

**Liquid crystals**—the mysterious expression used to describe the class of materials that can flow yet remain ordered—have a surprisingly long history reaching well back into the last millennium. The earliest days of liquid crystal existence and use are difficult to define because so little is recorded. And the most recent history of liquid crystals is difficult to track because so much is recorded. A recounting of the history of liquid crystals is like flying over mountains—it is easy to see the high points but the beauty of the details requires a closer look. In this fly-over of the field of liquid crystals, we will see the high points and be introduced to some of the scientists who trekked through the details.

# A Millennium of Liquid Crystals

By Eileen M. Korenic

## **Lyotropic liquid crystals**

Long before the liquid crystals (LC) of today were examined, synthesized, or microscopically scrutinized, a class of molecules existed that formed colorful thin films in sufficient concentration in water. Whipped with air, these films closed onto themselves forming bubbles of suds. These molecules, today called detergents, were commonly known as soaps. Even without understanding the chemistry of soaps, it was easy to see that with enough soap in water, bubbles formed.

As early as 1519, Leonardo da Vinci explored the capillary action of water. We now know that the hydrogen bonding responsible for that behavior is also the basis for soap films. Robert Hooke (late 1600s) and Isaac Newton (early 1700s) both investigated properties of such thin films. Even Benjamin Franklin (late 1700s) studied the action of lipid layers on the surface of water.

By 1840, mathematicians such as Joseph Plateau, despite his blindness, analyzed the regularities of soap film structures on polygonal frames.<sup>1</sup> He devised simple “bubble rules” that showed an elegance and simplicity unexpected from a random distribution of soap molecules distributed through water. These rules included such regularities as “Three films meet in a line” and “Four lines meet in a point.” These rules hold true even for bubbles in bubble bath as in the image on this page, suds in beer, and spaghetti starch in water—all examples of large molecules that organize into regular structures at the right concentration.

Within 30 years, Josiah Willard Gibbs<sup>2</sup> established interfacial thermodynamics from observations of soap films. By 1949, Bragg and Lomer<sup>3</sup> were using bubble rafts to study features such as dislocations in solid crystals. And still more recently (1984), very thin soap films known as black films have been used as beam splitters in neutron optical interferometry.<sup>4</sup>

The structure of a soap film is now understood to be a triple layer of soap-water-soap, in which the water molecules are hydrogen-bonded to each other, giving strength and flexibility to the film. The soap molecules are typically long hydrocarbon chains with a polar hydrophilic end dissolved in the water layer, and non-polar hydrophobic ends pointing towards the outside of the overall trilayer. It is this lamellar or layered structure that can properly be called a liquid crystal. We use the term liquid crystal to describe molecules that can flow like a liquid and yet maintain some kind of positional order like a crystal. This subgroup of liquid crystals that depends on a critical concentration for the ordered structure to form is called lyotropic, from the Greek for dissolving. Outside of the critical concentration which produces the structure, the soap-water mixture is a solution at low soap concentration or a gel at high soap concentration.

In addition to the soap-water type of lyotropic liquid crystals, there is a wealth of biological examples of order with flow. These biological liquid crystals include tobacco mosaic virus<sup>5</sup> and synthetic polypep-

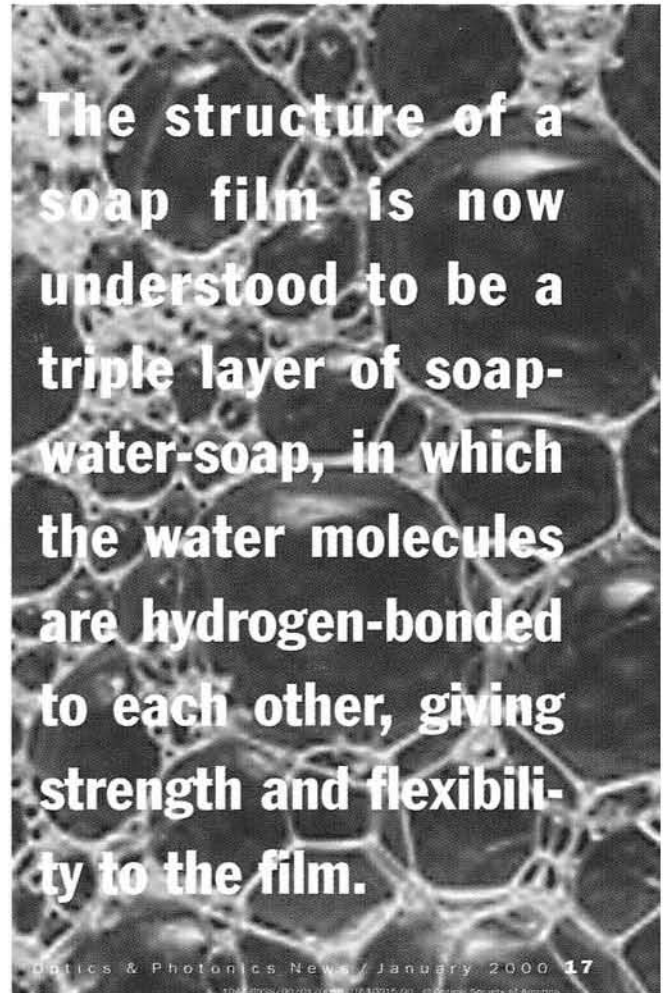
tides<sup>6</sup> in solution, usually with water. A particularly beautiful parallel of soap films and biological structures was illustrated in D’Arcy Wentworth Thompson’s *On Growth and Form*.<sup>7</sup> Some examples are shown in Figure 1.

Given the long history of soap molecules forming ordered structures out of solution, soap may be considered the first universally known liquid crystal. So, clearly, liquid crystals have existed and been used for longer than the last millennium, at least in the form of lyotropics.

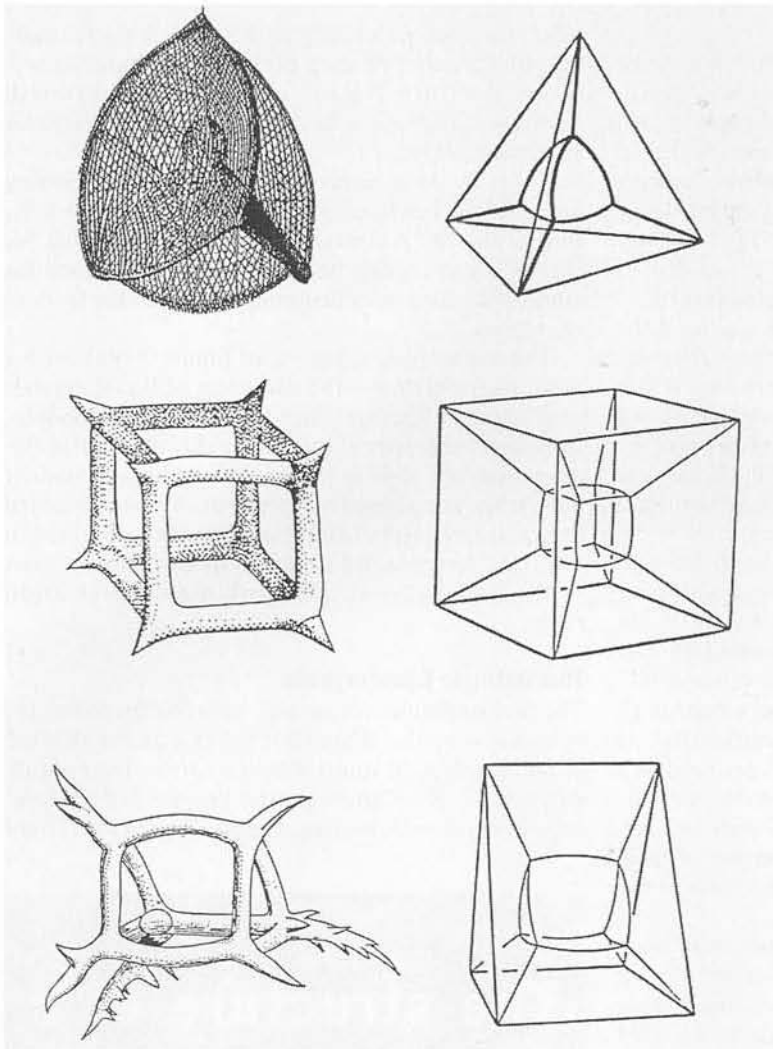
There is another subgroup of liquid crystals with a more recent history—the subgroup of liquid crystals used today in displays, shutters, spatial light modulators, and even artists’ media. In this class of molecules, ordered flow is not concentration-dependent but rather temperature-dependent. These are called thermotropics and exist as liquid crystals only within a specific temperature range, as lyotropics only exist in the liquid crystal state within a concentration range.

## **Thermotropic liquid crystals**

The first molecules recognized with this thermotropic behavior were the cholesteryl esters, which exhibited beautiful reflection colors within a narrow temperature window. In 1888, the botanist Friedrich Reinitzer<sup>8</sup> experimented with heating crystals of cholesteryl ben-



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**Figure 1.** D'Arcy Wentworth Thompson's book, *On Growth and Form*, compares the ordered structure of soap films on frames to the biological structure of sea animals called radiolarians.

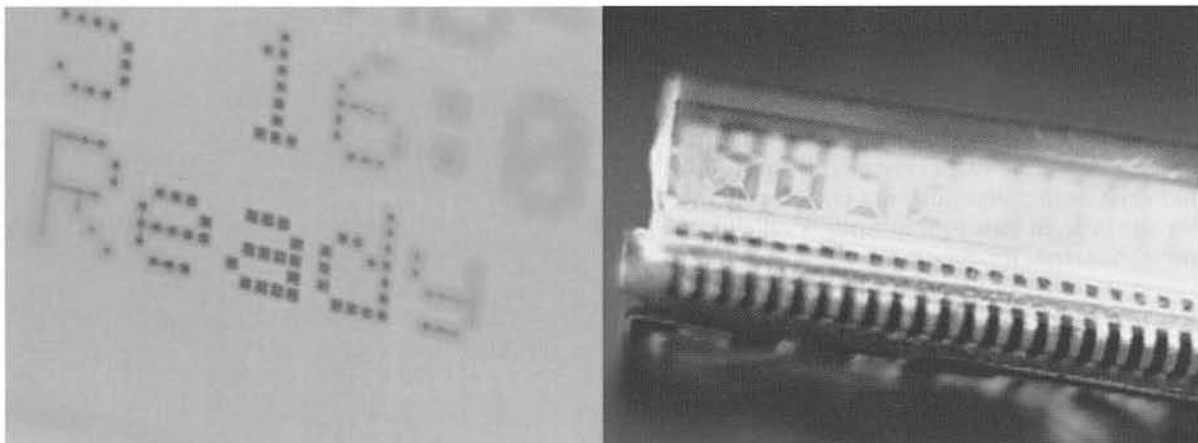
zoate and noticed that they passed through a cloudy melted state before clearing to an isotropic liquid. Otto Lehmann<sup>9</sup> showed this cloudy state to be a new phase of partially ordered molecules, a mesophase between liquid

and solid. In 1890, he coined the term "liquid crystal."

The cholesteral types of liquid crystals discovered by Reinitzer were the first to be thoroughly investigated, due in part to their beautiful appearance. These cholesteral-based liquid crystals, called cholesterics, show pure reflection colors. As other types of liquid crystal order began to emerge, many without colors, a classification scheme was developed to better understand these different types of optical behavior. In 1922, Friedel<sup>10</sup> proposed a scheme describing three classes of thermotropic liquid crystals: nematic, smectic, and cholesteric or chiral nematic.

Thermotropic liquid crystals are usually made of long, rod-like molecules. When they are ordered with the rods virtually along the same direction, the structure behaves like an anisotropic structure, exhibiting birefringence. This structure, shown in Figure 2a, is termed the nematic type of thermotropic liquid crystal. The direction of the molecules is given by the vector  $n$ , called the director. When the rods are pointing in the same direction but show an additional level of layered structure as in Figure 2b, they are termed smectic and also exhibit birefringence. As we will see, it is the birefringence of nematics and smectics that has made them exceptionally useful in practical applications.

In the third class of liquid crystal, the type Reinitzer observed, the molecules lie in layers in which the director slowly rotates through the thickness of the liquid crystal. The theory of this structure, proposed as early as 1911 by Mauguin,<sup>11</sup> was further



AMLCDs, active matrix liquid crystal displays, are popular in laptops and other display venues.

investigated in 1921 by Grandjean.<sup>12</sup> This structure is still referred to as the Grandjean texture in honor of this early work. Since then, other non-cholesteryl-based molecules have been found to show this helical formation. The chemical requirement for this is that the molecules themselves have a point that is non-superimposable on its mirror image. Such molecules are like right and left hands, and are therefore called chiral from the Greek for hand. Since the individual layers may be considered locally nematic, the cholesteric structure is sometimes also called chiral nematic. This structure is shown in Figure 2c. The length through which the director rotates  $360^\circ$  is called the pitch of the chiral nematic. The theory of the optical behavior of this specialized structure was described in 1950 by DeVries.<sup>13</sup> For unpolarized white light incident along the direction of the pitch axis, some wavelength in the medium will match the pitch and a circular polarization component will be superimposable on the twist of the helix. This match gives rise to constructive interference, producing a reflected wave with a narrow bandwidth and one handedness of circular polarization, as shown in Figure 3. Wavelengths may range from ultraviolet through the visible, to the infrared, with bandwidths in the visible typically ranging from 10-100 nm.

By the 1930s and 1940s, studies of all three types of liquid crystals were limited primarily to theoretical discussions of how the liquid crystal order arose. Two main theories to come out of these discussions by the 1960s were:

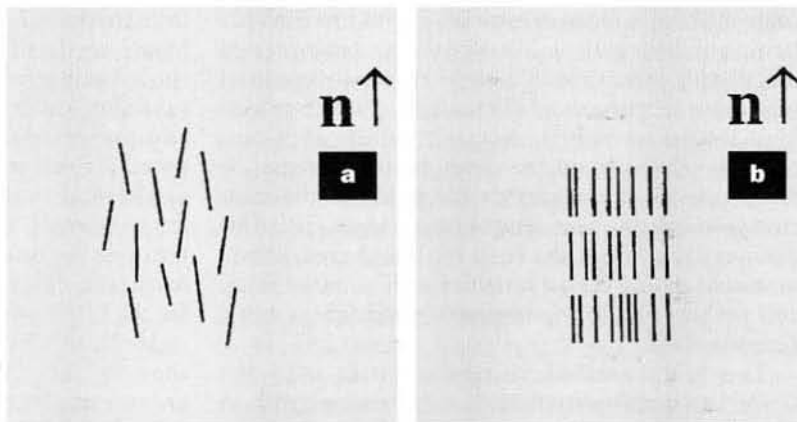
### 1 The continuum theory

First proposed by Oseen<sup>14</sup> in 1933, the liquid crystal state was modeled as a continuous medium. By 1958, Frank<sup>15</sup> had developed a theory of elasticity to calculate the strains of molecular orientation. Within two years, Leslie<sup>16</sup> and Ericksen<sup>17</sup> had formulated conservation laws and constitutive equations for describing the mechanics of a continuum of liquid crystals.

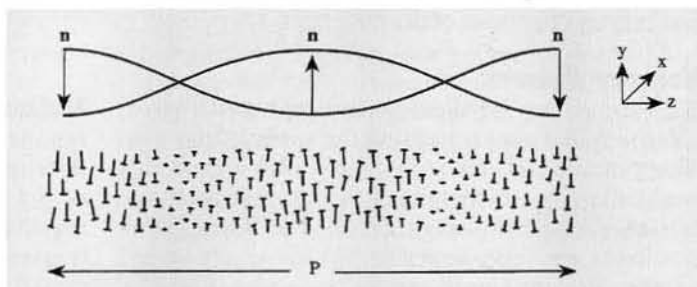
### 2 A statistical approach

In this type of theoretical treatment, liquid crystal molecules are modeled as rods in a lattice<sup>18</sup> or individually with a molecular field approximation as Maier and Saupe used.<sup>19</sup>

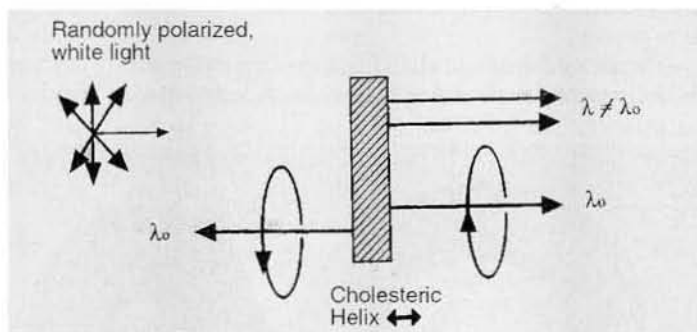
In the 1950s, as all of these theoretical approaches and variations were in the process of developing, a



**Figures 2a and b.** The classification of thermotropic liquid crystals into three types was proposed by G. Friedel in 1922. **a.** The nematic type has long, rod-like molecules aligned approximately along the same direction. **b.** The smectic type exhibits an additional lamellar level of ordering.



**Figure 2c.** The chiral nematic or cholesteric type exhibits a periodic rotation of the direction of the molecules.



**Figure 3.** Chiral nematic liquid crystals reflect one handedness of circularly polarized light of one wavelength. Other incident light is transmitted. The reflected light is produced by constructive interference of the component of incident light which is superimposable on the chiral nematic helix structure.

great resurgence in liquid crystal experimentation began. This rebirth of experimentation is credited to a review article published by Glenn Brown in 1956.<sup>20</sup> At the same time, Brown founded the Liquid Crystal Institute at Kent State University, an institution that has grown from one student working with Brown to an internationally recognized center of liquid crystal research.

By the mid-1960s, publications hinting at the possible uses of liquid crystals for display purposes had appeared. Fergason<sup>21</sup> showed the first temperature-

controlled color changes associated with low molecular weight cholesteric liquid crystals. He demonstrated that heating one of the cholesteric-type materials in its Grandjean texture caused the pitch to contract, reflecting a shorter wavelength. Not only did the pitch contraction relate directly to temperature increase, he found a series of cholesterics that produced the color changes over different temperature ranges. It is this discovery that forms the basis for liquid crystal thermometers, liquid crystal novelties such as mood rings, and perhaps use in liquid crystal display to achieve desired colors.

The alignment of chiral nematics into the Grandjean texture is relatively easy to accomplish. A drop of the material between glass plates which are then gently sheared is usually sufficient to produce the helix structure with the axis perpendicular to the glass surfaces. Nematics and smectics have no such straightforward alignment method and require the confining surfaces such as glass plates to be pre-treated to allow a preliminary alignment of the molecules.

### Molecular alignment

Early techniques for aligning the liquid crystal molecules included simply rubbing the surfaces of a confining surface, such as a glass plate, with a cloth.<sup>22</sup> It was not known whether this technique induced a surface charge on the glass or left residual fibers. Either possibility may have served to provide a starting orientation for the liquid crystal molecules. By 1973, Berreman<sup>23</sup> had developed a theory that grooves or microscratches produced by rubbing influence the surface energy of the molecules directly against them. Alignment then becomes a surface energy minimization process.

The second front in the effort to align molecules is the use of an alignment layer. In this process, a

thin coating of a polymer, typically a polyimide, is baked or dried onto the glass surfaces and then rubbed or buffed by hand or by means of a mechanical roller. Roller materials have included both woven and non-woven types of cloth. Mechanisms proposed for this technique providing alignment to liquid crystal molecules include the production of microgrooves, the presence of surface charge patterns, or the orientation of the alignment layer itself by plastic deformation into an anisotropic pattern for the LC to follow.<sup>24</sup>

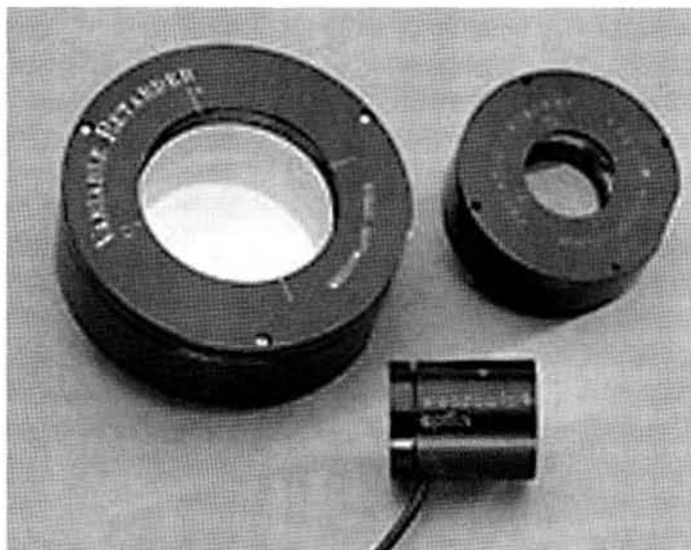
Work in this area continues, with experiments showing that alignment can be accomplished with grooves much smaller than the size of molecules or, indeed, even without any grooves at all. Most notably, in the latter case, Schadt *et al.* in 1992<sup>25</sup> showed that a coating of an alignment polymer can itself be aligned and polymerized by exposure to linearly polarized ultra-violet light. This alignment layer has been shown to align liquid crystals in contact with it, promoting orientation throughout the thickness of the LC sample.

### Applications

Among the most straightforward applications of LC structures are those that make use of the birefringence of the ordered liquid crystal. A typical geometry requires aligning all the molecules along a single direction and setting the thickness of the confined liquid crystal by means of spacers, such as glass beads or fibers. Such an ordered structure functions well as a waveplate or retarder.

By about 1967, simple sandwich-type cells of aligned nematics were also being tested within electric fields. A conductive coating on the glass surfaces, then overcoated with an alignment layer, provided the electrodes to apply an electric field to the liquid crystal molecules. In the preliminary tests, regions of turbidity developed, subsequently called Williams' domains and associated with the flow of ionic impurities, causing turbulence in the liquid crystal structure and thus the scattering of light. This state of "dynamic scattering" provided the first demonstration<sup>26</sup> of a liquid crystal capability useful for displays: liquid crystals change their alignment in response to an electric field, producing a scattering optical state, and return to their original alignment when the field is turned off, producing a transparent optical state.

The idea of applying an electric field was also used to purposely reorient liquid crystal molecules,<sup>27</sup> not simply create turbulence. This electro-optic control of liquid crystal molecule orientation has provided the ability to design continuously variable retarders and waveplates corresponding to user-controlled voltage settings. Such variable retarders and



Liquid crystal variable retarders are now commercially available. They are less expensive than traditional birefringent solid crystal retarders and waveplates, as well as more versatile.

waveplates, like those shown in the image on page 20, can be purchased commercially. This is extremely advantageous, in that it eliminates the expense associated with growing and precisely cutting traditional birefringent crystals whose useful wavelength must be predetermined.

Within two years of discovery of the dynamic scattering ability, Schadt and Helfrich<sup>28</sup> introduced a construction that would ultimately become the workhorse of the display industry. This is the construction which is now called the twisted nematic, or TN cell. In this geometry, one of the confining glass surfaces has an alignment layer oriented at 90° rotation to the alignment layer on the other surface. At each surface, the LC molecules nearest the surface align with the alignment layer. Between the surfaces, there is a slow twist, a gradual rotation through the thickness of the LC, of one alignment direction to the other. Variations of this geometry include rotation of one of the alignment layers 270° with respect to the other in the so-called super-twisted nematic, or STN cell. Placing the TN or STN cell between crossed polarizers with the field off, the liquid crystal serves to “waveguide” the polarization of incident light, rotating the plane of polarization through the LC thickness, transmitting the light. With the electric field on, the molecules align with the field, no longer waveguiding, and the cell effectively blocks the light. (See S. Shields, “The Allure of Liquid Crystal Displays,” *Optics & Photonics News*, 1994).

By 1973, the first commercially reliable nematics for use in display had been invented by George Gray.<sup>29</sup> The first liquid crystal display watches came onto the market in 1973 and the field of liquid crystal displays, LCDs, was launched.

### Improvements to display applications

The 30 years since the invention of the TN cell have witnessed dramatic improvements in the use of liquid crystal constructions for displays. These improvements have been in the areas of overcoming temperature sensitivity, speed of switching optical states, and development of more complex display geometries.

### Temperature sensitivity improvement

Up until 1980, low weight liquid crystals had been used in liquid crystal cell construction. In 1980, Tsutsui and Tanaka<sup>30</sup> proposed the use of liquid crystal polymers in applications. The higher weight molecules were designed to have mesophase temperature windows at higher than room temperature. This meant that, for example, the liquid crystals could be manipulated at elevated temperatures into a retarder or waveplate configuration, cooled, then used at room temperature without loss of structure as the temperature fluctuated. These early polymers cooled to a crystalline phase subject to changes in molecular order during the phase transition from mesophase to crystal. At about the same time, Finkelmann<sup>31</sup> introduced

a special class of liquid crystal polymers called “side-chain” polymers. These structures are made of liquid crystal-like structures attached to a main-chain polymer by flexible spacers, like multiple pendants on a chain. These side-chains behave like low-weight liquid crystals in their alignment capability, responding to electric fields. However, on cooling, they do not crystallize but remain glassy and so provide an excellent optical material.

### Switching speed improvement

As early as 1974, Meyer *et al.*<sup>32</sup> suggested that liquid crystals might show ferroelectricity, that is, a spontaneous electrical polarization arising from the alignment of the molecules. By 1980, the first ferroelectric liquid crystal display was demonstrated by Clark and Lagerwall.<sup>33</sup> Because of the existence of the polarization, switching times were enhanced to faster than a millisecond response.

Another avenue pursued in attempting to produce faster switching times was the development of composite systems. These include polymer-dispersed liquid crystals (PDLC) and polymer-stabilized liquid crystals. In PDLC, a polymer which may or may not be a liquid crystal itself creates a network of pockets filled with the liquid crystal of interest. These include reflective and transmissive displays in which nematic liquid crystals are confined to droplets. Electric fields may be used to control the alignment within the droplets, demonstrated for nematics in 1982 by Craighead, Cheng, and Hackwood.<sup>34</sup> Polymer-stabilized systems are similar in that polymers provide a structural network helping the partially confined liquid crystals to realign when an applied field is removed.

In the case of either PDLC or polymer-stabilized systems, the alignment of molecules within a droplet or confined area gives the liquid crystal an index of refraction which may or may not match the surrounding index of the medium. If there is a match, light passing through the system is not scattered or in any other way redirected. If there is an index mismatch, the light is effectively scattered, creating a milky appearance. This principle is behind the application of PDLC for switchable privacy windows.

Chiral nematics may also be used in composite systems. When confined to droplets, recent developments have shown that the helix formation within the droplet, albeit with minor distortions due to the confines of the droplet, produces the beautiful selective reflection of color and polarization associated with pure chiral nematics. With control of the electric field, the chiral nematic droplets can produce the choice of states of reflecting a specific color or scattering.

### More complex geometries

When TN sandwiches comprise individual segments of a display with each segment being separately

controlled, we see the basis of the simplest types of displays, commonly seen in digital displays like watches, cell phones, and messaging pagers.

For more complex images with faster response, passive matrix displays use stripes of electrodes, running in two directions. By controlling the voltage to each set of stripes, the overlap of a specific pair can reach a threshold voltage required to make the LC move in the pixel selected. Still better displays are the active matrix liquid crystal displays (AMLCDs) in which each pixel is controlled by a thin-film transistor. These displays use the high multiplexing ability of semiconductors to control the twisted nematic behavior, yielding superior image quality.

The display structures described thus far are functioning as spatial light modulators; that is, they allow light to pass or not in a pattern chosen by the user. For most displays, though, users want more than a mosaic of black and white pixels. Color was added by using a tricolor pixelated screen of red, green, and blue pigments. An example of an AMLCD with color filters is shown in the images on page 18.

### Future directions

Much work is still being done in the field of liquid crystals. Numerous composite systems are being studied, including so-called guest-host combinations. In these types of composites, the liquid crystal is only one component of a system that may include dyes and/or polymers. A dichroic dye aligned with a liquid crystal will orient as the liquid crystal molecules respond to an electric field. In this case, the liquid crystal serves as a mechanism to orient the dye rather than as an optical entity in and of itself. Liquid crystals are also being investigated for their nonlinear effects, including harmonic generation. And work continues in exploring the stability of liquid crystals for use with lasers.<sup>35</sup>

While liquid crystals in the form of lyotropics have been around for at least the last millennium, liquid crystals as a discipline, especially thermotropics, is only about 100 years old, which is relatively young. The growth of this field has been remarkable. Liquid crystal displays are taking significant market share from cathode ray tubes (CRTs) in displays around the world.<sup>36</sup> International validation of the importance of the study of molecular order came in 1991 when the Nobel prize in physics was awarded to Pierre-Gilles de Gennes for work on ordered systems including liquid crystals.

In the field of liquid crystal displays, work to improve color, contrast, and power usage, all with new and clever designs, will continue. Most importantly, the field of liquid crystals will maintain its unique ability to integrate the multiple disciplines of physics, chemistry, engineering, biology, and optics. From the invention of soap to one of the most powerful display tools on earth—liquid crystals have made a clean sweep!

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