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Formation of Optical Films by Photo-Polymerisation of Liquid Crystalline Acrylates and Application of These Films in Liquid Crystal Display Technology

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Photo-polymerisation of liquid crystalline di-acrylates is a very versatile method to produce homogeneously aligned polymer films. The orientation of the liquid crystals and hence the anisotropic optical properties of the films are frozen in by the photo-polymerisation process. Homogeneously aligned nematic liquid crystals form birefringent films that find application as retarders, while splayed nematic liquid crystalline mixtures form angle dependent birefringent films that find application as wide viewing angle foils. In addition, cholesteric liquid crystals form reflecting films that can be used as colour filters or polarisers and smectic liquid crystals form highly ordered films that find application as polarisers. Moreover, modulating the light during the manufacturing process either in lateral or in-depth direction of the film can create complex structures not attainable with liquid crystalline polymers. All these films are mechanically, thermally and chemically stable and therefore very suitable to be processed in liquid crystal display manufacturing as additional films or as in-cell optical components.

1. PHOTO-POLYMERISATION OF LIQUID CRYSTALS

In liquid crystal displays, the switchable liquid crystals are kept in a cell formed by two glass plates. Liquid crystalline materials can also be used as optical film needed for the functioning of liquid crystal displays or to improve the properties of such displays. In that case a stable not switchable material is needed. Liquid crystalline polymers can be used for this purpose. Two types of these polymers can be

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distinguished: rod-like molecules connected to a polymer chain referred to as side-chain polymers, or rod-like molecules connected head to tail, thus forming a polymer chain containing these rods, referred to as main-chain polymers. The first type of polymers is very popular to use because the polymerisation process is independent of the structure of the liquid crystal, which gives a lot of freedom in designing the chemical structure and thus the properties of the polymer.

Just as in the case of the low molecular-weight liquid crystals, liquid crystalline polymers exhibit optical anisotropy in the form of, for example, birefringence. A disadvantage of these polymers is their relatively high viscosity compared to the low molecular-weight liquid crystals. Due to this high viscosity, alignment over large surface areas is difficult. In most cases a so-called multi-domain structure in which the mutual local directors of these domains do not point to one direction is obtained, which optically is far from perfect.

To solve this problem, the in-situ photo-polymerisation of reactive liquid crystals has been proposed [1]. In this process a mixture of liquid crystalline (di)-acrylates with a small amount of a radical photo-initiator is molten or coated from a solution (e.g. spin-coating) on a surface that contains a very thin rubbed polymeric alignment layer. Due to the low viscosity of these monomers compared to the polymers, alignment in a mono-domain over a large surface area can easily be obtained. After alignment a fast UV induced polymerisation process

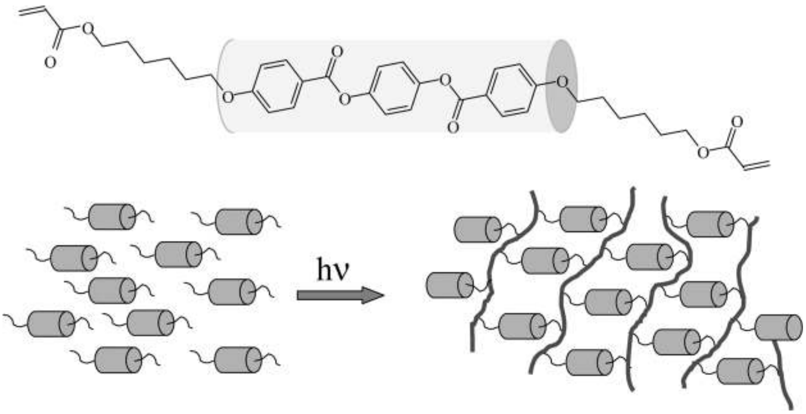

FIGURE 1.1 Structure of a liquid crystalline di-acrylate (top) and schematic representation of the photo-polymerisation reaction to obtain a crosslinked polymer network with retention of alignment (bottom).

is started (photo-polymerisation) to form a polymer and which in this way stabilises the anisotropic optical properties of the monomers. By using monomers with two or more polymerisable groups, a tightly crosslinked network is formed upon photo-polymerisation (Fig. 1.1). Such a network is stable over a large temperature range. The advantage of photo-polymerisation over thermally initiated processes is the freedom in choosing the polymerisation temperature enabling the selection of the most optimum phase and molecular order [2]. Anisotropic properties of liquid crystals which are observed in a relatively small temperature domain before polymerisation only, now become stable between –100 and + 200°C. An example of such a monomer is the liquid crystalline di-acrylate shown in figure 1.1. This material exhibits a nematic phase up to 155°C. Figure 1.2 shows the ordinary and extraordinary refractive index of the molten material after alignment as a function of temperature. The same figure shows that after polymerisation at 120°C the refractive indices become nearly temperature independent.

Another advantage of this photo-polymerisation process is that complex molecular architectures become possible. By using masks, photo-lithographic effects can be performed with the film. Well-defined

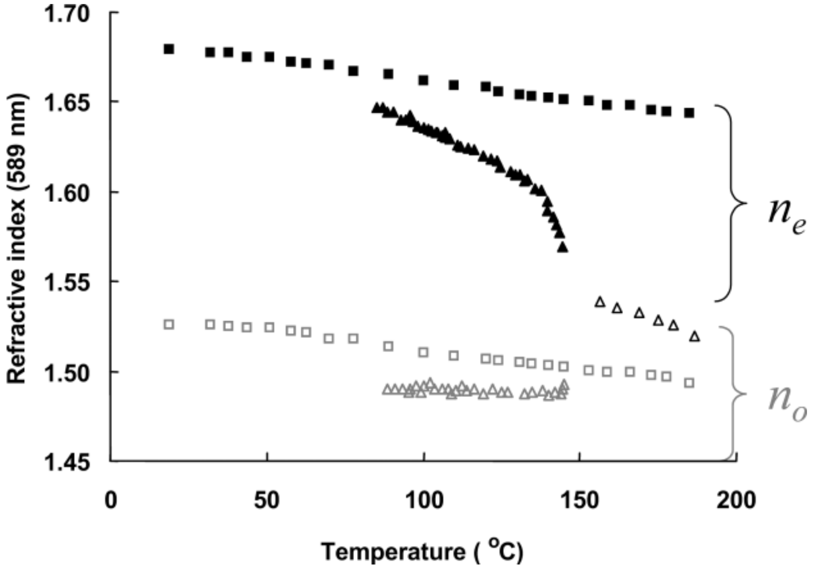

FIGURE 1.2 Refractive indices of the compound of figure 1.1 before (▲, △ and △) and after (■ and □) polymerisation at 120°C. (See COLOR PLATE IX)

local alignment deviations can be obtained by using an electric field during polymerisation [3]. Complex structures obtained by changing the tilt angle of the director with the surface as a function of the film thickness can be stabilised by the photo-polymerisation process too as will be shown in the next sections. Instead of nematic molecules, materials exhibiting various other liquid crystalline phases can be used too. In all those cases the photo-polymerisation process will stabilize anisotropic properties characteristic for such a phase. In this paper several examples are given with materials in various phases using simple, more complex irradiation techniques or even sequences of irradiation processes to perform the polymerisation. In this way advanced optical films for improvement of the liquid crystal display are made.

Many of the thin layers described in this paper are much thinner than the conventional optical components. These layers can be used inside the cell (in-cell). Thus, these layers reduce the thickness of the display. When used as in-cell layers, the glass plates form the exterior of the display, which gives a higher robustness. Furthermore, the optical properties of the glass plates become less critical and can for instance be replaced by plastics that often are birefringent. So these new thin in-cell components will play an important role in the development of flexible displays. Also, the optical function is brought in very close contact with the switching liquid crystal, which makes optimisation possible on pixel level avoiding parallax problems.

In the forthcoming sections several examples of optical films derived from liquid crystalline di-acrylates and application of these films in liquid crystal displays will be discussed in detail.

2. FILMS MADE FROM NEMATIC LIQUID CRYSTALS

2.1. Patterned Retarders by Photo-alignment

Birefringent films as described in the previous section are very suitable to make retarder films. These films that change the polarisation state of polarised light, find widespread application in liquid crystal displays. The ease of alignment due to the low viscosity of the liquid crystalline di-acrylates and the photo-polymerisation process, which makes patterning relatively simple, offers the possibility to produce relatively complex retarders. The extent in which a planar film retards polarised light (R), depends on the birefringence (Δn), the film thickness (d) and the angle (ϕ) between the optical axis of the film and the original polarisation direction of the light according to:

$$\mathrm{R} = \cos(\phi - 45^\circ)\mathrm{d}\Delta\mathrm{n} \tag{2.1}$$

Maximum retardation is obtained when the angle between the electric field vector of linearly polarised light and the optical axis of the nematic film equals 45 degrees.

If instead of a rubbed polyimide the alignment is performed with the aid of a patterned photo-alignment layer, the director of the nematic crystals before polymerisation is locally changed. This means that ϕ and thus the retardation is changed locally [4,5].

Figure 2.1 shows a photo-aligned patterned retardation film made by photo-polymerisation of liquid crystalline di-acrylates aligned on such a photo-alignment layer. This photo-alignment layer is exposed by polarised UV light in a patterned way in order to obtain the domains with different alignment direction. Then the liquid crystalline di-acrylates are applied which adapt the alignment of the photo-alignment layer, followed by photo-polymerisation. High resolution patterned retarders with 10 μm sized domains are obtained as shown in figure 2.1. These retarders are very thin (less than 2 μm) and are therefore very suitable to be used inside the cell. Such in-cell retarders have to withstand process conditions, such as application of ITO and polyimide, which are performed at high temperatures. These films indeed show a good thermal stability. Heating of these films at 210°C for 4 hours result in a reduction of the retardation value of only less than 2%.

Such a director patterned-retarder can be used in a transflective liquid crystal display to improve the performance under small viewing angles [6]. Figure 2.2 shows a simplified cross section of a transflective display. Each pixel consists of a reflective and a transmissive part. To achieve a white picture in the non-addressed state for the transmissive and reflective part simultaneously, a $\lambda/4$ retardation film is

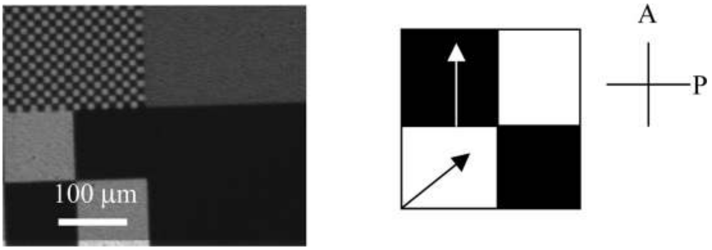

FIGURE 2.1 A patterned retardation film viewed in between two crossed polarisers (A and P). The domains are created by photo-alignment forcing the directors (shown on the right as arrows) to orient parallel to or at 45 degrees with respect to the transmissive axis of the polariser. The thickness of the film corresponds to 275 nm retardation of 550 nm light. (See COLOR PLATE X)

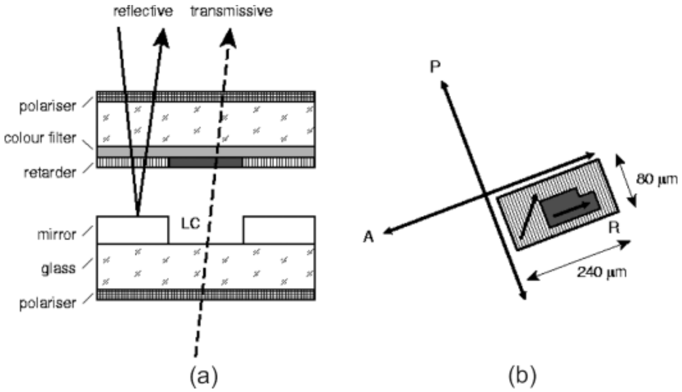

FIGURE 2.2 (a) A cross section of a transflective liquid crystal display and (b) a top view of the pixel layout demonstrating the transparent hole in the mirror, the position of the polarisers and the direction of the directors.

required in the reflective part, whereas the transmissive part does not need a retardation film at all. In order to manufacture a retarder with a patterned director, a mixture of liquid crystalline acrylates is spin-coated on top of a dual- domain photo-alignment layer made as explained before. The thickness of the liquid crystal film is such that the product of the thickness and the birefringence equals 138 nm (see Eq. (2.1)). The director orientation is chosen as demonstrated in figure 2.2b. The angle between the director and the transmissive axis of the polariser is 45 degrees in the reflective part, while in the transmissive part this angle equals zero.

However, director patterning leads to two domains having an intrinsic identical retardation value. As a consequence misalignment in the main optical axis of the retardation film with respect to the transmissive axis of one of the polarisers will result in light leakage and corresponding contrast reduction. Moreover, a disclination line with a width of about 4 μm appears at the interface of two adjacent domains with a different director as a consequence of minimization of the elastic energies in the system. In addition the optical properties of the retardation film are also viewing angle dependent in the transmissive part. The misalignment, disclination line and viewing angle dependence strongly reduce the performance of the display and are therefore disadvantageous. For an optimum performance, the transmissive part is preferred to be isotropic because an isotropic domain will eliminate the above-mentioned causes of contrast degradation. Such isotropic domains can be created by a technology called thermal patterning discussed in the next section.

2.2. Thermally Patterned Retarders

The principle of thermal patterning is demonstrated with the aid of figure 1.2. The birefringence of a non-crosslinked nematic liquid crystal depends on the temperature: The birefringence decreases with increasing temperature until the transition temperature is reached and the birefringence becomes zero. Consequently, a film crosslinked above this temperature does not show any optical retardation as the product of the film thickness and the birefringence is zero (see Eq.(2.1)).

The process steps to make a patterned retarder with $\lambda/4$ retardation and zero retardation needed for the application presented in figure 2.2 are as follows. First a glass substrate is provided with an alignment layer. On top of this alignment layer the mixture of liquid crystalline (di-)acrylates and the initiator is coated. The thickness of the film is chosen such that after polymerisation at the chosen temperature $d\Delta n = 138\,\text{nm}$. In the next step the nematic film of liquid crystalline di-acrylates is partially crosslinked by UV irradiation through a mask at this temperature in a nitrogen atmosphere. The

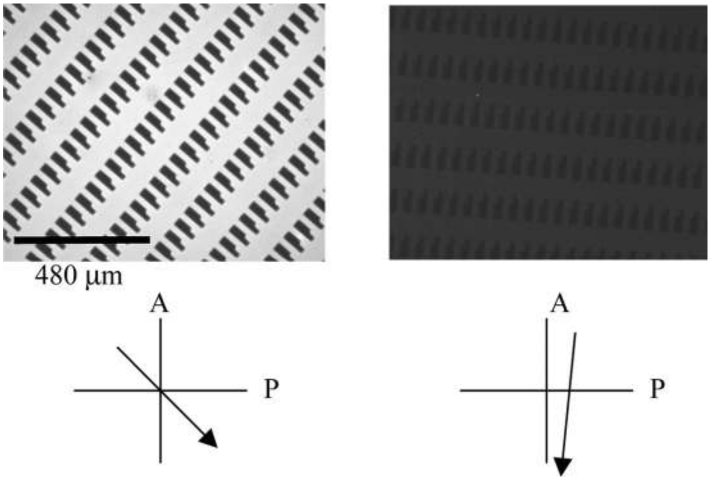

FIGURE 2.3 Thermally patterned retarder with isotropic part and nematic part between crossed polarisers. The orientation of the director (represented by the arrows) in the nematic domains with respect to the transmissive axis of the polariser (P) is 45 degrees in the left figure and 0 degrees in the right figure. The isotropic part does not show any optical retardation for both orientations, whereas the nematic part retards the light when viewed at 45 degrees. (See COLOR PLATE XI)

$\lambda/4$ retardation required for the reflective part in a transflective display is hence obtained after the mask exposure. Subsequently, the layer is heated above the transition temperature, so the non-crosslinked parts will become isotropic. The heated film is exposed to UV light to crosslink the isotropic parts. As a result a thermally patterned retarder with isotropic and nematic parts is obtained. A picture of such a patterned optical film is shown in figure 2.3.

The thermally patterned retarder is specifically well suited for application in transflective displays [6,7] such as the one shown in figure 2.2. Compared to displays with simple polymeric retarder films, the viewing angle has improved enormously by using this thermally patterned retarder. Moreover, the display is brighter due to light recycling in the transmissive mode, which is only possible as a result of the patterning technique. In conclusion, films made from nematic liquid crystalline di-acrylates can replace the retardation films applied in liquid crystal displays because the liquid crystals enable the fabrication of patterned retardation films that are crucial for a further improvement in the performance of these displays.

2.3. Wide Viewing Angle Film

A major imperfection of liquid crystal displays is their limited viewing angle in comparison to cathode ray tubes. Unintended effects of the liquid crystal layer on the polarisation state of the passing light limit the viewing angle of twisted nematic liquid crystal displays. The viewing angle dependence of the transmission in the display's driven state is connected to the birefringent nature of the liquid crystal material in a fundamental way. It is related to the viewer's position with respect to the director profile in the cell. Figure 2.4 shows schematically a pixel of an active matrix twisted nematic liquid crystal display. At full addressed state, a nearly complete homeotropic alignment of the switched molecules result in a black pixel (left). However, under an angle the molecules still exhibit retardation resulting in a grey pixel. At the half addressed state a grey pixel is obtained but for certain viewing angles this pixel becomes black (right). This grey scale inversion, which is also colour dependent, is one of the main drawbacks of these types of displays.

Improvement of the display performance on this aspect may be achieved by adding birefringent compensation layers that undo part of the undesired birefringent effect of the liquid crystal layer. A relatively straightforward solution is to add phase compensation films in which the molecular organization mimics that of the liquid crystal in the most sensitive state, e.g. the half addressed state of twisted

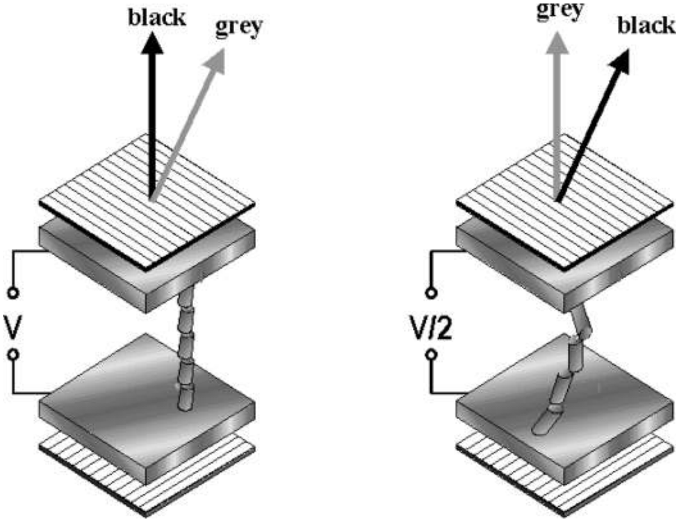

FIGURE 2.4 Schematic representation of a pixel of a twisted nematic display in the fully addressed state (left) and half addressed state (right).

nematic-liquid crystal display, in a complementary manner. Two types of these so-called wide-viewing-angle films have been demonstrated. Discotic polymeric network films with a tilted optical axis, applied between the liquid crystal display cell and the polariser, gave an enormous improvement on the angular dependence of contrast and grey scale inversion [8]. The technology described in previous sections with nematic liquid crystalline di-acrylates lead to comparable improvements of the optical performance. A film is made from two layers of crossed liquid crystalline networks that exhibit a tilt or a splay. Such birefringent films exhibit a lower refractive index in the direction of the tilt and higher indices in the plain perpendicular to the tilted axis [9].

These retarder films are produced from reactive liquid-crystalline (di-)acrylates. Figure 2.5 shows an example of a mixture that aligns planar at the polyimide interface but tends to become homeotropic at the air interface driven by the surface energy at this interface. Especially the cyano-containing compound shows this tendency. By controlling the composition of the mixture shown in figure 2.5, the temperature and the film thickness, a splayed layer is obtained where the average angle determines the tilt angle. The tilt angle is stabilized completely by the photo-polymerisation process. By mounting two of these films crossed (i.e. with mutual perpendicular directors) between

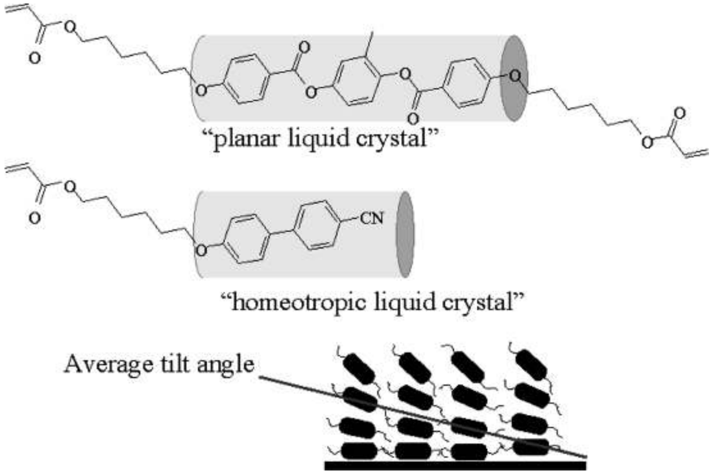

FIGURE 2.5 Example of a mixture of liquid crystals that form a splayed structure, which is stabilised by photo-polymerisation.

the active liquid crystalline switch and the analyser, a strong improvement in the viewing angle of the display is obtained.

3. FILMS MADE FROM CHOLESTERIC LIQUID CRYSTALS

The chiral nematic phase or cholesteric phase is characterised by a twist in the director as a function of the lateral position in the film. In this way the director describes a helix of which the pitch (p) is defined as the distance over which the director has rotated 360° as shown in Figure 3.1.

The rotation direction depends on the sign of the enantiomeric excess of the chiral moiety. The most important property of these materials is the ability to reflect light with reflection wavelength λ is given by:

$$\lambda = p * \bar{n} \tag{3.1}$$

where $\bar{n}$ is the mean refractive index of the polymer. The bandwidth of the reflection band ($\Delta\lambda$) is defined by the birefringence of the material (Δn) according to:

$$\Delta\lambda = p * \Delta n \tag{3.2}$$

The ability of a chiral compound to induce a twist is defined by the helical twisting power (HTP) which is a material dependent constant.

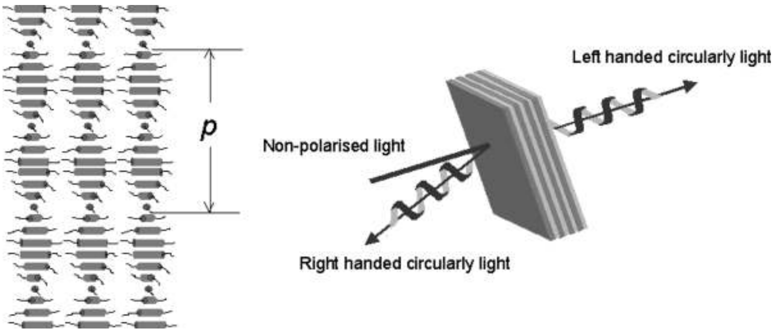

FIGURE 3.1 Representation of the cholesteric phase, the pitch p (left) and a cholesteric film as a circular polariser (right).

In first assumption the reflection wavelength of a mixture of nematic liquid crystals and chiral molecules is defined by:

$$\lambda = \overline{n}\Sigma_i(HTP_i * x_i)^{-1} \tag{3.3}$$

Where: x_i is the fraction of the chiral component. The reflected light is circularly polarised and the handedness of the polarisation of the reflected light is the same as the handedness of the helix of the cholesteric material. The other polarisation direction is transmitted through the material. These optical properties make cholesteric films very useful for colour separation and the formation of polarised light (figure 3.1). By changing the amount of chiral components (x_i) the reflection wavelength is changed. Figure 3.2 shows a chiral liquid crystal of which the pitch after polymerisation has a value of about 180 nm. By mixing it with for example the nematic compound also shown in figure 3.2, the reflection wavelength and thus the colour can be chosen by the fraction of the chiral compound also shown in this figure.

With this kind of mixtures thermally, chemically and mechanically stable films can be obtained [10] which find their applications in decoration or in optical components.

3.1. Broadband Circular Polarisers

Nearly all liquid crystal displays visualise their images by making use of polarised light. Therefore, one of the principal components of a liquid crystal display is the polariser. Normally such a polariser absorbs one polarisation direction of the backlight in the case of transmissive displays while the other polarisation direction is transmitted. This means a loss of the backlight intensity of at least 50%.

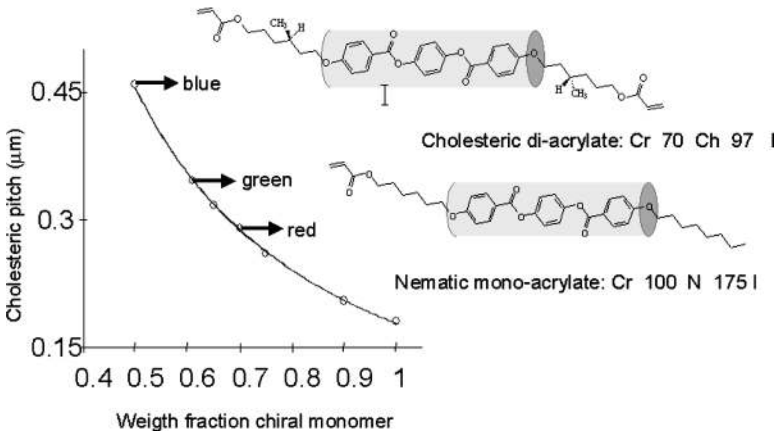

FIGURE 3.2 Dependence of the reflection wavelength of a cholesteric mixture after photo-polymerisation at 60°C as a function of the fraction of the chiral compound (left). Structure of the chiral d-iacrylate and nematic mono-acrylate (right).

Cholesteric films are capable of making polarised light by transmitting one polarisation direction and reflecting the other. If the reflected light is depolarised it can be used again and a much more efficient polarisation device can be made. Disadvantages of the cholesteric films are that they generate circularly polarised light instead of linearly polarised light and they are only effective for a certain colour and not for the whole visible spectrum. The first problem is solved easily by converting the circularly polarised light into linearly polarised light with the aid of a quarter wave plate. To solve the second problem, the bandwidth of the reflection band of the cholesteric films which normally amount to about 80 nm should be increased at least three times (see Eq. (3.2)). This would mean an increase in birefringence of the liquid crystals with the same factor. Such materials are difficult to make and may have disadvantages such as a low stability and absorption bands in the wavelength region of interest.

A better solution to this problem is the production of a cholesteric film in which the pitch and thus reflection wavelength has a gradient. To produce such a film use can be made of the kinetics of the photopolymerisation reaction. A film is made of a mixture of the cholesteric di-acrylate and nematic monoacrylate shown in figure 3.2. The composition is chosen such to obtain a green reflection band. If such a mixture is photo-cured, a green light reflecting layer is obtained. By

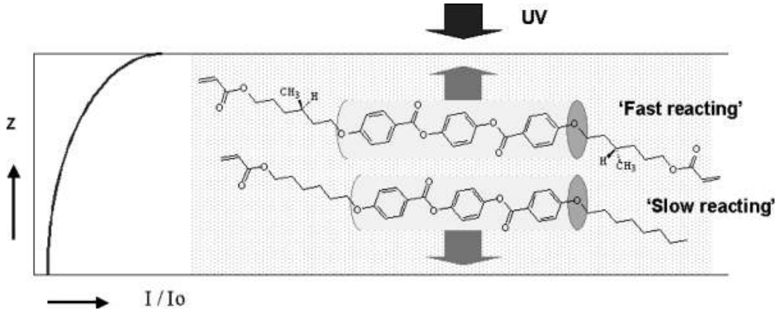

FIGURE 3.3 Intensity gradient for UV light in a cholesteric film (left) and diffusion direction of the different monomers in this film during polymerisation (right).

adding a UV absorbing dye, an intensity gradient of the UV light in the transverse direction is obtained shown on the left side of figure 3.3.

Due to the UV intensity gradient, the polymerisation at the top proceeds much faster than at the bottom of the layer. The cholesteric component is a di-acrylate, and therefore has a twice as high probability as the nematic mono-acrylate to be incorporated in the polymer. If the overall polymerisation rate is tuned to the diffusion kinetics (relatively low UV intensity), depletion of the chiral di-acrylate near the top of the layer generates a concentration gradient of this di-acrylate in the transverse of the film. This in turn starts diffusion of this compound towards the top of the layer. The ultimate result after complete photo-polymerisation is that the top of the layer contains more chiral material and thus has a shorter reflection wavelength than at the bottom of the layer, which is formed of relatively more of the non chiral compound. Although the film is made partly of a mono-acrylate, there are still enough crosslinks to obtain a similar stability as shown in figure 1.2.

SEM results show indeed a pitch gradient in the film [11]. The effect of the pitch gradient on the optical properties is apparent from figure 3.4 in which the green reflection band before polymerisation is shown together with the broad band reflection after polymerisation. It is clear that such a “molecular architecture” in the film is impossible to make with non-polymerisable liquid crystals or liquid crystalline polymers. The photo-polymerisation reaction is not only responsible for the formation of a stable film, but it also plays a role in the formation of this architecture. By selection of the right liquid crystalline structures it is possible to form sheets in a continuous coating process, which can be cut and incorporated in liquid crystal displays.

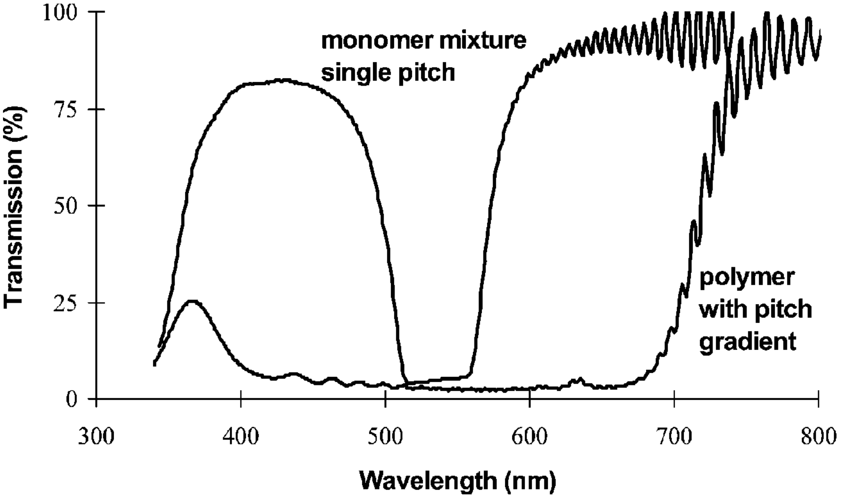

FIGURE 3.4 Reflection of right-handed circularly polarised light measured as transmission loss of a 1:1 mixture of the compounds of figure 3.2 before and after polymerisation using an UV intensity gradient.

The method of increasing the brightness using the recycling principle is schematically shown in figure 3.5. Light with the right polarisation direction is transmitted while the other polarisation direction is reflected to the lamp system. It is then depolarised and can in turn

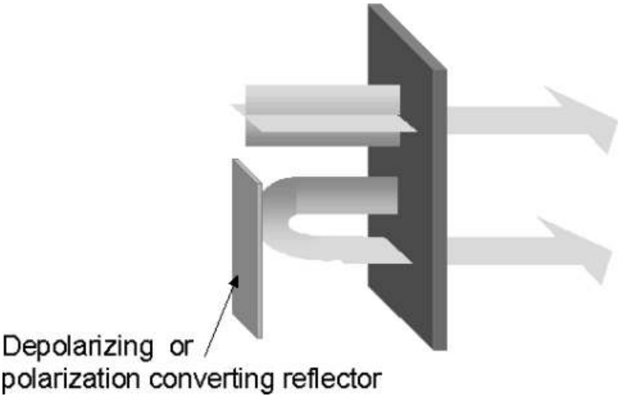

FIGURE 3.5 Principle of 100% conversion of unpolarised light into polarised light by recycling of light using a reflective polariser.

form again light with the right polarisation direction. Theoretically in this way a 100% gain in light intensity can be obtained.

The above-mentioned sheets were placed between the active switching part of a display and the backlight system, which was optimised for the use of these sheets. The brightness of such a display was 1.6 times as high as with a conventional polariser [11].

3.2. Cholesteric Colour Filters

The example described above is used to make films of which the properties are constant in the lateral direction. Alternatively, cholesteric materials can be applied to make films with patterned reflection colours. Apart from applications as decorative materials an interesting application is the use of these materials for colour filters in liquid crystal displays. Reflective liquid crystal displays are important components for mobile systems such as handheld computers or mobile phones. The advantage of such displays is that they are low energy consuming because no back-light is needed. Present technology drives reflective liquid crystal displays towards high reflectivity and full-colour. The advantage of using a cholesteric film as colour filter is that it not only generates colour, but also acts as polariser and reflector. Therefore the design of reflective displays can be simplified. For application in transmissive liquid crystal displays, cholesteric colour filters have an extra advantage. The reflective nature of the colour filter offers the opportunity to recycle the two unwanted primary colours from the backlight. In conventional transmissive liquid crystal displays unwanted light (i.e. at least 66%) is absorbed by the colourfilter. This means that when cholesteric colour filters are used in combination with the cholesteric polariser described in section 3.1, a six times higher light intensity can be obtained compared with the use of absorbing components [12]. A colour filter needs to consist of an array of red, green and blue pixels. In the manufacturing process of conventional colour filters these colours are applied successively by e.g. lithography, a very laborious process. Cholesteric materials offer the possibility to obtain a red-green-blue (RGB) array in one step, i.e. by changing the pitch (p) and thus the relative fractions of the chiral compounds locally in the layer.

A method to perform this is by the use of photo-chemically isomerisable chiral compounds. Figure 3.6 shows the structure of such a compound. The chiral groups are situated in the cyclohexanone moiety that is connected to an isomerisable double bond with E configuration. Upon irradiation, isomerisation to the Z configuration occurs. The compound with the E configuration has a relatively high HTP while

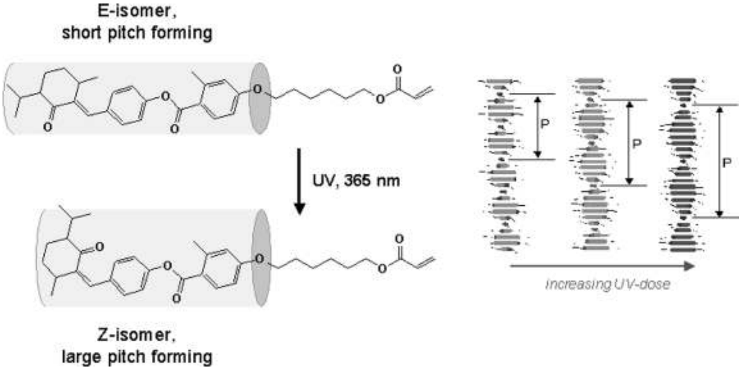

FIGURE 3.6 E-isomer of a chiral isomerisable compound derived from menthone in its Z-isomer obtained after irradiation (left). Increase of the pitch as a function of the irradiation time of a cholesteric mixture made with a photo-isomerisable compound (right).

the photo-isomerised compound (Z-isomer) has an HTP of nearly zero [13]. Thus by changing the relative fractions of the two isomers the pitch, and thus the reflection wavelength, changes according to Eq. (3.3).

By preparing a mixture with the right composition of the chiral isomerisable compound and a nematic di-acrylate shown in figure 2.5, a blue reflecting film is obtained after coating on an alignment layer, which upon irradiation will change gradually via green to red. Figure 3.7 shows how the three colours are made by one irradiation step using a grey-scale mask between the light source and a film of the material. Stabilisation of the film containing the pixelated reflection colours is again performed by photo-polymerisation.

Process circumstances have been found in which the two photochemical processes, namely isomerisation and polymerisation, do not interfere [14]. The kinetics of the photo-polymerisation reaction plays again an important role in the process. Photo-isomerisation is independent of the atmosphere present during the process. Photo-polymerisation will not start if air is present due to the inhibitive effect of oxygen on the acrylate polymerisation reaction. Combination of this effect and the relatively low UV intensity needed for isomerisation results in easy formation of the colours in the presence of air without noticeable polymerisation. For the photo-polymerisation a photo-initiator is chosen which absorbs UV light in the region outside the absorption band of the isomerisable compound, and the atmosphere is changed to an inert one (nitrogen or argon). In this way a rapid

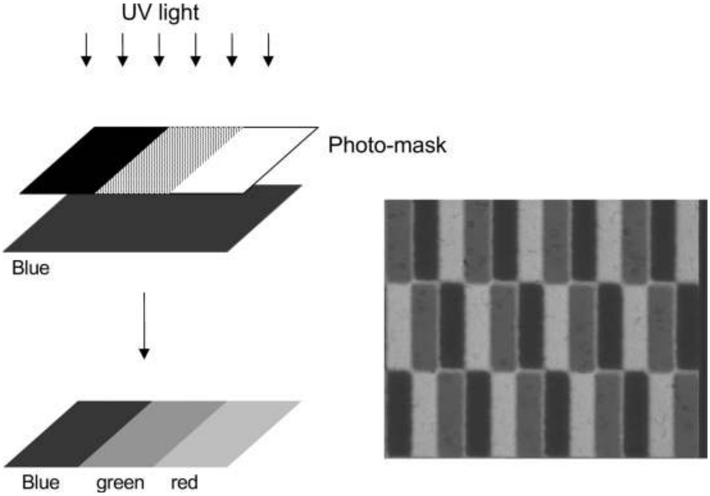

FIGURE 3.7 The colour formation process for isomerisable cholesteric mixtures and an example of a colour filter with $100 \times 300\,\mu m^2$ pixels.

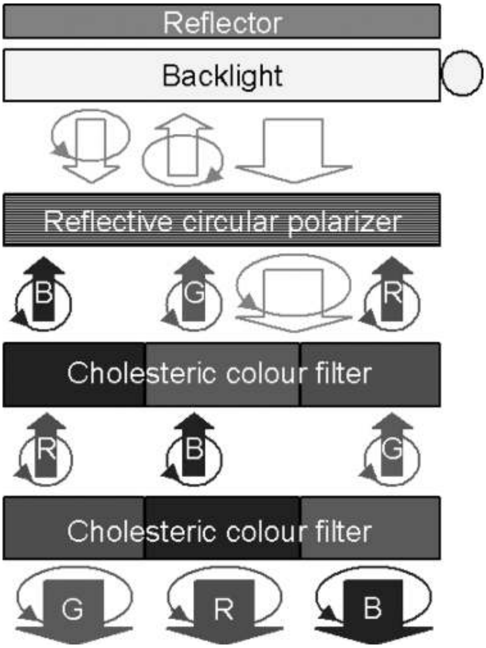

FIGURE 3.8 Schematic representation of light recycling using a reflective polariser and colour filter in transmissive liquid crystal display.

fixation of the patterned cholesteric structure is obtained. Due to the crosslinking a thermally stable material is obtained. Also the UV stability is very high. Post isomerisation will not have an effect on the helix because it is fixed by the crosslinks and thus the colour will not change upon post irradiation. These cholesteric colour filters (Fig. 3.7) reflect colours of high colour purity and are very promising materials for new generations of reflective liquid crystal displays [12,15].

For the application of cholesteric colour filters in transmissive liquid crystal displays, two primary colours have to be reflected so that the third is transmitted and reaches the viewer as shown in figure 3.8. This figure also shows the theoretically 6 times higher light intensity when all the light reflected by the reflective polariser (section 3.1) and the colourfilter is recycled completely.

Such a configuration can be achieved by stacking two cholesteric films on top of each other and carry out the processing of the two layers consecutively. By tuning the positions of the reflection bands to the red, green and blue emission lines of a fluorescent backlight, high colour purity can be obtained [15].

A 5” full-colour transmissive liquid crystal display with such a double-layer cholesteric colour filter was made. For this purpose, ITO and an alignment layer were applied on top of the colour filter. The high-temperature processing of these layers did not deteriorate the optical performance of the colour filter, confirming its good thermal stability in the same way as observed with the patterned retarder materials discussed in section 2.2. This stack was then used as one of the two substrates to construct the liquid crystal cell. The other substrate

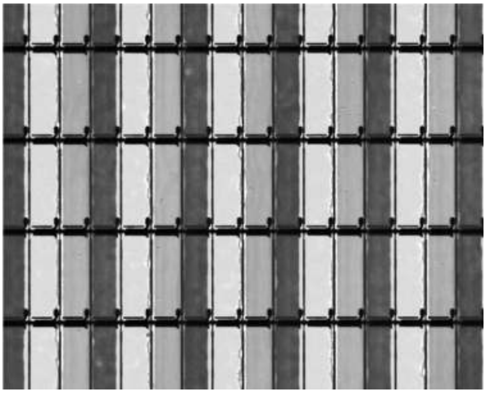

FIGURE 3.9 Microscopic image of the liquid crystal display showing the $100 \times 300\,\mu m^2$ pixels.

contained an active matrix array. The microscope picture in Figure 3.9 shows that the first pixelated cholesteric layer, the second one and the active matrix array are well-aligned with each other. Simple liquid crystal displays with good colour purity were manufactured with these layers. The good colour quality and the opportunity of light recycling in combination with a cholesteric polariser show the potential of applying cholesteric colour filters in transmissive liquid crystal displays.

4. POLARISERS MADE FROM SMECTIC MATERIALS

For most types of liquid crystal displays the performance is strongly influenced by the performance of the polariser. The most elegant way to define the polarisation performance is the dichroic ratio in absorbance. The dichroic ratio is a materials property and therefore, it is independent of the thickness of the polariser. The dichroic ratio in absorbance (DR) can be determined via polarised absorption spectroscopy and is defined as:

$$DR = \frac{A_{//}}{A_{\perp}} \tag{4.1}$$

Where $A_{//}$ and $A_{\perp}$ are defined as the absorbance parallel and perpendicular to the average orientation axis of the dye molecules, respectively. When the DR is determined, the order parameter for the dye molecules (S_{dye}) can be calculated under the assumption that the transition dipole moment is located along the long axis of the dye molecule:

$$S_{dye} = \frac{A_{//} - A_{\perp}}{A_{//} + 2A_{\perp}} = \frac{DR - 1}{DR + 2} \tag{4.2}$$

For low-end mobile applications of liquid crystal displays, polarisers with dichroic ratios of approximately 35 are standard in current products. For high-end mobile applications of liquid crystal displays and for non-mobile applications such as TFT-monitors and LC-TV, the requirements for the polarisation performance are more demanding. Polarisers with dichroic ratios exceeding 40–50 are currently used in these applications.

Currently, the most widely used polarisers for liquid crystal display applications consist of uniaxially stretched poly(vinylalcohol) which is impregnated with iodine or doped with dichroic dyes. The moisture sensitive poly (vinylalcohol) film is protected on both sides by a TAC-layer (triacetylcellulose). On one side an adhesive is applied in order to laminate the polariser to the display. The necessary use of protective layers and adhesive in these polarisers add unnecessary thickness to the liquid crystal display. Furthermore, it is not possible to apply these polarisers inside a liquid crystal cell, since the polariser stack is not resistant to the process conditions, which are required for liquid crystal display manufacturing.

Numerous advantages are foreseen when these traditional sheet polarisers are replaced by ultra-thin coatable polarisers situated at the inside of the cell (in-cell). Apart from a significant reduction in display thickness and weight, the positioning of the polarisers inside the cell eliminates all parallax related issues and is beneficial to the robustness of the display. Further, it allows use of a wide variety of substrates (including low-weight and strong plastics) that otherwise would be rejected because of their birefringence. A possible approach to obtain thin coatable polarisers is based on the use of reactive liquid crystals.

The principle behind this guest-host polariser approach can be explained with the aid of figure 1.1. By replacement of some of the liquid crystalline di-acrylates with dye molecules with an elongated structure, a dichroic mixture is obtained. Upon alignment of the host liquid crystalline di-acrylates, the dye molecules align along the director of the host liquid crystals, resulting in dichroic absorption of the dye molecules. Upon photo-polymerisation the anisotropic properties of the film are stabilised.

Thus, dissolving dichroic dye shown in Figure 4.1 in the nematic liquid crystalline di-acrylate of figure 1.1 can produce thin film polarisers. Polarisers made from these materials show dichroic ratios smaller than 10, as a result of the low order parameter (S = 0.6–0.7) of the LC and dye molecules in the nematic phase.

The order in the nematic phase is clearly insufficient to meet the requirements. Other liquid crystalline phases with higher order have to be used. If one of the aromatic rings of the nematic di-acrylate of

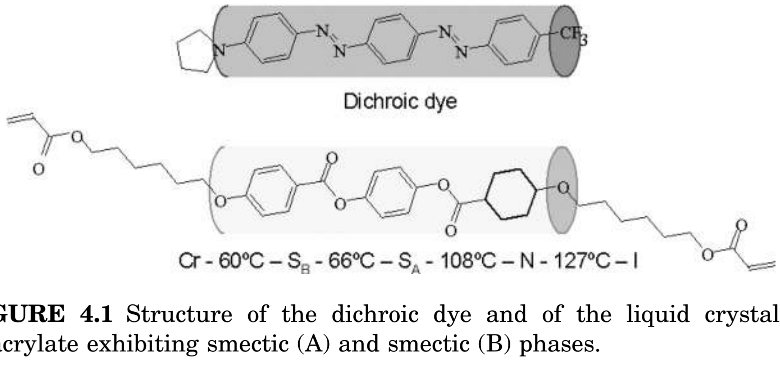

FIGURE 4.1 Structure of the dichroic dye and of the liquid crystalline di-acrylate exhibiting smectic (A) and smectic (B) phases.

figure 1.1 is replaced by a trans cyclohexane ring as shown in figure 4.1, a material is obtained that exhibits a nematic phase, a smectic-A phase as well as a smectic B phase[16].

Figure 4.2 shows the polarised UV/Vis absorption spectra of a small LC-cell containing a mixture of the liquid crystalline di-acrylate and dichroic dye shown in figure 4.1. At 140°C the mixture is above the nematic to isotropic transition and the molecules are randomly oriented. The polarised UV/Vis absorption spectra show an exact overlay for the two polarisation directions, as expected for isotropic media. At 120°C the mixture is in the nematic phase. At this temperature, the polarised UV/Vis absorption spectrum recorded parallel to the aligned direction of the LC-host shows a stronger absorption than in the direction perpendicular thereto. The dichroic ratio, as determined from the polarised absorption spectra is approximately 3 over the whole width of the absorption band. Upon further cooling the mixture enters the smectic-A phase. In this phase, at 80°C, the difference in absorption parallel and perpendicular to the alignment direction is more pronounced and the dichroic ratio has increased to approximately 10.

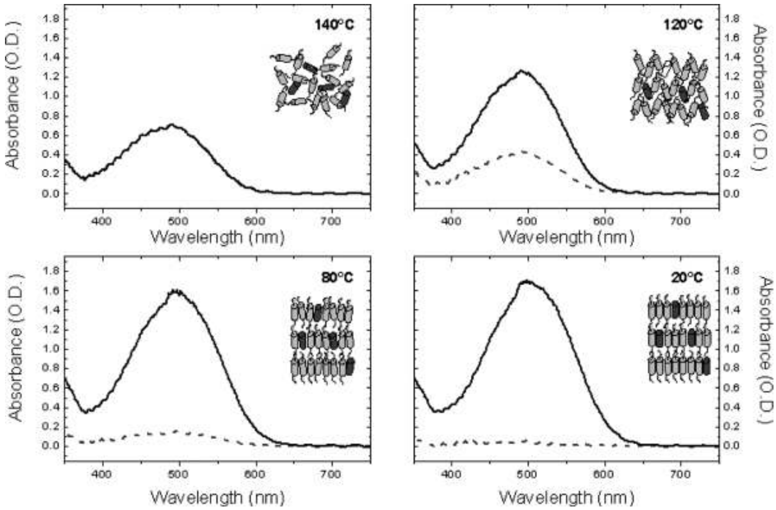

FIGURE 4.2 Polarised UV/Vis absorption spectra (——:parallel and, - - - - : perpendicular to molecular orientation) of an LC-cell filled with the liquid crystalline di-acrylate of figure 4.1 mixed with 2% of the dichroic dye shown in the same figure. The spectra were recorded at 140°C, 120°C, 80°C and 20°C, respectively. The insets give a schematic representation of the (liquid crystalline) order at these temperatures.

Below 65°C the smectic-B phase is entered and at 20°C a dichroic ratio as high as 50 is reached. From these results it is apparent that sufficiently high dichroic ratios are only observed in the smectic-B phase which exhibit a much higher order parameter S (see Eq. (4.2)) than the other two phases. Photo-polymerisation of the liquid crystalline di-acrylate at 20°C results in the formation of a highly crosslinked polymer network. During polymerisation a decrease in the dichroic ratio is observed from $DR = 50$ to $DR = 35$. The exact cause for this decrease in dichroic ratio is unknown at present. However a possible cause can be loss of order due to the polymer formation. The hexyl spacer between the mesogenic group and the acrylate group decouples the polymerisation process from the ordering of the mesogenic groups. In the case of nematic compounds like the ones of figures 1.1 and 2.5 normally an increase in order was observed upon polymerisation. However, in the case of the smectic compound of figure 4.1 the high order already present before polymerisation may be disturbed somewhat due to the polyacrylate formation. Despite the unwanted reduction in dichroic ratio the polarisation performance of the remaining polymer network is sufficient for use in low-end liquid crystal display applications. Current research is focused on further increasing the dichroic ratio, achieving colour neutral dye mixtures and obtaining freestanding films.

5. CONCLUSIONS

Optical films based on liquid crystalline (di-)acrylates can be applied to improve the performance and properties of liquid crystal displays. The main advantage in using these liquid crystalline (di-)acrylates lies in the fact that the optical function can be optimised by tuning the anisotropic properties and controlling the orientation and order of these compounds before polymerisation. The optimised optical functions are stabilised by the formation of a cross-linked network through photo-polymerisation of these compounds.

Using this methodology, ultra thin complex patterned retarders and wide viewing angle films can be produces from nematic (di-)acrylates. Cholesteric (di-) acrylate mixtures can be applied to make reflective polarisers and colourfilters. In addition, smectic mixtures can be applied to make thin polarisers.

Apart from the easy optimisation of complex optical functions, the films based on photo-polymerisation of liquid crystalline (di-)acrylates have the advantage that they are very thin and can be applied inside the cell (in-cell), facilitating the development of flexible displays.

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