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Polymer Films Derived From Aligned and Polymerised Reactive Liquid Crystals

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SUMMARY: The principles and methods of fabricating thin polymer films with particular optical properties via the process of *in-situ* photopolymerisation of reactive liquid crystals are described. The optical properties of these films are described in terms of their retardation profile. Some possible applications, such as compensation films for improving the viewing angle of a TN-TFT liquid crystal display are discussed. A novel way of combining the properties of a quarter wave foil and a compensation film for a broad band cholesteric brightness enhancement film is also described.

Introduction

Liquid crystal displays have become increasingly popular in recent years. Large area 15” displays can now be commercially manufactured and can compete with the dominant position that CRT’s have held in this area for many years. These displays are particularly popular as computer monitors[1]. Of the many types of liquid crystal display (LCD) mode used as monitor modules, the commonest and cheapest is the TFT-TN mode. This mode has some well-documented problems associated with it, namely poor viewing angle, inversion in the grey scale levels, and poor luminance yield because of the necessity of using crossed polarisers attached to the display cell[2]. During the last few years many workers have attempted to solve these problems by incorporating birefringent films of various designs into the LCD module[3,4,5]. The collections of birefringent films used to solve these problems are composed of two or more component films, usually, but not exclusively, one on each side of the display. The component films can in turn contain more than one basic film. This paper will describe the general method of fabricating these basic films, their optical properties, and their assembly into stacks that can be used in display devices.

There have been many ways of preparing these birefringent films, for example, some were made by either uniaxially or biaxially stretching a polycarbonate or polyvinyl alcohol film. The use of thin liquid crystal films has recently been shown to be one of the most promising ways of constructing these films.

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Liquid crystals are formed by anisotropic molecules such as rods, laths, discs etc. Two types of liquid crystals have been used in optical films, the rod shaped (or calamitic) system, and the disc shaped (or discotic) liquid crystals. This paper will confine itself to comments on films made from calamitic liquid crystals. Monoreactive polymerisable liquid crystals (often referred to as reactive mesogens) have been known for many years; they are often used to form oligomeric side chain liquid crystal polymers using solution polymerisation. However, in recent years it has been shown that if the polymerisation process is conducted *in-situ* i.e. within the liquid crystal phase of the reactive liquid crystal, then the liquid crystal structure can be retained in the polymer and, in general, very high molecular weight polymers are formed[6]. Crosslinking is possible, indeed it is normal and is achieved using direactive liquid crystals. The addition of reactive but non-liquid crystalline materials is also possible.

A special property of liquid crystals is that the short range order can be extended to long range order by aligning the molecules on some aligning surface so as to provide a 'single crystal' structure. This is the basis for most types of liquid crystal display. The combination of anisotropy and ordering leads to differences in macroscopic properties such as refractive index; this is different when measured along or across the molecular director. The difference between the two values is termed the birefringence (Δn); it is relatively high (up to about 0.2 in many cases, and 0.3 in rare cases). Similarly reactive liquid crystals can be aligned and then polymerised to provide polymers in which the long-range order is retained. Very often there is some slight or even gross reduction in ordering of the molecules leading to a change in the magnitude of the optical properties when such films are polymerised. Such films can be mechanically and thermally robust and have unique optical properties. The key feature is that the molecules of the liquid crystal phase are aligned. This paper will show that several types of liquid crystal alignment are possible and give rise to a range of optical products.

Several types of molecular architecture can be envisaged when constructing a thin film from rod shaped liquid crystal molecules. The molecules can be aligned such that they align parallel or perpendicular to a substrate, they can be made to tilt or splay away from a substrate, and, if a chiral molecule is introduced into the liquid crystal mixture, the molecules can be made to twist, and form a helix, which have useful optical properties. These are shown schematically in figure 1.

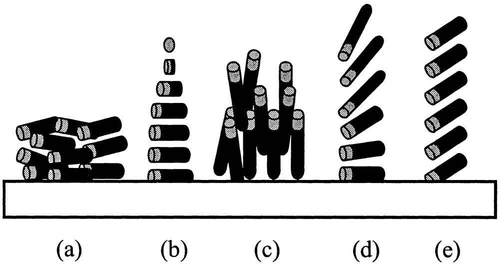

Fig. 1. Examples of different liquid liquid crystal molecular distribution possible in aligned thin LC layers. These are termed: - **(a)** planar (homogeneous) alignment, **(b)** cholesteric, **(c)** homeotropic **(d)** splayed and **(e)** tilted films.

Alignment of Liquid Crystals

The alignment of liquid crystals on different substrates has been extensively studied[7,8,9], but a comprehensive theoretical model for predicting liquid crystal alignment has yet to be realised. Many factors influence liquid crystal alignment, e.g. surface topography, surface active layers (alignment layers), the physical properties of the liquid crystals and the relative strength of the surface energies of the substrate and the surface tension of the liquid crystal. One theory, the Friedel-Creagh-Kmetz[10] rule, later modified by others[11,12], states that the nature of liquid crystal alignment can be predicted from considerations of the surface energies of the liquid crystal and substrate. If the surface tension of the liquid crystal is higher than the surface energy of the substrate, then homeotropic alignment will be achieved. This might be likened to the liquid crystal molecules being attracted to each other in the nematic phase more than being attracted to the surface and aligning parallel to it.

The FCK rule states:

$\gamma_S < \gamma_{LC}$	homeotropic alignment
$\gamma_S > \gamma_{LC}$	homogeneous alignment

However, many modifications to this rule have been made, including for example, factors such as anisotropy of surface tension in liquid crystals, along the long and short molecular axis. Splitting up the, surface tension of a liquid crystal and surface energy of a substrate into their polar and dispersive forces has also been considered[13].

Most of the work on alignment has been concerned with systems where two solid surfaces affect the liquid crystal alignment, e.g. a liquid crystal cell. However, less is known about systems that have only one solid layer influencing the alignment, the other surface being effectively air. An indication of the effect air has on alignment in such a system can be obtained by studying free standing films, in which only the liquid crystal-air interface has an influence. It has been found that the polarity of the terminal groups attached to the liquid crystal core group can influence the alignment[14]. Liquid crystal molecules with terminal alkyl groups tend to give homeotropic alignment, whilst molecules with polar terminal groups tend to give homogeneous alignment. These observations have been rationalised by considering the surface energy anisotropy of liquid crystals[15]. The molecules that have homeotropic alignment have:

$$\Delta\gamma = \gamma_{LC(parallel)} - \gamma_{LC(perpendicular)} > 0$$

and the molecules that have homogeneous alignment have:

$$\Delta\gamma = \gamma_{LC(parallel)} - \gamma_{LC(perpendicular)} < 0$$

The strength of alignment at the air-liquid crystal interface is considered to be weak, therefore the ultimate alignment obtained on a single substrate system is determined by the relative strength of the alignment from both surfaces. Careful choice of substrates, liquid crystal mixture composition and surface modification agents allow thin anisotropic polymer optical films with specific molecular distribution to be designed.

Homogeneous Alignment

Most conventional LCD's make use of a unidirectional 'rubbed' polyimide (or polyvinylalcohol or nylon) aligning layer. A strong interaction between the molecules of the liquid crystal phase and the aligning layer exist such that the molecules lie along the rubbing direction, usually with a small pre-tilt in the direction of rubing. Very often a microgrooved structure or polymer chain alignment, brought about by the rubbing actions, are invoked to account for this behaviour. Upon this surface is solvent coated a thin film of a nematic reactive liquid crystal (RLC) mixture (typically 1-5 microns) containing a photoinitiator. Polymerisation of the thin film is carried out by exposure to UV light usually generated by a medium pressure mercury lamp. The choice of photoinitiator is important, as some photoinitiators, that can polymerise a thin film of a commercial acrylate, do not give a satisfactory degree of polymerisation in RLC films when cured in air. Examples of photoinitiators that can effectively cure RLC films in air are Irgacure 907, and Irgacure 369. Other photoinitiators e.g. Irgacure 651 can cure RLC films, if a blanket of an inert atmosphere such as nitrogen covers it. Another way of overcoming this problem is to use a more powerful source of UV light, which emits shorter wavelength UV light, for example a Fusion microwave powered lamp[16]. Using this lamp photoinitiators such as Irgacure 651 also cure RLC film in the presence of air. The control of temperature is critical, as this must be within the nematic range of the reactive liquid crystal; the precise temperature affects the molecular ordering and thus the birefringence of the final film.

In films that have an open to the air surface the molecules can also have some tilt angle at the air interface, and this can be controlled by careful mixture development, in particular, adding using reactive liquid crystals which do not have a long terminal alkyl chain. In addition to this it has been found that addition of a suitable surfactant can help to reduce this tilt angle.

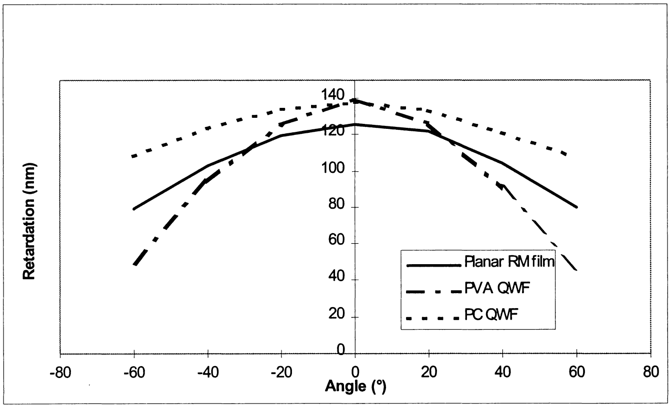

Fig. 2. Plot of retardation verses angle of planar reactive mesogen films measured along the rubbing direction compared to polycarbonate and PVA films.

The birefringence of such films is often in about 0.15. Thus to achieve the retardation values (80-150nm) often obtained in stretched polyvinylalcohol or polycarbonate films of 80-100μm thickness only 1-2 micron films of reactive liquid crystals are required.

Such films can be used for the same applications as stretched films, e.g. quarter wave foils, supertwisted nematic display compensation films and as components of twisted nematic compensation films.

Homeotropic Alignment

When liquid crystal films are coated onto low energy surfaces they often align such that the long axis of the molecules is arranged orthogonal to the surface. This is termed homeotropic alignment. A variety of surface active agents such as propyltrichlorosilane and stearate chrome complexes can give rise to this effect. Some evaporated inorganic materials such as magnesium fluoride can also do this. In this case some novel materials have been used to give good alignment to nematic films that are subsequently photocured.

Smectic liquid crystals prefer to form 'layers' of molecules in which the molecules are essentially orthogonal to the substrate. This feature can be taken advantage of if smectic A reactive liquid crystal mixtures are used. Such mixtures give rise to the same optical properties as the nematic films.

The retardation profile of a homeotropically aligned nematic RLC film is shown in Fig. 3. The on-axis retardation of this film is close to zero, but becomes more positive at more acute viewing angles. Figure 3 also shows the effect different film thickness have on the retardation profile. The on-axis retardation, at zero is independent of film thickness, however off axis, thicker films retard light more than thinner films. A film with this retardation profile is termed a positive C plate.

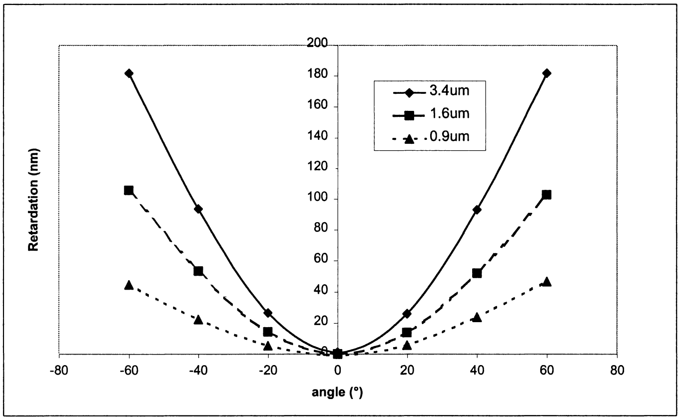

Fig.3 Retardation profile of a homeotropically aligned RLC film with different thickness

At non-normal angles of incidence such films have the property that they tend to convert elliptically polarised light to circularly polarised light, the extent of this being dependent on the film thickness and the angle from normal incidence. This feature has been used in the context of wide waveband cholesteric reflective polarisers to improve the off axis brightness of LCD's that are fitted with such a reflective polariser. This is shown in Figure 4 where the compensated reflective polariser shows a much higher luminance at wide angles but it has no effect on-axis. The optics of such films have been described elsewhere[25].

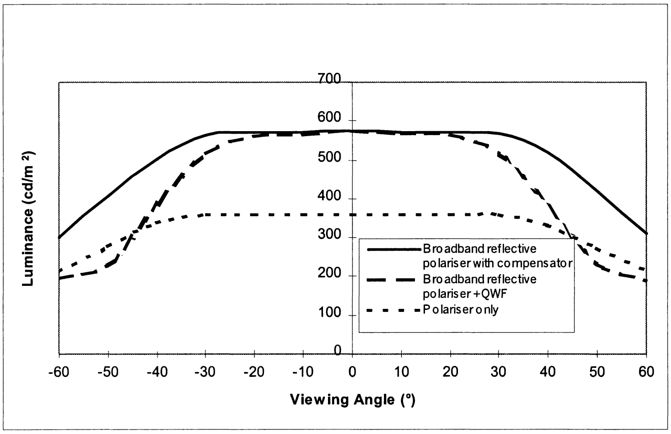

Fig. 4. Luminance of a LCD backlight fitted with a broad band cholesteric film with and without homeotropic compensator film.

Splayed and Tilted Alignments

This is a hybrid structure between homogeneous and homeotropic. All liquid crystals have a natural tilt angle with respect to a surface or an air interface. This can be tailored to give various tilt angles at the substrate or air surface. In the previous examples the two extreme cases have been shown, here we shall consider the intermediate situations. As was shown in figure 1, two types of tilted films can be formed, one with a constant tilt through the Z-direction of a film, and the other showing a gradation of tilt through the Z-direction. If the tilt angle at the solid substrate is optimised to be very low and the tilt angle at the air surface is allowed to be large or even homeotropic then the molecules between the two 'surfaces' will follow a 'splayed' structure. In part the elastic forces (namely the splay elastic constant K_{11}) defines the magnitude of this effect. To obtain a tilted structure, a tilt amplification layer can be used to further increase the pretilt obtained from the polyimide alignment layer. Such tilt-amplification layers are also made from very thin layers of nematic RLC ($<0.1\mu m$)[17,18]. In the case of the splayed films, it is particularly important that the solid substrate layer has a reasonable pre-tilt, otherwise, defects known as reverse tilt disinclination can occur. This defect occurs when the molecules are forming a splay in the Z-direction, but the direction of tilt can be in one of two degenerate states. The retardation profile a typical film is shown in figure 5

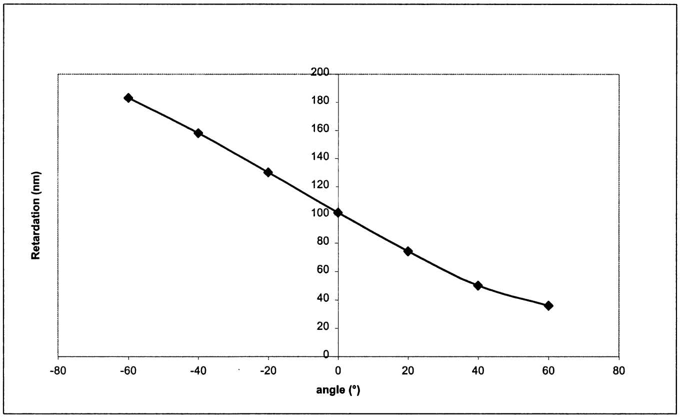

Fig. 5. Typical retardation profile of a splayed film, measured in the rubbing direction

Once again the structure can be locked in by photocuring of the film at an appropriate temperature with a UV beam of the appropriate energy and wavelength for the photoinitiator used.

One important application of these films is in the compensation of TN-TFT LCD displays. It is well documented that, at oblique angles of incidence, the viewing cone for a TN display becomes complicated and non-uniform. A combination of two tilted films with their rubbing direction crossed orthogonally to each other, and with one of the two rubbing directions parallel with the stretch direction of one of the polarisers, has on average the opposite optical properties of an addressed, normally white TN display[19,20]. This allows the viewing cone to become greatly enhanced and more uniform, and also eliminates grey scale inversion at most practical viewing angles, the exception being when the display is viewed from greater than 30° below the normal. Further improvements can be made if the tilted films are used in conjunction with homogeneously aligned RLC films.[21] Typical improvements in display characteristics are shown in table 1:

		Uncompensated	RLC film compensated
10:1 contrast area	horizontal	+30° to –30°	+60° to –60°
	Vertical	+20° to –25°	+60° to –60°
Grey scale inversion	horizontal	+25° to –25°	No inversion
	Vertical	+25° to –15°	+80° to –25°

Tab.1. Comparison of performance data between a typical compensated and uncompensated TN-TFT display

A novel use of splayed films is as a bilayer. A pair of splayed films at 180° to each other has a retardation profile similar to that of a quarter wave foil and a homeotropic compensator combined (figure 6).

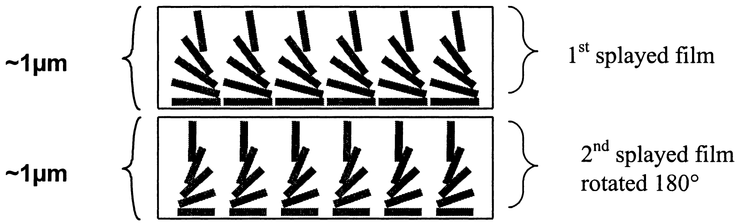

Fig 6. Schematic representation of two splayed films arranged such that they act as both a homeotropic compensator and a quarter wave plate.

Such a film stack can be used with a broad band polariser to improve the off axis brightness gain. The retardation profile is shown in figure 7, where it is compared to the retardation profile of a polycarbonate stretched film plus a homeotropic film. The splayed film is a better match for the polarisation state of light passing through the reflective polariser than a simple quarter wave foil, and therefore can increase the brightness of LCD's at wide angles that are fitted with a cholesteric wide waveband polariser (Figure.8).

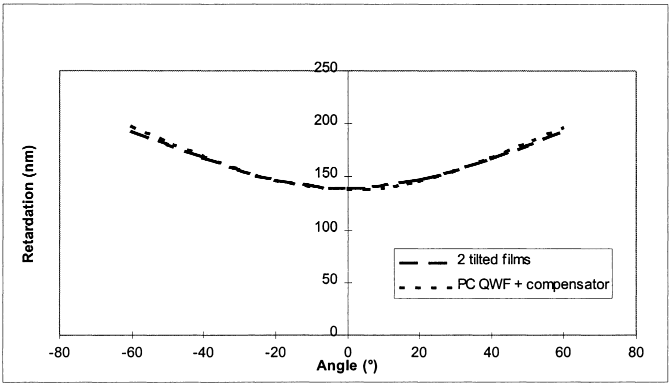

Fig.7. Comparison of the retardation profile of a bilayer of 2 splayed films and a combination of stretched polycarbonate film plus homeotropic film.

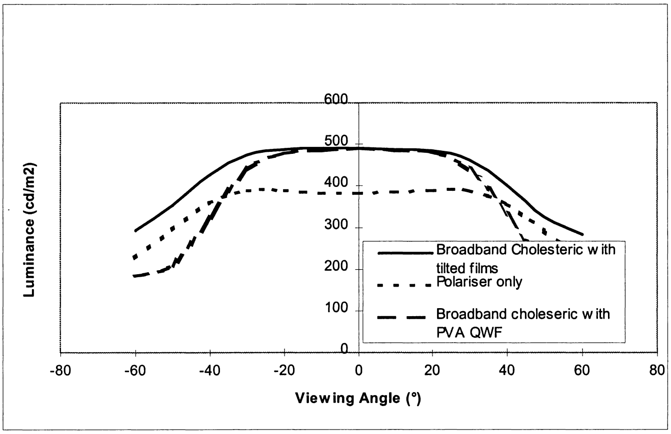

Fig. 8. Comparison in luminance for a LCD backlight fitted with a wide-waveband cholesteric film plus either a bilayer splayed film or a conventional PVA based quarter wave foil.

Cholesteric or Chiral Nematic Films

Chiral nematic (previously also called cholesteric) films exhibit a special optical property of reflecting a narrow band of incident light by Bragg reflection from the helical structure of the chiral nematic material. The pitch (P) of the helix is a critical parameter to determine the wavelength of reflected light according to the Equation 1

Equation 1 $\lambda = n.P \sin\theta$

where sin θ is the angle of incidence and 'n' is the mean refractive index of the chiral nematic phase; λ is the centre of the reflected wavelength of bandwidth Δλ = Δn.P. The reflected waveband is circularly polarised. Only 50% of this waveband is reflected, the other 50% is transmitted and circularly polarised in the opposite direction. All the other wavebands are transmitted and not circularly polarised. The wavelength can be, and often is, very temperature dependent leading to its use in thermometers etc. However, when reactive liquid crystals are used this optical property can be locked in such that the reflected wavelength is essentially temperature independent. Such films can be used as colour filters having a specific reflection bandwidth and may be especially useful if the incident light is circularly polarised. By adjusting the chirality of the mixture it is possible to change the pitch of the chiral nematic reactive mixture such that it reflects in the ultra violet, visible or infra red region. RLC films that reflect in the UV region have the property of retarding light of longer wavelength, rather than reflecting it. Such films are known as negative C films, and have the opposite retardation profile to that shown by a homoetropic RLC film. It has the retardation profile shown in figure 9. Increasing the thickness gives films with higher retardation off-axis, but remains zero on-axis. These films can be used to compensate TN-TFT[22].

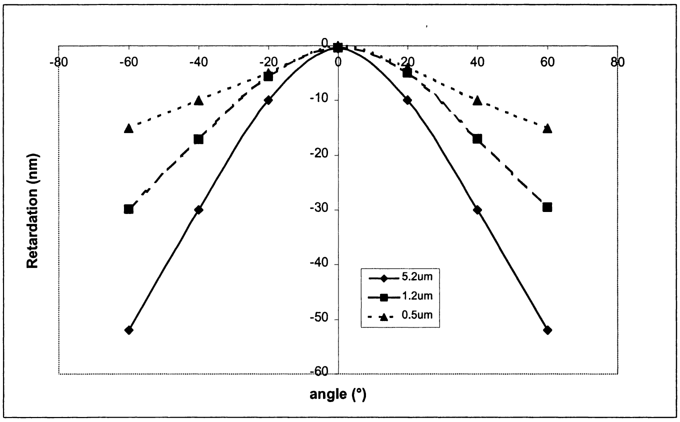

Fig. 9. Retardation profile of a homeotropically aligned RLC film with different thickness

An extension of this work was to show how broad bandwidth chiral nematic films could be made[23]. These can be used as reflective polarisers in LCD's to effectively prepolarise the light entering the first linear polariser of the display. The pre-polarisation process being affected by recirculating the light rather than an absorption process. The transmitted, circularly polarised light is then converted to linear polarised light using a uniaxial stretched film that retards the light by a quarter wavelength. This film can also be made from homogeneously aligned reactive liquid crystals as shown earlier. In this way more of the light from a backlight is transmitted through the display making it much brighter[24,25]. Figure 10 shows the effectiveness of a reflective polariser compared to a standard display. Note that the brightness is lower at wide angles of incidence. However, as has been shown, this can also be improved using a homeotropic reactive liquid crystal film or a bilayer splayed film that acts as both quarter wave foil and homeotropic compensation foil.

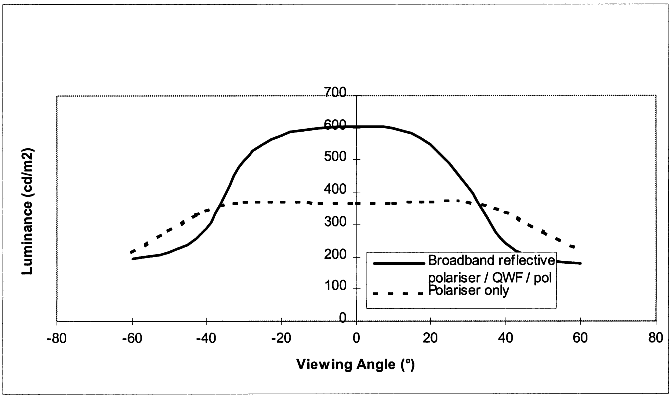

Fig. 10. Luminance vs viewing angle for a LCD backlight with a broadband reflective polariser plus linear polariser compared to the backlight with linear polariser only.

Summary

In this paper we have described the preparation and optical properties of several types of birefringent films. These films are prepared from reactive liquid crystals via the process of *in-situ* photopolymerisation. These films can be used to improve the performance of LCD's. We describe the novel use of a tilted liquid crystal layer film stack as a potential compensator and quarter wave foil for a wide bandwidth cholesteric brightness enhancement film.

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