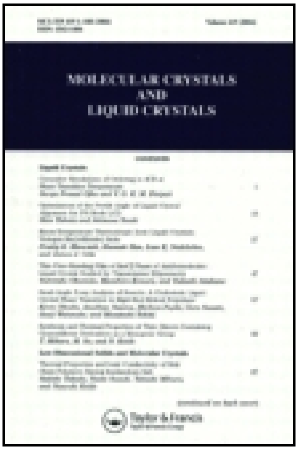

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Negative Birefringence Films From Non-Traditional Materials

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Version of record first published: 18 Oct 2010

To cite this article: T. Sergan, J. Kelly, O. Yaroshchuk & L.-C. Chien (2004): Negative Birefringence Films From Non-Traditional Materials, Molecular Crystals and Liquid Crystals, 409:1, 153-162

To link to this article: http://dx.doi.org/10.1080/15421400490431101

Mol. Cryst. Liq. Cryst., Vol. 409, pp. 153–162, 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490431101

NEGATIVE BIREFRINGENCE FILMS FROM NON-TRADITIONAL MATERIALS

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Polymer films possessing negative birefringence are used for the compensation of residual positive birefringence of liquid crystal displays in order to improve their viewing characteristics. We present several types of materials suitable for the fabrication of negative birefringence films and controllable distribution of optic axis. Films featuring a splayed optic axis can be made of discotic materials as a result of different anchoring forces acting at the film boundaries. Films with a planar optic axis can be made by shearing of thermotropic and lyotropic discotics and as a result of irradiation of photosensitive polymers with polarized light. Homeotropic alignment of optic axis can occur as a result of film shrinkage during solvent evaporation or photo-induced rotation of disk planes.

Keywords: discotics; light induced birefringence; lyotropic chromonic liquid crystals; optical retardation films

1. INTRODUCTION

Although nematic liquid crystal displays have enjoyed greater success than other types of liquid crystal displays, their introduction into certain high volume applications has suffered as a result of their poor viewing cone. The poor viewing angle performance and image inversion of the liquid crystal display is due to the positive birefringence of the liquid crystal layer incorporated between two dichroic polarizers. This residual birefringence

This research was supported by the NSF Science and Technology Center for Advanced Liquid Crystalline Optical Materials (ALCOM) under Contract No. DMR 89-20147, Ohio Board of Regents that provided support throughout a Research Challenge grant and a grant from 3M company. We thank O. D. Lavrentovich, T. Schneider, Yu. Nastushyn, J. C. Lee, and Yu. Bobrov for fruitful discussions, T. Gardner from 3M Co. for providing us with materials, M. Sonpatki, I. Gerus and S.-N. Lee for material synthesis, and M. Lavrentovich, Yu. Zakrevski and H. Wonderly for technical support.

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produces undesirable light leakage for off-normal viewing in display modes that use two crossed polarizers in the dark state. The idea of optical compensation using passive birefringent films was developed in order to overcome this shortcoming. The ideal compensation film for producing a good dark state has negative birefringence and an optic axis that mirrors that of the liquid crystal layer. The display compensated by using this approach shows a dark state similar to that one of crossed polarizers. In some cases further improvements are also possible by applying additional passive retardation films and compensating polarization effects at off-normal directions for two dichroic polarizers [1].

Negative birefringence materials have refractive index for ordinary wave n_o higher that for extraordinary n_e. One of the well-known representatives of negative crystalline materials is calcite or island spar with $n_o = 1.6584$ and $n_e = 1.4864$. However, it is impractical to use thin slabs of rock in display applications. Another candidate for optical compensation elements is a polymer film featuring negative birefringence. Partial success in manufacturing was achieved for negative films with optic axis perpendicular to the film surface (negative C-plates) [2] as a result of film shrinkage during solvent evaporation process. Even a more challenging task was to make films with controllable optic axis distribution. In 1996 Fuji Photo Film introduced a negative birefringence film with splayed optic axis configuration featuring discotic liquid crystalline material [3,4]. Further efforts in film development have shown that the film structure was very rigid and did not allow varying the film's characteristics such as pretilt angles and thickness. We also started our work by researching discotics potential in building negative films with pre-determined optical axis distribution and further progressed into studies of other materials with similar capabilities. This paper summarizes our efforts and findings.

2. EXPERIMENTAL TOOLS

In order to estimate the optic axis distribution in thin oriented layers we applied a null ellipsometry technique based on the Senarmont method. The details of the technique can be found in the reference [5]. The result of the measurement is an experimental curve that represents phase shift in a birefringent sample versus incidence angle of a testing laser beam. The curve is very characteristic to the film. For example, in case of splay optic configuration, the curve is asymmetric regarding normal direction (Figure 1), with high birefringence effects for the light incident perpendicularly to the average optic axis and low birefringence values for light propagating along the average optic axis. Film with an optic axis that is perpendicular to the film plane shows no birefringence for head-on direction

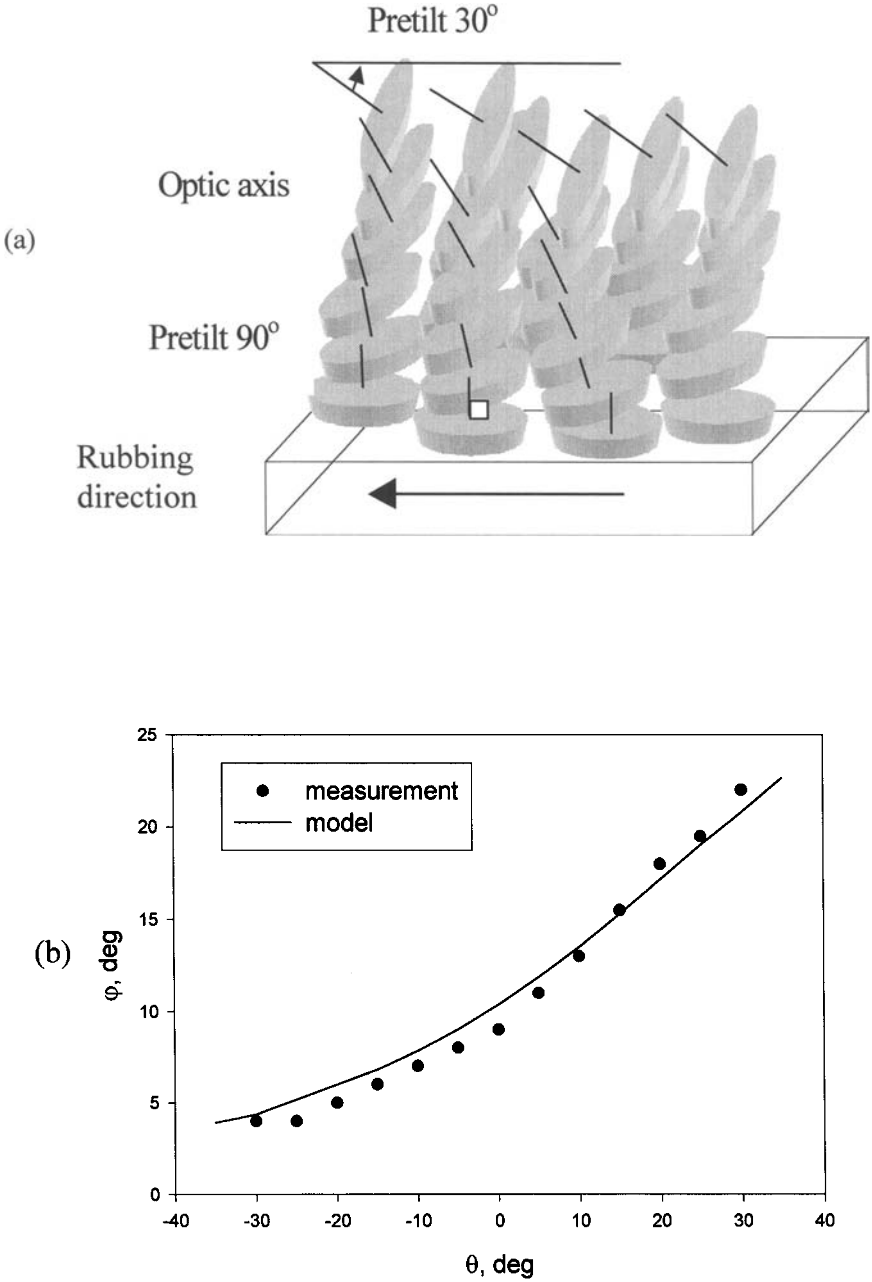

FIGURE 1 Orientation of discotic molecules in a splay film (a) and phase shift φ versus incidence angle θ curve for the discotic splay film (b).

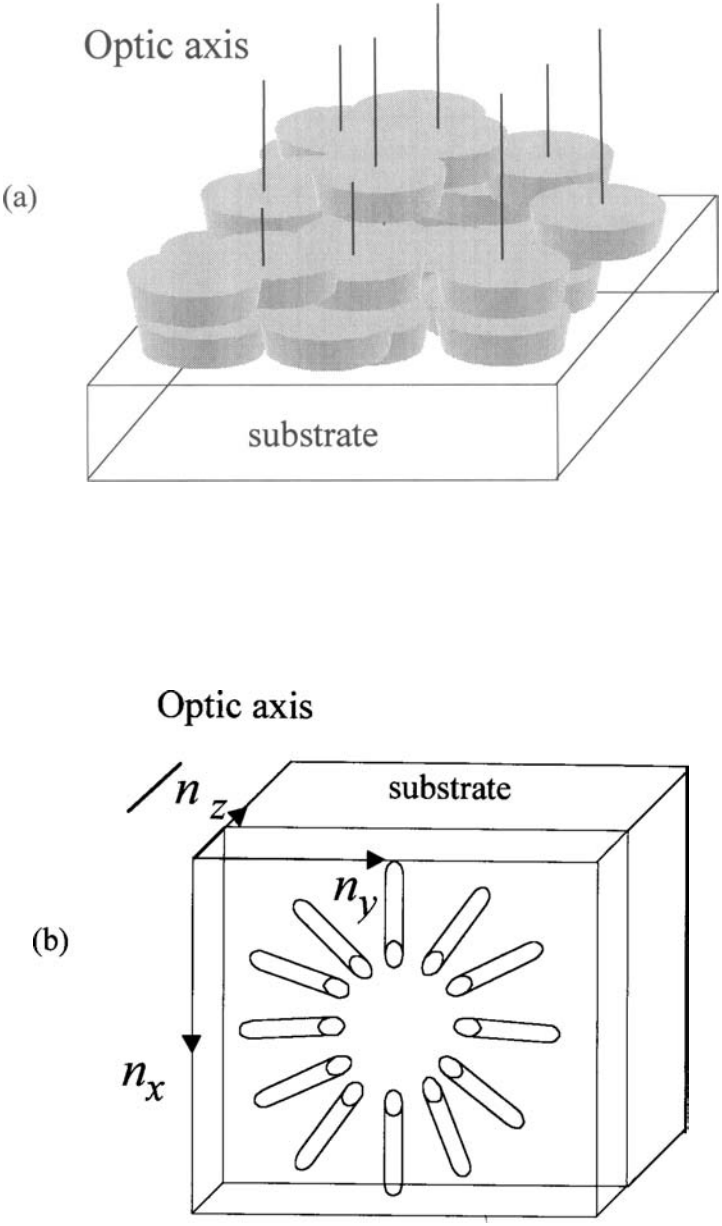

FIGURE 2 Homeotropic alignment of discotic molecules (a), degenerated in-plane distribution of azobenzene fragments and cross-linked bonds in poly (vinil-cinnamate) (b), and phase shift φ versus incidence angle θ curve for negative C-plate formed from azopolymers (c).

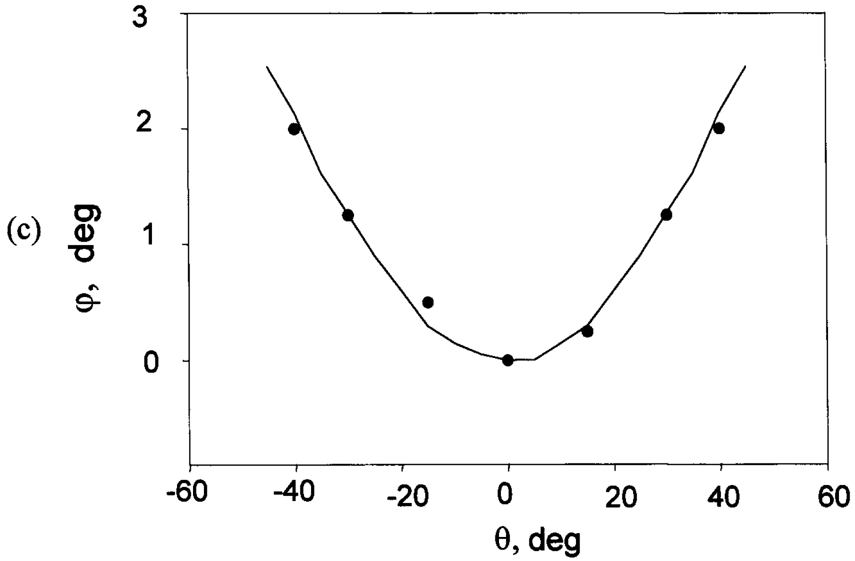

FIGURE 2 (Continued).

and substantial birefringence effects for off-normal directions (Figure 2). Film with optic axis in the film plane features high and comparable birefringence for both head-on and off-normal directions (Figure 3). Mathematical sign of the phase shift in a certain laboratory frame depends on birefringence sign: from the shape of the curve it is possible to determine the absolute values of birefringence, the sign of the birefringent medium (negative or positive), and alignment of the optic axis. The birefringence measurements are performed far from absorption bands of each material.

Sample thickness was estimated by measuring film profiles with Alpha-Step 200 profilometer by Tencor Instruments and via atomic force microscopy.

3. FILMS FROM DISCOTIC LIQUID CRYSTALS

Discotic mesophases are usually formed by coin-shaped molecules that can assemble into stacks (D phases) or layers with no long-range order (nematic-like N_D phase) [6]. Most discotic molecules possess π-electrons whose conjugation is in the disk plane. Since the refractive index of the compound is related to the electron polarization, these materials possess a lower refractive index (n_e) for the light polarized perpendicularly to

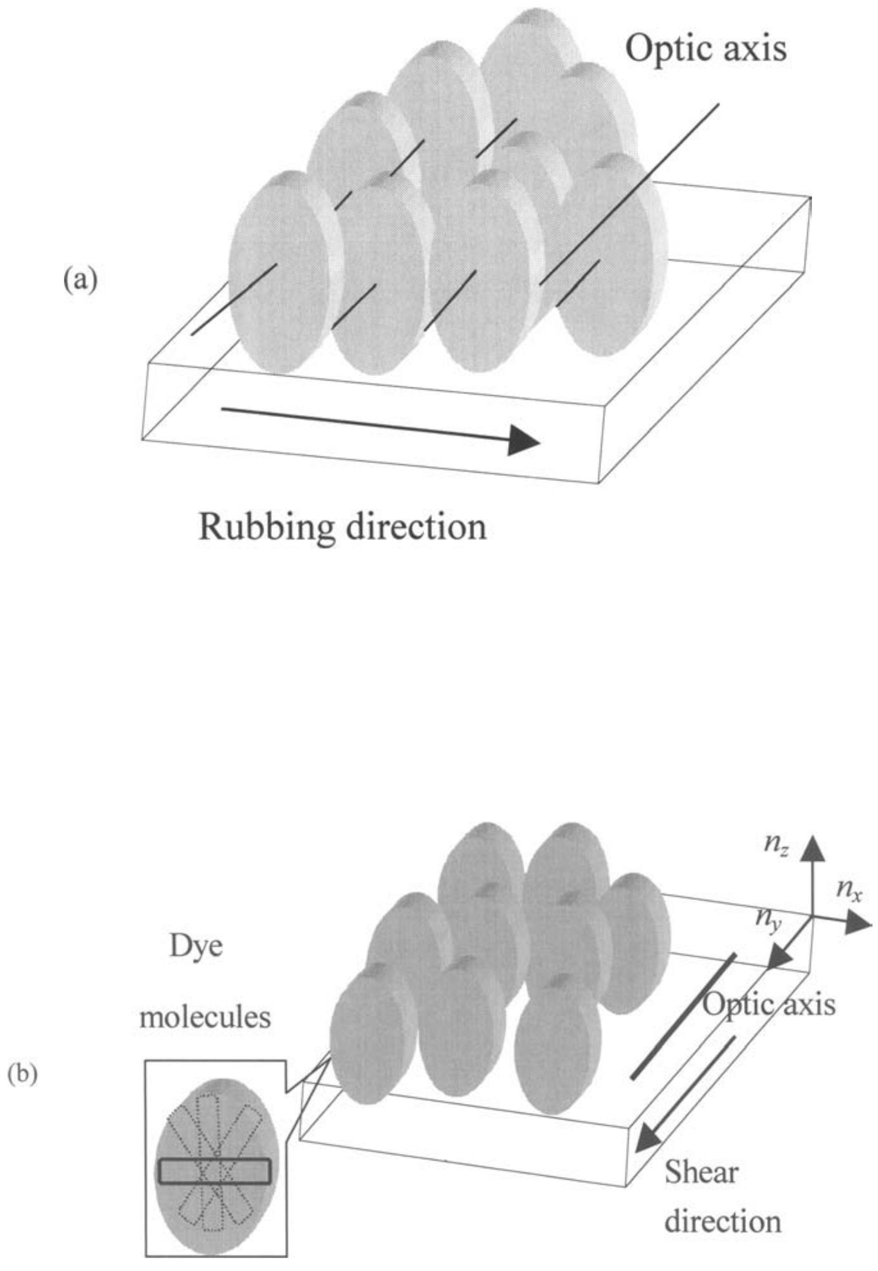

FIGURE 3 Molecule distribution in the negative A-plate made of discotics (a) and lyotropic dyes (b), and phase shift φ versus incidence angle θ curves for cromolyn film (c).

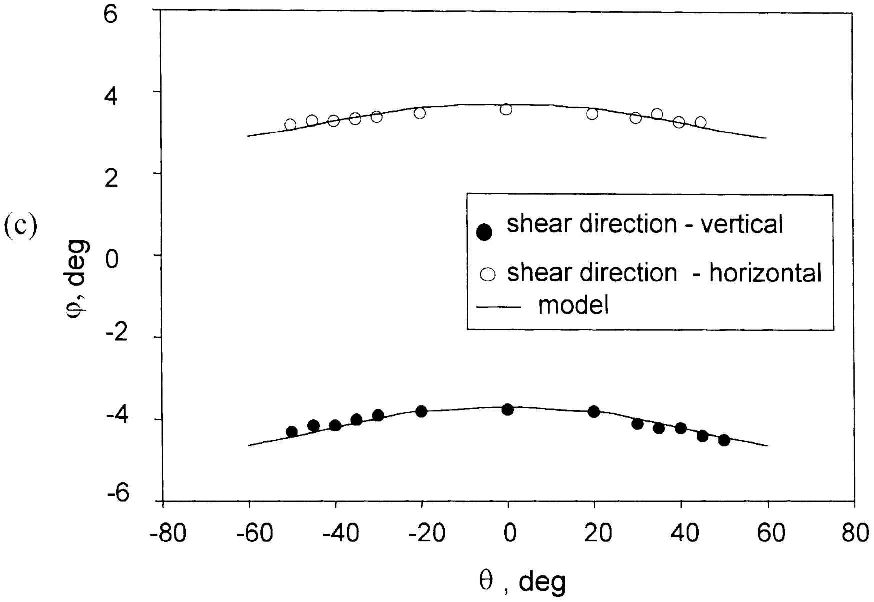

FIGURE 3 (Continued).

the molecular plane comparing to the refractive index for the light polarized in the disk plane (n_o). Thus, the material shows negative birefringence $n_e < n_o$ and features an optic axis perpendicular to the planes of molecular cores.

In our work we studied a discotic compound from the group of 2, 3, 6, 7, 10, 11 hexa-alkoxytriphenylenes. The functional groups produce a wide temperature range nematic phase T = 104–180°C. The material features typical schlieren textures under polarizing microscope [7]. The films with thickness of 0.5–8 microns were sheared from 10–20% solution in toluene on substrates covered with different alignment layers. Photo-polymerization of triphenylene epoxy monomers occurred during subsequent irradiation of the films with non-polarized UV light in the wavelength range $\lambda = 320$–$475\,\text{nm}$ in the presence of a photoinitiator (Irgacure 261 by Ciba Additive Inc.). Most rubbed polyimides and polyvinyl alcohol layers yield a splayed distribution of optic axis within the film. We found that the optic axis changed its orientation from almost homeotropic alignment near the rubbed substrate to a 30° tilt at the film-air interface (Fig. 1). The splayed films are optically uniform and have a birefringence of $\Delta n \sim -0.04$ and optical retardation Δnd about $-100\,\text{nm}$ [8]. The homeotropic alignment of optic axis (Fig. 2) can be induced in the initially splayed layers during the polymerization process at the concentration of photoinitiator above 0.5% (wt) [8]. The photo-polymerization process involves the rotation of molecular discs and leads to the formation of negative C-plates with birefringence of $\Delta n \sim -0.03$ and $\Delta nd = -60 \div -40$ nm. The lower values of birefringence indicate the lower order parameters for the homeotropic alignment comparing with splay layers. The planar alignment of the optic axis can be realized by using fluorinated polyimides as alignment layers [8] (Fig. 3). In the latter case, the optic axis of the film is in the plane of the film and perpendicular to the rubbing direction (negative A-plate). The birefringence of the planar films varies in the range $\Delta n = -0.1 \div -0.07$. It is set by the order parameter of the film and depends on the preparation conditions. We obtained films with the in-plane retardation value of $\Delta nd = -120 \div -60$ nm. The applications of the splayed discotic films are described in the works of Fuji Photo Film Co. [3,4] and our works [8,9].

4. CHROMONIC LYOTROPIC LIQUID CRYSTALS

Negative birefringence films can be made from a water mixture of plank-like dye molecules such as disodium cromoglycate (cromolyn), that do not absorb visible light [11,12] and materials introduced by Optiva Inc. [10], some of them transparent in the region of $\lambda = 550$–700 nm (yellow 12). At concentrations above 5% (wt), their aqueous solution forms a nematic phase. The molecules of the compound have a polyaromatic rigid core and a hydrophilic ionic solubilizing group at the periphery. Because of the hydrophilic properties of the molecule periphery they assemble into stacks with degenerate molecule orientation in the molecular plane. The resultant phase is uniaxial with the lower refractive index in the direction that is perpendicular to molecular cores, and the higher refractive index in the molecular plane. As a result of averaging over possible molecular orientations the material has optical characteristics similar to discotic liquid crystals. We studied thin films made as a result of shearing and subsequent drying of the chromonic liquid crystals. The ellipsometry also revealed that the films are negative and uniaxial with the following relationship between three principal dielectric indices $n_y = n_e < n_x = n_z = n_o$ and $(n_o - n_e)d = 13$ nm (Fig. 3(b)). The higher in-plane refractive index appears in the direction perpendicular to the shearing, and the optic axis of the film coincides with the shearing direction (negative A-plate). The application of yellow dye film is described in our work [9]. Detailed studies and applications of cromolyn films and cells are presented elsewhere [13].

5. FILMS OF AZOPOLYMERS

Negative birefringence medium can be obtained from rod-like molecules that possess positive birefringence. In this case the rods should be distributed in parallel planes with random distribution of molecular axes within the planes. Thus, the optic axis of the system is perpendicular to molecular planes and the index for extraordinary wave n_e for the light polarized along the optic axis is lower than the index for the light polarized along any direction in the molecular plane n_o. We created the negative C-plates [5] by providing degenerated distribution of azobenzene fragments in the plane of the film as a result of spin-coating of polymers dissolved in toluene (Fig. 2(b)).

Azopolymers possess strong absorption of near UV light (in our case, emitted by a Xe lamp). As a result of light irradiation within the absorption band, the azobenzene fragments overcome a series of *trans-cis* conformational transitions that result in the reorientation of the fragments. The photo-steady state of the material is characterized by the distribution of azobenzene fragments oriented preferably perpendicularly to the polarization of the exciting beam. This molecular distribution gives rise to the birefringence for the light outside the absorption band. We irradiated the films with polarized light at normal beam incidence. As a result of multiple absorption cycles the fragments accumulate in the direction that is perpendicular to the direction of light polarization and preferably in the film plane. However, after the rotation of polarization on the angle of 90° to the initial one, we induced out-of-plane movement of azo-groups. The result is the formation of a negative A-plate (Fig. 3(b)). The detailed study of other possible light – induced structures in azopolymer films can be found in our work in the reference [5].

6. FILMS OF POLY(VINILCINNAMATE)

We also fabricated a negative A-plate as a result of the irradiation of initially isotropic films of poly(vinylcynnamate) by polarized UV light. In the latter case the irradiation breaks chemical bonds along the direction of light polarization. However, the bonds in the directions that are perpendicular to the light polarization remain intact. As a result, fragments with high polarizability can be found in all directions that are perpendicular to the direction of UV light polarization (Fig. 3(b)) creating a negative uniaxial film with optic axis along the UV light polarization (negative A-plate) [14]. Contrarily to the case of azopolymers, this structure was obtained as a result of irradiation of initially isotropic material that did not have any preferential alignment of functional fragments. We successfully applied several of the obtained films for compensation of twisted nematic displays. Compensated displays demonstrate high contrast ratio (up to 50:1) at wide viewing angles (up to 50° for polar angle), uniform gray scale, and improved color performance.

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