varying factors such as the UV light irradiation intensity, curing temperature, and cell thickness will affect the diffusion rate, viscosity and degree of polymerisation for the photo-polymerisation-type monomer and LC molecules, thereby impacting the structure and visual appearance of the PSCOF. Therefore, one can vary the process

*Corresponding author. Email: ketcer2009@gmail.com

parameters to obtain different polymer structural types, such as a polymer film with smooth surface or a PDLC film with rough surface.

In this study, we have followed the layered phase separation technology [82] and PIPS method [94, 106, 148–151] pioneered by Kumar *et al.* to vary the process parameters in order to obtain polymer films of different structural types. To obtain PSCOF with a smooth surface, we replicated their experimental procedures with the appropriate process parameters, i.e. UV light irradiation intensity, curing temperature, and cell thickness, to obtain a photo-polymerisation type acrylic monomer/LC mixture solution with lower overall viscosity, satisfactory fluidity, rapid molecular diffusion and slower copolymerisation and finally vertical alignment copolymer films (VACOF) with a smooth surface [152]. The layered structure diagram for the photo-polymerisation type acrylic monomer/LC molecules phase separation process is shown in Figure 1.

The focus of this experiment was the production of vertical alignment (VA) mode LC devices with high pre-tilt angle. Several past reports in the literature have studied extensively the important relationship between the LC molecules pre-tilt angle and the alignment film surface properties, the most famous of which is the Friedel–Creagh–Kmetz Rule [153, 154], which determines the alignment mode of the LC molecules based on the relative magnitudes of the LC surface tension and alignment film surface tension. Namely, when the LC surface tension is greater than the alignment film surface tension (hydrophobic surface with low surface tension), the LC molecules would be vertically aligned; for the converse, they would be horizontally aligned. In addition, the means through which one can control the pre-tilt angle of the LC molecules include applying differential unidirectional rubbing on the polymer alignment film [11, 14, 15, 22, 23, 26, 27, 155, 156], importing alkyl long carbon side chain or hydrophobic functional groups into the polymer alignment film in order to reduce the polarity of the alignment film surface and increase the pre-tilt angle of LC molecules [43, 71, 74, 81, 157–162], and the use of UV light irradiation or plasma treatment to process the alignment film surface [22, 74, 163]. In this study, we conducted a preliminary investigation of the interactions between the LC molecules and the alkyl long carbon chains through measurements of the electro-optical characteristics, by varying the different carbon chain lengths of the alkyl acrylic monomer (to simulate the functions of the alkyl side chains of the traditional vertical alignment type PI).

2. Experimental details

2.1 Materials

The materials we used included alkyl acrylic monomers with different carbon chain lengths: A_{C4} , A_{C10} , A_{C14} (to simulate the alkyl side chains' function of the traditional vertical alignment type PI, SeaEn); acrylic monomer B (to simulate the main chain function of the traditional vertical alignment type PI, SeaEn), photoinitiator (Ciba) and negative dielectric anisotropy nematic liquid crystal (N-type LC, NLC) ($\Delta\epsilon = -4.1$, $\Delta n = 0.0899$, $\eta_1 = 0.21 \text{ kg m}^2 \text{ s}$, $K_{\text{eff}} = 18.1 \text{ pN}$, Merck). The chemical structures of the acrylic monomers and the photoinitiator are shown in Figure 2.

2.2 Vertical alignment mode principle

In the experiment, we made use of the non-contact photo-polymerisation method to achieve VA of the LC molecules. In the traditional VA mode, due to the use of a VA film with side chain type polymer and N-type LC materials, the LC molecules will be vertically aligned with the glass substrate surface in the absence of an applied voltage ($V = 0$). When the polarisers and the top and bottom glass substrates are placed orthogonally, no light can be transmitted, giving rise to a dark state (Normally Black, NB); at the applied threshold voltage ($V > V_{\text{th}}$), other than the LC molecules closest to the glass substrate surface that are constrained by the alignment film, the long axes of the rest of the LC molecules would tilt an angle Φ toward the direction of the electric field. This tilt angle Φ would increase with increasing voltage, and the incident linearly polarised light would become elliptically polarised due to birefringence effects [162]. Part of the light would be transmitted through the analyser and give rise to a bright display, with the transmitted light intensity dependent on the magnitude of the applied voltage. The principles behind the electro-optical effects of the VA mode [163, 164] are shown in Figure 3(a) and (b) and the transmitted light intensity, I , is given by (see [165, 166]):

$$I = I_0 \sin^2 2\theta \sin^2(\pi d \Delta n(V) / \lambda), \quad (1)$$

where I_0 is the incident light intensity, θ is the angle between the polarisation direction of the incident light and the long axes of the LC molecules, d and $\Delta n(V)$ are the cell thickness and birefringence under a voltage V respectively. Here, $d \Delta n(V)$ is the retardation R of the LC, and λ is the wavelength of the incident light.

In this kind of LC device, the tilt angle Φ of the LC molecules would increase with increasing voltage, and so

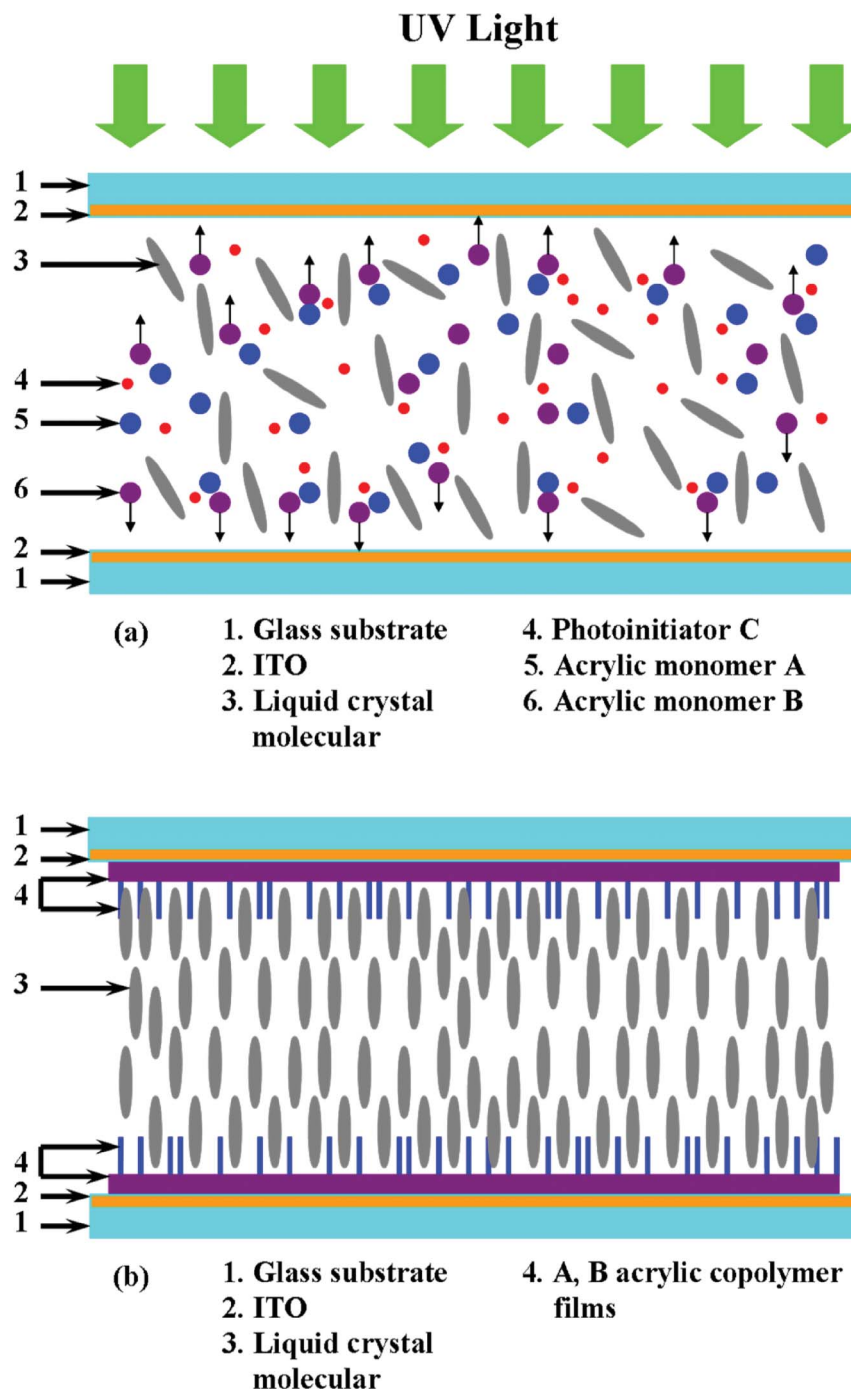


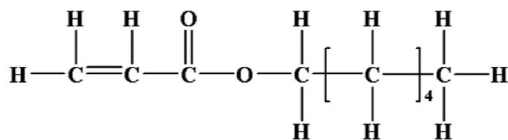
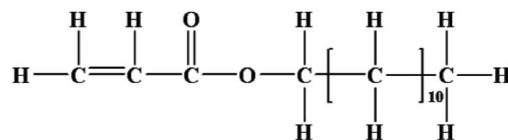
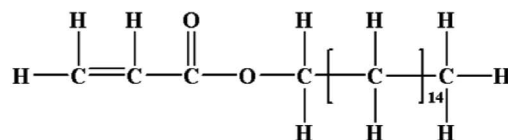
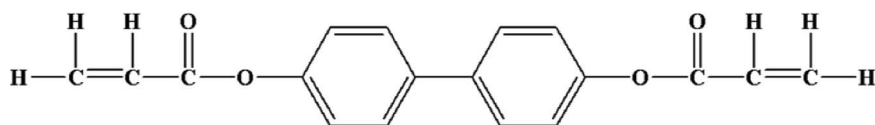
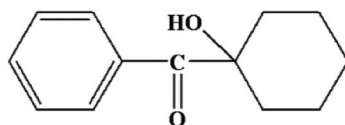
Figure 1. The vertical alignment copolymer films (VACOF) were formed after UV light irradiation. (a) The copolymerisation occurred after the acrylic monomers A, B and the photoinitiator had been irradiated by UV light. (b) The double layers VACOF film emerged after phase separation was completed (colour online).

would the retardation. For a fixed cell thickness, to obtain the maximum light transmission T_{\max} ($T = II_0$), the tilt angle between the LC molecules and the crossed polarisers must be 45° [167] when a voltage is applied to the LC cell. Also, in Equation (1), II_0 stands for the transmittance. Therefore, when $\theta = 45^\circ$, the value of

$\sin 2\theta$ is 1, and the transmittance depends only on the magnitude of the applied voltage.

2.3 Preparation of the NLC mixture materials

We first selected a LC mixture system (NLC2) of acrylic monomer with alkyl carbon chain length

**Acrylic monomer A_{C4}*****Acrylic monomer A_{C10}****Acrylic monomer A_{C14}****Acrylic monomer B****Photoinitiator*** **Number of alkyl carbon**Figure 2. Chemical structures of the acrylic monomers A (A_{C4}, A_{C10}, A_{C14}), B and photoinitiator.

between A_{C4} and A_{C14}: A_{C10}. From our experiments, we found that this mixture system gave rise to vertical alignment of the LC molecules after UV light irradiation [152]. The preparation of the material was as follows: 1.8 wt% acrylic monomer A_{C10} was mixed into the LC with five different ratios of acrylic monomer B (0.28, 0.29, 0.30, 0.31 and 0.32 wt%, respectively), and 0.1 wt% photoinitiator at room

temperature, followed by ultrasonic vibration and stirring for about 1 h at an environment temperature of 90° (the clear point of the LC) to obtain five LC mixture solutions (NLC2) with different mix ratios, as shown in Table 1. From preliminary experimental results and observations, we determined that 0.3 wt% content of the acrylic monomer B yielded the optimum electro-optical properties. Therefore, we settled on this

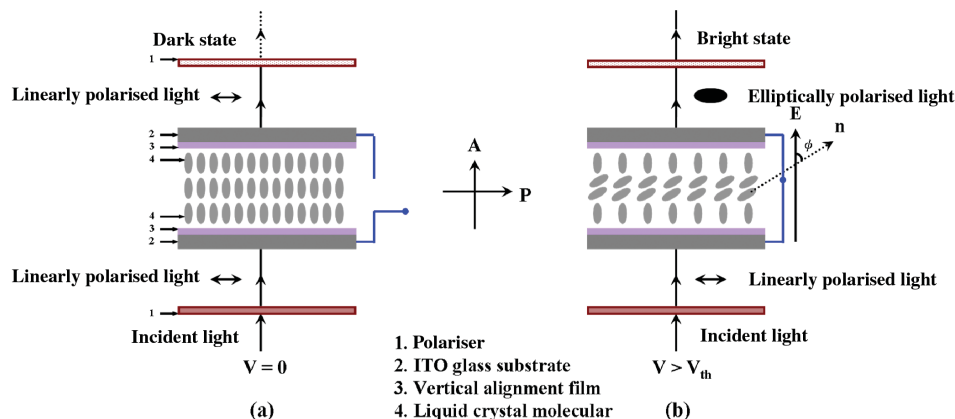


Figure 3. Principles of the electro-optical effects after photo-alignment. (a) Dark state before applied voltage. (b) Bright state after applied voltage (colour online).

Table 1. Components and ratios of the NLC2 mixture solution.

LC mixture solution	Acrylic monomer $A_{C_{10}}$ * (wt%)	Acrylic monomer B (wt%)	Photoinitiator (wt%)
NLC2	1.8	0.28	0.1
	1.8	0.29	0.1
	1.8	0.30	0.1
	1.8	0.31	0.1
	1.8	0.32	0.1

Note: *Number of alkyl carbon

ratio (1.8 wt% acrylic monomer A, 0.30 wt% acrylic monomer B, and 0.1 wt% photoinitiator) and conducted follow-up studies and investigations for mixture systems of the LC and alkyl acrylic monomer A_{C_4} , $A_{C_{10}}$ and $A_{C_{14}}$ with different carbon chain lengths. The mixed contents and relative ratios of each system are shown in Table 2.

2.4 Detailed procedures

From the studies of Kumar *et al.* [89], one can change the rate of phase separation and degree of monomer polymerisation, and thus alter the appearance and structural type of the film, by varying factors such as

Table 2. Components and ratios of each LC mixture system.

LC mixture system	Acrylic monomer (wt%)				Photoinitiator (wt%)
	A_{C_4} *	$A_{C_{10}}$	$A_{C_{14}}$	B	
NLC1	1.8	-	-	0.3	0.1
NLC2	-	1.8	-	0.3	0.1
NLC3	-	-	1.8	0.3	0.1

Note: *Number of alkyl carbon

the UV light irradiation intensity, curing temperature and cell thickness. Therefore, to obtain VACOF with smooth surface, we standardised all experiment conditions, as shown in Table 3.

After heating the LC mixture solution to the nematic-isotropic transition temperature, we infused this into empty cells with $4\ \mu\text{m}$ diameter glass fibre spacers (the most commonly used cell thickness in the LCDs industry) via capillary action, and obtained double-layered VACOF via phase separation due to copolymerisation after UV light irradiation ($\sim 5\ \text{mW cm}^{-2}$) treatment [152]. The LC molecules would be vertically aligned (VA mode) with the glass substrate surface, as shown in Figure 1. The experiment was carried out at the appropriate UV light intensity, curing temperature and cell thickness to lower the overall viscosity of the LC mixture solution, achieve rapid molecular diffusion and slower copolymerisation [84, 89], and finally obtain VACOF with smooth surface.

We then dissolved the NLC2 mixture solution in methanol solvent (concentration = $3.3 \times 10^{-6}\ \text{mol L}^{-1}$), treated it with UV light irradiation, and measured the absorption values over a 0–30 min interval with the use of a UV-Vis absorption spectrometer (VARIAN, Inc., Cary 100 Conc.) to obtain the conversion percentage (CP) of the LC mixture system [168–178].

A polarising optical microscope (POM, OLYMPUS Optical Co. Ltd., Models BHSP-2, BX-51) can also be

Table 3. Experiment settings and parameters.

Experiment parameter	UV light irradiation intensity (mW/cm^2)	UV light irradiation time (min)	Curing temperature ($^{\circ}\text{C}$)	Cell gap (μm)
Value	~ 5	~ 15	90*	~ 4

Note: *Clear point of liquid crystal

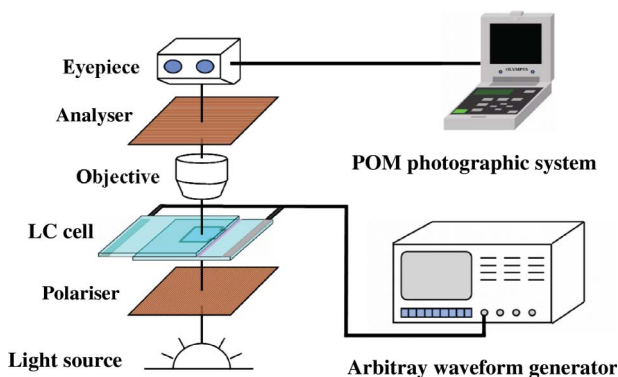


Figure 4. Setup for observation of the LC cell with polarising optical microscopy (colour online).

used to observe under the crossed polarisers the dark and bright states of the LC cell before and after the applied voltage, to determine the alignment of the LC molecules. The setup is as shown in Figure 4. In addition, one can use a scanning electron microscope (SEM, JEOL, JSM-6390LV) to observe the types of the VACOF microstructures formed on the conductive indium-tin oxide (ITO) glass substrate surface by the LC cell after UV light irradiation. The observation process is as follows: prise open the LC cells to be observed, remove the LC with hexane, cut them into $1\text{ cm} \times 1\text{ cm}$ samples to be placed on the evaporation pedestal, and coat a layer of platinum on the cell surface by sputtering for future observation.

The setup for measuring properties such as the transmittance and contrast ratio is shown in Figure 5. We placed an empty cell under the crossed polarisers before measurement, and defined the transmittance of this state to be 0%, and the transmittance when the polarisers were parallel to be 100%, for the purpose of calibration. After the completion of the calibration process, we next placed the LC cell under the crossed polarisers of the POM, applied an AC voltage (0–6 V, 60 Hz, square

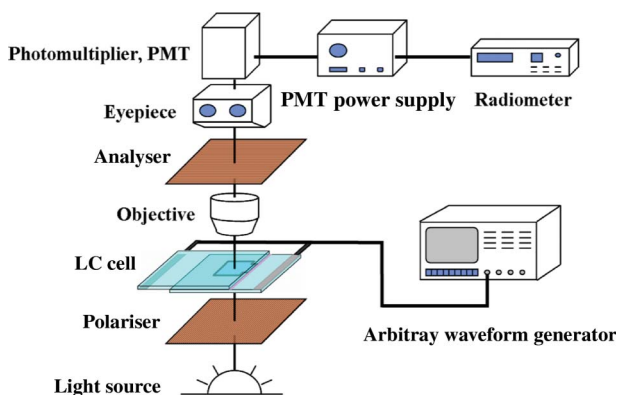


Figure 5. Setup for measurement of the transmittance and contrast ratio of the LC cell (colour online).

wave), and recorded the variation of the transmittance with the slowly increasing voltage with a radiometer [179].

From the transmittance versus applied voltage curve, we can further obtain the threshold voltage (V_{th} , defined to be the voltage when the transmittance reached 10%) and driving voltage (V_{on} , defined to be the voltage when the transmittance reached 90%) of the LC cell. The measurement of the contrast ratio was similar, with the use of the radiometer (International Light Inc., Models IL1700) to record the transmittance in the dark and bright states followed by conversion to the Contrast Ratio (CR) with (see [97, 180]):

$$\text{Contrast Ratio} = T_{\text{bright}}/T_{\text{dark}}, \quad (2)$$

where T_{bright} and T_{dark} are the transmittance of the LC cell in the dark and bright states respectively. From Equation (1), we can see that in order to obtain the maximum transmittance, the angle between the tilt of the LC molecules and the crossed polarisers must be 45° when the saturation voltage is applied to the LC cell [167]. In addition, other than the dark and bright states before and after a voltage has been applied to the LC cell, the intensity of the incident light can also affect the contrast ratio.

Figure 6 shows the setup for measuring the response time of the LC cell [179]. We used a He-Ne laser ($\lambda = 632.8\text{ nm}$, 10 mW) as the incident light source, and placed the LC cell between the crossed polarisers for measurement. By applying an alternating saturation voltage ($V_{\text{sat}} = 6\text{ V}$, 10 Hz, square wave), the signal would be received and transformed by the photodiode (Electro-Optics Technology Co. Ltd.,

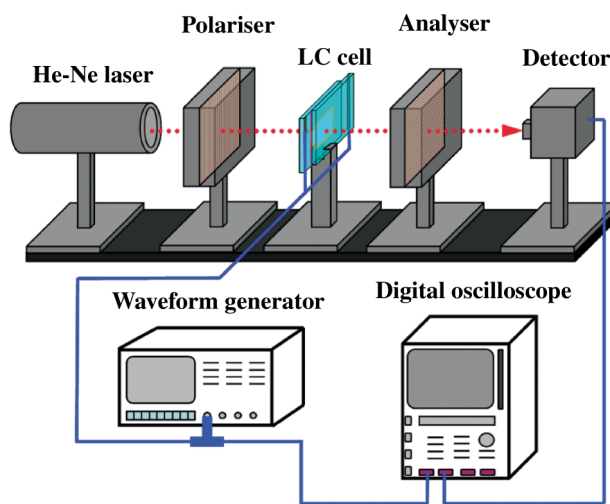


Figure 6. Setup for measurement of the response time of the LC cell (colour online).

Models ET-2000) and displayed on the oscilloscope (Yokogawa Electric Co. Ltd., Models DL1200A).

From the detected shapes of the waveform, we calculated the total response time, defined to be the sum of the rise time (T_r) and fall time (T_f):

$$\text{Total response time} = T_r + T_f. \quad (3)$$

In this study, the acrylic monomer B functioned as the main chain to be combined with acrylic monomer A, which served as the alkyl side chain for the vertical alignment of the LC device. To investigate the interactions resulting from the UV light irradiation between the VACOF and the LC, we therefore examined the VA and electro-optical properties of the LC molecules such as transmittance, contrast ratio and response time, for alkyl acrylic monomer A with different carbon chain lengths after UV light irradiation.

3. Results and discussion

3.1 Conversion percentage of the NLC2 system

After dissolving the NLC2 system in methanol solution followed by UV light irradiation for 0–30 min, we measured the absorption values over the time interval with a UV-Vis absorption spectrometer, as shown in Figure 7(a). During the UV light irradiation, free radicals would be produced by the photoinitiator, and subsequently attack the unsaturated acetyl double bonds, leading to copolymerisation between the acrylic monomers A and B and thus lowering the LC solubility. Phase separation would then occur, resulting in the formation of layered structures. Therefore, whenever copolymerisation (destruction of unsaturated acetyl double bonds) occurred, the UV absorption would decrease with increasing UV light irradiation time until all such reactions were terminated and the saturation point was reached. We thus

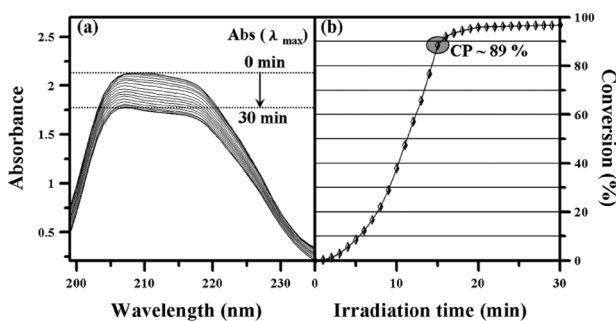


Figure 7. (a) Absorption spectrum of the NLC2 mixture system with UV light irradiation time. (b) Conversion percentage (CP) of the absorption of the NLC2 mixture system with UV light irradiation time.

substituted the largest UV absorption λ_{\max} over the time interval (0–30 min) for calculating the CP, as shown in Figure 7(b). If the UV light irradiation time was too short, the phase separation between the photo-polymerisation-type monomer and the LC molecules would be incomplete. When the irradiation time was too long, leading to increased degree of crystallisation for the photo-polymerisation type monomer, and thus larger cross-linking density, the brittleness of the alignment film might significantly increase. Therefore, we selected a CP of $\sim 89\%$ (UV light irradiation for ~ 15 min) [152] for performing measurements of electro-optical properties and investigations of the LC mixture system.

3.2 POM and SEM observations of the NLC2 system alignment film surface microstructures and the LC molecules alignment mechanism

First, the NLC2 system was exposed to UV light irradiation for ~ 15 min and allowed to cool to room temperature before being placed under a POM for observation of the display state of the LC cell before and after voltage was applied. When the polarisers were orthogonal, the LC molecules were vertically aligned to the glass substrate surface (due to the interactions between the LC molecules and the alkyl side chains). Therefore, no light was transmitted, and we obtained a uniformly dark state, as shown in Figure 8(a). In addition, the conoscopic pattern shown in the inset further indicates that the cell was uniformly vertically aligned and exhibited a very dark state under the crossed polarisers (Figure 8 (a)). The application of an alternating saturation voltage (6 V, 60 Hz, square wave) resulted in a tilt angle Φ between the long axes of the LC molecules (at 45° with the crossed polarisers, and thus the highest transmission) and the direction of the electric field. Due to the birefringence effect, light would

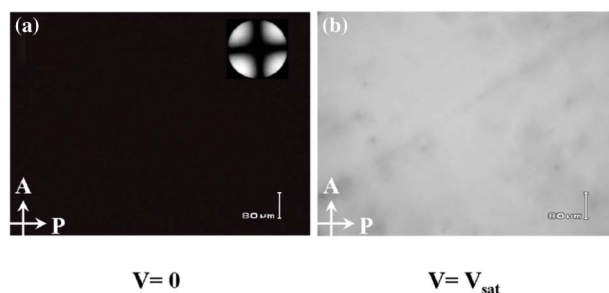


Figure 8. Polarising optical microscopy observation of the LC cell (with acrylic monomer B content of 0.30 wt%). (a) Uniformly dark state before applied voltage (Inset: conoscopic pattern) and (b) Single-domain uniformly bright state after applied voltage.

penetrate and result in a single-domain uniformly bright state, as shown in Figure 8(b). Since the LC cell was in a nearly uniform dark state before the application of voltage, we could therefore infer that the LC molecules were stacked neatly in a VA on the side chain-type VACOF surface. Based on the above observations, we expected to obtain a better contrast ratio.

After rigorous repetition of the experiments, we postulated that at the point of infusion of the LC into the cells, effects similar to directional rubbing alignment would occur due to the directional flow of the LC mixture solution [24]. Further exposure to UV light irradiation would assist in the neat VA of the LC molecules toward the same direction (photo-polymerisation-type acrylic monomer congregating towards the direction of the UV light irradiation) [35], as shown in Figure 9. In addition, the presence of alkyl long carbon chains in both the LC molecules and the acrylic monomer A_{C10} means that the similar polarity led to mutual attraction between the two (van der Waals forces) [17, 25, 67, 152, 181], with the results that the LC molecules could also produce VA effects. From current preliminary research and observations, it can be inferred that such an injection method might promote an overall uniaxial and uniform single-domain display for the LC molecules, as shown in Figure 8 (b).

The surface pattern of the alignment film as observed under a SEM after the LC cell was prised open is shown in Figure 10(a) and (b). One can clearly discern the VACOF produced by the copolymerisation of the acrylic monomers A and B on the ITO conductive glass substrate surface. Due to the UV irradiation on the surface of the LC cell, some of the photo-polymerisation-type acrylic monomers

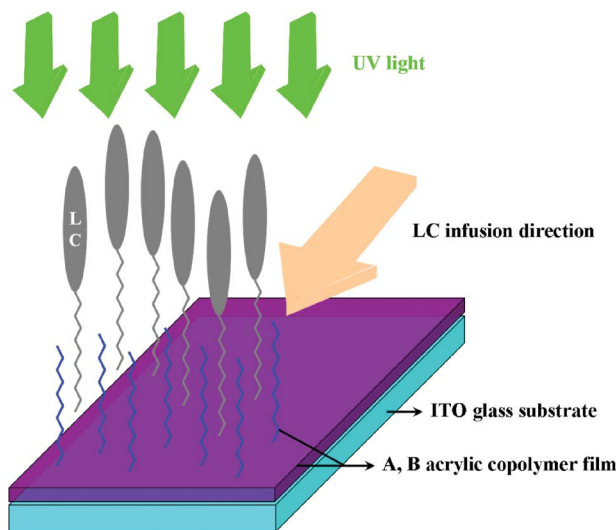


Figure 9. Vertical alignment mechanism for LC molecules (colour online).

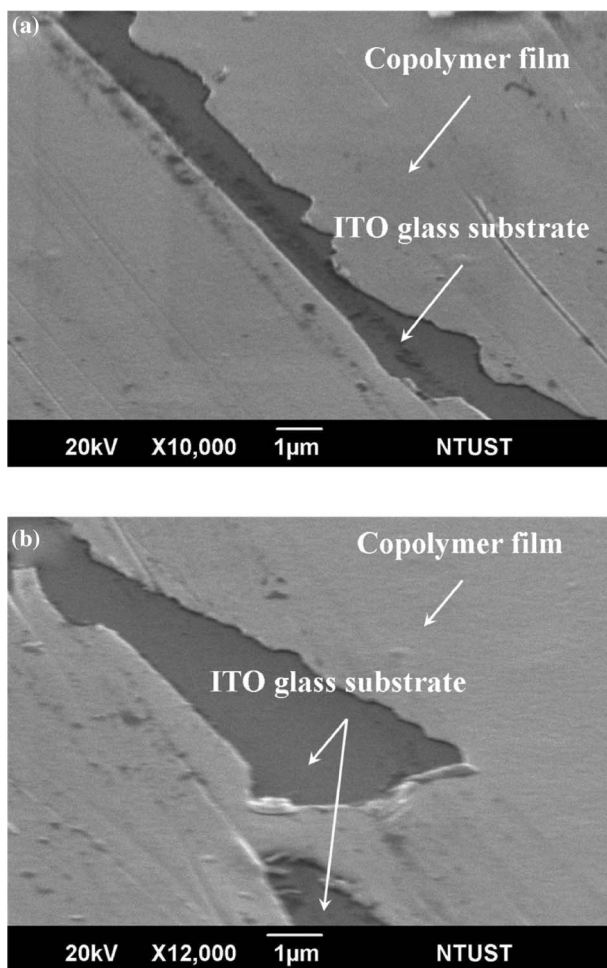


Figure 10. Scanning electron microscopy pictures of the vertical alignment copolymer films (VACOF) (with acrylic monomer B content of 0.30 wt%). (a) The upper and (b) the lower VACOF on the surface of the ITO glass.

congregated towards the direction of UV irradiation while the rest would be precipitated (likely due to its micro-gravity) [127, 152] and deposited on the lower glass substrate surface to form double-layered VACOF. Therefore, from POM and SEM observations, we verified that VACOF with smooth surface would be formed on the glass substrate surface after UV light irradiation treatment. However, when the LC cell was taken apart, the VACOF was very thin and damage to the alignment film surface was likely to occur (Figure 10 (a) and (b)).

The difference in the photo-alignment technology we proposed and the model by Kumar *et al.* is that there is no need for processes such as the coating of polymer alignment agent, rubbing alignment, etc., for both the upper and lower glass substrate surfaces in our experiment. The most unique feature was the observation by SEM of VACOF on both the upper and lower double layers of the glass substrate surface.

Therefore, we boldly postulate that similar effects occurred during the studies of Kumar *et al.* In other words, during the polymerisation-induced phase separation of the photo-polymerisation-type monomer and LC mixture systems, while most of the photo-polymerisation-type monomers congregated toward the direction of UV light irradiation, the rest would be precipitated due to micro-gravity effects and deposited on the polymer alignment film surface of the lower ITO glass substrate coating.

In addition, according to the surface tension ($\Delta\gamma$) relationship between liquid and solid proposed by Creagh *et al.*, one can infer that the LC molecules were either horizontally or vertically aligned, as described by (see [153, 154]):

$$\Delta\gamma = \gamma_L - \gamma_S, \quad (4)$$

where γ_L and γ_S are the surface tension of the liquid (LC) and solid (alignment film), respectively. One can deduce the alignment of the LC molecules from the positive or negative value of $\Delta\gamma$, i.e. when $\gamma_L > \gamma_S$, the LC molecules are vertically aligned. For the converse, they would be horizontally aligned. From Equation (4) and the experimental results and observations, one can infer that the surface tension of the LC molecules was greater than that of the VACOF, which was one of the reasons for the vertically aligned state of the LC molecules.

3.3 Electro-optical properties of the NLC2 system

We next measured the transmittance and contrast ratio of the LC cell, as shown in Figure 11 (a) and (b). The threshold voltage (V_{th}), driving voltage (V_{on}), as well as contrast ratio of LC cells with different mix ratios are shown in Table 4. Figure 11(a) shows that when the acrylic monomer B content of the LC mixture solution was 0.30 wt%, the transmittance was the highest, due to the better uniformity of the VACOF formed. In the absence of an applied voltage, the LC molecules were neatly vertically aligned on the VACOF surface (presumably due to the appropriate quantities of alkyl side chain per unit surface area present in the acrylic monomer A_{C10}) [152]. Under the influence of an electric field, the LC molecules assumed a uniform arrangement, and became tilted towards the same direction. Under a crossed POM, the transmittance ratio of the dark state measured in the absence of an applied voltage was lower than those of the other groups.

Conversion by Equation (2) yielded a contrast ratio of up to 1300:1 (if one can further increase the intensity of the incident light source in a sufficiently dark state, one could presumably increase the contrast ratio significantly), as shown in Figure 11(b) and

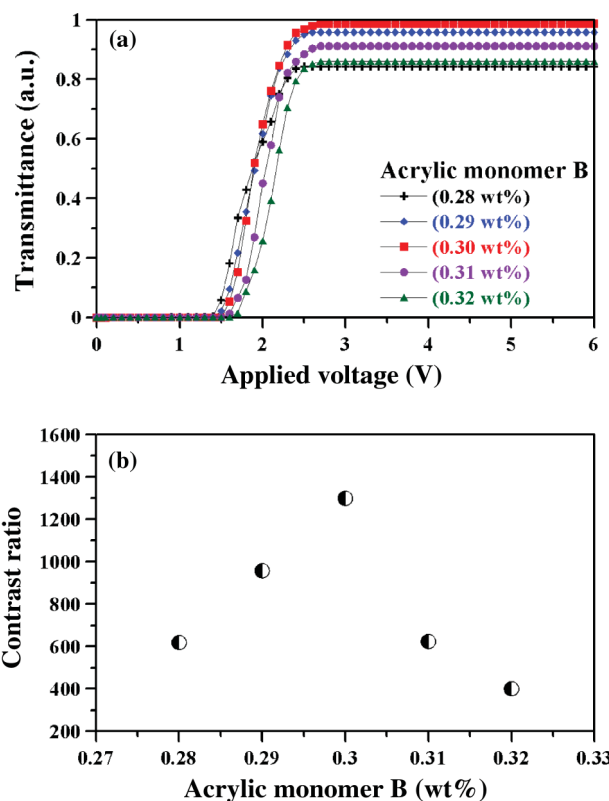


Figure 11. The results of the transmittance and contrast ratio measurements of the LC cells. (a) Transmittance vs. applied voltage, and (b) contrast ratio versus acrylic monomer B content (colour online).

Table 4. Threshold voltage, driving voltage and contrast ratio of the NLC2.

NLC2 (B wt%)	V_{th} (V)	V_{on} (V)	Contrast ratio
0.28	1.52	2.22	619:1
0.29	1.61	2.24	958:1
0.30	1.64	2.27	1300:1
0.31	1.73	2.30	624:1
0.32	1.79	2.37	401:1

Table 4. Thus, we concluded that the uniformity of the VACOF at this ratio was better than those of the other groups and yielded the highest contrast ratio. Also, by Equation (5), one can calculate the theoretical value of the V_{th} of the LC used in the experiment to be ~ 2.22 V [182, 183]:

$$V_{th} = \pi \sqrt{K_{eff}/\epsilon_0 |\Delta\epsilon|}, \quad (5)$$

where V_{th} is the threshold voltage of the LC, K_{eff} is the effective elastic constant, ϵ_0 is the free space permittivity and $\Delta\epsilon$ is the dielectric anisotropy of the LC. From

Equation (5), we can see that V_{th} does not depend on the cell thickness.

Comparison of the theoretical and experimentally measured values of the LC (Table 4) revealed that the LC mixture system used in this study lowered the V_{th} of the LC (Equation (5)). After the LC cell had undergone photo-alignment, the weaker anchoring energy or larger pre-tilt angle of the alignment film surface could effectively reduce the V_{th} and achieve rapidly driven display effects [126, 184–187]. In addition, we surmised from Equation (5) that the K_{eff} of the LC itself increased with the incorporation of the acrylic monomer. The VACOF thus formed was not an electro-conductive material; therefore, as the alignment film became thicker, the applied voltage required also became larger. The increase of the acrylic monomer content is thus also a factor affecting the magnitude of the V_{th} .

Thereafter, for the response time measurement, we defined the rise time (T_r) of the LC molecules to be the time required for the transmittance to rise from 10% to 90% as the dark state shifts to the bright state, and the fall time (T_f) to be the time required for the transmittance to fall from 90% to 10% as the bright state shifts to the dark state, as shown in Figure 12. The T_r and T_f of the LC molecules are given by the following equations (see [182, 183]):

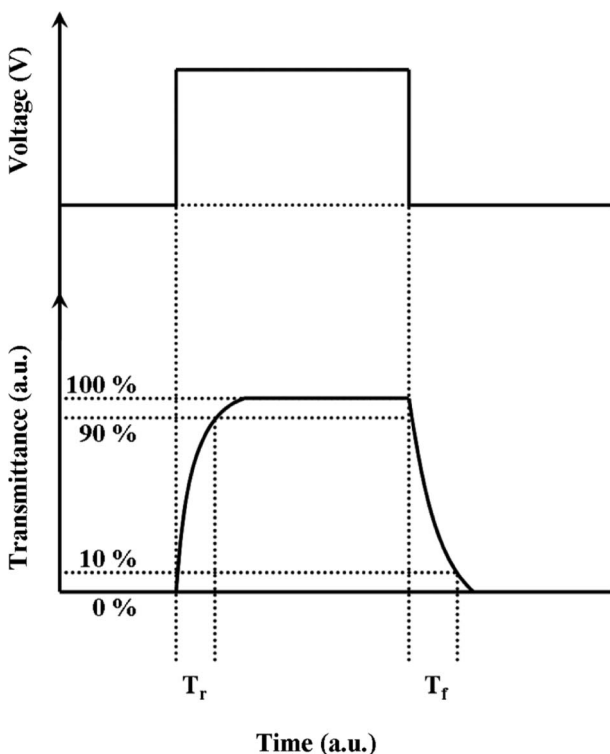


Figure 12. Definition of the rise time and fall time of the LC molecules.

$$T_r = \eta_1 d^2 / (\epsilon_0 |\Delta\epsilon| V^2 - K_{eff} \pi^2), \quad (6)$$

$$T_f = \eta_1 d^2 / K_{eff} \pi^2, \quad (7)$$

where η_1 is the rotation viscosity of the LC and V is the applied voltage. One can see from the response time measurements in Table 5 that T_f was slightly larger than T_r .

The main reason was that the rise time is the time required for the LC molecules to generate electro-optical effects after being acted on by the electric field, while the fall time is the time required for the LC molecules to be restored to their original locations on their own after removal of the electric field. Therefore, Equation (7) does not involve the applied voltage. However, from Equations (6) and (7) we can see that when using the same LC materials, the physical parameters of the LC itself aside, T_r and T_f are proportional to the square of the cell thickness d . Therefore, using a smaller cell thickness would increase the total response time of the LC cells.

Since the anchoring energy of the alignment film surface formed after UV light irradiation was weaker [126, 183, 184], the time required for vertical rotation of the LC molecules was shorter. Therefore, the T_r measured for each group of LC cells was around 8–9 ms. When the electric field was removed, the time required for the LC molecules to return to their original locations was slightly longer than the rise time. However, from our experimental results, changing the ratio of the photo-polymerisation-type acrylic monomer in the LC would likely increase the K_{eff} but would not have much impact on the viscosity of the overall system. The total response times ranged from around 16 to 18 ms (Figure 13 and Table 5), and were consistent with the current response speed required in LCDs. In addition, the magnitude of the dielectric anisotropy is one of the factors affecting the response time, threshold voltage and driving voltage.

Table 5. Response time measurements for the NLC2.

NLC2 (B wt%)	Rise time (ms)	Fall time (ms)	Total response time (ms)
0.28	8.13	8.21	16.34
0.29	8.18	8.35	16.53
0.30	8.21	8.50	16.71
0.31	8.58	8.88	17.46
0.32	8.73	9.13	17.86

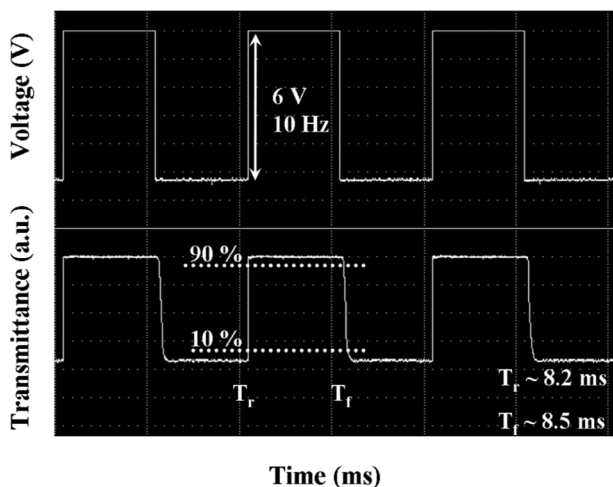


Figure 13. The measurement of the response time with the acrylic monomer B content at 0.30 wt%.

3.4 The interaction of alkyl acrylic monomers with different carbon chain lengths with the LC and the study of resulting electro-optical characteristics

The VA of the LC molecules and the electro-optical characteristics, when alkyl acrylic monomers with different carbon chain lengths were attached to the main chain type acrylic monomer B, were investigated. We mixed alkyl acrylic monomer A with three different carbon chain lengths (A_{C4} , A_{C10} , A_{C14}) in this experiment to obtain the NLC1, NLC2 and NLC3 LC mixture systems, respectively, with the ratios as shown in Table 2. From the interactions between the LC molecules and the alkyl carbon chain [71, 157, 158], one can infer that the longer the alkyl carbon chain length, the better the solubility of the oxygen-alkyl side chains with the LC molecules (the stronger the mutual interactions, the larger the contact area with the alkyl carbon chain, and thus the greater the van der Waals force) [17, 25, 67, 152, 181]. This way, the LC molecules could be more easily vertically aligned on the VACOF surface; in short, one could control the pre-tilt angle of the LC molecules by changing the alkyl carbon chain length [22, 71, 154, 162].

After UV light irradiation for ~ 15 min, the NLC1, NLC2 and NLC3 LC mixture systems were further observed under the POM (Figure 14). One could see that for the NLC1 mixture system, due to the shorter alkyl carbon chain for NLC1, the contact area with the LC molecules was smaller, and the mutual interactions were lower. Therefore, from this result and Equation (5), one could infer that the anchoring energy for the VACOF was weaker.

Other than slightly reducing the V_{th} and V_{on} (Table 6), the shorter alkyl carbon chain of the NLC1 system also affected how the LC molecules were vertically

aligned on the VACOF surface. Therefore, in the absence of an applied voltage, the overall dark state was not dark enough due to minor light leakage in the LC cell (Figure 14(a), $V = 0$). Also, when the LC molecules were rotated, minute discontinuous black stripes (schlieren structure) would be formed, resulting in a multi-domain rather than a uniform single-domain image for the LC cell (Figure 14(a), $V_{sat} = 6$ V). The transmittance and CR were further reduced, as shown in Figure 15 and Table 6.

In addition, observation of the NLC3 mixture system under POM in the absence of applied voltage revealed that the measured transmittance of the dark state was similar to that of the NLC2 (Figure 14(c), $V = 0$), but the LC molecules also exhibited slight defects after rotation by the electric field (Figure 14(c), $V_{sat} = 6$ V). Most likely, the longer (and thus more flexible) alkyl carbon chains of the NLC3 (A_{C14}) led to some of them being entangled, resulting in the formation of defects and lowering slightly the transmittance and CR (Figure 15 and Table 6). In addition, the longer alkyl side chains of the NLC3 resulted in a larger anchoring energy, and the slightly larger measured values of the V_{th} and V_{on} than for NLC1 and NLC2 [126, 184, 185].

Finally, from the definition of Figure 12, we measured the response time of the three LC mixture systems NLC1, NLC2 and NLC3 (Table 7). For the NLC1 mixture system, the anchoring energy was weaker due to the shorter alkyl carbon chains, and the time required for the rotation of the LC molecules by the electric field was shorter ($T_r \sim 7$ ms). When the electric field was removed, the time taken for the LC molecules to return on their own to the original locations was longer ($T_f \sim 11$ ms). Increasing the alkyl carbon chain length therefore enhances the overall anchoring energy of the VACOF surface and accelerates the response time. From the preliminary results in this section, we therefore concluded that a mixture system with the appropriate alkyl carbon chain length, such as the NLC2 mixture system, would yield better electro-optical properties than say NLC1 and NLC3.

4. Conclusions

Based on the report by Kumar *et al.*, we know that the effective control of parameters such as the UV light irradiation, curing temperature and cell thickness would yield PSCOF with smooth surface. Therefore, in this study, we attempted to obtain structures such as VACOF with smooth surface by replicating their experimental procedures. In the experiment, we mainly mixed different types of acrylic monomers and photoinitiator at the proper ratios, and created

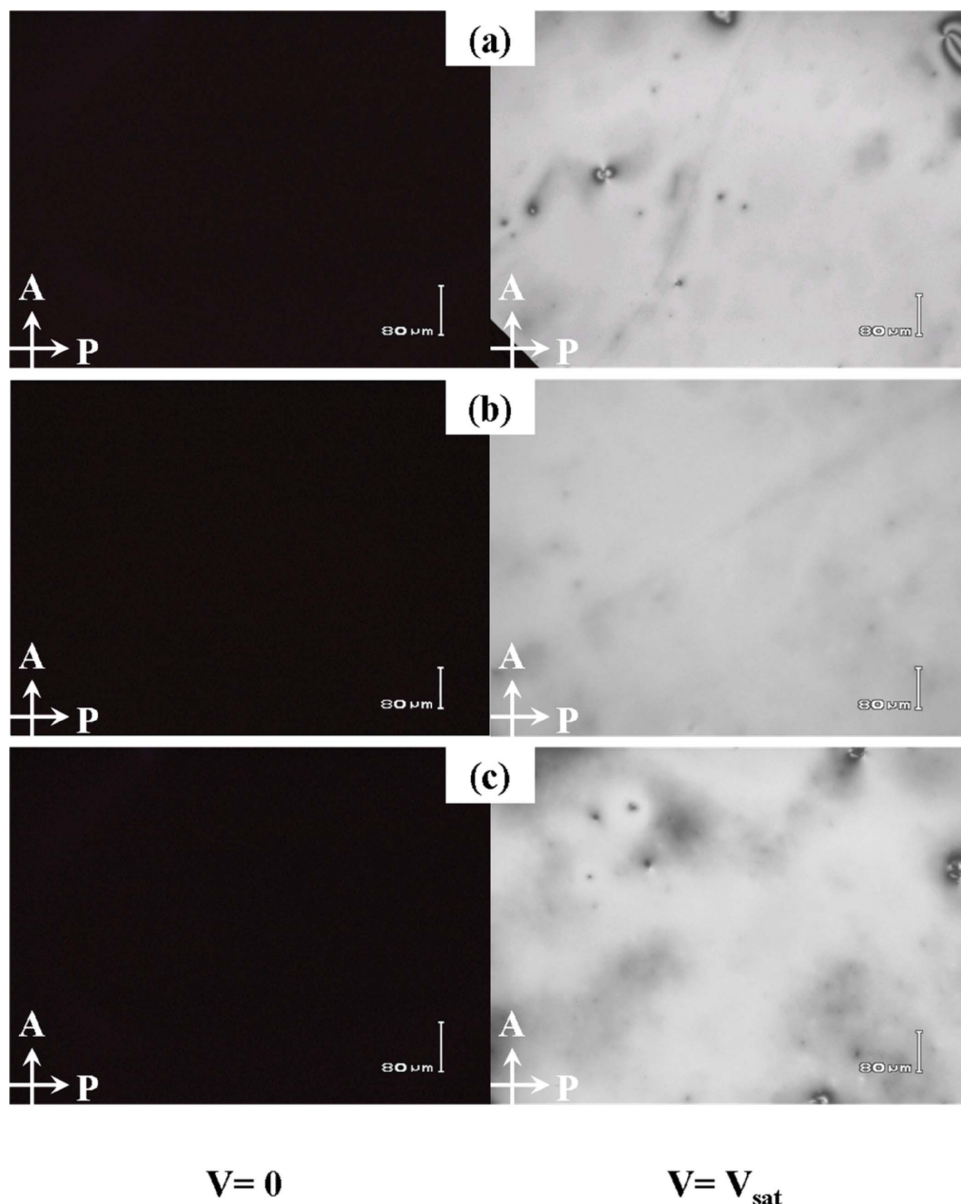


Figure 14. Polarising optical microscopy of the 3 LC mixture systems: NLC1, NLC2 and NLC3. (a) A_{C4} , (b) A_{C10} , (c) A_{C4} display state before and after applied voltage.

Table 6. Threshold voltage, driving voltage and contrast ratio of the three LC mixture systems: NLC1, NLC2 and NLC3.

LC mixture system	V_{th} (V)	V_{on} (V)	Contrast ratio
NLC1	1.57	2.20	650:1
NLC2	1.64	2.27	1300:1
NLC3	1.69	2.33	1050:1

double-layered VACOF with the use of polymerisation-induced phase separation and UV light irradiation, to simulate such traditionally used PI methods as the polymer alignment film. We also conducted

further studies of the electro-optical properties for the VA system.

First, from the experiment, we found that when the LC mixture solution was infused into the empty cell, the directional flow of the solution resulted in effects similar to rubbing alignment, enabling the LC molecules to be aligned toward the same direction. After UV light irradiation and application of a voltage on the LC cell, the LC molecules exhibited an overall uniaxial orientation and yielded a uniform single domain, a preliminary identification of the photo-alignment mechanism for the LC molecules. In the NLC2 system, we found that when the content of the acrylic monomer B was 0.3 wt%, the contrast ratio

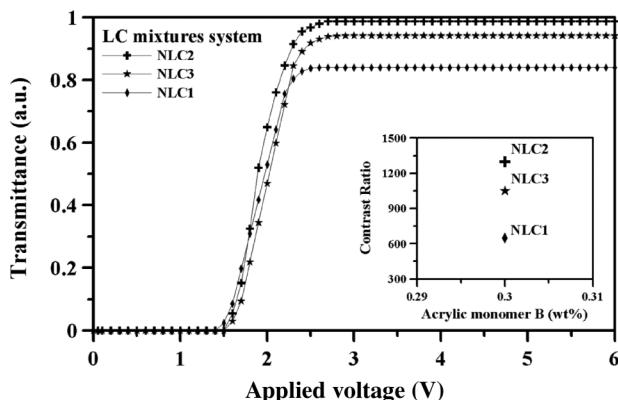


Figure 15. The results of the transmittance and contrast ratio measurements of the three LC mixture systems: NLC1, NLC2 and NLC3. (a) Transmittance versus applied voltage, and (b) contrast ratio versus acrylic monomer B content.

Table 7. Response time measurements for the three LC mixture systems: NLC1, NLC2 and NLC3.

LC mixture system	Rise time (ms)	Fall time (ms)	Total response time (ms)
NLC1	7.13	10.79	17.92
NLC2	8.21	8.50	16.71
NLC3	8.03	8.33	16.36

reached a value of around 1300:1. The presence of appropriate quantities of the alkyl side chain on the VACOF surface had resulted in the optimum VA state for the LC molecules. After the mixing of the LC with the acrylic monomer, the threshold voltage (V_{th}) of the LC was significantly reduced due to the weaker anchoring energy of the photo-alignment film surface, resulting in fast driving and energy efficiency. In addition, the total response time of the NLC2 system was around 16–18 ms, and consistent with the current needs and applications for LCDs.

This study also examined in-depth the interactions between the LC molecules and alkyl acrylic monomers with different carbon chain lengths. From our experiment, the alkyl carbon chain length yields considerable impact on the VA state of the LC molecules. For the NLC1 system, due to the shorter alkyl side chains for the VACOF, there existed smaller contact area with the oxygen-alkyl side chains of the LC molecules. The smaller mutual interaction resulted in a smaller anchoring energy, and thus the VA of the LC molecules as a whole was poorer. This in turn affected such electro-optical properties of the LC cell as transmittance, contrast ratio and the total response time. In comparison to the NLC3 system, we also found that if one were to improve these shortcomings, in addition

to enhancing the anchoring energy of the alignment film surface, increasing the alkyl carbon chain length alone would not suffice and alkyl carbon chains of the appropriate length are also needed. Summarising the above preliminary experiment results, we believe that this photo-alignment technology holds great potential and promise for future applications, and we look forward to using this technology to produce LC devices with characteristics such as high contrast ratio.

Acknowledgements

The authors would like to express their gratitude to Mr. Kai-Neng Yang, from SeaEn Special Material Co. Ltd, for supplying the acrylic monomers A and B, and photoinitiator for the experiment, as well as for his advice and suggestions which helped to facilitate the smooth completion of the experiment.

References

- [1] Haaren, J.V. *Nature* **2001**, *411*, 29.
- [2] Chatelaine, P. *Bull. Soc. Franc. Crist.* **1943**, *66*, 105.
- [3] Berremam, D.W. *Phys. Rev. Lett.* **1972**, *28*, 1683.
- [4] Berremam, D.W. *Mol. Cryst. Liq. Cryst.* **1973**, *23*, 215.
- [5] Wolf, U.; Greubel, W.; Kruger, H. *Mol. Cryst. Liq. Cryst.* **1977**, *23*, 187.
- [6] Cheng, J.; Boyd, G.D. *Appl. Phys. Lett.* **1979**, *35*, 444.
- [7] Clark, N.A.; Lagerwall, S.T. *Appl. Phys. Lett.* **1980**, *36*, 899.
- [8] Nakamura, M. *J. Appl. Phys.* **1981**, *52*, 4561.
- [9] Aoyama, H.; Yamazaki, Y.; Matsuura, N.; Mada, H.; Kobayashi, S. *Mol. Cryst. Liq. Cryst.* **1981**, *72*, 217.
- [10] Castellano, J.A. *Mol. Cryst. Liq. Cryst.* **1983**, *94*, 33.
- [11] Becker, M.; Kilian, R.A.; Kasmowski, B.B.; Mlynski, D.A. *Mol. Cryst. Liq. Cryst.* **1986**, *132*, 167.
- [12] Geary, J.M.; Goodby, J.W.; Kmetz, A.R.; Patel, J.S. *J. Appl. Phys.* **1987**, *62*, 4100.
- [13] Nakajima, K.; Wakemoto, H.; Sato, S.; Yokotani, F.; Ishihara, S.; Matsuo, Y. *Mol. Cryst. Liq. Cryst.* **1990**, *180B*, 22.
- [14] Sugiyama, T.; Kuniyasu, S.; Seo, D.S.; Fukuro, H.; Kobayashi, S. *Jpn. J. Appl. Phys.* **1990**, *29*, 2045.
- [15] Seo, D.S.; Muroi, K.; Kobayashi, S. *Mol. Cryst. Liq. Cryst.* **1992**, *213*, 223.
- [16] Mada, H.; Sonoda, T. *Jpn. J. Appl. Phys.* **1993**, *32*, L1245.
- [17] Ito, T.; Nakanishi, K.; Nishikawa, M.; Yokoyama, Y.; Takeuchi, Y. *J. Poly.* **1995**, *27*, 240.
- [18] Toney, M.F.; Russell, T.P.; Logan, J.A.; Kikuchi, H.; Sands, J.M.; Kumar, S.K. *Nature* **1995**, *374*, 709.
- [19] Kihuchi, H.; Logan, J.A.; Yoon, D.Y. *J. Appl. Phys.* **1996**, *79*, 6811.
- [20] Pidduck, A.J.; Bryan Brown, G.P.; Haslam, S.; Bannister, R.; Kitely, I.; McMaster, T.J.; Boogaard, L. *J. Vac. Sci. Technol. A* **1996**, *14*, 1723.
- [21] Lee, K.W.; Paek, S.H.; Lien, A.; Durning, C.J.; Fukuro, H. *Macromolec.* **1996**, *29*, 8894.
- [22] Lee, K.W.; Lien, A.; Stathis, J.H.; Paek, S.H. *Jpn. J. Appl. Phys.* **1997**, *36*, 3591.

- [23] Paek, S.H.; Durning, C.J.; Lee, K.W.; Lien, A. *J. Appl. Phys.* **1998**, *83*, 1270.
- [24] Seo, D.S. *J. Kor. Phys. Soc.* **1999**, *43*, 359.
- [25] Ge, J.J.; Li, C.Y.; Xue, G.; Mann, I.K.; Zhang, D.; Wang, S.Y.; Harris, F.W.; Cheng, S.Z.D.; Hong, S.C.; Zhuang, X.; Shen, Y.R. *J. Am. Chem. Soc.* **2001**, *123*, 5678.
- [26] Sinha, G.P.; Wen, B.; Rosenblatt, C. *Appl. Phys. Lett.* **2001**, *79*, 2543.
- [27] Stöhr, J.; Samant, M.G.; Lüning, J.; Callegari, A.C.; Chaudhari, P.; Doyle, J.P.; Lacey, J.A.; Lien, S.A. Purushothaman, S.; Speidell, J.L. *Science* **2001**, *292*, 2299.
- [28] Macdonald, B.F.; Zheng, W.; Cole, R.J. *J. Appl. Phys.* **2003**, *93*, 4442.
- [29] Behdani, M.; Keshmiri, H.S.; Soria, S.; Bader, A.M.; Ihlemann, J.; Marowsky, G.; Rasing, Th. *Appl. Phys. Lett.* **2003**, *82*, 2553.
- [30] Lee, G.J.; Lee, J.J.; Lee, G.; Kim, J.S.; Hwang, U.J.; Oh, C.H.; Song, S.H.; Kim, P.S.; Lee, Y.P. *J. Kor. Phys. Soc.* **2004**, *45*, 71.
- [31] Kumar, S.; Kim, J.H.; Shi, Y. *Phys. Rev. Lett.* **2005**, *94*, 077803.
- [32] Egerton, P.L.; Pitts, E.; Reister, A. *Macromolec.* **1981**, *14*, 95.
- [33] Ichimura, K.; Suzuki, Y.; Seki, T.; Hosoki, A.; Aoki, K. *Langmuir* **1988**, *4*, 1214.
- [34] Gibbons, W.M.; Shannon, P.J.; Sun, S.T.; Swetlin, B.J. *Nature* **1991**, *351*, 49.
- [35] Schadt, M.; Schmitt, K.; Kozinkov, V.; Chigrinov, Switzerland, *Jpn. J. Appl. Phys.* **1992**, *31*, 2155.
- [36] Nishikawa, M.; Yokoyama, Y.; Bessho, N.; Seo, D.S.; Iimura, Y.; Kobayashi, S. *Jpn. J. Appl. Phys.* **1994**, *33*, L810.
- [37] Shannon, P.J.; Gibbons, W.M. *Nature* **1994**, *368*, 532.
- [38] Ichimura, K.; Akita, Y.; Akiyama, H.; Hayashi, Y.; Kudo, K. *Jpn. J. Appl. Phys.* **1996**, *35*, L992.
- [39] Schadt, M.; Seiberle, H.; Schuster, A. *Nature* **1996**, *381*, 212.
- [40] Wang, Y.; Xu, C.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J. Appl. Phys.* **1998**, *84*, 181.
- [41] Wang, Y.; Xu, C.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J. Appl. Phys.* **1998**, *84*, 4573.
- [42] Wang, Y.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Appl. Phys. Lett.* **1998**, *72*, 545.
- [43] Nishikawa, M.; West, J.L. *Jpn. J. Appl. Phys. Part 1* **1999**, *38*, 5183.
- [44] Han, K.J.; Jung, Y.; Choi, H.H.; Hwang, H.K.; Lee, S.; Humjang, S. *J. Appl. Phys.* **1999**, *86*, 1854.
- [45] Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847.
- [46] Contoret, A.E.A.; Farrar, S.R.; Jackson, P.O.; Khan, S.M.; May, L.; O'Neill, M.; Nicholls, J.E.; Kelly, S.M.; Richards, G.J. *Adv. Mater.* **2000**, *12*, 971.
- [47] Perny, S.; Barny, P.L.; Delaire, J. *Liq. Cryst.* **2000**, *27*, 349.
- [48] Wang, Y.; Xu, S.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Matsuki, Y.; Takeuchi, U. *Liq. Cryst.* **2001**, *28*, 473.
- [49] Fang, Y.J.; Chen, S.M.; Shashidhar, R. *Langmuir* **2001**, *17*, 1549.
- [50] Lee, B.; Clark, N.A. *Science* **2001**, *291*, 2576.
- [51] Choi, D.H.; Cha, Y.K. *Bull. Kor. Chem. Soc.* **2002**, *23*, 587.
- [52] Huang, D.D.; Pozhidaevl, E.P.; Chigrinov, V.G.; Cheung, H.L.; Ho, Y.L.; Kwok, H.S. *Displays* **2004**, *25*, 21.
- [53] Parka, J.H.; Khoo, I.C.; Yu, C.J.; Jung, M.S.; Lee, S.D. *Appl. Phys. Lett.* **2005**, *86*, 021906.
- [54] Janning, J.L. *Appl. Phys. Lett.* **1972**, *21*, 173.
- [55] Urbach, W.; Boix, M.; Guyon, E. *Appl. Phys. Lett.* **1974**, *25*, 479.
- [56] Uchida, T.; Ohgawara, M.; Wada, M. *Jpn. J. Appl. Phys.* **1980**, *19*, 2127.
- [57] Heffner, W.R.; Berreman, D.W.; Sammon, M.; Meiboom, S. *Appl. Phys. Lett.* **1980**, *36*, 144.
- [58] Chaudhari, P.; Lacey, J.A.; Lien, S.C.A.; Speidell, J.L. *Jpn. J. Appl. Phys.* **1998**, *37*, L55.
- [59] Chaudhari, P.; Lacey, J.; Doyle, J.; Galligan, E.; Lien, A.S.; Callegari, A.; Hougham, G.; Lang, D.N.; Andry, S.P.; John, R.; Yang, H.K.; Lu, M.; Cai, C.; Speidell, J.; Purushothaman, S.; Ritsko, J.; Samant, M.; Stöhr, J.; Nakagawa, Y.; Katoh, Y.; Saitoh, Y.; Sakai, K.; Satoh, H.; Odahara, S.; Nakano, H.; Nakagaki, J.; Shiota, Y. *Nature* **2001**, *411*, 56.
- [60] Gwag, J.S.; Park, K.H.; Kang, D.J.; Jhun, C.G.; Kim, H.; Cho, S.J.; Yoon, T.H.; Kim, J.C. *Jpn. J. Appl. Phys.* **2003**, *42*, L468.
- [61] Lu, X.M.; Lu, Q.H.; Zhu, Z.K.; Yin, J.; Wang, Z.G. *Chem. Phys. Lett.* **2003**, *377*, 433.
- [62] Saunders, F.C.; Staromlynska, J.; Smith, G.W.; Daniel, M.F. *Mol. Cryst. Liq. Cryst.* **1985**, *122*, 297.
- [63] Gupta, R.K.; Suresh, K.A.; Guo, R.; Kumar, S. *Anal. Chim. Acta.* **2006**, *568*, 109.
- [64] Wasserman, S.R.; Tao, Y.T.; Whitesides, G.M. *Langmuir* **1989**, *5*, 1074.
- [65] Gupta V.K.; Abbott, N.L. *Langmuir* **1996**, *12*, 2587.
- [66] Gupta V.K.; Abbott, N.L. *Phys. Rev. E* **1996**, *54*, R4540.
- [67] Miller, W.J.; Abbott, N.L. *Langmuir* **1997**, *13*, 7106.
- [68] Evans, S.D.; Allinson, H.; Boden, N.; Flynn, T.M.; Henderson, J.R. *J. Phys. Chem. B* **1997**, *101*, 2143.
- [69] Wu, C.G.; Chen, J.Y. *Chem. Mater.* **1997**, *9*, 399.
- [70] Chung, D.H.; Fukuda, T.; Takanishi, Y.; Ishikawa, K.; Matsuda, H.; Takezoe, H.; Osipov, M.A. *J. Appl. Phys.* **2002**, *92*, 1841.
- [71] Ha, K.; West, J.L. *Liq. Cryst.* **2004**, *31*, 753.
- [72] Ha, N.Y.; Woo, Y.K.; Park, B.; Wu, J.W. *Adv. Mater.* **2004**, *16*, 1725.
- [73] Zhurin, V.V.; Kaufman, H.R.; Robinson, R.S. *Plasma Sources Sci. Technol.* **1999**, *8*, R1.
- [74] Newsome, C.J.; O'Neill, M. *J. Appl. Phys.* **2002**, *92*, 1752.
- [75] Yaroshchuk, O.; Kravchuk, R.; Dobrovolsky, A.; Qiu, L.; Lavrentovich, O.D. *Liq. Cryst.* **2004**, *31*, 859.
- [76] Chou, S.Y.; Krauss, P.R.; Renstrom, P.J. *Science* **1996**, *272*, 85.
- [77] Xia, Y.; Whitesides, G.M. *Angew. Chem. Int. Ed.* **1998**, *37*, 551.
- [78] Marzolin, C.; Smith, S.P.; Prentiss, M.; Whitesides, G.M. *Adv. Mater.* **1998**, *10*, 571.
- [79] Chou, S.Y.; Keimei, C.; Gu, J. *Nature* **2002**, *417*, 835.
- [80] Chiou, D.R.; Yeh, K.Y.; Chen, L.J. *Appl. Phys. Lett.* **2006**, *88*, 133123.
- [81] Chiou, D.R.; Chen, L.J. *Langmuir* **2006**, *22*, 9403.
- [82] Vorflusev, V.; Kumar, S. *Science* **1999**, *283*, 1903.
- [83] Vorflusev, V.; Kim, J.H.; Kumar, S. *Pramana-J. Phys.* **1999**, *53*, 121.
- [84] Qian, T.; Kim, J.H.; Kumar, S.; Taylor, P.L. *Phys. Rev. E* **2000**, *61*, 4007.
- [85] Kim, I.; Kim, J.H.; Kang, D.; Agra-Kooijman, D.M.; Kumar, S. *J. Appl. Phys.* **2002**, *92*, 7699.

- [86] Kim, J.H.; Kumar, S. *Jpn. J. Appl. Phys.* **2004**, *43*, 7050.
- [87] Kim, J.H.; Vorflusev, V.; Kumar, S. *Displays* **2004**, *25*, 207.
- [88] Wang, Q.; Kumar, S. *Appl. Phys. Lett.* **2005**, *86*, 071119.
- [89] Wang, Q.; Park, J.O.; Srinivasarao, M.; Qiu, L.; Kumar, S. *Jpn. J. Appl. Phys.* **2005**, *44*, 3115.
- [90] Kim, J.H.; Kumar, S. *J. Lightwave Technol.* **2005**, *23*, 628.
- [91] Wang, Q.; Guo, R.; Daj, M.R.; Kang, S.W.; Kumar, S. *Jpn. J. Appl. Phys.* **2007**, *46*, 299.
- [92] Choi, H.; Kim, D.W.; Rhie, K.W.; Hong, M.P.; Shin, S.T.; Kumar, S.; Jang, W.G.; Lee, B.W.; Kim, K.H. *Jpn. J. Appl. Phys.* **2008**, *47*, 1008.
- [93] Craighead, H.G.; Cheng, J.; Hackwood, S. *Appl. Phys. Lett.* **1982**, *40*, 22.
- [94] Doane, J.W.; Vaz, N.A.; Wu, B.G.; Zumer, S. *Appl. Phys. Lett.* **1986**, *48*, 269.
- [95] Drzaic, P.S. *J. Appl. Phys.* **1986**, *60*, 2142.
- [96] Vaz, N.A.; Smith, G.W.; Montgomery Jr., G.P. *Mol. Cryst. Liq. Cryst.* **1987**, *146*, 1.
- [97] Vaz, N.A.; Smith, G.W.; Montgomery Jr., G.P. *Mol. Cryst. Liq. Cryst.* **1987**, *146*, 17.
- [98] Vaz, N.A.; Montgomery Jr., G.P. *J. Appl. Phys.* **1987**, *62*, 3161.
- [99] West, J.L. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 427.
- [100] Doane, J.W.; Golemme, A.; West, J.L.; Whitehead Jr., J.B.; Wu, B.G. *Mol. Cryst. Liq. Cryst.* **1988**, *165*, 511.
- [101] Chidichimo, G.; Arabia, G.; Doane, J.W.; Golemme, A. *Liq. Cryst.* **1989**, *131*, 352.
- [102] Smith, G.W. *Mol. Cryst. Liq. Cryst.* **1991**, *196*, 89.
- [103] Yamaguchi, R.; Sato, S. *Jpn. J. Appl. Phys.* **1991**, *30*, L616.
- [104] Jiang, P.; Asada, T. *Mol. Cryst. Liq. Cryst.* **1992**, *222*, 87.
- [105] Radianguenebalid, M.; Sixou, P. *Mol. Cryst. Liq. Cryst.* **1992**, *220*, 53.
- [106] Shimada, E.; Uchida, T. *Jpn. J. Appl. Phys.* **1992**, *31*, L352.
- [107] Nolan, P.; Tillin, M.; Coates, D. *Liq. Cryst.* **1993**, *14*, 339.
- [108] Takiazawa, K.; Kikuchi, J.; Fujikake, H.; Narnkawa, Y.; Tada, K. *Jpn. J. Appl. Phys.* **1994**, *33*, 1346.
- [109] Lovinger, A.J.; Amundson, K.R.; Davis, D.D. *Chem. Mater.* **1994**, *6*, 1726.
- [110] Tondiglia, V.P.; Natarajan, L.V.; Sutherland, R.L. *Opt. Lett.* **1995**, *20*, 1325.
- [111] Fung, Y.K.; Yang, D.K.; Ying, S.; Chien, L.C.; Zumer, S.; Doane, J.W. *Liq. Cryst.* **1995**, *19*, 797.
- [112] Kato, K.; Tanaka, K.; Tsuru, S.; Sakai, S. *Jpn. J. Appl. Phys. Part 1* **1995**, *34*, 554.
- [113] Rajaram, C.V.; Hudson, S.D.; Chien, L.C. *Chem. Mater.* **1995**, *7*, 2300.
- [114] Rajaram, C.V.; Hudson, S.D.; Chien, L.C. *Chem. Mater.* **1996**, *8*, 2451.
- [115] Cheng, S.X.; Bai, R.K.; Zou, Y.F.; Pan, C.Y. *J. Appl. Phys.* **1996**, *80*, 1991.
- [116] Liu, J.H.; Liu, H.S.; Tsai, F.R. *Polym. Int.* **1997**, *42*, 385.
- [117] Takizawa, K.; Fujii, T.; Kawakita, M.; Kikuchi, H.; Fujikake, H.; Yokozawa, M.; Murata, A.; Kishi, K. *Appl. Optics* **1997**, *36*, 5732.
- [118] Chung, D.B.; Tsuda, H.; Chida, H.; Mochizuki, A. *Mol. Cryst. Liq. Cryst.* **1997**, *304*, 81.
- [119] Legerange, J.D.; Carter, S.A.; Fuentes, M.; Boo, J.; Freeny, A.E.; Cleveland, W.; Miller, T.M. *J. Appl. Phys.* **1997**, *81*, 5984.
- [120] Carter, S.A.; Legerange, J.D.; White, W.; Boo, J.; Wiltzius, P. *J. Appl. Phys.* **1997**, *81*, 5992.
- [121] Tondiglia, V.P.; Natarajan, L.V.; Neal, R.M.; Sutherland, R.L.; Bunnings, T.J. *Mat. Res. Soc. Symp. Proc.* **1997**, *479*, 235.
- [122] Nephew, J.B.; Nihei, T.C.; Carter, S.A.; *Am. Phys. Soc.* **1998**, *80*, 3276.
- [123] Nastal, E.; Zuranska, E.; Mucha, M. *J. Appl. Polym. Sci.* **1999**, *71*, 455.
- [124] Patnaik, S.S.; Pachter, R. *Polym.* **1999**, *40*, 6507.
- [125] Bhargava, R.; Wang, S.Q.; Koenig, J.L. *Macromolecules* **1999**, *32*, 8989.
- [126] Prk, N.H.; Cho, S.A.; Kim, J.Y.; Suh, K.D. *J. Appl. Polym. Sci.* **2000**, *77*, 3178.
- [127] Whitehead Jr., J.B.; Crawford, G.P. *Polym. Prepr.* **2000**, *41*, 1067.
- [128] Nicoletta, F.P.; Lanzo, J.; Filpo, G.D.; Chidichimo, G. *Langmuir* **2001**, *17*, 534.
- [129] Du, F.; Wu, S.T. *Appl. Phys. Lett.* **2003**, *83*, 1310.
- [130] Chen, T.J.; Chen, Y.F.; Sun, C.H.; Wu, J.J. *Jpn. J. Appl. Phys.* **2004**, *43*, L557.
- [131] Gelinck, G.H.; Huitema, H.E.A.; Veenendaal, E.V.; Cantatore, E.; Schrijnemakers, L.; Putten, J.B.P.H.V.D.; Geuns, T.C.T.; Beenhakkers, M.; Giesbers, J.B.; Huisman, B.H.; Meijer, E.J.; Benito, E.M.; Touwslager, F.J.; Marsman, A.W.; Rens, B.J.E.V.; Leeuw, D.M.D.; *Nat. Mater.* **2004**, *3*, 106.
- [132] Kihara, H.; Miura, T.; Kishi, R.; Kaito, A. *Polymer* **2004**, *45*, 6357.
- [133] Kihara, H.; Miura, T. *Polym.* **2004**, *46*, 10378.
- [134] Buyuktanir, E.A.; Mitrokhin, M.; Holter, B.; Glushchenko, A.; West, J.L. *Jpn. J. Appl. Phys.* **2006**, *45*, 4146.
- [135] Blinov, L.; Chigrinov, V. *Electrooptical Effects in Liquid Crystal*; Springer: Berlin, 1993.
- [136] Drzaic, P.S. *Liquid Crystal Dispersions*; World Scientific: Singapore, 1995.
- [137] Crawford, G.P.; Zumer, S. *Liquid Crystals in Complex Geometries*; Taylor and Francis: London, 1996.
- [138] Hikmet, R.A.M. *J. Appl. Phys.* **1990**, *68*, 4406.
- [139] Krongauz, V.V.; Schmelzer, E.R.; Yohannan, R.M. *Polym.* **1991**, *32*, 1654.
- [140] Hikmet, R.A.M.; Boots, H.M.J. *Phys. Rev. E* **1995**, *51*, 5824.
- [141] Dierking, I. *Adv. Mater.* **2000**, *12*, 167.
- [142] Kossyrev, P.A.; Qi, J.; Priezjev, N.V.; Pelcovits, R.A. *Appl. Phys. Lett.* **2002**, *81*, 2986.
- [143] Murashige, T.; Fujikake, H.; Ikehata, S.; Sato, F. *Jpn. J. Appl. Phys.* **2003**, *42*, 1614.
- [144] Fan, Y.H.; Ren, H.; Wu, S.T. *Appl. Phys. Lett.* **2003**, *82*, 2945.
- [145] Fan, Y.H.; Ren, H.; Wu, S.T. *Opt. Express* **2003**, *11*, 3082.
- [146] Fan, Y.H.; Lin, Y.H.; Ren, H.; Gauza, S.; Wu, S.T. *Appl. Phys. Lett.* **2004**, *84*, 1233.
- [147] Fan, Y.H.; Ren, H.; Liang, X.; Lin, Y.H.; Wu, S.T. *Appl. Phys. Lett.* **2004**, *85*, 2451.
- [148] Stannarius, R.; Crawford, G.P.; Chien, L.C.; Doane, J.W. *J. Appl. Phys.* **1991**, *70*, 135.
- [149] Takatsu, H.; Takeuchi, K.; Umezu, Y. *Mol. Cryst. Liq. Cryst.* **1993**, *225*, 81.
- [150] Noh, C.H.; Jung, J.E.; Kim, J.Y.; Sakong, D.S.; Choi, K.S. *Mol. Cryst. Liq. Cryst.* **1993**, *237*, 299.
- [151] Smith, G.W. *Mol. Cryst. Liq. Cryst.* **1994**, *241*, 77.

- [152] Lin, F.H.; Ho, C.Y.; Lee, J.Y. *J. Technol.* **2009**, in press.
- [153] Creagh, L.T.; Kmetz, A.R. *Mol. Cryst. Liq. Cryst.* **1973**, *24*, 59.
- [154] Kahn, F.J.; Taylor, G.N.; Schonhorn, H. *Proc. IEEE* **1973**, *61*, 823.
- [155] Wan, J.T.; Tsui, O.K.; Kwok, H.S.; Sheng, P. *Phys. Rev. E* **2005**, *72*, 021711.
- [156] Yeung, F.S.; Ho, J.Y.; Li, Y.W.; Xie, F.C.; Tsui, O.K.; Sheng, P.; Kwok, H.S. *Appl. Phys. Lett.* **2006**, *88*, 051910.
- [157] Seo, D.S.; Kobayashi, S.; Nishikawa, M.; Yabe, Y. *Jpn. J. Appl. Phys.* **1996**, *35*, 3531.
- [158] Seo, D.S.; Kobayashi, S. *Liq. Cryst.* **2000**, *27*, 883.
- [159] Lee, W.C.; Chen, J.T.; Hsu, C.S. *Liq. Cryst.* **2002**, *29*, 907.
- [160] Hwang, J.; Lee, S.H.; Peak, S.K.; Seo, D. *Jpn. J. Appl. Phys.* **2003**, *42*, 1713.
- [161] Lee, Y.J.; Choi, J.G.; Song, I.S.; Oh, J.M.; Yi, M.H. *Polym.* **2006**, *47*, 1555.
- [162] Lackner, A.M.; Margerum, J.D.; Miller, L.J.; Smith, W.H. *Proc. SID* **1990**, *31*, 321.
- [163] Moore, J.A.; Dasheff, A.N. *Chem. Mater.* **1988**, *1*, 163.
- [164] Bahadur, B. *Liquid Crystal: Applications and Uses*; World Scientific: Singapore, 1990.
- [165] Yeh, P.; Gu, C. *Optics of Liquid Crystal Displays*; John Wiley and Sons: New York, 1999.
- [166] de Gennes, G.P.; Prost, J. *The Physics of Liquid Crystals*; Clarendon: Oxford, 1993.
- [167] Crandall, K.A.; Fisch, M.R.; Petschek, R.G.; Rosenblatt, C. *Appl. Phys. Lett.* **1994**, *65*, 118.
- [168] Kaczmarek, H.; Decker, C. *J. Appl. Polym. Sci.* **1994**, *54*, 2417.
- [169] Kim, Y.S.; Sung, C.S.P. *J. Appl. Polym. Sci.* **1995**, *57*, 363.
- [170] Decker, C. *Polym. Int.* **2002**, *51*, 1141.
- [171] Mequanint, K.; Sanderson, R.D. *Macromol. Symp.* **2003**, *193*, 169.
- [172] Zhong, R.; Yang, J.; Zeng, Z.; Chen, Y. *Polym. Int.* **2006**, *55*, 650.
- [173] Kong, J.; Fan, X.; Zhang, G.; Xie, X.; Si, Q.; Wang, S. *Polym.* **2006**, *47*, 1519.
- [174] Chen, X.; Hu, Y.; Jiao, C.; Song, L. *Prog. Org. Coat.* **2007**, *59*, 318.
- [175] Zhang, X.; Yang, J.; Zeng, Z.; Wu, Y.; Huang, L.; Chen, Y.; Wang, H. *Polym. Eng. Sci.* **2007**, *47*, 1082.
- [176] Kilambi, H.; Reddy, S.K.; Bowman, C.N. *Macromolecules* **2007**, *40*, 6131.
- [177] Chen, X.; Hu, Y.; Song, L.; Jiao, C. *Polym. Adv. Technol.* **2008**, *19*, 322.
- [178] Xiao, P.; Dai, M.; Nie, J. *J. Appl. Polym. Sci.* **2008**, *108*, 665.
- [179] Spurge, G.; Pringle, R.D. *Mol. Cryst. Liq. Cryst.* **1988**, *154*, 307.
- [180] Montgomery Jr., G.P.; Vaz, N.A. *Appl. Optics* **1987**, *26*, 738.
- [181] Byoung, H.H.; Han, J.A.; Soon, J.R.; Soo, S.C.; Hong, K.B. *Langmuir* **2009**, *25*, 8306.
- [182] Jakeman, E.; Raynes, E.P. *Phys. Lett.* **1972**, *39A*, 69.
- [183] Nastishin, Y.A.; Polak, R.D.; Shiyanovskii, S.V. *Appl. Phys. Lett.* **1999**, *75*, 202.
- [184] Li, X.T.; Kawakami, A.; Akiyama, H.; Kobayashi, S.; Iimura, Y. *Jpn. J. Appl. Phys.* **1998**, *37*, L743.
- [185] Chiang, C.H.; Tzeng, S.Y.T.; Sie, F.C.; Huang, R.H.; Wu, P.C.; Wu, J.J.; Lin, T.Y.; Liu, A.S.; Hsu, L.H.; Liao, W.L.; Len, S.C. *J. Appl. Polym. Sci.* **2007**, *46*, 5917.
- [186] Nie, X.; Xianyu, H.; Lu, R.; Wu, T.X.; Wu, S.T. *J. Display Technol.* **2007**, *3*, 280.
- [187] Jiao, M.; Ge, Z.; Song, Q.; Wu, S.T. *Appl. Phys. Lett.* **2008**, *92*, 061102.