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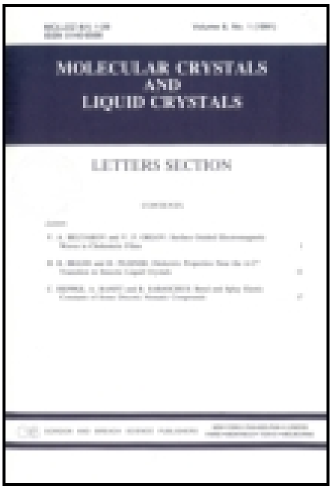

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Photo Alignment and Patterning of Liquid Crystal Polymer Films and Optical Devices by Side-Chain Photopolymers

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Prerequisite for virtually all nematic field-effects on which liquid crystal displays (LCDs) are based is stable, uniaxial surface alignment with defined bias tilt angle between the long liquid crystal (LC) axes and their display boundaries. Since the invention of the TN-LCD [1] in 1970 until recently this was achieved by confining liquid crystals between mechanically brushed surfaces [2–4]. We have first shown in the 1990s that, non-mechanical, uniaxial, tilted and patterned LC-alignment is possible by anisotropic Van der Waals surface interactions [5], namely by directional polymerization of photo-sensitive side-chain polymers films [5, 6] by linear polarized UV light. The LPP model is reviewed and its applications enabling high resolution multi-domain liquid crystal displays operated in transmission and reflection are discussed. Examples are given for optical retarders integrated into LCDs, anisotropic liquid crystal polymer (LCP)-films for 3D imaging, interference color filters, wide-view films and anisotropic polymer surface topologies.

Keywords Photo-alignment of liquid crystal devices; liquid crystal displays (LCDs); optical patterning of thin-film polymer liquid crystal films; multi-domain LCDs; integrated liquid crystal polymer retarders

The Beginnings of Photo-Alignment of Liquid Crystals

Uniaxiality, surface anchoring energy and bias tilt angle between nematic LC-director and display substrate(s) define the alignment boundaries of field-effect LCDs [7]. Prior to photo-alignment, LCD-substrates were mainly aligned by mechanically buffed polyimide films [8–10]. Since buffing is a macroscopic process, patterned LCD-alignment in arbitrary azimuthal directions and/or with different bias tilt angles is not possible. Moreover, brushing generates dust, electric charges and alignment defects which are detrimental for display manufacturing and high-quality LCD performance. Despite the simplicity of mechanical brushing, its surface interactions are still not really understood; brushing is more of a craft than a science. The origin of the complex anisotropic forces causing liquid crystal molecules to align on surfaces has intrigued the author since his research on the twisted nematic (TN)-effect [1]. The finding that some molecular functional groups and molecular LC-configurations align well, whereas others—such as supertwisted nematic [11, 12], ferroelectric [13, 14] and phase-change cholesteric configurations [15]—are delicate to align, often proved frustrating. In his search for correlations between molecular

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*Address correspondence to Martin Schadt, MS High-Tech Consulting, CH-4411 Seltisberg, Switzerland. E-mail: martin.schadt@bluewin.ch structural elements, their influence on macroscopic LC-order and electro-optical LCD performance, and from the few observations reported for brushed main-chain polymer films [8, 16], he suspected that—apart from the rather well understood topological [17, 18] and steric LC-interactions—anisotropic Van der Waals interactions play an important role in LC-alignment. It was known that 90° vertical surface alignment induced by steric LC-interactions can be achieved on surfaces coated with fatty acids or siloxanes [19]. From the steric switching experiments of the nematic director in free standing LC-films with linear polarized light of Ichimura *et al.* [20] it was also known that cis-trans isomerization of azobenzene dopants changes the direction of LC-alignment. Gibbons *et al.* [21] used this effect for realizing re-writable optical LC-storage devices. However, and despite first experiments made in collaboration between the author and NIOPIK with polyvinyl cinnamate (PVMC) [10], it was unknown in early 1990 whether and how stable surface alignment of molecular liquid crystal configurations with defined bias tilt could be achieved by molecular/optical means; the mechanism causing LC-alignment on (unstable) PVMC films was mysterious.

Optical Alignment of Liquid Crystals by Directionally Photo-Sensitive Side-Chain Polymer Films

Although the optical and thermal stability of PVMC-aligned cells were poor [6], the author developed a quantitative molecular LC-alignment model [6, 10]. The model is based on the idea that photo-chemical excitation of double-bonded π-electrons of cinnamoyl moieties of adjacent molecules must be *directional* dependent; i.e. the cross-linking probability is largest for bonds parallel to the plane defined by the electric field vector E and the propagation direction of incident polarized UV-light [6]. As a result linear polarized excitation results in directional 2+2 cyloaddition of pre-polymer pairs generating photo-isomers whose distribution is also directional dependent. As a result initially isotropic distributed pre-polymers are converted into an anisotropic distribution of photo-isomers and also anisotropically distributed non-crosslinked pre-polymer molecules [6]. The anisotropic molecular LPP-distribution exhibits anisotropic Van der Waals interactions enabling adjacent LC-molecules to uniaxially align [6] (Fig. 1a).

Last but not least, simultaneous *fixation* of the anisotropic molecular surface distribution occurs via increase of the glass transition temperature of the LPP-film due to UV-cross-linking. Photo-alignment experiments confirmed the linear photo-polymerization (LPP)-model and showed that the double-bonds of cinnamoyl moieties in PVMC indeed undergo directional cross-linking under linear polarized UV-light causing uniaxial LC-alignment by anisotropic Van der Waals interactions [6, 10] (Fig. 1a). Moreover, it was found that 2+2 cyloaddition indeed stabilizes LC-alignment, thus enabling alignment patterning by sequential substrate exposure through photo- masks [6] (Fig. 1b). However, thermal and light stability as well as surface LC-anchoring of PVMC proved to be far from sufficient for practical use and it was questionable whether stable directional photo-sensitive side-chain polymers could be developed. Moreover, LC-alignment on PVMC occurred *perpendicular* to the polarization direction of incident polarized UV-light [6]; i.e. in the same direction as caused by the cis-trans isomerization of azobenzenes [20–23]. Due to this cylinder symmetry it was impossible to simultaneously generate uniaxiality *and* bias tilt with PVMC [6]. At this stage the collaboration with NIOPIK terminated [10]. Even though the odds were against the conviction of the author that optically stable photo-polymers with *non-cylinder*

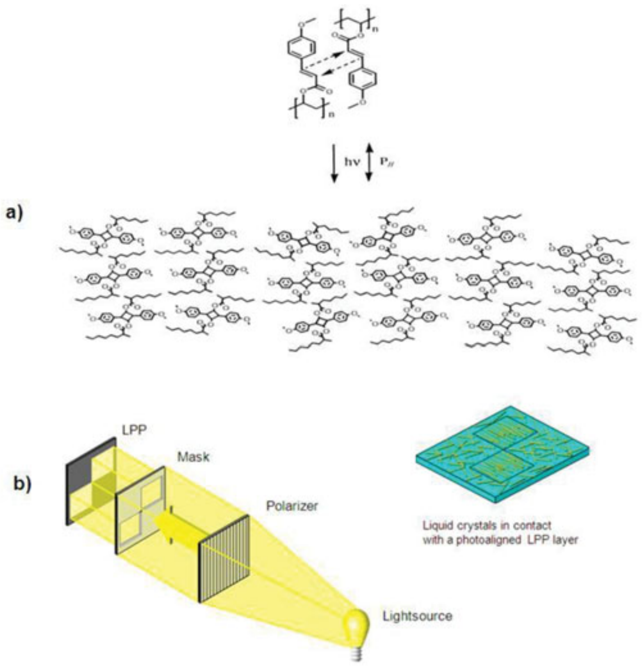

Figure 1. a) Photo-alignment of LCs by directional side-chain photo-polymers (LPPs): Directional cross-linking under linear polarized UV-light of double-bonds in PVMC generating anisotropic Van der Waals surface-interactions and uniaxial LC-alignment. b) Photo-patterning of LC-alignment through photo-mask.

symmetry are feasible, he continued the search for stable, non-cylinder symmetric photo-aligning polymers with his co-workers at Roche. Four years later, they discovered the first side-chain photo-polymer material combining non-cylinder symmetry and uniaxiality [5] upon oblique polarized UV-exposure (Fig. 2a).

This paved the way for stable photo-alignment and alignment pattering of field-effect LCDs enabling multi-domain LCDs with markedly improved fields of view [5, 24], higher brightness and much improved optical resolution as well as shorter response times compared with fringe-field multi-domain generation [9]. Moreover, novel liquid crystal polymer thin-films with large optical anisotropy became feasible [7, 25]. The findings justified further development of side-chain photo-polymers with the goal of covering the full range of bias tilt angles on which field-effect LCD-modes are based [7, 10, 17–19]; i.e. $00 \leq \Theta < 90^\circ$. Figure 2b schematically depicts different molecular LC-alignment functions of a side-chain photo co-polymer [26].

LPP Photo-Alignment Multi-Domain LCDs

LPP-photo-alignment enables generating multi-domain field-effect LCDs with broad fields of view. This was first demonstrated by Schadt and co-workers in 1996 with a photo-aligned four-domain TN-LCD [5]. Figure 3a schematically depicts the LC-director configuration of a partially switched picture element (pixel) of such a display. The four reverse twist domains in the sub-pixels—each rotated by $\pi/2$—result from different bias tilt angle directions at the two substrates; where the different tilt directions were realized by sequential UV-exposure

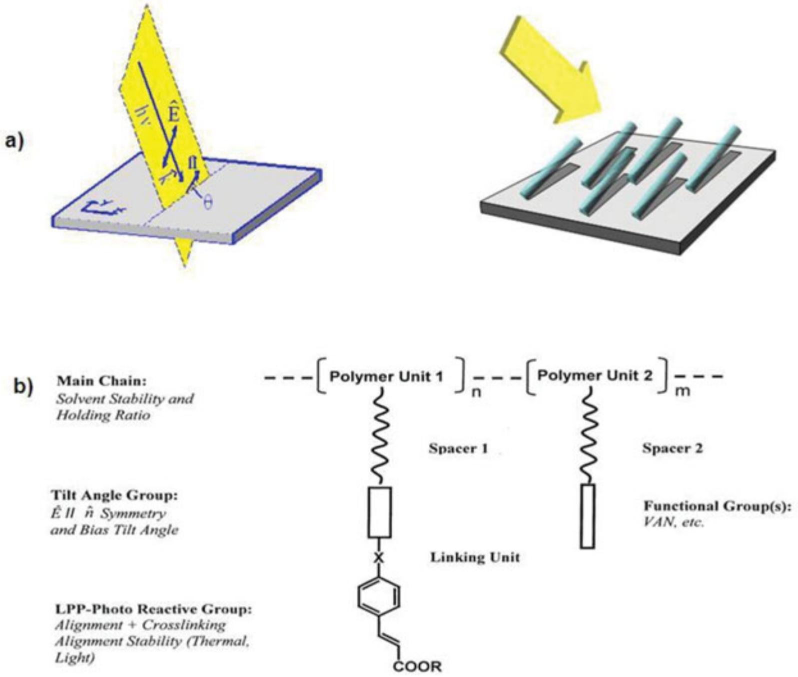

Figure 2. a) Non-cylinder symmetry and uniaxiality of LPP-photo-aligned long molecular LC-axes under oblique polarized UV-exposure. b) Generic molecular LC-aligning functions of directional photo-aligning side-chain co-polymers.

of the substrates under different angles of incident polarized UV-light through a photomask [5]. Figure 3b shows a microphotograph of the angular dependence of four sub-pixels whose different contrasts average in the eyes of the viewer [5]. Figure 3c shows an actual photo-aligned dual-domain TFT-addressed TN-LCD with its considerably improved field of view compared with the conventional single-domain counterpart at the bottom of the Figure [27].

In the late 1990s multi-domain LCD-alignment, thin-film transistor (TFT)-development and LC-material progress opened up the possibility to base TFT-LCD-manufacturing not only on the twisted nematic effect [1] and in-plane switching [28] but also on vertically aligned nematic (VAN) configurations whose single-domain version [29, 30] was known since 1971. However, poor viewing properties, fluctuations of contrast and color caused by birefringence effects due to inadequate cell manufacturing and negative dielectric anisotropic liquid crystals with insufficient material properties prevented their commercialization for more than 30 years [7, 10]. In the late 1990s progress enabled increasingly large size TFT-TN-LCDs for computer monitors and first LCD-TVs which spurred the demand for larger size TFT-LCDs [10]. This required increased off-state contrast and broader fields of view beyond those of optical film-compensated TN-LCDs [31]. The realization of multi-domain vertical aligned (MVA) LC-configurations in 1998 by LPP-photo-alignment [24] and independently in the same year by lateral fringe-fields [9] enabled the development and manufacturing of TFT-addressed MVAN-LCDs. Due to virtually optical uniaxiality of the slightly off-vertically aligned LC-configuration of MVAN-LCDs in their off-state ($\Theta = 89°$), a large off- state contrast results [7, 24]. Figure 4a depicts the

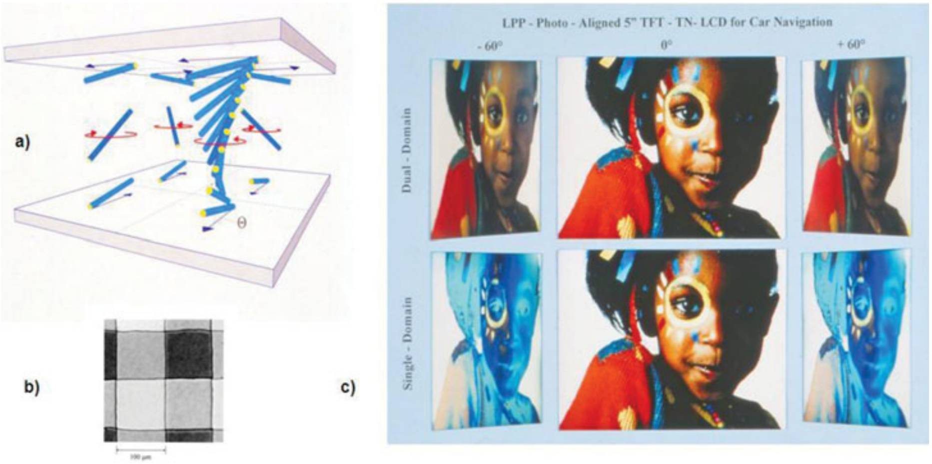

Figure 3. a) LC-director configuration of a partially switched four-domain TN-LCD pixel. b) Microphotograph of its four sub-pixels. c) Fields of view of two-domain photo-aligned/patterned TFT-addressed TN-LCD (top) and conventional single-domain counterpart (bottom).

slightly off-vertical LC-director configuration of a partially switched LPP-photo-aligned four-domain VAN-LCD developed by Seiberle and Schadt [24] in 1998.

Figure 4b depicts the virtually angular independence of the 4-domain VAN-LCD whose off-axis birefringence for oblique angles of view in the off-state is compensated by a photo-aligned, negative birefringent biaxial cholesteric liqid crystal polymer film. Also in 1998 year Takeda *et al.* at [9] published a multi-domain MVAN-LCD based on a completely different approach, namely on fringe-field electrode patterning. Fringe-field

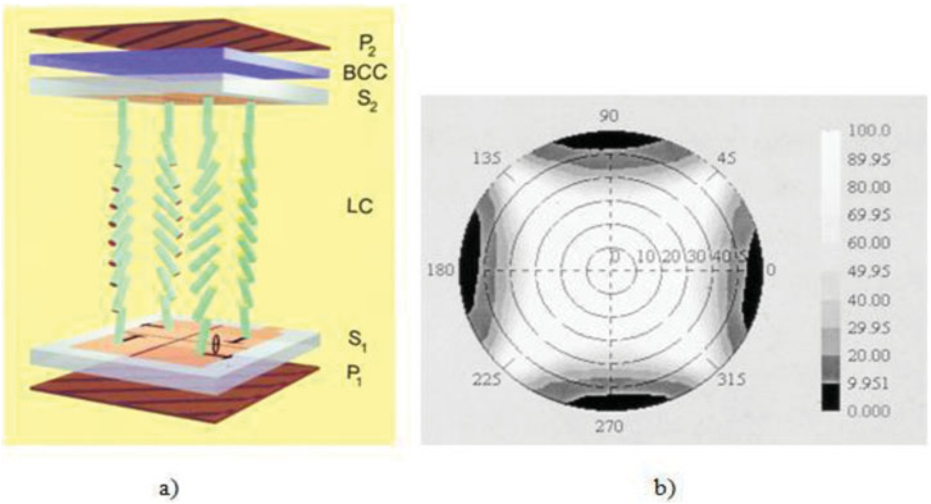

Figure 4. a) Partially switched (20%), slightly off-vertical LC-director configuration of an LPP-photo- aligned four-domain VAN-LCD. b) Azimuthal viewing angle dependence of 4-domain VAN-LCD whose off-axis birefringence at oblique angles of view in its off-state is compensated by a biaxial negative birefringence LCP-optical wide-view film.

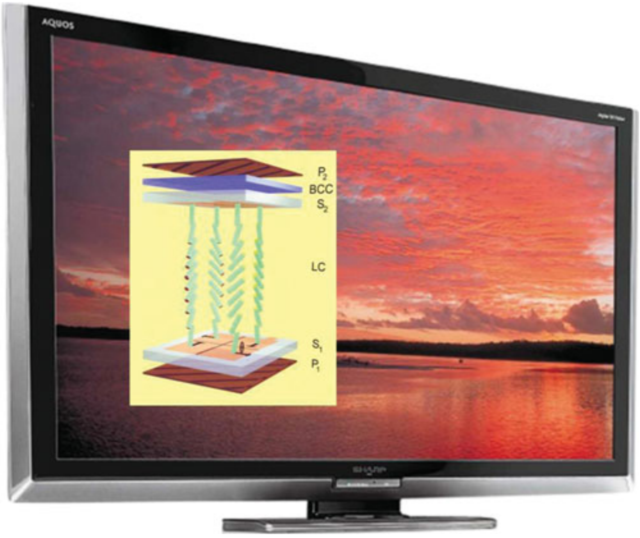

Figure 5. LPP-photo-aligned, 40″ Sharp TFT-MVAN-LCD TV; partly switched 4-domain MVAN director configuration (insert).

patterns add complexity to the electrode structure of TFT-substrates; they induce additional LC-dislocations, reduce LCD brightness and increase response time [7, 10]. However, since electrode patterning was a continuation of established manufacturing processing, fringe-field patterned TFT-MVAN-LCDs for large size television LCDs were introduced first by Sharp, Samsung and others in 2000. In order to reduce the power consumption and the response time of TFT-LCDs and simultaneously increase display brightness, Sharp changed in 2009 to side-chain polymer photo-alignment in its gen 10 Sakurai plant which they renamed UV2A technology. Figure 5 shows an LPP-photo-aligned, 40” Sharp TFT-MVAN TV; the insert depicts a partly switched, LPP-photo-aligned 4-domain MVAN director configuration [24].

Photo-Alignment/Patterning of Liquid Crystal Polymers (LCP) on Single Substrates

The LC-molecules in field-effect liquid crystal displays are surface-aligned by *two* substrates; i.e. they are confined in a sandwich configuration which exerts uniaxial aligning forces to bottom *and* top adjacent LC-layer (Fig. 3a). During his research on photo-alignment of LCDs, the author wondered whether and to what extent anisotropic photo-aligning forces could be transferred into the bulk of a liquid crystalline film deposited on a *single* aligned substrate. Moreover, if not only monomer LCs but also liquid crystal polymers (LCPs) could be photo-aligned on a single substrate without optical defects he envisaged interesting liquid crystal polymer configurations and anisotropic optical thin-film devices [10, 25]. However, in 1995 it was unknown how far the aligning information on a single aligned surface would extend into a pre-polymer LCP-film whose top surface is exposed to air. It was also unknown whether adjacent photo-patterned pixels exhibiting different aligning directions would maintain their respective surface alignment information in the bulk of the LCP-film. Director coalescence due to interfering elastic deformations at

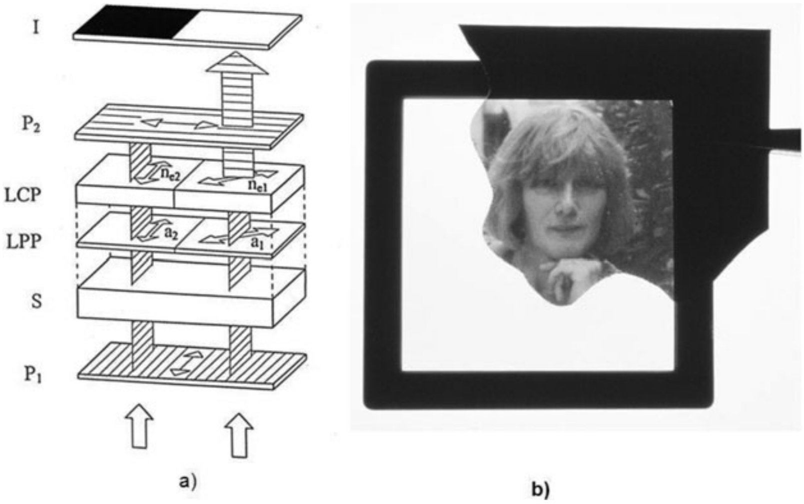

Figure 6. a) Photo-aligned/patterned LCP-retarder on substrate S between crossed polarizers. b) LCP- retarder image visible only between crossed polarizers.

the pixel- boundaries [32] and thermal disorder were likely to occur. Moreover, it was questionable whether photo-patterned pre-polymer configurations would survive subsequent polymerization without destruction of the macroscopic order of director configurations causing optical defects. Based on the above photo-alignment technology, the author started the development of photo-alignment of liquid crystal polymer films on single substrates with co-workers in the early 1990s [7, 10]. The target was photo-alignment and optical patterning of liquid crystal polymers on single substrates of glass, plastic, metal, silicon, paper, etc. Copying the molecular surface alignment information (uniaxiality and bias tilt) and transferring it into the bulk of adjacent pre-polymer LCP films via long range LC-order was first achieved in the mid 1990s [33, 34]. Fixation of the pre-polymer configurations by subsequent polymerization at room temperature by unpolarized UV-light without optical defects proved feasible for LCP film thicknesses up to $\sim$10 μm. Moreover, due to optical bias tilt generation the direction of the slow optical axes of LCP films enabled arbitrarily 3D-director alignment in space [34]. The concept is illustrated by the following examples.

The two LPP-aligned and photo-patterned LCP pixels in Fig. 6a schematically depict the operating principle of a 1.2 μm thin photo-aligned/patterned half-wave LCP-retarder (birefringence $\Delta n = 0.22$) on a transparent substrate S between crossed polarizers [33]. The LCP-director in the right pixel defines the slow optical retarder axis ne_1 of the birefringence ellipsoid. The direction of n_{e1} copies the underlying photo-aligning direction a_1 of the photo-patterned, 40 nm thin photo-alignment film.

The angle between a_2 and a_1 is 45°. Therefore, incident linear polarized light P_1 rotates by $\pi/2$ in the right pixel rendering it transmissive. Since the alignment direction a_2 and the slow optical axis n_{e2} in the left pixel are parallel to P_1, the polarization state of the left pixel is not affected and appears black between crossed polarizers (Fig. 6a). By combining the optical LCP-retarder patterning concept of Fig. 6a with photo-alignment via digital photo-masks, not only high resolution retarder images with grey scale reproduction became feasible but also photo-patterned retarders for 3D-LCDs [25, 33]. Figure 6b shows an early example of a photo-patterned LCP-retarder image made 1995 between partly crossed polarizers [25]. Since optical retarder images are only visible in polarized light,

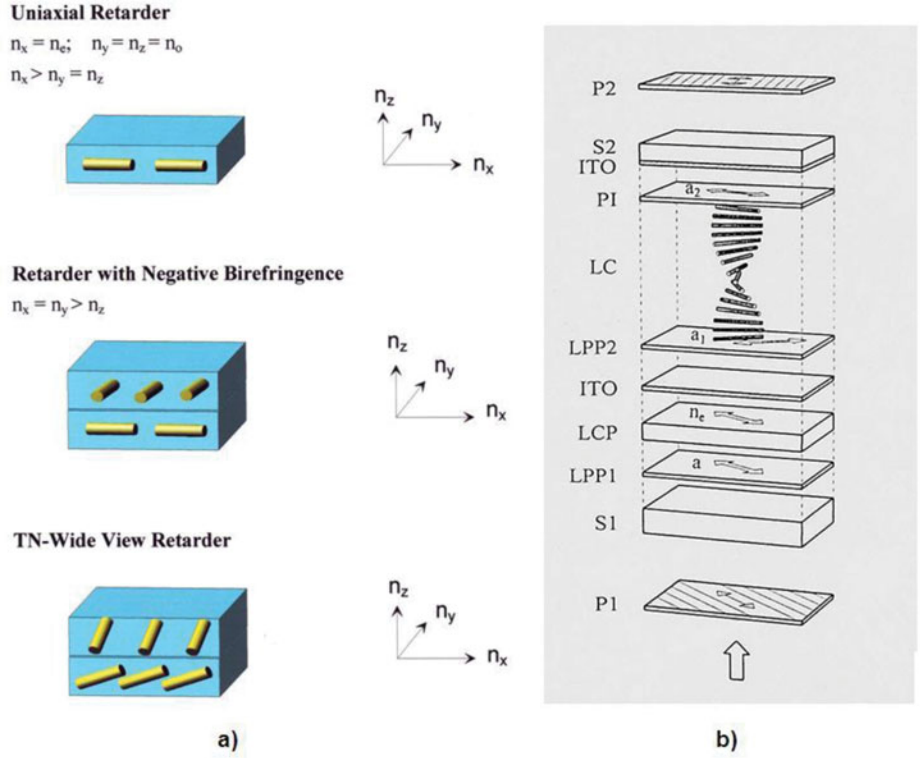

Figure 7. a) Photo-aligned LCP-retarder integrated onto the substrate of a photo-aligned LCD. b) Black-white supertwisted nematic (STN)-LCD with integrated color compensating a-plate LCP-retarder.

photo-aligned/patterned LCP-films enable transmissive and reflective optical security elements [25].

Due to the large optical anisotropy of LCP-molecules, alignment and photo-patterning of LCP films enables very thin, complex, chiral and non-chiral optical polymer retarder films and LCP film-stacks with photographic resolution, patterned dichroic guest-host polarizers, loss-free polarization interference filters for projection optics, etc. [25]. Moreover, due to LPP bias tilt generation the direction of the slow optical axes of LCP films can be arbitrarily photo-aligned in space and different films can be stacked [33, 34]. Examples for different LCP director configurations in optical retarders are depicted in Fig. 7a. Fig. 7b shows the first photo-aligned a-plate LCP- retarder directly integrated onto the substrate of a photo-aligned LCD [33]. The retarder converts the interference colors of a super-twisted nematic (STN)-LCD into a black-white STN-LCD.

Last but not least, the above optical generation of anisotropic surface interactions on single substrates and their transfer into adjacent liquid crystalline materials developed by the author and co-workers also enables anisotropic phase-separation and anisotropic surface diffusion in binary liquid crystalline mixtures consisting of monomer and cross-linkable pre-polymer components. In 2001 Ibn-Elhaj and Schadt have shown that anisotropic 3D phase-separation can optically be induced in films of liquid crystal mixtures coated on uniaxial aligned/patterned surfaces. In principle monomer corrugation (MC)-mixtures consist of a monomer liquid crystal (LC) and a liquid crystal pre-polymer (LCP), where only the latter is photo-cross-linkable [35]. After film-coating, directional phase-separation is induced

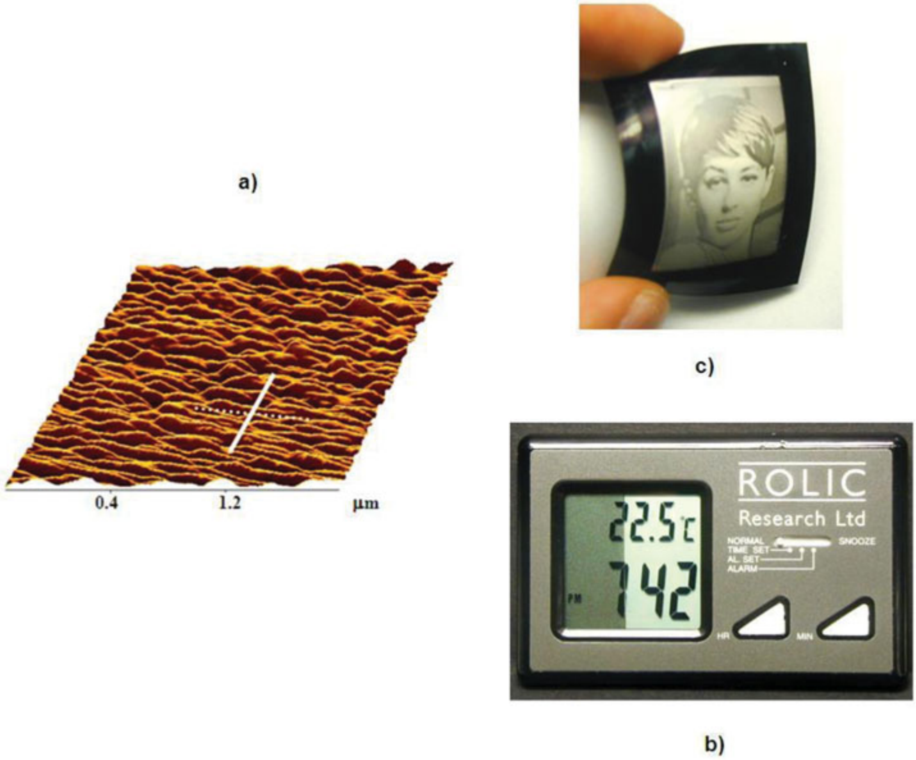

Figure 8. a) AFM-profile of a uniaxial aligned nano-corrugated LCP surface topology. b) Reflective TN-LCD clock whose conventional diffuse reflector is replaced by a high-gain metalized diffuse directional MC-reflector (right). c) High-resolution directional diffuse MC-reflector image on plastic substrate.

in the MC-mixture by cross-linking its LCP- component with flush UV-light. Subsequent removal of the (liquid) LC-component leaves uniaxial aligned nano- and micro-corrugations in the remaining cross-linked solid LCP-film. The AFM profile in Fig. 8a shows a uniaxial aligned nano-corrugated LCP surface topology, exhibiting elongated grooves aligned parallel to the underlying LPP-photo-alignment direction of the substrate [35]. Photo-aligned and patterned nano- and micro-topologies on substrates enable interesting optical thin-film devices, such as efficient directional diffuse broad-band reflectors which preserve polarization, high resolution directional diffuse reflectors, diffractive polymer film topologies, uniaxial polymer nano-topologies enabling liquid crystal alignment via minimizing the elastic deformation energy of adjacent LC-films [12, 35], etc.

The photograph in Fig. 8b shows a digital clock with a TN-LCD whose conventional diffuse reflector (right) is replaced by a metalized diffuse directional MC-reflector which markedly improves brightness [35]. Fig. 8c shows a photo-aligned and photo-patterned high-resolution directional diffuse MC-reflector image on a plastic substrate [35].

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