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### Displays

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# Displays

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A display represents a true man-machine interface (MMI). Several types of displays are analyzed, including nematic (twisted, supertwisted, active matrix) and smectic (heat addressed, ferroelectric). Polymer-dispersed liquid crystals (LCs) including heat-addressed PLCs are considered also, as well as ferroelectric PLCs. On this basis, construction of PLC displays (also called polymeric LCDs) is described; they include also portable displays.

*Keywords:* Man-machine interface; MMI; nematic displays; twisted displays; smectic displays; heat addressed displays; ferroelectrics; polymer-dispersed liquid crystals; construction of PLC displays; portable displays

## 1. INTRODUCTION

When confronted with liquid crystals, the vast majority of the public imagine the digital watch or pocket calculator. Indeed it would be rare if anyone initially thought of an application of liquid crystals not concerned with some form of information display. Of course there are a great deal of applications for liquid crystal (LC) materials that do not involve display systems, but I think it is fair to say that the LC revolution has been led by the liquid crystal display (LCD). That is perhaps not surprising when one considers that the discovery of optical effects in LC materials [1–3] predated even the discovery of the first room temperature stable materials [4–6].

A display probably represents the most common method of transmitting information from a device to a human and is thus a

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true man-machine interface (MMI). However the development of displays has long lagged behind the development of the technology to which they are attached. For example the MMI in the most advanced desk top computers are the same as in the common television set, namely a cathode ray tube (CRT), based on the principle of a beam of electrons striking a phosphor material with consequent emission of light. Unfortunately, these displays all tend to be fragile (being constructed of an evacuated glass chamber), heavy, both in mass and in power consumption and are typically geometrically awkward. It is factors such as these which have driven the research toward a new display device.

In order to appreciate the role of the LC materials and how polymer liquid crystals (PLC) can further the applications of LCDs, it would perhaps be helpful for us to consider the various types of LCD currently available, their modes of operation, the limitations as to their application and the improvements necessary to achieve a universally applicable display.

## 2. THE NEMATIC DISPLAY

The basic operating principle is relatively simple. In the nematic phase there is a tendency for the long axis of the molecules to be aligned parallel to one another [7, 12] as illustrated below in Figure 1.

As we can see, the nematic phase lies between the solid and liquid phases. While the material still behaves in a liquid like manner, *i.e.*, it undergoes flow, takes the shape of its container, *etc.*, there is still some degree of order between the LC molecules. However, the first LC phase identified was the Cholesteric phase [8, 9], in the cholesteric

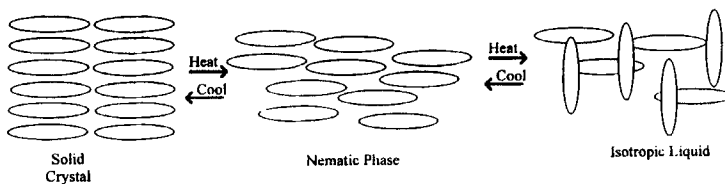


FIGURE 1 Transition from crystal to LC and isotropic liquid phases.

phase nematic layers assemble themselves with their director twisted with respect to the preceding layer. This gives a helical superstructure, which can selectively reflect incident light, and finds applications in thermochromic materials, among others. Nevertheless, nematics were essentially the first LC materials to find major commercial application [3, 10–13].

The application of liquid crystal materials to displays involves controlling the orientation of the molecules by the application of electric fields. However, there are a number of parameters we must first satisfy. It has long been known that aligned LC molecules have the ability to twist polarised light [14] and if the material has a positive dielectric anisotropy, ( $\epsilon_{\parallel} > \epsilon_{\perp}$ , where  $\epsilon_{\parallel}$  is the dielectric constant parallel to the long molecular axis and  $\epsilon_{\perp}$  is the dielectric constant perpendicular to the long molecular axis) then, when a certain threshold field, which exceeds the elastic forces within the cell is applied the molecule will align its director parallel with the applied field, to minimize electrostatic energy. Only the molecules which are not constrained by the surface are free to reorientate in this way, but this is still sufficient to prevent rotation of the plane of incoming polarised light. Producing such a device led to the twisted nematic display.

## 2.1. The Twisted Nematic (TN) Display

In a twisted nematic cell the liquid crystal molecules are aligned by a surface alignment layer. This is typically a thin layer of polymer which has been unidirectionally rubbed with cloth. The exact physics of this phenomenon is as yet not fully understood, but for the sake of simplicity we can assume that the molecules lie along the direction of the grooves created during the rubbing process and that the molecules acquire a slight pre-tilt at one end. When the cell is constructed, the top plate is placed such that the rubbing directions on either plate are perpendicular to one another and the gap between the two plates is sufficient to allow the long axis of the molecules to undergo a twist angle of  $\pi/2$  rads as we travel from one surface to the other. Then, when light polarised in the plane of the lower plate rubbing direction enters the cell and passes through the twisted layer of nematic liquid crystal the plane of the polarised light twists along with the molecules and when it emerges from the top plate it is in the correct orientation

to pass through an analyser, which is rotated through  $90^\circ$  with respect to the lower plate rubbing direction. However, on application of an electrical field the molecules at the centre of the cell become orientated with the direction of the field and can therefore no longer interact with the incoming polarised light. The light cannot then pass through the analyser and the cell appears black. When the field is removed the molecules relax back to their original positions, directed by the surface layers, and polarised light can again pass through the cell, thus the application of a field can switch between a light and dark state, as shown in Figure 2 below.

This simplistic effect holds true as long as the "mauguin Limit" is not approached [15], this can be expressed as below:

$$u = (2d\Delta n)/\lambda \gg 1 \quad (1)$$

where  $d$  is the cell spacing and  $\Delta n$  is the optical birefringence at wavelength  $\lambda$ . In reality however, this is difficult to achieve and often light leaks between the two modes of propagation resulting in the optical light being elliptically polarised [16, 17] and it is then imperfectly transmitted by the analyser. In practice it is found that optimum behaviour is achieved for  $u$  values of  $\sqrt{3}$ ,  $\sqrt{15}$ ,  $\sqrt{35}$ , etc. and any

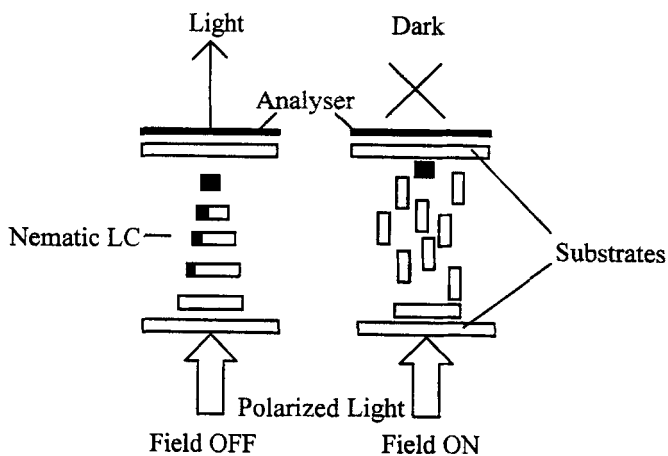


FIGURE 2 Field effects.

deviation will bring about a reduction in contrast. Also, as  $u$  is wavelength dependent, undesirable coloration may also appear in the off state [18, 19].

Direct drive and low complexity TN displays achieved dominance in the watch and calculator markets, but when one considers displays more complex than this, the simple cell design becomes severely limited, primarily by the number of connections that would have to be made in order to produce a reasonably complex display capable of showing varied information. Thus, instead of having each individual LC pixel connected directly to the electronic drivers, as in the early watch and calculator displays, in more complex devices the electrodes on the top and bottom plates are arranged in a grid pattern and when constructed they form a matrix where each pixel occupies an intersection of the matrix. The displays are then addressed by sending voltages down the columns and along the rows, as illustrated in Figure 3.

A strobe signal is sent along the row and a data signal is sent down the column. The row and column voltages meet at the pixel and the two voltage pulses combine to give an overall applied voltage. It is the rms level of this combined voltage over the frame time which

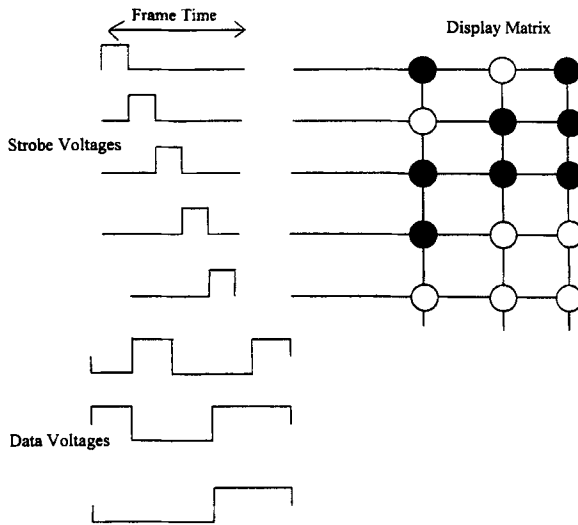


FIGURE 3 Displays addressing.

determines whether the pixel is on or off. Although the optimum driving scheme for this type of display was first identified by Nehring and Kmetz [20], an earlier, but less complex scheme put forward by Alt and Pleshko [21] is used for TN displays.

Clearly these driving schemes are quite complex and are well beyond the scope of this chapter, but one must be aware that the technique of active addressing has a complexity limitation for TN devices. If one examines the mid layer tilt angle ( $\theta_m$ ), defined as the tilt angle mesogens in the centre of the cell, against applied voltage for a TN material as shown in Figure 4.

Then as  $\theta_m$  is directly related to the change in optical transmittance through the cell, there is clearly a  $V_1$ , where the cell is black and a  $V_0$ , where it is light and the material can be defined in terms of its ratio  $M$ ;

$$M = V_1/V_0 \quad (2)$$

Thus the material drive requirements are defined and the drive scheme must be capable of delivering voltages which satisfy this requirement for an efficient display. However, as the display complexity, or the number of lines which have to be addressed ( $N$ ) increases the ability of

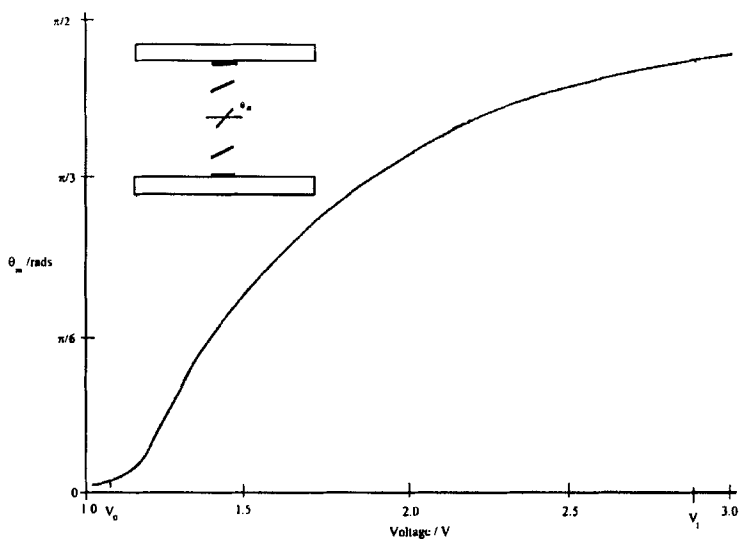


FIGURE 4 Twisted nematic behavior.

the drive scheme to deliver this full ratio falls. So the change in transmission from the off to the on state rapidly becomes negligible above about  $N = 20$  to 30. This can be described by the following relationship [21, 22];

$$(V_0/V_1) = ((N^{1/2} - 1)/(N^{1/2} + 1))^{1/2} \quad (3)$$

This clearly places an upper limit on the definition achievable by any given TN display. Although this is the basic operating principle of the most common displays, further development was clearly desired, in order to achieve more complex displays.

## 2.2. The Supertwist Nematic (STN) Display

This type of display represents a major improvement on the TN display. In the supertwist cell the long axis of the molecules undergo anything from a 180 to 360° twist, as illustrated in Figure 5.

This extra twist causes a change in the mid layer tilt angle,  $\theta_m$ , versus applied voltage curve as shown in Figure 6.

At  $3\pi/2$  rads, for instance, there is a distinct step and the gradient of the slope of the transmission versus applied voltage curve approaches infinity, in theory allowing an infinite number of addressed lines.

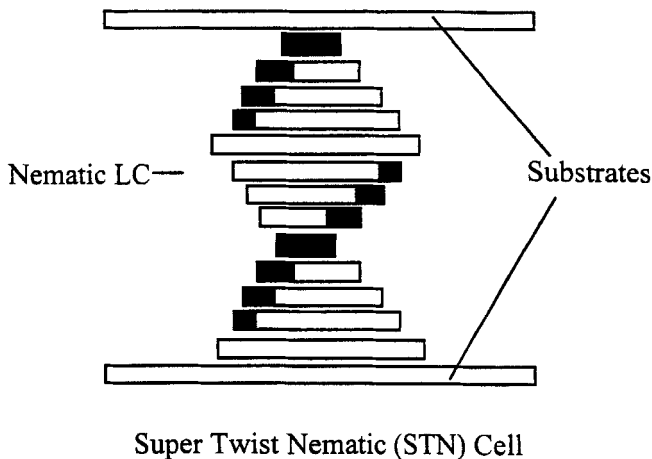


FIGURE 5 Super twist nematic (STN) cell.



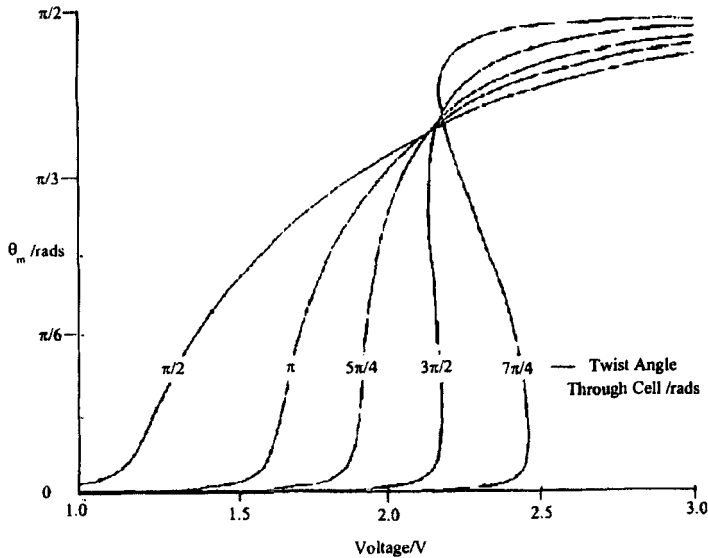


FIGURE 6 Consequences of the extra twist.

However, this ability to produce a high level of complexity is at the expense of the levels greyscale achievable in the simple TN cells. While true analogue greyscale can be achieved in a STN display, the voltage levels become critical and therefore averaging effects are often preferred. These averaging effects are generally either temporal or spatial dither techniques. Firstly temporal greyscale, if we consider the time of address of a display pixel as the frame time, and the pixel is to appear black then an rms voltage,  $V_{on}$ , is applied to the pixel for the full frame time and if it is to appear white, then an rms voltage,  $V_{off}$ , is applied during the frame time, thus, we can achieve grey by applying  $V_{on}$ , for part of the frame time and  $V_{off}$ , for the remainder. By varying the fraction of the frame time in which the pixel is black we can achieve an appearance of greyness. Secondly, spatial greyscale. If we subdivide the pixel into a number of subpixels, then when we require levels of greyness we select an appropriate number of subpixels. The disadvantages of these methods are that in the temporal technique the achievable level of greyscale is limited by the response time of the material and the available frame time; for the spatial technique the effects of subpixelating to

produce a clear image can be prohibitive in terms of the number of LC elements that have to be addressed, thus limiting the overall size of the display. Nevertheless, the development of the supertwist nematic display allowed the development of the first viable laptop computers and is still the most widely used display in this technology.

### 2.3. The Active Matrix TFT Display

In order to achieve colour in a LCD we must either utilise the subpixels to give us red green and blue light, or use a temporal technique whereby three images, a red image, green image and a blue image are displayed over one frame time. Usually for spatial colour the three primary colour filters are laid down as strips on the glass substrate within each column of subpixels. This allows for up to eight colour combinations, but by adding varying levels of greyscale for more colour combinations can be achieved. Obviously, in light of the above discussion, achieving colour in the STN display by this method involve increasing the number of elements which have to be addressed and therefore the number of connections in the display. If we use the temporal method then the display is synchronised with three coloured backlights. This is at the expense of temporal greyscale and again will limit the frame time for the display. Thus color STN screens can appear weak and washed out as the colour is almost always produced at the expense of greyscale. However, the development of amorphous silicon has led to the generation of thin film transistors [23] or TFT. The active matrix TFT (AMTFT) display has a small transistor positioned in the corner of each pixel. This allows the full  $V_1/V_0$  voltage ratio for the material to be developed at each individual pixel and overcomes the limitations of display complexity associated with the material. By going back to the TN design and optimizing the slope of transmission against rms voltage, true analogue greyscale can be achieved, leaving the subpixels free to generate the colour. Therefore AMTFT screens offer the brightest colours and sharpest images of any currently available LCD, and they stand comparison with the best CRT displays. However, as most consumers are aware the cost of AMTFT displays is relatively high. Initially this was due to rather poor production yields, as in producing an AMTFT you are working at the current limits of processing technology, and the extremely large

numbers of transistors, around 1–2 million for a typical laptop computer screen, all have to be fully operational. Clearly this can account for a great deal of wastage. Despite this AMTFT display manufactures are steadily increasing the yield from their production plants by increasing plant investment and developing new processing technologies. Nevertheless, of all the LCD types the AMTFT has the largest number and most complex processing steps. It will therefore spend the longest time at the manufacturing stage. As the raw material costs for all LCDs are approximately the same, the AMTFT will always have the highest unit cost. However, as mentioned above the AMTFT offers the best performance of all the nematic based displays, but this leaves a market area for a LCD which offers the performance of an AMTFT but, with the processability of the STN display.

### 3. THE SMECTIC DISPLAY

LCDs that utilise the smectic phase of liquid crystals include those at the current edge of research, and it is into this category that most polymeric liquid crystal based displays come. The bistability and fast ( $\mu\text{s}$ ) response times of ferroelectric displays enable complexity without the need for TFTs. However, there are only a few displays commercially available.

Firstly, however we must consider the nature of the smectic phase for it is not simply just one phase, but there are many smectic mesophases [24, 25]. The simplest to consider first is the smectic  $A$  phase ( $S_A$ ) a simple representation of which is given in Figure 7.

As can be seen the molecules have arranged themselves into distinct layers. Although there is generally no positional ordering within each

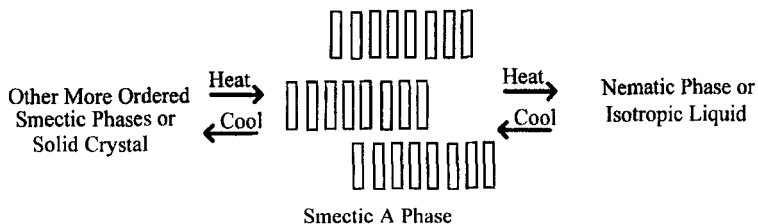


FIGURE 7 The smectic displays.

layer there is an average overall director orientation, as with a nematic phase. The  $S_A$  phase has the highest entropy of all the smectic mesophases and in materials that exhibit formation of a  $S_A$  phase it will form immediately after cooling from either the isotropic liquid or from a nematic mesophase.

### 3.1. The Heat Addressed Smectic A Display

If a material which has the phase sequence isotropic to nematic to smectic  $A$  is aligned between two glass substrates coated and patterned with indium tin oxide (ITO) electrodes, then, by selectively heating and cooling a localised point we can disrupt the alignment and create an area of scattering. While this type of effect was first demonstrated by using a laser [26] to produce texture changes in nematics and cholesterics. It was soon extended to smectic  $A$  materials, as being of smaller size and higher density the scattering achieved in the  $S_A$  phase is more intense and of sharper resolution [27–29].

The basic device begins in a clear state of a uniformly aligned LC layer [30–32]. The areas of the display which are to be written to are heated above the clearing temperature and then undergo rapid cooling by heat dissipation through the glass substrates. This regenerates the  $S_A$  phase *via* the  $N$  phase and produces a light scattering texture in the areas where the display has been written to. The whole display can be erased by heating to the isotropic and either allowing slow cooling or more usually applying a short dc pulse to one of the conducting plates. This aligns the material as it passes through the  $N$  phase and this in turn causes the  $S_A$  phase to be homeotropically aligned. Selective erasure is achieved by applying the short pulse while the area is heated by the laser.

The image produced by this type of display has a sharp contrast and high resolution and this has been utilised in projection systems [33–36]. Greyscale has also been produced by applying smaller voltages as the material cools through the  $N$  phase [35].

### 3.2. The Ferroelectric Display

The next smectic phase down the entropy ladder is the smectic  $C$  ( $S_C$ ) phase again this is illustrated below;

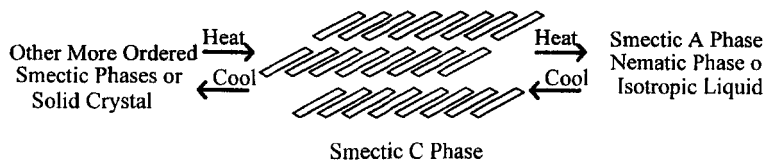


FIGURE 8 The ferroelectric displays.

In the  $S_C$  mesophase there is a universal tilt of the long molecular axis and therefore there is a certain degree of ordering within each of the smectic layers. If the molecule contains a chiral centre near the mesogenic unit then the layer tilt angle will form either a right or left handed helix when considered over a large number of layers. In the case of low molar mass LC this effect can also be induced by adding a chiral dopant to a  $S_C$  forming material [37]. Meyer showed by an elegant symmetry argument [38, 39] that when the helix is unwound, either by the application of an electric field or by the surface alignment forces, there is a net imbalance of the direction of the polarisation vector. Thus, when there is no field present there is still a degree of polarisation present. This is known as the spontaneous polarisation ( $P_s$ ) and results in the appearance of ferroelectricity. When an external electric field is applied and the polarisation of the system measured, a hysteresis loop similar to that illustrated in Figure 9 is set up.

The molecular reorientations which occur during this switching process cause the mesogenic molecule to describe the outline of a cone, (Fig. 10).

If a planar aligned sample is placed between polarizers with one of the polarisers aligned parallel to one side projection of the cone described by the switching molecules, then the device forms a birefringent slab [40]. The light transmitted by such a device, when placed between crossed polarisers, can be described by the following equation;

$$I = I_0 \sin^2(2\alpha) \sin^2((\pi \cdot \Delta n_{\text{eff}} \cdot d)/\lambda) \quad (4)$$

Where  $I$  is the fraction of the incident light  $I_0$  transmitted through the slab,  $\alpha$  is the angle between the mesogens and the polariser,  $\Delta n_{\text{eff}}$  is the effective in plane birefringence,  $d$  is the slab thickness and  $\lambda$  is the wavelength of the incident light. Thus, if the mesogens are parallel to

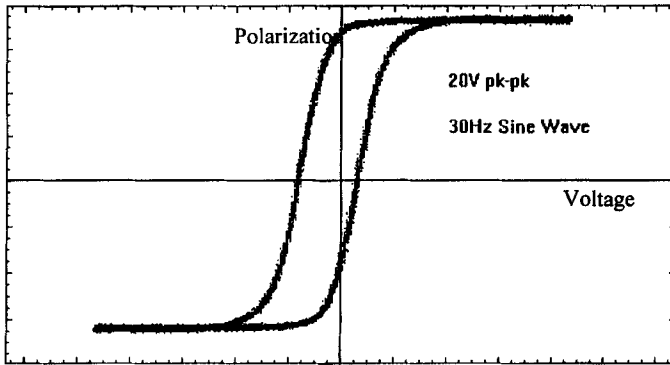


FIGURE 9 The hysteresis loop for ferroelectric.

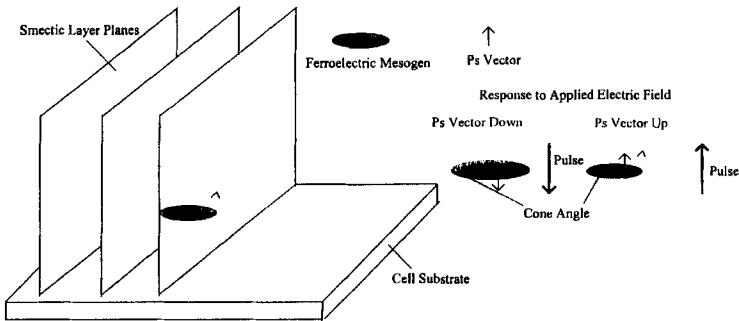


FIGURE 10 Molecular reorientation.

the polariser then  $\alpha$  is zero and  $\sin^2(2\alpha)$  is zero, thus no light is transmitted. When the molecules switch to the other side of the cone then  $\alpha$  becomes equal to  $2\theta$ , *i.e.*, twice the cone angle, If  $2\theta$  is equal  $\pi/4$  rads, then  $\sin^2(2\alpha)$  is equal to one. The transmitted light is therefore only limited by the optical retardation of the device. Also, as far as the molecules are concerned either side of the cone is of equal internal energy, and they are therefore thermodynamically equivalent. Thus, energy is only required to switch between either state, and the devices are said to be bistable, unlike nematic devices where a constant voltage had to be maintained to hold the molecules in their switched positions. Also the relative amount of molecular reorganisation required by the switching process is far less than for nematic devices and causes much

less disruption to the packing. Consequently the switching process is considerably faster, indeed two orders of magnitude faster in many cases [40–45]. However, the alignment in low molar mass ferroelectric displays is extremely sensitive to mechanical shock, and any display built from a ferroelectric LC will require to be protected against mechanical damage.

## 4. POLYMERS IN LCDs

### 4.1. Polymer Liquid Crystals

Until 1956, when Robinson [46] observed birefringence in a solution of poly- $\gamma$ -benzyl-L-glutamate, all known liquid crystal materials were effectively monomeric liquid crystal (MLC) systems. Soon after this, research into producing “polymer liquid crystals” (PLC) by covalently stitching together small liquid crystal units and polymer chains was undertaken. Much of this early work was reviewed by Elias [47]. However, true systematic studies of PLCs were not undertaken until Ringsdorf and co-workers [48, 49] and independently Shibaev and Platé [50] showed, in 1978, that the necessity to insert a flexible spacer between the main chain and the mesogen, in order to preserve the LC phase behaviour.

In general all the useful display materials to date, are side chain polymer liquid crystals, as opposed to the more common main chain PLCs. Primarily the difference is in the positioning of the mesogenic LC core. As the names suggest this is incorporated within the main chain or is attached as a pendant group *via* a side chain. Schematically we can represent each of the two types as in Figure 11.

The systematic synthesis of main chain polymer liquid crystals began in the 1970's when it was observed that fibres spun from anisotropic solutions exhibited extraordinarily high mechanical properties [51–53]. This improvement in mechanical properties forms the basis for the major application of these materials and as such they are used primarily as strengthening additives in polymer blends or indeed as high strength polymers in their own right; *e.g.*, Kevlar<sup>®</sup>. The interested readers attention is drawn to the extensive reviews of PLCs by Brostow [54] and elsewhere [55].

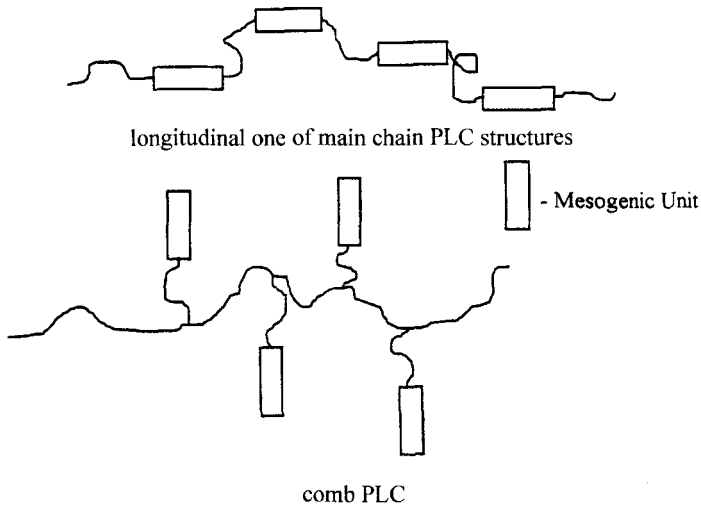


FIGURE 11 Selected molecular structures of PLC.

On the other hand, side chain PLCs have been specifically designed to allow for freedom of motion of the mesogen and thus facilitate electro-optic switching. On a molecular scale this has been achieved by employing a flexible spacer group between the mesogen and the main chain, there have been many studies carried out on the effects of length and nature of this spacer group [48–50, 56–59] and in certain cases these effects can be quite dramatic, causing the change from ferroelectric to antiferroelectric (where the direction of molecular tilt alternates from layer to layer in the  $S_C$  phase) by changing the length of the spacer group by just one unit [58, 59].

Despite this early research PLCs could never seemingly produce the properties desirable for display applications, and other types of displays employing polymeric materials were pursued.

#### 4.2. Polymer-dispersed Liquid Crystals

In 1986 it was first shown that displays consisting of droplets of a low molar mass nematic liquid crystal encapsulated in a bulk polymer could be produced [60]. Due to the refractive index mismatch between



the polymer and the low molar mass LC a film produced by this process appears opaque. However, as a liquid crystal system has two refractive indices; one when switched and one when unswitched. We can carefully match one of the refractive indices with the refractive index of the supporting polymer and the produced film can then be made to switch between clear and opaque in response to an applied field. This led to the development of the polymer-dispersed liquid crystal display (PDLC).

However, as this system has been fully covered, by Simoni in this volume, and it is I feel beyond the scope of this work.

### 4.3. Heat Addressed Polymer Displays

As we discussed above a display can be produced by uniformly aligning a layer of LC material then heating localised areas above the clearing temperature and allowing rapid cooling through a nematic phase. This process is obviously suitable also for PLC materials, provided they have the correct phase sequence and can be uniformly aligned on the substrates.

This type of effect has been demonstrated with a polysiloxane material [61] and as one would expect, the written image is very stable, even though the glass transition temperature ( $T_g$ ) of the polymer, the temperature above which the polymer chains can possess some degree of mobility, is well below ambient temperatures.

### 4.4. Ferroelectric Polymers

The response time of a liquid crystal device, where the response time is typically defined as the time taken for a change in transmittance from 10% to 90% in an aligned sample between crossed polarizers, induced by a given electric field, is inversely proportional to the product of  $Ps$  and applied field and directly proportional to the viscosity, thus;

$$\tau \approx \eta / Ps \cdot E \quad (5)$$

Naturally in polymers the viscosity,  $\eta$  is considerably higher than in low molecular weight LCs, while clearly this adversely effects the switching time it adds stability to the overall device. Nevertheless, as

ferroelectric LCs are inherently faster than their nematic counterparts, there exists a window of opportunity to utilise ferroelectric polymer liquid crystals. In 1984, Shibaev [62]; who has also contributed two articles to this volume, followed by many others, succeeded in synthesising side chain polymer liquid crystals with a chiral  $S_C$  phase, and in 1987, Uchida *et al.* [63, 64] reported the first  $P_s$  and response time measurements on a PLC.

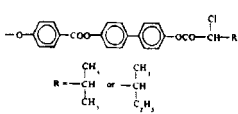
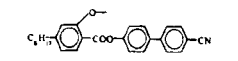
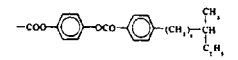
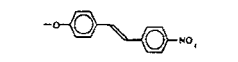
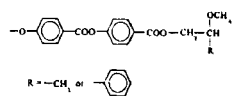
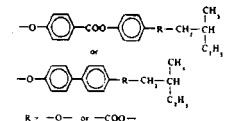
#### 4.5. Development of Ferroelectric Polymers for Display Applications

Side chain PLCs are generally synthesised in one of two ways, either directly from the suitably substituted monomer or by grafting the mesogenic side groups onto pre-prepared backbones. Either route will give polymers of the general structure indicated in Figure 10 above, but generally the target polymer defines the route by which it is prepared, for example polysiloxane materials are usually produced by grafting side groups onto a chemically active polysiloxane backbone, whereas polyacrylates can be produced by polymerization of a suitably substituted acrylic acid derivative. In Table I below is a farfrom exhaustive list of the typical PLC materials which have been synthesised with a view to producing a polymeric display device.

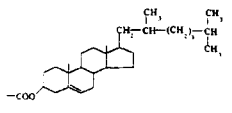
In general, the PLC has to be designed to allow for flexibility of the mesogens, thus, the polymer mainchain is chosen so as to reduce  $T_g$ . However, as  $T_g$  is increased by increasing side group substitution [109, 110], the very action of attaching the LC mesogens increases the value of the glass transition temperature. Hence, siloxanes and acrylates are preferred as these systems have inherently low  $T_g$  values when unsubstituted. As mentioned above Ringsdorf and Shibaev have shown [48–50] that to maintain the LC phases it is necessary to include a flexible spacer, this can be thought of as decoupling the mesogen from the mainchain, but this effect is explained in more detail in the following section. Of all the smectic phases the most desirable for electro-optic displays is the chiral smectic  $C$  phase,  $S_C^*$  where the asterisk denotes chirality. Since 1976, several hundred low molar mass LC (MLC) materials have been prepared which exhibit the  $S_C^*$  phase [111]. The mesogenic core contains at least two aromatic groups which may or may not be laterally substituted with various halogens. There is

Polymer	Spacer	Mesogen	Ref.
$\left[ \text{CH}_2 - \underset{\text{CO}_2}{\text{CH}} \right]$ <p>or</p> $\left[ \text{Si} \begin{array}{c} \text{CH}_3 \\   \\ \text{O} \\   \\ \text{CH}_3 \end{array} - \text{O} - \left[ \text{Si} \begin{array}{c} \text{CH}_3 \\   \\ \text{O} \\   \\ \text{CH}_3 \end{array} - \text{O} \right] \right]$	$-(\text{CH}_2)_n-$ <p>n = 2 to 10</p>	<p>R = H or CH<sub>3</sub></p>	65, 66, 67, 68, 69, 70.
$\left[ \text{Si} \begin{array}{c} \text{CH}_3 \\   \\ \text{O} \\   \\ \text{CH}_3 \end{array} - \text{O} - \left[ \text{Si} \begin{array}{c} \text{CH}_3 \\   \\ \text{O} \\   \\ \text{CH}_3 \end{array} - \text{O} \right] \right]$	$-(\text{CH}_2)_6-$		71.
$\left[ \text{Si} \begin{array}{c} \text{CH}_3 \\   \\ \text{O} \\   \\ \text{CH}_3 \end{array} - \text{O} \right]$	$-(\text{CH}_2)_n-$ <p>n = 4 or 6</p>		68, 70, 72, 73.
$\left[ \text{Si} \begin{array}{c} \text{CH}_3 \\   \\ \text{O} \\   \\ \text{CH}_3 \end{array} - \text{O} - \left[ \text{Si} \begin{array}{c} \text{CH}_3 \\   \\ \text{O} \\   \\ \text{CH}_3 \end{array} - \text{O} \right] \right]$	$-(\text{CH}_2)_n-$ <p>n = 6, 8 or 11</p>		74.
$\left[ \text{CH}_2 - \underset{\text{CO}_2}{\text{CH}} \right]$	$-(\text{CH}_2)_n-$ <p>n = 2, 6, 8, 10 or 11</p>		75, 76.
$\left[ \text{CH}_2 - \underset{\text{CO}_2}{\text{CH}} \right]$	$-(\text{CH}_2)_1 - \text{O} - \underset{\text{CH}_3}{\text{CH}}$		77.

a chiral centre, usually located in the terminal alkyl chain and the structure typically contains only one asymmetric carbon. As we see from the table above, to produce the desired smectic phases for ferroelectric display applications in PLCs researchers have tended to follow these design rules classified for MLC.

Polymer	Spacer	Mesogen	Ref.
$\left[ \text{CH}_2 - \underset{\text{CO}_2}{\text{CH}} \right]$	$-(\text{CH}_2)_{10}-$		78, 79, 80.
$\left[ \text{Si} \begin{array}{c} \text{CH}_3 \\   \\ \text{O} \\   \\ \text{CH}_3 \end{array} \right] \text{---} \left[ \text{Si} \begin{array}{c} \text{CH}_3 \\   \\ \text{O} \\   \\ \text{CH}_3 \end{array} \right]$ <p style="text-align: center;">or</p> $\left[ \text{Si} \begin{array}{c} \text{CH}_3 \\   \\ \text{O} \\   \\ \text{CH}_3 \end{array} \right]$	$-(\text{CH}_2)_n-$ n = 5 or 6		81.
$\left[ \text{Si} \begin{array}{c} \text{CH}_3 \\   \\ \text{O} \\   \\ \text{CH}_3 \end{array} \right]$	$-(\text{CH}_2)_{10}-$		82.
$\left[ \text{CH}_2 - \underset{\text{CO}_2}{\text{CH}} \right]$	$-(\text{CH}_2)_6-$		83.
$\left[ \text{CH}_2 - \underset{\text{CO}_2}{\text{CH}} \right] \text{ or } \left[ \text{CH}_2 - \underset{\text{CO}_2}{\overset{\text{CH}_3}{\text{C}}} \right]$	$-(\text{CH}_2)_6-$		84.
$\left[ \text{CH}_2 - \underset{\text{CO}_2}{\text{CH}} \right] \text{ or } \left[ \text{Si} \begin{array}{c} \text{CH}_3 \\   \\ \text{O} \\   \\ \text{CH}_3 \end{array} \right]$	$-(\text{CH}_2)_n-$ n = 8, 10 or 12		85, 86, 87, 88.

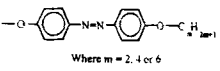
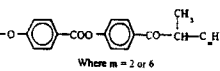
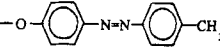
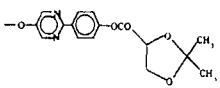
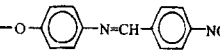
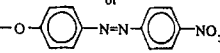
Despite this apparent wealth of materials there are still stringent requirements for any materials that hope to find application in LCD's. Firstly they must show a good operating temperature range, which is preferably centred around room temperature; secondly, they require a

Polymer	Spacer	Mesogen	Ref.
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \text{CH}_3 \end{array} \right] \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \text{CH}_3 \end{array} \right]$	$\text{---}(\text{CH}_2)_6\text{---}$	$\text{---} \begin{array}{c} \text{O} \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{COO} \end{array} \text{---} \begin{array}{c} \text{C}_6\text{H}_4 \\   \\ \text{R} \end{array}$ $\text{R} = \begin{array}{c} \text{C}_6\text{H}_4 \\   \\ \text{CN} \end{array} \text{ or } \begin{array}{c} \text{C}_6\text{H}_4 \\   \\ \text{COO} \end{array} \text{---} \begin{array}{c} \text{C}_6\text{H}_4 \\   \\ \text{CN} \end{array}$ $\text{or } \begin{array}{c} \text{OCH}_3 \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{CN} \end{array}$	68, 89.
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \text{CH}_3 \end{array} \right]$	$\text{---}(\text{CH}_2)_n\text{---}$ $n = 4 \text{ or } 10$	$\text{C}_6\text{H}_4\text{---} \begin{array}{c} \text{O} \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{CO} \end{array} \text{---} \begin{array}{c} \text{O} \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{CO} \end{array} \text{---} \text{C}_6\text{H}_4\text{---} \text{O---C}_6\text{H}_4\text{---}$ $n = 4 \text{ or } 6$	90, 91.
$\left[ \begin{array}{c} \text{---CH}_2\text{---CH---} \\   \\ \text{CO}_2 \end{array} \right]$	$\text{---}(\text{CH}_2)_n\text{---}$ $n = 1 \text{ to } 5, 7, 9, 10, 11 \text{ or } 15$		92.
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \text{CH}_3 \end{array} \right] \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \text{CH}_3 \end{array} \right]$ or $\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \text{CH}_3 \end{array} \right]$	$\text{---}(\text{CH}_2)_{10}\text{---}$	$\text{---} \begin{array}{c} \text{C}_6\text{H}_4 \\   \\ \text{COO} \end{array} \text{---} \begin{array}{c} \text{C}_6\text{H}_4 \\   \\ \text{O---CH---CO---C}_6\text{H}_4 \end{array}$	93, 94.
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \text{CH}_3 \end{array} \right] \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \text{CH}_3 \end{array} \right]$ or $\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---O---} \\   \\ \text{CH}_3 \end{array} \right]$	$\text{---}(\text{CH}_2)_n\text{---}$ $n = 5 \text{ or } 6$	$\text{---} \begin{array}{c} \text{C}_6\text{H}_4 \\   \\ \text{COO} \end{array} \text{---} \begin{array}{c} \text{C}_6\text{H}_4 \\   \\ \text{R} \end{array}$ $X = \text{F} \text{ and } Y = \text{H} \text{ or } X = \text{H} \text{ and } Y = \text{F}$ $R = \text{F}, \text{CN} \text{ or } \text{CF}_3$	95.
$\left[ \begin{array}{c} \text{---CH}_2\text{---CH---} \\   \\ \text{CO}_2 \end{array} \right] \text{ or } \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---CH}_2\text{---C---} \\   \\ \text{CO}_2 \end{array} \right]$	$\text{---}(\text{CH}_2)_{10}\text{---}$	$\text{---COO---} \begin{array}{c} \text{C}_6\text{H}_4 \\   \\ \text{OCO} \end{array} \text{---} \begin{array}{c} \text{C}_6\text{H}_4 \\   \\ \text{COO---R} \end{array}$ $R = \begin{array}{c} \text{CH}_3 \\   \\ \text{---CH}_2\text{---CH---} \\   \\ \text{C}_6\text{H}_4 \end{array} \text{ or } \begin{array}{c} \text{CH}_3 \\   \\ \text{---CH---CH---} \\   \\ \text{CH}_3 \end{array}$	96.

reasonable response time, although this requirement is quantified by the type of display to which they are applied, for video rate displays response times in the microsecond region are preferred. At this time it

Polymer	Spacer	Mesogen	Ref.
$\text{CH}_3 \left[ \begin{array}{c} \text{CH}_2 - \text{CH} \\   \\ \text{O} \end{array} \right] \text{OCH}_3$	$-(\text{CH}_2)_n-$ $n = 2, 3, 4, 6, 8 \text{ or } 10$		97, 98.
$\left[ \begin{array}{c} \text{CH}_2 - \text{CH} \\   \\ \text{CO}_2 \\ \text{A} \end{array} \right] \left[ \begin{array}{c} \text{CH}_2 - \text{C} \\   \\ \text{O} \\ \text{B} \end{array} \right] \text{CH}_3$ $\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si} - \text{O} \\   \\ \text{C} \end{array} \right] \left[ \begin{array}{c} \text{O} \\   \\ \text{P} = \text{N} \\   \\ \text{O} \\ \text{D} \end{array} \right]$ <p>Either A, B, C, or D</p>	$-(\text{CH}_2)_n-$ $n = 3, 6, 8 \text{ or } 11$	<p>Either X = H and Y = CH<sub>3</sub> or Y = H and X = CH<sub>3</sub></p>	99.
$\left[ \begin{array}{c} \text{CH}_2 - \text{CH} \\   \\ \text{CO}_2 \\ \text{a} \end{array} \right] \left[ \text{CH}_2 - \text{N} - \text{N} - \text{O} - \text{CH}_2 - \text{COO} - \text{CH} - \text{CO} \right]$	$-(\text{CH}_2)_6-$		100.
$\left[ \begin{array}{c} \text{CH}_2 - \text{CH} \\   \\ \text{CO}_2 \\ \text{or} \\ \text{OCH}_2 - \text{CH} \\   \\ \text{CO}_2 \end{array} \right]$	$-(\text{CH}_2)_n-$ $n = 10 \text{ or } 12$	<p>R = -COO-C<sub>2</sub>H<sub>5</sub> or -C<sub>2</sub>H<sub>5</sub>COO- Where n = 7 or 9</p>	101.
$\left[ \begin{array}{c} \text{CH}_2 - \text{CH} \\   \\ \text{CO}_2 \end{array} \right]$	$-(\text{CH}_2)_n-$ $-(\text{CH}_2)_2 - \text{O} - \text{CH}_2 - \text{O} - (\text{CH}_2)_2 -$		102.

is hard to envisage any polymeric material offering this sort of response speed, as even the best polymeric materials show switching times of tens of milliseconds. However, for other less complicated displays re-

Polymer	Spacer	Mesogen	Ref.
$\left[ \text{CH}_2 - \underset{\text{CO}_2}{\overset{\text{CH}_3}{\text{C}}} \right]$	$-(\text{CH}_2)_n-$ $n = 6 \text{ or } 8$	 Where $m = 2, 4 \text{ or } 6$	103.
$\left[ \text{Si} - \underset{\text{O}}{\overset{\text{CH}_3}{\text{C}}} \right]$	$-(\text{CH}_2)_8-$	 Where $m = 2 \text{ or } 6$	104.
$\left[ \text{CH}_2 - \text{CH}_2 - \underset{\text{H}}{\text{N}} \right]$ or $\left[ \text{CH}_2 - \text{CH}_2 - \underset{\text{H}}{\overset{\text{Br}^-}{\text{N}^+}} \right]$	$-(\text{CH}_2)_6-$		105.
$\left[ \text{CH}_2 - \underset{\text{CO}_2}{\text{CH}} \right]$	$-(\text{CH}_2)_{10}-$		106
$\left[ \text{CO}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{CO}_2 - \text{CH} - \text{CH}_2\text{CH}_2 \right]$	$-(\text{CH}_2)_6-$	 or 	107. 108.

sponse times of up to hundreds of msec are acceptable. Finally, and most importantly the PLC must offer some advantage over any existing technology. All of these factors serve to limit the number of materials shown in Table I which are suitable for display applications. Nevertheless, the nature of polymer science is such that we have many variables to adjust, spacer length, mesogen type, backbone type are the

more obvious, but there is also the possibility of copolymers [112–115], elastomers [116–121], cyclic polymers [122–125], combined main chain and side chain PLC [126], to name but a few. Also as this table was compiled only from the open literature there are almost certainly other materials under development, which may show excellent properties and will soon become suitable for display applications.

#### 4.6. The Nature of Ferroelectric Polymers

As the field of ferroelectric liquid crystal polymers has only come to prominence over the last decade or so, it is perhaps not surprising to find that our understanding of the physics of these systems is still very much in its infancy.

A major facet associated with all polymeric materials is the relationship between virtually all physical properties and the molecular weight, below certain values of  $M_w$  many of the materials properties vary dramatically with only a relatively small molecular weight changes [109, 110]. In the field of PLCs this effect has been widely observed, particularly with regard to transition temperatures and response times [127, 128]. This effect can then lead to difficulty in batch to batch reproducibility when one is working with short chain polymers or oligomers.

There is also the more general question of the effects the backbone has on the mesogenic ordering within the liquid crystal phases. This can simplistically be described by the fact that the polymer chain has a desire to adopt a random coil configuration and incorporation of the long spacer allows the polymer chain to do this without disruption of the mesogenic ordering within the LC phase. Generally, to a first approximation, this may be consistent with a nematic phase, where mesogenic side chains are statistically disordered with respect to their centre of gravity. However, measurements have shown that the polymer chain is anisotropically deformed from its random coil configuration [129] even in the nematic phase. In a smectic phase this deformation will be increased and the chain deformation has to adapt to the layered arrangement of the mesogens. A possible explanation has been suggested involving two dimensional ordering between the smectic layers [130]. Clearly, this anisotropic deformation of the chain packing can serve to increase the  $T_g$  of the resultant polymer and hence the smectic



PLC tend to be characterised by high clearing temperatures and high  $T_g$  values [131]. If we consider a very short chain length of a relatively flexible backbone, then one can imagine that the tendency for the chain to coil will be suppressed by the mesogenic ordering and the chain will be confined almost entirely between the smectic layers. However on going to higher molecular weights and thus, longer chain lengths, the desire for the chain to coil must eventually overcome this restriction and the chain will either pass through the smectic layers or form a hairpin defect both causing a disruption to the LC ordering. In general, the polymer backbone is distributed between the smectic layers, over relatively short range, but is distributed through the layers over longer ranges. There has been some experimental evidence published to support this [132].

In simple terms the molecular design of PLCs is chosen so that the liquid crystal mesogens generally behave as normal MLC over short range and the polymeric backbones behave as polymers over long ranges. Thus intrinsic molecular properties are dominated by the mesogens such as response times and  $P_s$  characteristics, but the bulk material properties are predominantly those of polymers *e.g.*, thermal and rheological behaviour. In conclusion, however, the combination of these properties are not totally exclusive of one another. The bulk properties are affected by the presence of the mesogen and conversely the intrinsic LC properties are affected by the presence of the polymer chain. They are not therefore polymers with some liquid crystal behaviour, nor are they liquid crystals with some polymer characteristics, they are truly liquid crystal polymers and deserving of their own material classification.

## 5. CONSTRUCTION OF A POLYMERIC LCD

### 5.1. General Display Construction

As discussed earlier a LCD consists of a thin layer of aligned molecules constrained between two substrates, usually glass. The substrate has the required electrode pattern etched onto it in ITO and then an alignment layer, typically rubbed poly(imide). Sheets of polariser are fixed to the outside of the substrates and thus the display is completed as shown below;

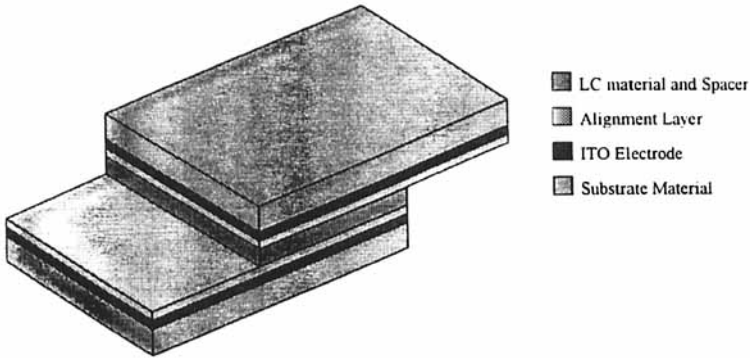


FIGURE 12 Displays structure.

The two substrates are assembled using spacers and finally the liquid crystal material is allowed to flow fill the cell, usually under vacuum. There exist a number of problems with the construction of displays in this way when using polymer liquid crystals; not the least of which is the fact that the viscosity of polymers is too high to give adequate flow filling and secondly only a few polymers will be aligned by the simple surface forces in a rubbed polymer cell. In order to combat this researchers have turned to the use of shear forces for alignment. By sandwiching the polymer between substrates and then applying a shear force, typically by bending the device [133], the shear applied to the polymer causes alignment of the molecules and thus produces an aligned device, as illustrated in Figure 13.

This method also negates the need for flow filling as the polymer can be coated down onto one of the substrates. Idemitsu Kosan Co. Ltd., recently displayed a prototype ferroelectric liquid crystal polymer display [134] based on this principle. Although the rather limited response time of the polymers used gives only a 5 ms/line response time, which represents a 2 Hz frame rate, still far behind video frame rate, typically about 30 Hz/frame. Nevertheless, we must bear in mind that while flat screen televisions require video frame rate this is not a necessary requirement for the bulk of displays. Indeed Idemitsu's display is capable of most of the current applications such as information display terminals *etc.* However, this market is already well established and polymer displays do not offer a significant advantage to cover the extra cost in development.

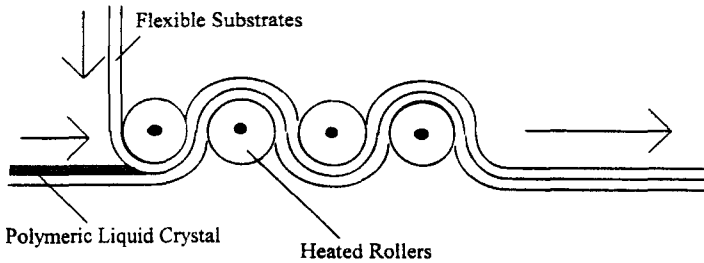


FIGURE 13 PLC alignment.

The advantages of using a polymer based display are primarily in flexibility and robustness. However, this is paid for in terms of response time which manifests itself in device complexity.

Eventually however, polymers may offer the opportunity for a free standing film of display material. In such a device the polymer would be produced as an aligned film and then electrodes and polarising filters coated down and on top. This in turn will greatly reduce the cost of displays and thus the cost of devices which utilise them.

## 5.2. Other Display Components

All displays can be categorised as either emissive or passive displays. An emissive display is one which emits its own light typically by converting electrical energy into light energy as in light emitting diodes (LED), or by using a beam of electrons to excite some photosensitive material as in the common CRT. On the other hand, a passive display simply modulates the light which passes through it, typically by changing the light's polarisation direction. Thus when an aligned film of liquid crystal material is placed between crossed polarising filters a switch from light to dark can be observed. This therefore requires an LCD to have a light source, if one wishes to use natural light the LCD is placed onto a reflector and incident light passing through the display is reflected back out and can be modulated by the liquid crystal to give a light to dark contrast. Clearly this type of display is limited and so it is more common to mount the display onto some backbit substrate. The advantages of this type are firstly it can be used in low light

conditions and secondly a much better level of transmission is achieved because the light is only passing through the display once instead of twice as in the reflective display. However, backlighting adds considerably to the cost, weight and power consumption. Indeed one of the greatest drains on a laptop computer's battery is the backlights for the display, which is why most power manager systems switch off the backlights to conserve power when the computer is inactive. Despite these drawbacks, the LCD is still one of the most power efficient display on the market, including backlights.

A further necessary addition to the completed display system is the actual driver electronics and the cost of the drivers is related to the complexity of the display. As discussed above, most display systems are multiplex driven there are therefore row and column drivers which supply the signals to the lines of the display. Alternatively the active matrix display requires connections to each of the thin film transistors, these connections have to be routed between the pixels to the outside edge of the display. This requires a finite amount of space between the pixels to allow for the connections. Also the number of connections limits the number of pixels in a display. An alternative option, especially for large area displays is to utilise a projection device. However, the limitations of interpixel gap, which will be magnified along with the image, are clearly much more crucial. Sharp Corporation recently announced the production of a 53 cm diagonal active matrix TFT display [135]. This gives video frame rate, full colour, TV quality images. At the other end of the scale, Sony Japan have also released a hand held projection TV. This is based on a 4.5 cm diagonal TFT display which can be magnified up to produce a 1.2 m image before the inter pixel gap becomes apparent.

## **6. POLYMER DISPLAY MARKET**

### **6.1. The Role of the Polymeric LCD**

In order to become a commercially successful technology a product must open a new market or offer an improvement on an existing capability. This ideology can be summed up in the diagram showed in Figure 14.

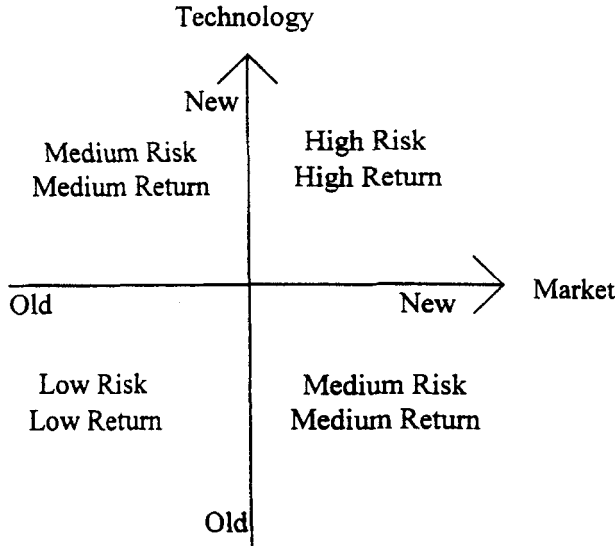


FIGURE 14 Economics and technology.

Flat panel LCD's are now well established in the market place. In order for a new technology such as Polymeric LCD's (PLCD's) to be successful they must offer something new and product enabling. As it is described above PLC's have some inherent problems when applied to displays, particularly with the achievable response speed, thus any PLCD will be restricted by frame time and thus will probably not offer full video capability. Nevertheless, there are still many applications which do not require video speed, such as very large public information displays for airport, and railway display boards; personal data assistant displays (PDA); rolling maps; *etc.* The qualities of robustness, non volatile memory and processability inherent with pseudosolid state PLCD's are potentially very interesting to display products.

## 6.2. Large Area Displays

Large screen displays are typically either direct view or projection type systems. As far as direct view is concerned, AMTFT displays are getting larger 25 cm and 35 cm, full colour video rate screens are readily available from several Japanese manufacturers and larger

devices, capable of video frame rate, full colour, TV quality images are becoming available. Although they are approaching the current upper size limit of a single TFT active matrix display, the issue is whether large area TFT displays can be manufactured and sold at a price the market will bear.

A second, more cost effective approach to large area direct view displays is by tiling small screens; for example, in 1985 Matsushita Electric Co. (Panasonic), developed a large screen LCD constructed from upto 154 individual AMTFT modules [136], each module was  $200 \times 267$  mm, and each pixel was  $5 \text{ mm}^2$ . The drawback with tiled displays is that seams between each module can detract greatly from the image quality.

On the other hand, projection LCD's are now common place with options from high definition TV to briefcase portable units. One of the smallest is the Sony hand held projection TV, discussed above. At the other end of the scale Barco Data Systems Ltd., market a projection display for cinema use. This consists of three TFT modules (one for each of the three primary colours) and can produce images up to 9 m across. All of these displays utilise TFT modules and are therefore capable of producing video frame rate images and are clearly well in advance of anything yet possible with PLC's. However, they represent the top of the range information display systems. Most large screen displays are required to show only alphanumeric characters or simple dot matrix type graphics, *e.g.*, airport and railway information boards, variable message traffic control signs, *etc.* All of these are direct view, large area screens, and given the simplicity of displayed information the TFT module is over complex and not cost effective. In the large screen low information content market there are many established technologies: MLC direct view displays; LED message signs; electro-magnetic disc displays; plasma displays; electroluminescent displays; moving dielectric displays; even incandescent lamp displays. In order to be competitive in this market PLCD's must demonstrate in manufacture their advantage in processability and in performance. However, roll to roll production of PLCD's, as outlined in a recent patent [133], would involve a large capital investment in plant, and would soon saturate the market. For example, if the roll to roll plant produces around 10 m per hour of display, then in a working year it will produce about 25 km of PLCD. This clearly well outstrips the

market demand for this type of product and the manufactures would therefore be unable to get a reasonable rate this type of product and the manufactures would therefore be unable to get a reasonable rate of return on their investment.

### **6.3. Portable Displays**

This represents the growth end of the display market, and one into which the PLCD fits extremely well. A portable display must be lightweight and rugged, clearly polymeric materials are well suited to those criteria. However, the display must not be an awkward shape as this severely limits portability and it must also have a low power consumption in order to prolong battery life. Considering a ferroelectric PLCD it is lightweight and rugged, the ferroelectric nature offers bistability and therefore low power consumption and because of the in-built flexibility in these systems they offer the possibility of being rolled up or folded away when not in use.

This could well lead to applications in the form of rolling map displays, personal data assistant displays and electronic paper. Clearly they represent major market opportunities for the polymeric liquid crystal display. In turn the PLCD has the necessary properties and advantages over other techniques to allow for the future development of these products. I am sure that it is in this area that we shall see the first PLCD device.

## **7. CONCLUSIONS**

Currently the display industry serves a multibillion pound market and within this market the LCD has emerged as the foremost challenger to the dominance of the CRT. Within this technology area exists PLCD research and development. Ferroelectric MLC offer the next generation of LCD's superfast response times and low power bistability. However, at present, they suffer from poor mechanical shock resistance. On the other hand, PLC had notoriously slow response times, but in turn were not as sensitive to mechanical damage. What has occurred in PLC over the past few years is a combination of these

two technologies to produce ferroelectric PLC. Thus, the high speed of the ferroelectric switching process compensates for the long response time of the polymers and the high dimensional stability of the polymers compensates for the mechanical sensitivity of the ferroelectric mesogens.

This wealth of research, both into materials and devices is now at the stage of being formed into prototype devices. Generally, these displays consist of plastic film with the PLC sandwiched between. The display is therefore lightweight, flexible and rugged. Hopefully, these displays will soon find the commercial market worthy of the vast amount of research and development that has gone into this class of novel materials.

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