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### Milestones in Physics (6)

#### Liquid Crystals, LCDs and Optical Alignment of Molecules

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# Milestones in Physics (6)

## Liquid Crystals, LCDs and Optical Alignment of Molecules

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### Introduction

Since the invention of the twisted nematic (TN) field-effect by Schadt and Helfrich in the Central Research Laboratories of Roche, Basel, in 1970 [1], the liquid crystal display (LCD)-technology has made remarkable progress. Electric field-effects determine the operating principles of today's LCDs. They are based on macroscopic molecular liquid crystal (LC)-configurations with specific boundary conditions whose voltage dependent polarization states switch virtually loss-free [2].

The building block concept of LCDs enables the integration of silicon-driving electronics and complex optical thin-films. LCDs cover virtually all applications of the communication between man and machine, ranging from reflective displays in digital watches to ultra-high resolution television LCDs. Interdisciplinary R&D between physics, material sciences, synthetic chemistry, semiconductor electronics, and engineering spurred progress since the beginnings in 1970. The turnover of the LCD industry reached \$130billion in 2013.

Apart from the twisted nematic effect continued interdisciplinary R&D of the author and collaborators mainly at Roche, led to new electro-optical effects, new liquid crystal materials and to a contact-free, optical alignment technology for LC-molecules. For details of the article c.f. ref. [2]

### State of the art of electronic displays in 1970

The first observation of a liquid crystalline phenomenon was made in 1888 by the Austrian botanist Reinitzer, Graz. However, it was realized only in the 1930s that liquid crystals are not suspended micro-crystals but a new state of matter exhibiting long-range molecular order. In 1918 Björnstahl published the first study of an electro-optical effect in liquid crystals. Upon ion-flow through a negative dielectric anisotropic liquid crystal (LC)-film he observed light scattering under his microscope. In the mid-1960s industrial research groups in the US and in Europe became interested in liquid crystals for potential electronic display applications. The few liquid crystals known at the time were unstable, and their melting temperatures were far above room temperature and/or covering too narrow temperature ranges for practical use. Only few of the numerous anisotropic LC-material properties, which are relevant for LCDs, were known, and reliable

experimental means for their determination had yet to be developed.

Most scientists considered liquid crystals to be exotic and of primarily academic interest. In 1963, i.e. 45 years after Björnstahl, Williams re-discovered current-induced light scattering in liquid crystal films at RCA Princeton. In 1968 Heilmeyer and Zanoni [3] extended his work towards practical liquid crystal displays and denominated their display dynamic (light) scattering (DS)-LCD. Their work triggered interest in liquid crystals. However, dynamic scattering suffered from serious drawbacks such as electro-chemical decomposition, poor optical contrast and power consumption.

Spurred by scientific curiosity and by the advancing semiconductor industry in the late 1960s, research groups around the globe started searching for new physical concepts for electronic displays. A flat shape and compatibility with the low voltage and power requirements of emerging complementary metal oxide semiconductors were some of the visions. However, none of the many different research strategies followed by scientists and engineers met the demanding goals. Compared with Nixie tubes, the emerging inorganic light emitting diodes (LEDs) used in digital matrix displays were most advanced (Fig. 1). Even exotic ideas at the time, such as a display based on organic light emitting diodes (OLEDs) were pursued. The first primitive OLED prototype was made by the author during his post-doctoral studies at the Canadian National Research Council, Ottawa (Fig. 1). With their reputation of being unstable and poorly visible, liquid crystals were only one of many options.

### Invention of the twisted nematic (TN) field-effect

Triggered by the dynamic scattering work of Heilmeyer and in line with the trend of business diversification at the time, the pharmaceutical company Roche, Basel, established a liquid crystal research group in 1970. It included collaboration with former Brown Boveri (now ABB) for jointly developing dynamic scattering LCDs for medical electronics equipment. The experimental physicist Schadt had joined the R&D group of Roche shortly before Helfrich also joined from RCA. When the two scientists met, they took advantage of the freedom at Roche to select and pursue individual research topics. Both scientists questioned the performance of the current-induced dynamic scattering and started searching for new display operating principles. Their goals were macroscopically ordered LC-configurations which change their polarization state in electric fields. However, loss-free molecular switching required polarization detection and surface-alignment of the long molecular LC-axes at the display boundaries. They were aware of the additional complications which this implied, namely the use of sheet polarizers and potential lifetime problems due to LC-alignment. Polarizers reduced brightness by more than 60%, and LC-alignment of the display substrates by mechanical brushing was a mysterious procedure. Moreover, they both added complexity and costs.



Fig. 1: Electronic displays end of 1960s: a) Nixie tubes, b) dot matrix LEDs, c) first OLED prototype of 1969 (~20x20x1mm).

Intrigued by a twisted polarization microscopy observation by the French crystallographer Mauguin [4] in 1911, Helfrich had the idea to apply a voltage to a positive dielectric anisotropic twisted nematic liquid crystal film for untwisting the helix into a vertically aligned on-state. Contrary to the management of RCA, and despite many open questions, Schadt was attracted by the idea and began to design and perform a series of experiments. Questions were whether dynamic scattering would prevent vertical field-alignment and whether repetitive switching was possible. Due to the lack of positive dielectric anisotropic room temperature liquid crystals Schadt first used the high melting PEBAB known from the literature since 1910 and synthesized by his chemist colleague Scherrer. Most of the initial TN-experiments of the author failed. Retrospectively, failure was due to a combination of inadequate LCs, unknown impurities, weak and irregular molecular surface anchoring and erratic wave-guiding.

On a Saturday morning in the fall of 1970 the author succeeded for the first time to reproducibly switch and observe polarization changes in a twisted nematic configuration between crossed polarizers. Now, as so often happens in physics, new surprising findings were made. Other than initially thought Schadt found that to achieve optical extinction it was not necessary for the electric field to fully unwind the liquid crystal helix. To his great surprise 2.5 volts were sufficient to block light transmission; i.e. twenty times less than the saturation voltage which estimates from elastic theory for untwisting suggested. The experiments also showed no interference effects; the helix acted as an achromatic waveguide. Moreover, he found that it was sufficient for the electric field to deform essentially only the central part of the helix for complete suppression of wave-guiding, and neither elastic fatigue of surface alignment nor dynamic scattering occurred. This confirms the saying of Niels Bohr that nothing exists before it is measured. Schadt and Helfrich immediately filed a Swiss TN-LCD patent application on 4<sup>th</sup> December 1970 and published their results in the February 1971 issue of Applied Physics Letters [1]. The reason for the rush of patent filing and submission of a short article with preliminary results was an information leak at Brown Boveri.

Figure 2 illustrates the threshold voltage and the big difference between the optical and the mechanical response of a 90° twisted nematic LCD versus applied voltage. The computed LC-director configurations in Fig. 2 depict the respective mechanical and optical on- and off- states. A theory

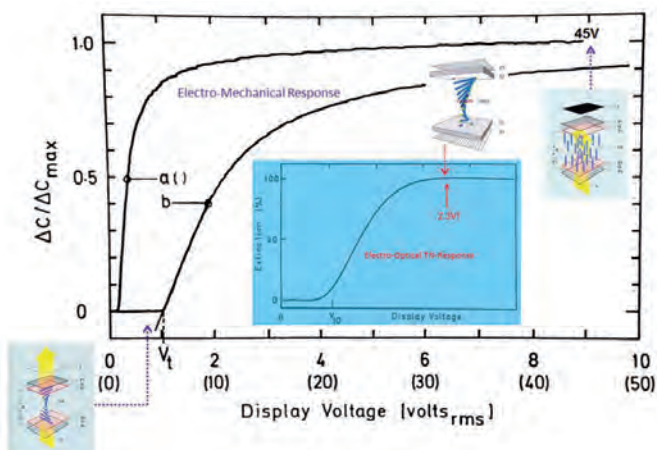


Fig. 2: Mechanical nematic helix director deformation (graphs a, b) and optical TN-LCD transmission (insert) between crossed polarizers versus applied voltage.

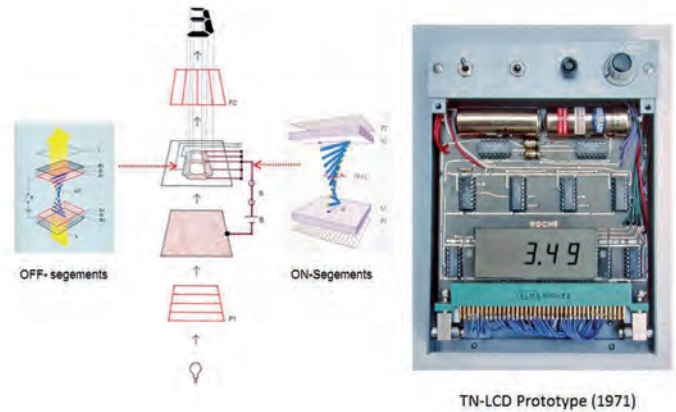


Fig.3: Schematic of a 7-segment addressed TN-LCD director-configuration in its off- and on-state. TN-LCD prototype made by the author (1971).

describing the complex electro-optics of twisted nematic LC-configurations did not exist at the time. A computer model based on the Stokes 4x4 matrix formalism was developed by Berreman at Bell labs three years after the publication of the TN-effect. Fig. 3 shows the first TN-LCD prototype made by the author and its seven-segment addressing scheme. Wave-guiding enables low operating voltages, achromatic optical response, broad field of view and small cell gap dependence of TN-LCDs. This paved the way for industrial implementation of the new technology.

#### Stop and new start of liquid crystal R&D at Roche

The publication of the twisted nematic effect spurred a strong interest of the scientific community and the electronics industry in field-effects. However, the potential of TN-LCDs and the use of liquid crystals in electronic devices continued to be questioned by many for years to come. One of the skeptics of the Roche LC-project was a new manager of its Central Research Labs. He declared liquid crystals to be "überflüssige Kristalle" (superfluous crystals) and ordered to stop liquid crystal research. The collaboration with BBC was terminated; Schadt was about to leave Roche and Helfrich left for the Freie Universität Berlin where he changed fields. The head of global Roche research convinced Schadt to stay. In the next two years the author searched for electro-optical effects and charge-transport phenomena in biophysics.

In the mean-time, leading Japanese watch and electronics companies had realized the potential of the TN-invention. In the spring of 1973 the head of the legal department of Roche asked Schadt to explain the relevance of the pending Swiss TN-LCD patent. The reason was an offer by Seiko to buy the TN-patent rights. The author outlined its big potential, the importance of liquid crystal materials and suggested licensing the TN-patent non-exclusively world-wide. Roche reactivated its liquid crystal activities, established a TN-licensing group and started manufacturing liquid crystals. This led to the first commercial TN-LCD mixtures. The author was given the opportunity to establish an interdisciplinary liquid crystal research team consisting of physicists and synthetic chemists. His research on electro-optical effects and new liquid crystals continued. One intriguing puzzle was the alignment of LC-molecules at display boundaries which – as shown below – initiated the LPP photo-alignment technology 20 years later. Because the physics of field-effect LCDs and LC-material properties were in their infancy, the author and his team started developing new experimental

techniques for identifying and determining all relevant liquid crystal material parameters. This provided the basis for their search for correlations between molecular structural elements, LC-material properties and display performance. Goals were better LCs and the establishment of a solid intellectual property basis for Roche's emerging liquid crystal material business. Apart from TN-licensing Roche became a leading LC-material manufacturer.

### Progress towards increased information content of LCDs

Important goals from the beginnings were improved optical performance and increased information content of LCDs. To achieve these goals, the development of dedicated LC-materials, new electro-optical effects and new display addressing schemes was crucial. Moreover, efficient backlighting, polarization recovering reflectors, color filters, optical retarders and wide-view films had to be developed and integrated into LCDs.

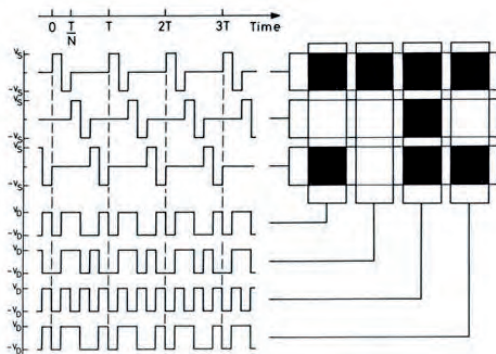


Fig.4: Time-multiplexed addressing scheme of the line and column electrodes of a TN-LCD (top). Time-multiplexed TN-LCD with 1200 pixels but only 96 connections (~1980).

Progress made in device physics and LC-materials enabled the development of medium information content TN-LCDs in the 1980s. The increase of information content broadened their applications from seven-segment digital watch displays to calculators, portable games, etc. Another step towards LCDs with increased information-content was the development of time-multiplexed addressing of matrix electrode arrays by Kawakami and Alt and Pleshko (Fig. 4). The development of more than 90° twisted nematic configurations with steeper electro-optical characteristics, i.e. super-twisted nematic (STN)-LCDs, by Scheffer and Nehring and others enabled – together with the development of infinitely steep and fast-responding STN-mixtures by the author and co-workers – a strong increase of the information content of LCDs (Figs. 5, 6). LCDs started to challenge the bulky cathode ray tube computer monitors. However, limited con-

trast, colored off-states, not yet developed wide-view compensation films, and the inherently slow response times of STN-LCDs hampered the development of flat panel LCD television. Parallel to the development of thin-film transistor (TFT)-addressing of the TN-LCDs the search started for planar- and vertically aligned electro-optical LC-configurations with broader fields of views.

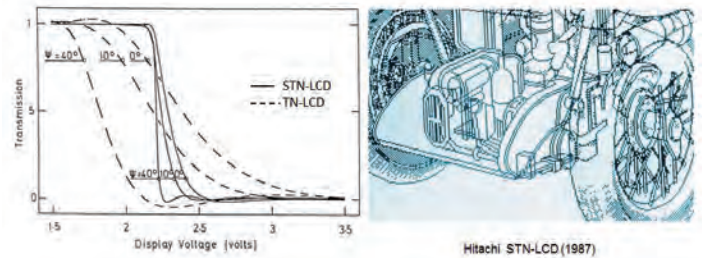


Fig.5: Voltage and viewing angle dependence  $\Psi(V)$  of a TN-LCD and an early STN-LCD (1987).

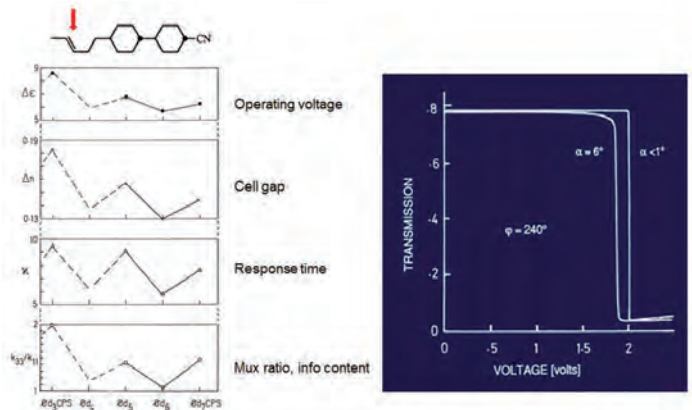


Fig.6: Left: Odd-even effects in alkenyl liquid crystals versus double-bond position in the side-chain. Dielectric anisotropy  $\Delta\epsilon$ , birefringence  $\Delta n$ , visco-elastic ratio  $\kappa$  and splay/bend elastic constant ratio  $k_{33}/k_{11}$ . Right: alkenyl LC-mixtures enabling infinitely steep transmission-voltage characteristics of STN-LCDs (1991).

Already in 1974 Brody et al had realized the compatibility of the TN-LCD with thin-film-transistor (TFT)-addressing. They made the first TFT-addressed TN-LCD with the driving TFTs integrated onto the LCD glass substrate. Pulse-sequential TFT-addressing of TN-pixels enabled the transfer of the multiplexing problem into the driving electronics. This resolved the contradicting STN-requirements between high-information content, gray scale reproduction and fast response (Fig. 7). However, it took R&D more than another twenty years until TFT-addressed TN-LCDs had reached a stage in the 1990s justifying large scale investment in TFT-LCD manufacturing.

### Information content, short response and LC-material properties

The introduction of double-bonds into specific side-chain positions of liquid crystal molecules by Schadt and co-workers in 1987 led to numerous important commercial liquid crystal families and provided new scientific and technological insights into correlations between molecular structural elements, LC-material properties and display performance. Alkenyl LCs enabled – for the first time – efficient molecular tuning of virtually all LC-material properties via shifting C=C double-bonds in flexible hydrocarbon side-chain(s) from odd to even positions (Fig. 6). This enables for instance LC-mixtures with broad nematic temperature range and large bend/spay elastic constant ratios  $k_{33}/k_{11}$  for infinitely steep



Fig.7: Thin-film transistor (TFT)-addressing scheme and microphotograph of the R, G, B color filters pixels of an early television TFT-TN-LCD.

electro-optical LCD-characteristics and maximum multiplexability (Fig. 6). The author attributed the odd-even effects to the formation of molecular nano-ensembles whose shapes depend on the position  $d_x$  of C=C double-bonds in the side-chain (Fig. 6). Because small viscoelastic ratios  $\gamma_1/\kappa$  are prerequisite for fast LCD-response, optimization of this parameter without sacrificing temperature range is crucial for instance for television (TV)-LCDs. This became possible by combining non-polar, short-chain alkenyls with LCs comprising long rigid cores.

#### Non-mechanical surface alignment of liquid crystals by optical means

Uniaxiality, anisotropic surface anchoring forces and the generation bias tilt angles between the long axes of liquid crystal molecules (LC-director) and the display substrates characterize field-effect LCDs. Prior to photo-alignment by side-chain photo-polymers, LCD-substrates were aligned by mechanically buffed polyimide films. Since buffing is a macroscopic process microscopic alignment patterning cannot be achieved. Moreover, brushing generates dust, alignment defects and reduces LCD contrast. Despite the relative simplicity of mechanical brushing, its surface interactions are not really understood even today; brushing is more of a craft than a science. The origin of the complex anisotropic interaction forces causing liquid crystal molecules to align on surfaces has intrigued the author since his early twisted nematic (TN)-experiments. In his search for correlations between molecular structures, LC-material properties and LCD performance, he suspected that – apart from the rather well understood topological and steric interactions – anisotropic Van der Waals interactions to play a crucial role. However, apart from perfect vertical LC-alignment via steric interactions, it was unknown whether and how stable LC-alignment could be realized by molecular means. In the late 1980s Schadt started several new R&D projects with his liquid crystal research team at Roche. One was the collaboration with the research group of the late Professor Titov, NIOPIK, Moscow, on fast responding ferroelectric electro-optical effects and first attempts towards photo-alignment. Two different types of LC-photo-alignment materials were known, namely azobenzenes and polyvinyl cinnamate (PVMC). The aligning mechanism of azobenzenes due to a conformation change upon exposure to linear polarized light was well understood, whereas the mechanism causing LC-alignment on PVMC was unknown.

#### Photo-alignment and alignment patterning by side-chain photo-polymers

Although the stability of LCDs that were photo-aligned by PVMC was poor, the author attempted to elucidate the underlying LC-aligning-mechanism and developed an opto-molecular LC-alignment model. This linear photo-polymerization (LPP)-model is based on the idea that optical excitation of  $\pi$ -electrons in double-bonds of nearest neighbor cinnamoyl moieties in a pre-polymer film must be (3D) direction-dependent. Therefore, the probability for 2+2 cycloaddition of C=C double bonds is largest for bonds lying parallel to the plane defined by the electric field vector  $E$  of incident polarized UV-light and its propagation direction (Fig. 8). As a consequence anisotropic molecular distributions result which generate sufficiently strong anisotropic Van der Waals interaction to align adjacent LC-molecules. Moreover, 2+2 cycloaddition simultaneously stabilizes the film enabling patterning of the LC-alignment along different directions via a single photo-mask. However, the poor performance of PVMC made it questionable whether side-chain photo-polymers with sufficient light-stability could be developed. Moreover, LC-alignment on PVMC occurred – as with azobenzenes – *perpendicular* to the polarization direction of incident polarized UV-light. Due to this cylinder symmetry it was impossible to simultaneously achieve uniaxiality and bias tilt with PVMC. Four years later, the author and co-workers succeeded in developing the first side-chain photo-polymers which combined uniaxiality with non-cylinder symmetry under oblique polarized UV-exposure (Fig. 8). This paved the way for stable photo-alignment and multi-domain alignment patterning of all types of field-effects.

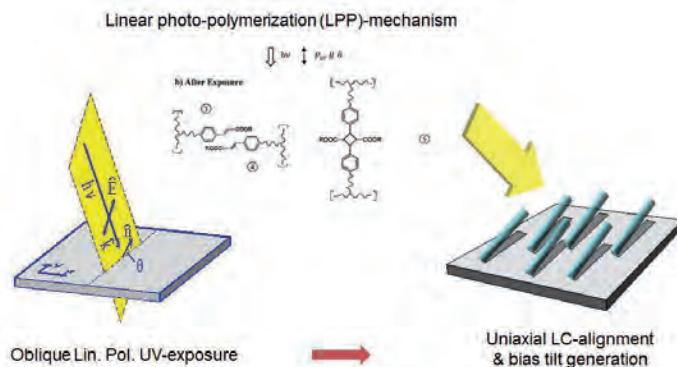


Fig.8: Molecular model of linear photo-polymerized (LPP) LC-alignment by polarized UV-light. Oblique polarized UV-exposure of LPP-substrate generates tilted, uniaxial LC-alignment.

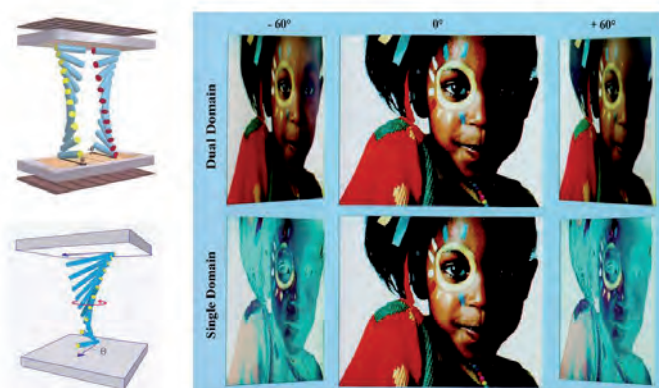


Fig.9: Single- and dual-domain photo-aligned TFT-addressed TN-LCD and corresponding nematic director configurations in the on-state; c.f. the much enhanced field of view of the dual domain configuration.

As a result, LCDs with broad fields of view (Fig. 9), shorter response times, ultra high resolution and improved brightness became possible. Fig. 10 shows the four-domain vertically aligned nematic (VAN)-configuration of a LPP-photo-aligned, television LCD.



Fig. 10: LPP-photo-aligned/patterned TFT-TV-LCD (Sharp, 2009) with partly switched four-domain MVAN-molecular configuration (insert).

### Photo-alignment/patterning of anisotropic liquid crystal polymer (LCP)-films

The LC-molecules in the sandwich configurations of an LCD are surface-aligned by two substrate boundaries; i.e. uniaxial aligning forces act on bottom and top of the LC-layer. The author wondered whether anisotropic surface interactions would not only align the LC-monomers in LCDs but also liquid crystal pre-polymer (LCP) films deposited on a single aligned substrate. However, in 1993 it was unknown how far the aligning information would extend into a pre-polymer LCP-film with its top surface exposed to air. Because liquid crystals were reported to vertically align at LC-air interfaces it was uncertain whether uniform LCP director configurations could be realized. Moreover, it was unknown whether photo-patterning of the alignment of adjacent LCP-pixels along different directions was possible. Director-deformation due to interfering elastic deformations at pixel-boundaries and thermal disorder were likely to occur. It was also questionable whether photo-patterned pre-polymer LC-configurations would survive subsequent polymerization without destruction of macroscopic LC-order. Despite these uncertainties the author and his co-workers started the development of photo-aligned liquid crystal polymer films on single substrates in the early 1990s. The goals were photo-aligned and photo-patterned optically anisotropic LCP thin-films with photographic resolution. The copy of surface alignment and its defect-free transfer into the bulk of adjacent LCP films proved feasible in the mid-1990s. Moreover, optical bias tilt generation enabled arbitrary alignment of the slow optical axes of the index ellipsoids of LCP films in space.

The optics is illustrated in Fig. 11. The two LPP-aligned and photo-patterned LCP pixels in Fig. 11 are photo-aligned by a 40 nm LPP-alignment film (not shown) on a transparent plastic substrate under  $90^\circ$  and  $45^\circ$  respectively. The respective LCP-directors (slow optical axes) copy the underlying alignment. Due to its optical retardation  $\Delta n d = \lambda/2$ , the right-hand pixel rotates incident linear polarized light P by  $\pi/2$  rendering it transmissive between crossed polarizers. The slow optical axis of the left pixel is parallel to P, therefore, its polarization state is not affected and it appears black (Fig. 11). LCP photo-alignment via digital photo-masks ena-

bles ultra-high resolution retarder images with grey scale reproduction (Fig. 11). Moreover, the technology enables numerous other chiral and achiral optical thin-films, such as photo-patterned retarders for 3D-LCDs, optical security elements, cholesteric band-pass filters, etc.

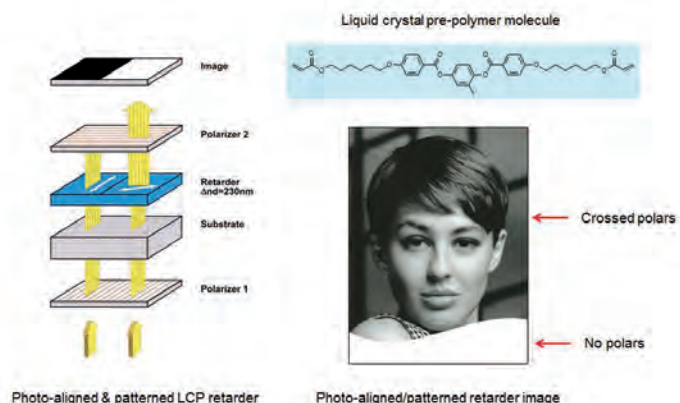


Fig. 11: Left: Photo-aligned and photo-patterned liquid crystal polymer (LCP)-retarder pixels (1  $\mu\text{m}$  thin). Right: Digitized LCP-retarder image between crossed polarizers (upper part) and no polarizers (bottom part). Top: Pre-polymer liquid crystal molecule (optical anisotropy  $\Delta n \sim 0.25$ ).

### Roche sells its liquid crystal business; foundation of Rolic

In 1994 Roche decided to focus its core business on life sciences, terminating or selling its non-pharmaceutical business activities, including its liquid crystal business. The entire nematic liquid crystal material patent portfolio of 64 LC-families, each granted in 10-12 countries, was sold to Merck KGaA, in 1996. Based on the strong intellectual property (IP) position on photo-aligned LCDs, optical thin-films and materials which the author had developed with his interdisciplinary research team since the late 1980s, the spin-off company Rolic (Roche liquid crystals) was founded in 1994. Forty-four basic photo-alignment patents on devices and new materials, each filed in 10-12 countries, were transferred from Roche into the new company. Analogous to the TN-licensing business of Roche 30 years before, the photo-alignment portfolio of Rolic provided the basis for its licensing and technology transfer business. The author acted as its first CEO. He and his co-workers continued R&D on photo-alignment, started licensing the new technologies and collaborating with LCD manufacturers and optical film-companies world-wide. In line with Roche's exit strategy, Rolic was sold to a Swiss investor end of 1996.

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**Martin Schadt** is one of the pioneers of modern LCD displays, honoured among others by the European Inventor Award for Lifetime Achievement. His impressive biography can be found under [http://de.wikipedia.org/wiki/Martin\\_Schadt](http://de.wikipedia.org/wiki/Martin_Schadt).