

CHEMISTRY, PHYSICS AND TECHNOLOGY FOR NEW LIQUID CRYSTAL DISPLAYS

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Abstract

Polymerization induced diffusion has been successfully applied to create new display components. Based on this principle a new technique to produce polymer covered liquid crystal layers on a single substrate, called photo-enforced stratification, allows cost-effective production of ultra-thin LCDs. The two-step photopolymerization-induced phase separation of a liquid crystal and a polymer precursor can be performed on a variety of substrates and provides freedom in display design.

1. Introduction

Polymerization induced diffusion processes in liquid crystal (LC) systems has proven to be a very useful tool to create a variety of optical elements that can be successfully applied in liquid crystal displays. Some examples are the formation of wideband reflective polarizers based on cholesteric networks [1], cholesteric polarizers with integrated retardation to transmit linearly polarized light without the need of additional quarter wave plates [2] and polarization sensitive diffractive filters [3]. Polymerization induced diffusion can also be applied to induce phase separation of an LC blend from an in-situ formed polymer network into well-controlled layers. This technique, called photo-enforced stratification (PES), may be used to build up an LCD on a single substrate by stacking the various layers on top of each other. The key process that enables layer stacking is the formation of a thin polymer covered LC layer. It comprises a two-step photopolymerization-induced phase separation of an LC blend and a polymer precursor. It can be carried out on a variety of substrates and provides freedom in display design as well in production methodology. The display

thickness of the resulting devices, referred to as stratified LCDs or PES-LCDs, is dominated by one substrate instead of two, hence gives ultra-thin and potentially real flexible displays.

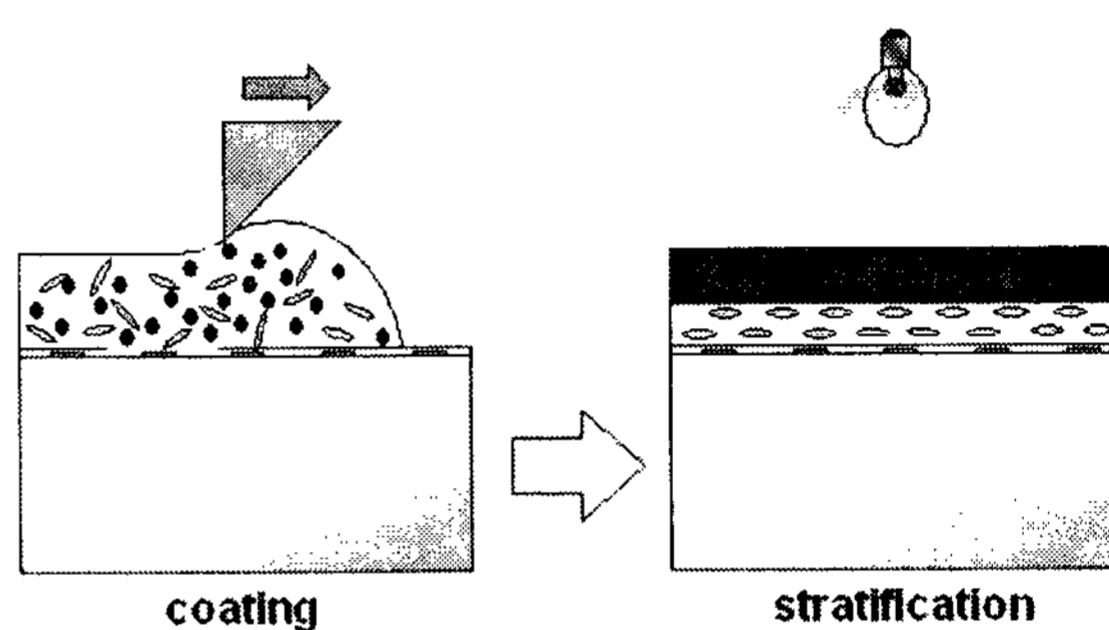


Figure 1. Schematic representation of the stratification process. Two parallel layers are formed from a coated film by photopolymerization-induced phase separation. The LC layer at the bottom can be switched by (in-plane) electrical fields. On top of the polymer cover which provides mechanical stability other functional layers (e.g. polariser, reflector) can be stacked.

2. Principle

PES-LCDs are formed by a directionally controlled photopolymerization-induced phase separation of a homogeneous mixture of an LC and a polymer-forming material. Phase separation in liquid crystal systems induced by polymerization has been utilized to produce PDLCs [4-6] and other electro-optical shutters of complex geometries [7-11]. Normally these processes are carried out in glass or plastic cell configurations where interfacial properties may enhance the formation of layers at the predestined

surfaces [9,10]. Directionality with respect to polymerization induced diffusion can be achieved by using a UV intensity gradient over the layer thickness by adding a chromophore that absorbs in the same wavelength region as the photoinitiator [1,10,11].

We have realized the formation of phase separated LC and polymer layers by the photopolymerization of a thin film (tens of microns) coated on a single substrate. The processing sequence is illustrated in figure 1. Film-forming techniques such as the doctor blade technique or slot die coating that are known for fast coating of both small and large areas, can be used to apply the film. The film is subsequently exposed to UV light in an inert atmosphere. Due to the UV intensity gradient across the film the polymerization predominantly takes place near the film surface that is directed towards the UV source. This in turn induces a diffusion of monomers in the film in the upward direction and a concomitant diffusion of LC molecules in the reverse direction. At the moment of the phase separation, pure LC droplets start to grow at the bottom of the film. The polymerization conditions (e.g. intensity, temperature) have been chosen such that coalescence of the LC droplets can take place which results in the desired continuous LC layer with a hard polymer film on top.

3. Experimental

A reactive blend is made consisting 50 wt% E7 (set of cyanobiphenyls-Merck), 44.5 wt% isobornylmethacrylate, 5wt% stilbene dimethacrylate and 0.5 wt% benzildimethylketal (Irgacure 651-Ciba Geigy) as photoinitiator. This mixture is isotropic before polymerization. Isobornylmethacrylate combines high solubility and low viscosity before polymerization, high diffusion rates and controlled phase separation during polymerization and rigidity after polymerization. The stilbene dimethacrylate provides an intensity gradient over the film thickness for the wavelength region around 340 nm. This wavelength region is used to irradiate the film during the stratification step. The stilbene functionalized dimethacrylate monomer combines a high absorption of the desired wavelength (extinction coefficient at 340 nm is $25000 \text{ M}^{-1}\text{cm}^{-1}$) with the ability to provide crosslinks (figure 2a,b). It is found that providing crosslinks between the poly-(isobornylmethacrylate) chains further enhances the directionally controlled phase separation.

The reactive blend is applied as a thin film of about $20 \mu\text{m}$ onto a glass substrate that has been provided with electrodes and a polyimide orientation layer. In order to obtain a stable device that can withstand lateral forces, it is essential that the polymer topcoat and the substrate be mechanically coupled. This is realized by using a two-step UV exposure for the photo-enforced stratification. The wet film is exposed through a mask with high-intensity light of 400 nm. This wavelength is outside the absorption region of the stilbene dimethacrylate (figure 2b) and therefore there is no intensity gradient over the film thickness. Polymerization in the exposed areas results in the formation of polymer walls (figure 2c). Subsequently, the unexposed areas are cured by a flood exposure with UV light of 340 nm. At this wavelength the stilbene dimethacrylate exhibits

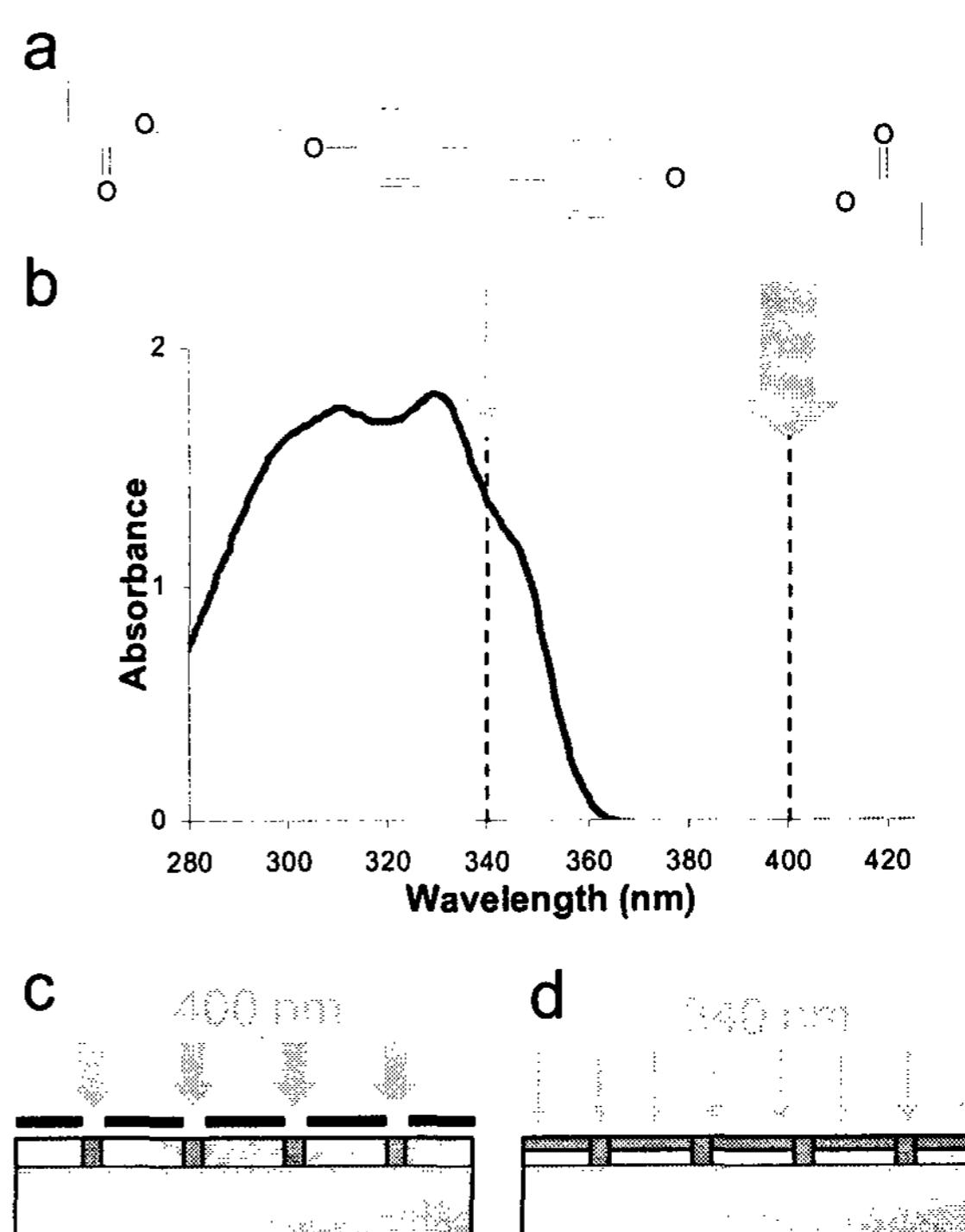


Figure 2. UV light distribution in the film. The structure of the stilbene-dimethacrylate which is used as absorber/crosslinker (a), its absorption spectrum and the wavelengths that are used in the two-step UV exposure (b). The polymer cover is mechanically coupled to the substrate by polymer walls. During the first step (c) the walls are formed and during the second step (d) the polymer cover is polymerised.

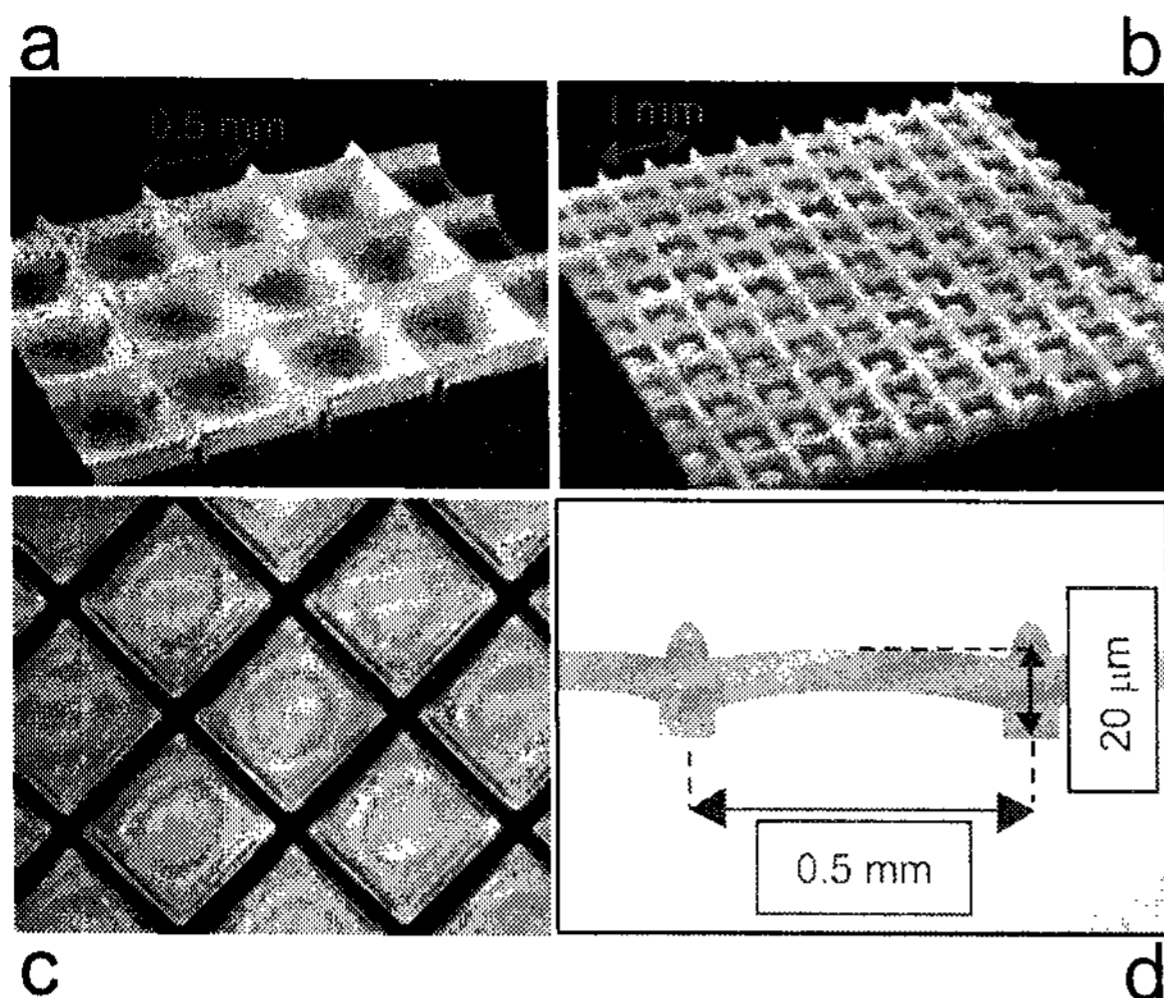


Figure 3. Shapes of the LC-filled boxes. Observed by interferometric microscopy after polymerisation of the walls (a) and after the stratification step (b). The pictures show a slight increase of the thickness of the film at the positions of the walls. A stratified LCD observed by polarisation microscopy (c) and a schematic cross-section (d). Note that the vertical dimensions are largely expanded with respect to the horizontal dimensions (a, b, d).

significant absorption. A much lower intensity is chosen to slow down the polymer network formation which gives the materials time to stratify in the vertical direction (figure 2d). The whole process finally leads to the formation of polymer boxes filled with pure LC. The boxes consist of polymer walls that have been formed during the first phase separation step and the polymer cover that has been formed at the second phase separation step, i.e. the stratification step. In the examples shown here the boxes are of the order of $0.5 \times 0.5 \text{ mm}^2$ wide and $10 \text{ }\mu\text{m}$ high, the walls are about $100 \text{ }\mu\text{m}$ wide and the polymer cover is about $10 \text{ }\mu\text{m}$ thick.

4. Results and Discussion

The surface profile of the film after the formation of the polymer walls is visualized in figure 3a. Due to the diffusion of monomeric material into the irradiated areas the polymer walls are a few microns higher than the rest of the film. The profile after the stratification step is shown in figure 3b. The LC was chosen to follow a planar director profile imposed by the alignment layer at the bottom. Figure 3c shows a

polarization microscope picture of a stratified LCD placed at 45° with respect to the crossed polarisers. The birefringence colors give information about the variations of the thickness of the LC domains. By analyzing figures 3b and 3c a schematic cross-section as shown in figure 3d can be deduced.

A photograph of a display produced by the two-step stratification process is shown in figure 4a. Interdigitated electrodes switch the LC by in-plane electrical fields[12,13]. Typical switching characteristics are shown in figure 4b and 4c. The whole display thickness is determined by the sum of the thickness of a single glass substrate, which can be as thin as 0.4 mm , and the thickness of the stratified layer, which is less than $30 \text{ }\mu\text{m}$ thick. When applied on a plastic substrate the display can even become thinner ($< 150 \text{ }\mu\text{m}$) and can be made flexible. To round off the whole concept, the stratified LCD can be coated with two 600 nm polariser films that are applied by shear-orientation of a sulphonated perylene dye doctor bladed from a water solution [14].

Besides the many advantages that can be ascribed to the PES-display technology also a number of limitations can be recognised. There will be some aperture reduction, leading to a somewhat lower front-of-screen brightness, because of the presence of the polymer walls. These walls therefore need to be placed at the inactive areas of the displays, e.g. at pixel edges. In addition, the contrast of the display remains still somewhat limited because the thickness and the shape of the LC areas have not been optimised yet. Preliminary experiments have shown that much flatter polymer-liquid crystal interfaces can be obtained by improved exposure conditions (collimation, intensity distribution) and materials (non-linear response to UV light by added inhibitor). Increasing the aperture by using smaller electrodes compared to the spacing between the electrodes (now 1:1) will also add to a better contrast ratio. Another issue that might play a role in the acceptance of this new technology might be the sensitivity towards mechanical forces exerted on the top layer. In order to improve the PES-displays on robustness they might be provided with a high-modulus top coating, for instance on top of the coated polariser layer. Even improved mechanical performance is obtained by a two-layer coating where the top layer has a high-modulus and is wear resistant and the lower layer is soft and able to absorb small point loads.

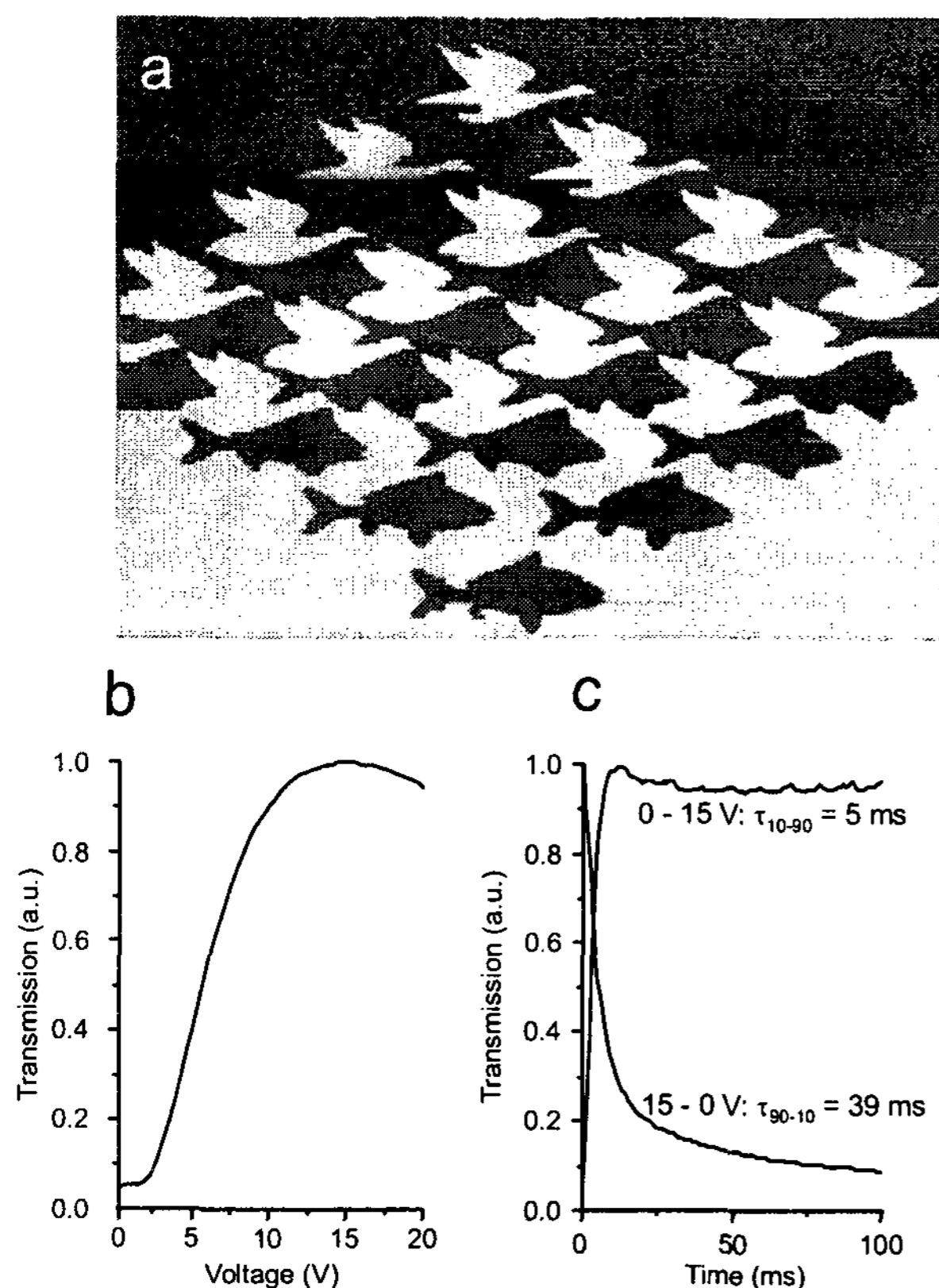


Figure 4. LCD produced by the PES-process. A photograph of a simple device (a). It is operated in the transmissive mode between two polarisers. The LC is switched by in-plane electrical fields. Transmission voltage (b) and switching rate (c) of the stratified LCD are measured in transmission. The LC (E7, Merck) is driven by in-plane switching. The electrode structure has a pitch of $18 \mu\text{m}$ and a spacing of $9 \mu\text{m}$.

5. Conclusions

In conclusion, this paper presents the new photo-enforced stratification technique (PES) to manufacture LC switches. Pixel sizes, optical and switching characteristics compatible with display and shutter applications were demonstrated using this technique. Based on a two-step photopolymerization induced separation of LC and polymer, PES radically departs from the standard LCD cell technology, enabling the production of liquid crystal displays in an extremely cost-effective way and paving the road for future 'paintable' displays.

6. References

- [1] Broer, D. J., Lub, J. & Mol, G. N. Wide-band reflective polarizers from cholesteric polymer networks with a pitch gradient. *Nature* 378, 467-469 (1995).
- [2] Broer, D. J., Mol, G. N., Van Haaren, J. A. M., Lub, J. & Huck, N., Spatially resonated excitation of a dichroic photoinitiator to form a deformed-helix cholesteric network. *Polymer Preprints (ACS, Div. of Polymer Chemistry)* 43, 526 (2002).
- [3] Broer, D. J., Lub, J., van Nostrum & C.F., Wienk, M.M. Photo-induced diffusion during the formation of liquid-crystalline networks. *Recent Res.Dev.Polym.Sci.* 2 (part 2), 313-324 (1998).
- [4] Vaz, N. A., Smith, G. W. & Montgomery, G. P. A light control film composed of liquid crystal droplets in a UV-curable polymer. *Mol. Cryst. Liq. Cryst.* 146, 1-15 (1987).
- [5] Doane, J. W., Vaz, N. S., Wu, B. G. & Zumer, S. Field controlled light scattering from nematic microdroplets. *Appl. Phys. Lett.* 48, 269-271 (1986).
- [6] Hirai, Y., Niiyama, S., Kumaim, H. & Gunjima, T. Phase diagram and phase separation in LC/prepolymer mixture. *Proc. SPIE-Int. Soc. Opt. Eng.* 1257, 2-8 (1990).
- [7] Bowley, C. C., Yuan, H. & Crawford, G. P. Morphology of holographically-formed polymer dispersed liquid crystals (H-PDLC). *Mol. Cryst. Liq. Cryst. Technol., Sect. A* 331, 2069-2076 (1999).
- [8] Yamada, N., Kohzaki, S., Funada, F. & Awane, K. Axially symmetric aligned microcell (ASM) mode: electro-optical characteristics or new display mode with excellent wide viewing angle. *J. Soc. Inf. Disp.* 3, 155-158 (1995).
- [9] Park, E.Y., Taheri, B., West, J.L. & Palffy-Muhoray, P. Surface Induced Polymer Walls and Islands Using a Polymer/Liquid Crystal Mixture. *SID 00 DIGEST* 782-785 (2000).
- [10] Vorflusev, V. & Kumar, S. Phase-separated composite films for liquid crystal displays. *Science* 283, 1903-1905 (1999).
- [11] Qian, T., Kim, J.-H., Kumar, S. & Taylor, P. L. Phase-separated composite films: Experiment and theory. *Phys. Rev. E* 61, 4007-4010 (2000).
- [12] Kiefer, R., Weber, B., Windscheid, F. & Baur, G. In-plane switching of Nematic Liquid Crystals. *Proc. 12th IDRC, Japan Display '92*, 547-550 (1992).
- [13] Oh-e, M., Ohta, M., Aratani, S. & Kondo, K. Principles and characteristics of electro-optical behaviour with in-plane switching mode. *Proc. Asia Display '95* 577-580 (1995).
- [14] Bobrov, Y. A. et al. Novel dichroic polarizing materials and approaches to large-area processing. *Mater. Res. Soc. Symp. Proc.* 508, 225-228 (1998)