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Photoinduced Surface Alignment for Optical Thin Films and Liquid Crystal Displays

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Abstract: Over the past few years, photoinduced surface alignment of liquid crystal layers has evolved into a mature technology which enables the production of high-quality liquid crystal displays and functional optical thin films. Owing to its versatile possibilities to control the azimuthal and polar orientation of liquid crystals without mechanical intervention, photoalignment (PA) brings along considerable advantages over alternative alignment methods and opens up a plethora of novel applications. Improved optical performances, high production throughputs and yield increases are additional benefits of this technology. PA materials undergoing anisotropic photochemical crosslinking reactions have now reached technological maturity and are entering the market on a large commercial scale.

Keywords: Linear photopolymerizable polymer (LPP) \cdot Liquid crystal display (LCD) \cdot Optical anisotropy \cdot Optical film \cdot Photoalignment

Introduction

Alignment layers provide a well-defined orientation of liquid crystal (LC) molecules in contact with the aligning surface. A means to adjust the alignment is required for most applications of LCs to control and design the anisotropic properties which are to be exploited. Rubbed polyimide films are still the mainstream alignment layers for common liquid crystal displays (LCDs). The mechanical brushing carried out to induce the preferred orientation can, however, lead to the generation of dust and static electricity which adversely affects the production yield. Furthermore, well-defined pretilt angles are difficult to reach and azimuthal aligning patterns cannot be achieved using standard systems. Several other processes to control LC alignment have been proposed but are not practical for processing large-area substrates and may also present other limitations.

All the above problems and limitations can be circumvented with photoalignment (PA). A photoaligned layer is functionalized solely by light exposure, *i.e.* without any mechanical contact and consequently

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enables an arbitrary orientation to be transferred to the LC molecules. PA technology using linearly polarized UV light (LP-UV) not only opens up simplified access to interesting display- and non display-applications such as patterned retarders, polarizers, interference color filters or brand protection devices, but also improves the performances of existing optical films and displays.^[1] The versatility of PA allows the properties of any LC-based device to be tailored to specific requirements: both the azimuthal alignment direction and the polar director orientation can be freely adjusted and patterned with a resolution on the micrometer scale.

Photoalignment Materials and Mechanisms

Photoalignment involves the illumination of a photoactive thin film with linearly polarized light. The absorption probability of the incident polarized light is proportional to $\cos^2\theta$, where θ is the angle between the transition moment of the chromophore and the polarization direction of the incident light. In other words, the molecules which have their absorption oscillator parallel to the light polarization will to a greater extent be prone to photoreact than those oriented perpendicularly. This angle-selective reaction within the photoactive thin film consequently induces a surface anisotropy in the layer.

Three main groups of materials are used to induce LC PA. They can be classified ac-

cording to the photomechanisms responsible for the alignment, which are mainly dimerization, *trans/cis* isomerization and photodegradation.^[2–4] PA using photodegradation of polyimide by LP-UV light typically at 257 nm is attributed to the anisotropic depolymerization of the polyimide chains parallel to the light polarization.^[5] The main limitations of this technique are the low photosensitivity of the materials and the contamination of the layer by degradation products generated by the photodecomposition of the polymer film.

Preferably, the PA technique involves well-designed photosensitive materials undergoing controlled reactions, for example dimerization or isomerization. Materials such as azo dyes undergoing photoreversible trans/cis isomerization can be used for the preparation of alignment layers.^[2] For example, self-assembled monolayers of azobenzene can switch on alternate exposure with UV and visible radiation between the homeotropic and the homogeneous planar alignment. Unfortunately, these surfaces called 'command surfaces' due to this reversible behavior have several disadvantages such as the azimuthal degeneration between the homeotropic and planar configurations.

Particularly suitable materials for the preparation of alignment layers are those undergoing dimerization reactions, the so-called LPPs (linear photopolymerizable polymers). The most prominent of the crosslinkable materials are derivatives of polyvinylcinnamate (PVCi) which was first known as a negative photoresist. Schadt *et*



Fig. 1. Polycinnamate-based polymers undergoing photoinduced [2+2] cycloadditions

al. showed in 1992 that PVCi films exposed to LP-UV were capable of inducing homogeneous LC alignment perpendicular to the polarization direction of the light.^[6] Alignment is believed to result from the anisotropic depletion of the cinnamates as a consequence of the [2+2] cycloaddition as shown in Fig. 1.

The alignment performances for these materials are strongly structure- and exposure energy-dependent. Depending on the LPP structures, both perpendicular and parallel alignment with respect to the electric field of the incident light were observed and some structures showed a transition in alignment direction from parallel to perpendicular depending on the irradiation conditions.^[3,10] The most robust and stable alignment layers in terms of thermal and mechanical stability are those prepared with materials undergoing dimerization and leading to parallel LC alignment. An additional advantage of these materials is their very high photosensitivity; typically between 5 and 50 mJ/cm² are sufficient to obtain a homogeneous and stable alignment layer. In addition to the cinnamatebased LPPs, many other functional polymers bearing for example coumarin, benzylidenephtalimidine, diphenylacetylene, chalcone, and more recently cyanostilbene moieties were shown to induce uniaxial alignment on exposure to LP-UV light.[3,6-10]

The alignment mechanism is thought to involve complex anisotropic surface

anchoring interactions between the PA layer and the liquid crystal. There remains some debate regarding the origin of the azimuthal anisotropy and particularly the nature of the chemical moieties controlling the orientation.^[2-4,8-12] UV absorption spectroscopy allows the identification of the photoreaction(s) taking place within the thin film when irradiated with LP-UV light. Fig. 2 shows an isotropic UV absorption spectrum for a 50 nm-thick LPP film, which was recorded for different exposure energies with LP-UVA light. The loss of absorption of the chromophore at 365 nm correlates well with the absorption increase at lower wavelengths, which was attributed to the formation of the dimer resulting from the [2+2] cycloaddition.^[13] Furthermore, the isobestic points indicate that a single photoreaction is taking place in the LPP film. The determination of the photoinduced dichroism is achieved by measurement of polarized UV absorption spectra, in particular of the absorbances at the wavelength of maximum absorption of the chromophore in parallel (A_{μ}) and perpendicular (A_{\perp}) to the electric vector of the LP-UV light as a function of the exposure doses. They are converted into values of dichroic ratio defined as $(A_{\perp}-A_{\perp})/(A_{\perp}+A_{\perp})$ and values typically below 10% are measured whatever the chromophore structure and the incident energy, which means that the optical anisotropy induced in the LPP

thin film and required to control the LC alignment is quite minute.

Photoalignment Applications, Processes and Devices

In comparison with alternative technologies, the field of applicability for photoinduced surface alignment is considerably broadened by the possibility to realize multi-domain orientation of LC and the flexibility regarding pretilt angle generation. Using LPP PA technology, tilt angles covering the complete span from 0° to 90° can be adjusted according to the requirements of the respective application. Such films with inclined LC directors, *i.e.* o-plate films, are required for several applications such as for viewing angle compensation films. Alignment patterns of the azimuthal orientation and the polar inclination of the optical axis can be generated by structured PA. Thus, a high resolution photopatterned alignment layer is induced, which carries and transfers the orientation information to the LC brought in contact with the alignment laver. In switchable LC cells, the LC medium typically consists of non reactive LC molecules. For the preparation of optical films, the LC molecules can be immobilized by photocrosslinking of polymerizable LC monomers (Fig. 3).

Processing of Photoaligned Optical Films

The sample preparation begins with the coating of the LPP formulation. After drying the LPP layer, the film is irradiated with LP-UV light, either with UVA or UVB depending on the chromophore absorption. An orientation pattern can be induced by area-selectively exposing the alignment layer to differently conditioned LP-UV light *i.e.* with varying intensities, incidence angles or polarization directions. The area-selectivity can *e.g.* be achieved by successive exposure steps through black/white masks.



Fig. 2. Isotropic UV-absorption spectra of a poly(cyanostilbene)-based photopolymer before and after irradiation with LP-UVA light



Fig. 3. Liquid crystalline pre-polymers (LCP) for the realization of retarders

In a second step, the anisotropic LPP layer is coated with a formulation of LCP monomer containing also a photoinitiator. After aligning the LCP by the subjacent LPP layer, the film is crosslinked with unpolarized light. The dry thickness of the LPP layer is typically between 20 and 100 nm, whereas the thickness of the LCP layer depends on the optical function in the final application. For example, a quarter wave plate prepared with a typical LCP formulation has a thickness of around 1 μ m.

Characterization of Optical Films

The coating and alignment quality of an optical film can be inspected by means of a polarization microscope. In combination with a Berek compensator module, the polarization microscope in addition allows a measurement of the optical retardation. For a detailed characterization of optical films, generalized anisotropic ellipsometry represents a very powerful tool.^[14] It permits all major characteristics to be determined such as the optical retardation and the tilt distribution of the optical axis of the film along the surface normal direction.

Devices

PA technology has been used in the production of photopatternable and high-resolution optical liquid crystal displays as well as of liquid crystal polymer elements such as optical retarders, polarizers, anti-reflective coatings or cholesteric band-modulation filters for color generation in imageprojection systems.^[15–19]

The working principle of optical security elements based on photopatterning technology is illustrated in Fig. 4.^[16] The left pixel does not affect the polarization of the incident light which consequently is not transmissive. The right segment acts as a half wave plate rotating the incident polarization direction by 90° and is transmissive. Such security devices cannot be photocopied but are machine-readable and personalized: a latent image, not visible under normal conditions, appears when observed between crossed polarizers. As a further feature of the security device, the rotation of the polarizer or of the device itself leads to contrast inversion.

With LCP formulations containing dichroic dyes, which have the capability of co-aligning with the LCP molecules, linearly polarizing thin films can be realized thus giving access to security and brand protection devices.

Furthermore, LCP materials may be doped with chiral additives to realize cholesteric filters, which optically act as reflective, wavelength-selective circular polarizers. Their characteristic optical effect and especially the viewing angle dependence of their color appearance make them attractive for security and brand protection applications. Moreover, retarders with tilted optical axis allow the compensation of the residual off-axis retardation of LCDs, thus reducing the viewing angle dependence of the contrast ratio, color and gray levels. Using numerical simulations, the optical properties of the retarder can be optimized for the respective type of LCD.^[19]

PA can be used not only to control passive, polymerized LC layers but also in active, *i.e.* switchable LCDs. In this case, the requirements on the alignment layer are considerably higher since it has to maintain its alignment capability over the device's complete life-time and the electro-optic properties of LCDs are highly sensitive to any kind of internal disturbance. In most of the electro-optical LCD modes, a polar angle between the director axis and the substrate is required to avoid the development of disclination defects upon switching.^[3,4,13] As explained above, PA technology is predestined to fulfill this requirement. In addition, the possibility to realize alignment patterns easily allows production of multi-domain LCDs which are needed to accomplish the viewing angle performance standards.

Conclusion

Rolic's LPP photoalignment technology provides a high level of flexibility to transfer specifically designed homogeneous or patterned orientation profiles to LC layers. As a consequence, the spectrum of applications of PA very broadly ranges from brand protection devices over viewing angle compensation films to LCD flat panel television sets.

The PA material can be applied by standard wet coating or printing techniques. The remarkable LP-UV photosensitivities of the LPP materials furthermore provide for a high production efficiency and/or a lowered investment threshold regarding the LP-UV exposure setup. Thus, the major driving forces for the current large scale industrial implementation of PA are the feasibility of novel optical devices, the improvement in performance of optical films or LCDs and the enhancement in production throughput and yield.

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