

Lyotropic Chromonic Liquid Crystals in Aligned Films for Applications as Polarizing Coatings

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Abstract

We describe dried oriented films with anisotropic structural and optical properties prepared from the aqueous solutions of plank-like molecules, the so-called Lyotropic Chromonic Liquid Crystals (LCLCs). The dried LCLC films may be used as optical elements, such as polarizers, compensators, color filters, or retardation plates in the UV, visible, or infrared parts of spectrums. The optical quality of the films is determined by the uniformity of the molecular alignment, which often distorted by periodic variations of the director field. We describe different ways to improve the alignment properties of the films by using additives. We present compositions capable of polarizing effects in visible and UV parts of spectrum.

Keywords : LiquidCrystal, Lyotropic, Chromonic, Polarizer, Shear-deposition

1. Introduction

Liquid Crystals (LCs) may be classified as thermotropic or lyotropic. Thermotropic LCs are orientationally ordered (or mesomorphic) within a specific temperature range. In contrast, lyotropic LC materials become mesomorphic when dissolved in a solvent (such as water) within an appropriate concentration (and temperature) range [1, 2].

Lyotropic LCs are typically formed by amphiphilic materials (surfactants) with molecules that have a polar (hydrophilic) head and a non-polar (hydrophobic) aliphatic tail. This dual character of the molecules leads to self-organization, for example, micelle formation, when they are dissolved in a solvent such as water or oil [1, 2]. When the lyotropic LC molecules are in contact with a substrate, their amphiphilic nature generally results in a perpendicular orientation of the molecule with respect to the plane of the substrate. Either the polar head of the lyotropic LC is attracted to a polar substrate or the hydrophobic tail of the lyotropic LC molecule is attracted to a non-polar substrate. Either orientation might result in a perpendicular alignment of the molecule with respect to the substrate and thus the

so-called homeotropic alignment of the whole sample, in which the optical axis (or director) is perpendicular to the substrate. However, it can be difficult to align the surfactant-based lyotropic liquid crystal in a planar fashion where the director is parallel to the plane of the solid substrate.

Lyotropic chromonic liquid crystals (LCLCs) differ in their structure from conventional lyotropic LCs. The LCLC molecules, as shown in Fig. 1, are generally plank-like or disk-like rather than rod-like, rigid rather than flexible, and aromatic rather than aliphatic. The term chromonic, according to Lydon[1], is a short hand for phrases such as "lyotropic mesophase formed by soluble aromatic mesogens" that additionally was intended to carry connotations of dyes and chromosomes and of the bis-chromone structure of disodium cromoglycate (DSCG), also known as cromolyn, one of the first identified solutes that form LCLCs. The LCLC molecules have a relatively rigid plank-like or disc-like polyaromatic core with polar solubilizing groups at the periphery. Aggregation of these molecules, caused by face-to-face arrangement of aromatic cores, results usually in cylindrical stacks with molecular planes being more or less perpendicular to the axis of the aggregate. The geometry of the basic structural unit in LCLCs is thus very different from the closed micelles, spherical or cylindrical, and bilayers formed by amphiphilic (surfactant) molecules in the regular lyotropic liquid

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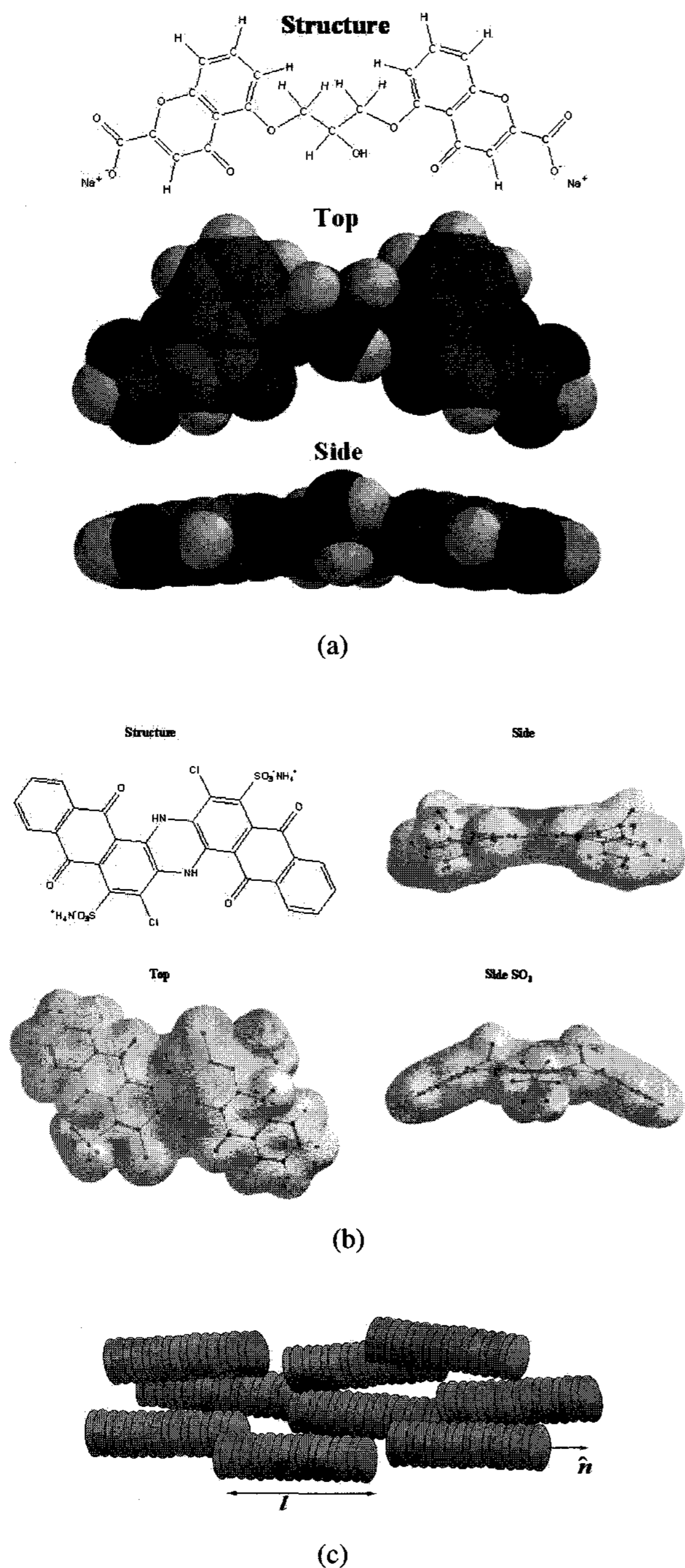


Fig. 1. (a) Molecular structure and shape of disodium cromoglycate (DSCG, cromolyn) and (b) Blue 27. (c) Rod-like aggregates of LCLCs aligned along the director.

Crystals [2]. The tendency to aggregate is observed even in very dilute solutions, thus LCLCs do not show a distinct threshold concentration similar to the critical micelle concentration in amphiphilic systems, except, perhaps, at the very early stages of aggregation. In contrast to the closed micelles formed by a well defined number of

molecules, the LCLC aggregates do not have a clearly defined size (length), as there is no geometrical restriction to the addition of another molecule to the existing stack. Such a behavior, first observed in the studies of nucleic acid bases and nucleosides, is called “isodesmic”; see the review by Lydon for more details [1].

Although π - π interactions are thought to be the main mechanism contributing to the face-to-face stacking of molecules, the details of molecular interactions within and between the aggregates are far from being well understood [1]. Clearly, the hydrophilic ionic groups at the periphery of the molecules make the material water-soluble, Fig. 1. The aggregates in water solution tend to be parallel to each other and (within the appropriate concentration and temperature region) form the nematic state, in which the axes of rods are on average aligned along the same direction called the director, Fig. 1c.

2. LCLC Background

Cromolyn (structural formula shown in Fig. 1a) remains the most studied LCLC. One of the reasons is that this material is used as an effective anti-asthmatic drug, although there is no clear link between its therapeutical activity and mesomorphic properties. When dissolved in water, cromolyn forms two basic mesomorphic phases, labeled N and M. The details of the molecular aggregation in these two phases are still the subject of discussions, see e.g., the reviews by Lydon [1]. The first structural X-ray data by Hartshorne and Woodard [3] suggested that the cromolyn molecules are arranged in cylindrical aggregates with their core regions being predominantly perpendicular to the axis of the cylinder. The intermolecular separation is about 0.34 nm along the axis of aggregate. In the M phase, the aggregates are parallel to each other and arrange into a hexagonal lattice. In the N phase, formed at larger dilutions (Fig. 1c), this lattice disappears but the aggregates retain the orientational order, which makes the N phase similar to a regular nematic phase in thermotropic (solvent-free) materials composed of elongated rod-like molecules. The scalar orientational order of the cromolyn aggregates is very high, in the range 0.76-0.97, depending on the

concentration [4].

The details of molecular packing within the LCLC aggregates, including cromolyn, are still debated (see, for example, [5, 6]). Originally, Hartshorne and Woodard [3] assumed that in cromolyn aggregates, there is one molecule per circular cross-section of the cylinder. They estimated the cylinder diameter to be about 1.6 nm; this value is somewhat smaller than the extended length of the flat cromolyn molecule (which is about 1.9 nm, see Fig. 1). Later, Lydon et al., [7, 8] proposed that the aggregate is of a hollow square-shaped chimney shape formed by four molecules linked by electrostatic salt bridges. Hui and Labes argued [9,10] that the structure is close to that of regular micelles. Namely, there are four cromolyn molecules in the cross section of the aggregate; these molecules have a shape of a sharp letter V with the OH group at the apex. The OH groups point towards the axis of the cylinder while the eight zwitterionic COONa groups point outward to the water continuum [9, 10].

Despite the lack of full understanding of supramolecular self-organization in LCLCs, it became clear recently that some of these materials can be of practical use precisely because of their mesomorphic properties. Following the early works of Dryer [11, 12], different research groups explored the possibility of using the dye-based LCLCs in fabrication of polarizing [13-23]; optical imaging [24]; optical compensating [25, 26], and biological sensing elements [27-29].

All these applications take advantage of the fact that the structure of LCLC materials in the LC state is orientationally ordered. As the result, the LCLC samples exhibit useful structural and optical properties, such as birefringence, polarization ability, polarization-dependent absorption and polarization-dependent light transmittance, ability to align other materials (such as thermotropic LCs, as described in [13], etc. In most cases, the LC state is used to prepare the LCLC films with uniform alignment through some deposition technique that implies shear. Shear induces specific alignment of the director and thus the structural units (molecules or their aggregates) with respect to the shear direction. Once the aligned structure is created by shear in the LC state, it can be “frozen” by evaporating the solvent. If the material is too diluted so that it is in the isotropic fluid state during the shear, the alignment is often lost[30]. However, it is important to realize that the final (“dried”) state of the material is not necessarily the state

that satisfies the thermodynamic definition of the liquid crystalline or mesomorphic state.

In many of the applications above, such as polarizing, imaging and optical elements, one uses the dried-down films that are not necessarily in their liquid crystalline “mesomorphic” state anymore. Upon drying, the LCLC might display a variety of behaviors, as they might (a) crystallize; (b) form an amorphous solid in which the orientational order is largely preserved or “frozen”, the material, however, cannot easily flow; (c) remain in the LC state, either the same state (that was originally prepared by dissolving the LCLC material in solvent) or a different state that exists at lower concentrations of solvent.

The main feature allowing many LCLC applications in “dried” form is that when water evaporates, the resulting dry film still preserves an orientational order and thus anisotropic optical properties. For example, as stated in [24], page 5, “...the advantageous spectral and physical properties of the dye liquid crystalline phases formed in the wet hydrophilic colloid (e.g., aqueous gelatin) are largely retained in the dried-down (evaporated) gelatin coatings of an imaging element.” Preserved in-plane long-range orientational order has been demonstrated not only for films of micron thickness but also for nano-films comprised of just one or few stacked LCLC monolayers and fabricated by electrostatic layer-by-layer deposition technique [30, 31].

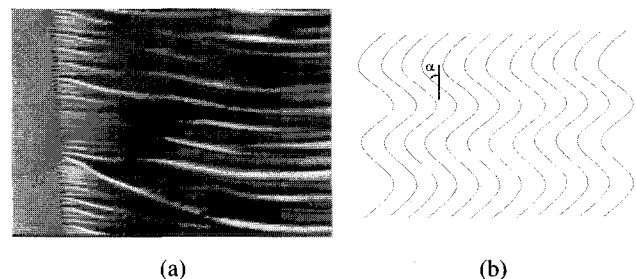


Fig. 2. (a) Polarizing microphotograph showing the banded or “tiger stripe” texture of the LCLC. (b) A schematic representation of the tiger stripes in the film; the thin lines depict the director pattern. Note that a complementary pattern with the director perpendicular to the lines is also possible.

2.1 Film defects

In practical applications of LCLC there is a great need for a uniform alignment of LCLC materials and the dried films formed from LCLC when water (or other solvent) is evaporated, with the director in the plane of the cell or

slightly tilted relative to the plane of the cell. One of the biggest problems is that the LCLC director might develop a periodic pattern of distortions, that is often called “tiger stripes” or “banded textures” because of their characteristic textures under the polarizing microscope, see Fig. 2a. Polarizing microscopy and Atomic Force Microscopy of the texture reveals that it is caused by the director distortions shown in Fig. 2b. Fig. 2b shows that the director is not uniform (as is desired for the best performance in optical and other applications) but periodically distorted.

Let us characterize the director orientation at the substrates with two angles. The angle θ is the angle between the normal to the substrate and the director. The angle α is the angle between the director projection onto the substrate and the fixed axis x in the substrate. The tiger strips can be, in principle, characterized by modulation of both these angles. However, even when θ is constant, for example, $\theta = \pi/2$, the stripes can still exist because of the spatial variations of the angle α characterizing the director distortions in the plane of the substrate. Fig. 2b. illustrates such a case, with α changing periodically in the direction perpendicular to the “tiger stripes”. It is desired in many applications that the LCLC and the dried version of it align with $\alpha = \text{const}$ and $\theta = \text{const}$ everywhere in the sample.

2.2 Aligning LCLCs

Methods to align the thermotropic LCs are well known. A substrate may be coated with a polymer treated, for example, by mechanical rubbing [32]. The treated polymer film then provides an orientation direction for an overlaying thermotropic liquid crystal layer. Such alignment techniques are not necessarily applicable to lyotropic LCs because of the structural (molecular) differences between thermotropic and lyotropic LCs. However, there is a method of stable, planar alignment of LCLCs by an aligned polymer layer or by a vapor deposited layer of silicon oxide or a similar compound on a substrate [28, 29]. This technique is applicable when the LCLC remains in its dissolved form, i.e. the solvent (water) remains within the sample.

Other techniques have also been suggested to impart a desired alignment to LCLCs. For example, it has been suggested to add a non-ionic surfactant to an LCLC, which can then be aligned by photo-treating an azobenzene-containing polymer to align the mixture of surfactant

and LCLC [19]. It is also known to align LCLCs in bulk solutions using a strong magnetic field applied to the LCLC cell. However, this field-induced alignment is only temporary as the degenerate (no fixed direction of molecular orientation) orientation returns within tens of minutes once the magnetic field is removed. Additionally, alignment of LCLC material was accomplished by shear depositing alternating layers of polyion and LCLC on a substrate [30, 33].

Aligned LCLC material may be used for the creation of polarizing films in LCDs, especially, of the flexible plastic type as demonstrated in [13]. One of the known techniques of preparing polarizing films is by using water-soluble dye solutions that form LCLCs on glass or polymer substrates, see for example [13, 22, 34]. These films are visible to the human eye as they absorb in the visible part of the electromagnetic spectrum. The dyes form liquid crystal phases and tend to orient uniformly during the deposition of the solution on the substrate. However, closer inspection reveals numerous defects in the texture of the resulting film, such as the tiger stripes shown in Fig. 2a,b. Under a polarizing microscope and between cross polarizers, these director variations look like stripes of varying intensity of the transmitted light, Fig. 2a. Because of the director deviation from a unidirectional texture, the optical uniformity of the resulting dry films and their performance as optical elements are poor.

There is, therefore, a need to improve the alignment of the LCLC materials, to eliminate the defects such as stripes and thus to improve optical properties, specifically, LCLC-based alignment films that have a more uniform alignment.

3. Improving Alignment Polarizing Films

3.1 General additives

To improve the alignment of dried films prepared from the liquid crystalline state of LCLC we propose adding different dopants to the LCLC material, where the dopant reduces or eliminates formation of defects such as tiger stripes and improves the uniformity of the director alignment. We identified two classes of such additives: block co-polymers or low molecular weight materials with molecules capable of intercalation into the rod-like aggregates of the host LCLC material. To date, additives

used in the production of thin dried films of the LCLC materials were surfactants such as Triton X-100 that improve wetting of the LCLC solution on the substrate [21], salts such as NaCl that change the phase diagram of the mesomorphic state of LCLC materials [35], pH-adjusting additives such as ammonium hydroxide [23], dyes to change the spectral characteristics of the films, pretilt agents such as Glucopon 225 to provoke a suitable orientation of an adjacent liquid crystal material [23], the cross-linking agents to improve chemical resistance of the chromonic materials [23]; 4-(dimethylamino) pyridine (DMAP) that "improves the optical clarity of the liquid crystalline material" [23]. However, there are no known additives to decrease or eliminate the appearance of "tiger stripes".

3.2 Block copolymer additives

We have found that block copolymers can be effective in preventing the formation of "tiger stripes". A block copolymer is essentially a linear copolymer with chains composed of different homo-polymeric chains linked together. These homo-polymer blocks can be either regularly alternating or random. Preferably, when the dopant is a block co-polymer, the monomeric blocks of the polymer differ in their hydrophilicity. A diblock copolymer contains two (generally chemically dissimilar) homo-polymeric chains.

It seems that a diblock copolymer may establish a close polar orientation at the bottom and the top surfaces of the liquid crystal dye film, thereby providing a uniform orientation, characterized by a lessening or even eliminating 'tiger stripe' formation as observed under a polarizing microscope. One of the physical mechanisms of the appearance of "tiger stripes" in nematic liquid crystals is the difference in polar angle θ that the director makes with the normal to the top surface of the LC film and the normal to the bottom surface of the LC film [36]. The role of the block copolymer is then to reduce the difference in the values of θ at the top (LCLC-air) and bottom (LCLC-substrate) interfaces. The diblock copolymer may also provide additional advantages in preparation of the aligned films. For example, the block copolymer may decrease the evaporation rate of water during the drying of the film, improve the wetting of the liquid crystalline film on the substrate, and prevent sticking of the dye material to the coating edge of the doctor blade or other deposition tool. The block copolymer can also promote a better wetting of

the deposited LCLC film at different substrates.

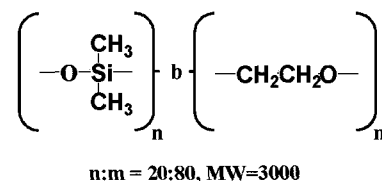


Fig. 3. PDMS-b-PEO diblock copolymer used as an additive to reduce or eliminate tiger stripes.

A small amount (0.01 gram) of poly (dimethylsiloxane-b-ethylene oxide) block co-polymer, Fig. 3., [MW = 3000; 20 : 80 PDMS : PEO] (PMDS-b-PEO) purchased from Polysciences Inc, Warrington, PA was added to 0.40 grams of 7.5 % Blue 27 dichroic dye (Optiva, Inc. of San Francisco, CA) aqueous solution. The components were mixed, and the mixture was deposited onto a glass substrate with a doctor blade and allowed to dry. The resulting film was then examined between crossed polarizers under a polarizing microscope. As shown in Fig. 2a, in a film from a dye solution without block copolymer deposited on a glass substrate, the above-mentioned "tiger stripes" are evident. However, with the block co-polymer (Fig. 4), the bands do not appear in the Blue 27 film. In addition to glass, the block co-polymer/blue 27 solution was also deposited onto polyester films (3M) and the resulting film showed no banded textures.

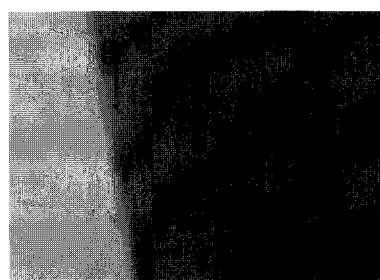


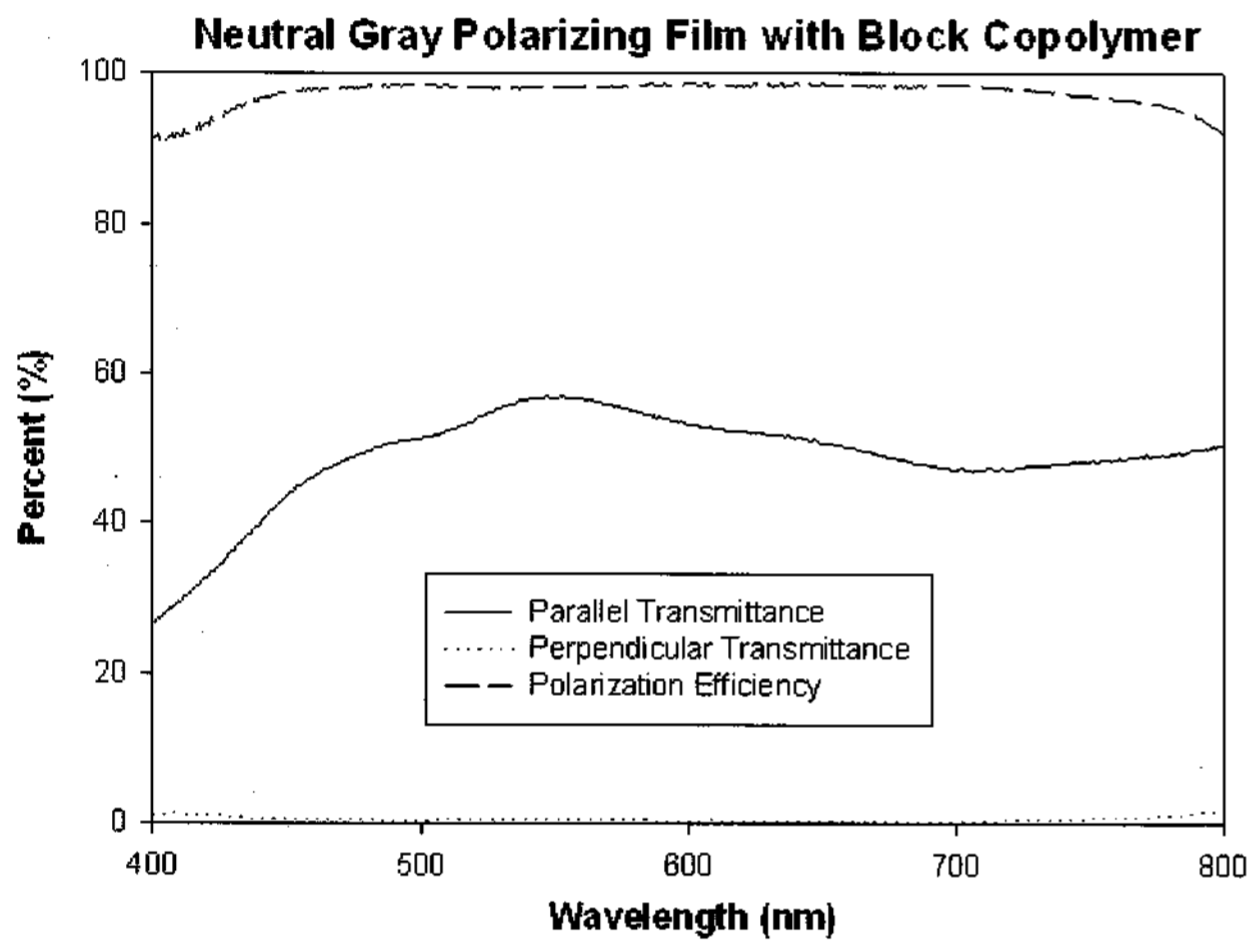
Fig. 4. A film of Blue 27 cast using a small amount of PDMS-b-PEO additive. Notice there are no tiger stripes as in Fig. 2a.

When a film of LCLC and block co-polymer mixture is cast, it is believed that the polymer with the lowest surface tension generally appears at the boundary of the free surface in order to minimize the surface free energy. Poly(dimethylsiloxane) (PDMS) has a low surface tension (~20 dyne/cm) at room temperature relative to poly(ethylene oxide) (PEO) (~43 dyne/cm), which has a surface tension of about twice that of PDMS. Also, PEO is

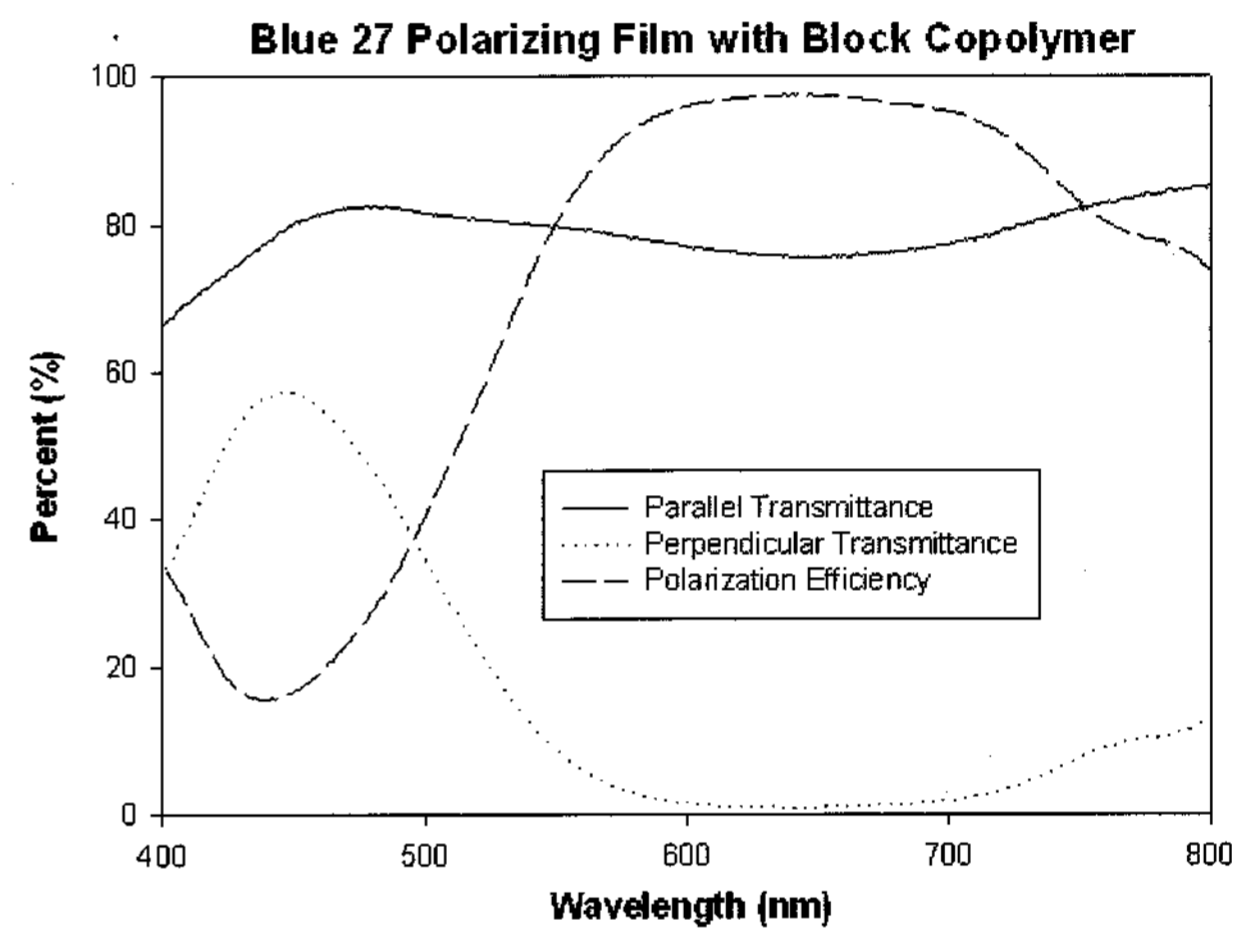
hydrophilic whereas PDMS is non-polar. When a small amount of this block co-polymer is mixed with the Blue 27 dye solution, the hydrophilic PEO has an affinity for the bulk of the dye solution while the PDMS has an affinity for the surface, minimizing the surface tension. Hence an effect is created where the dye is isolated from the bounding air interface and predominantly interacts with the hydrophilic PEO. It is also possible that the PDMS also has an affinity for the glass surface as well, because it has a siloxane end group, in which case, there are identical boundary conditions on both the top and the bottom of the film. This would allow the dye to be sheared and relax without

director changes.

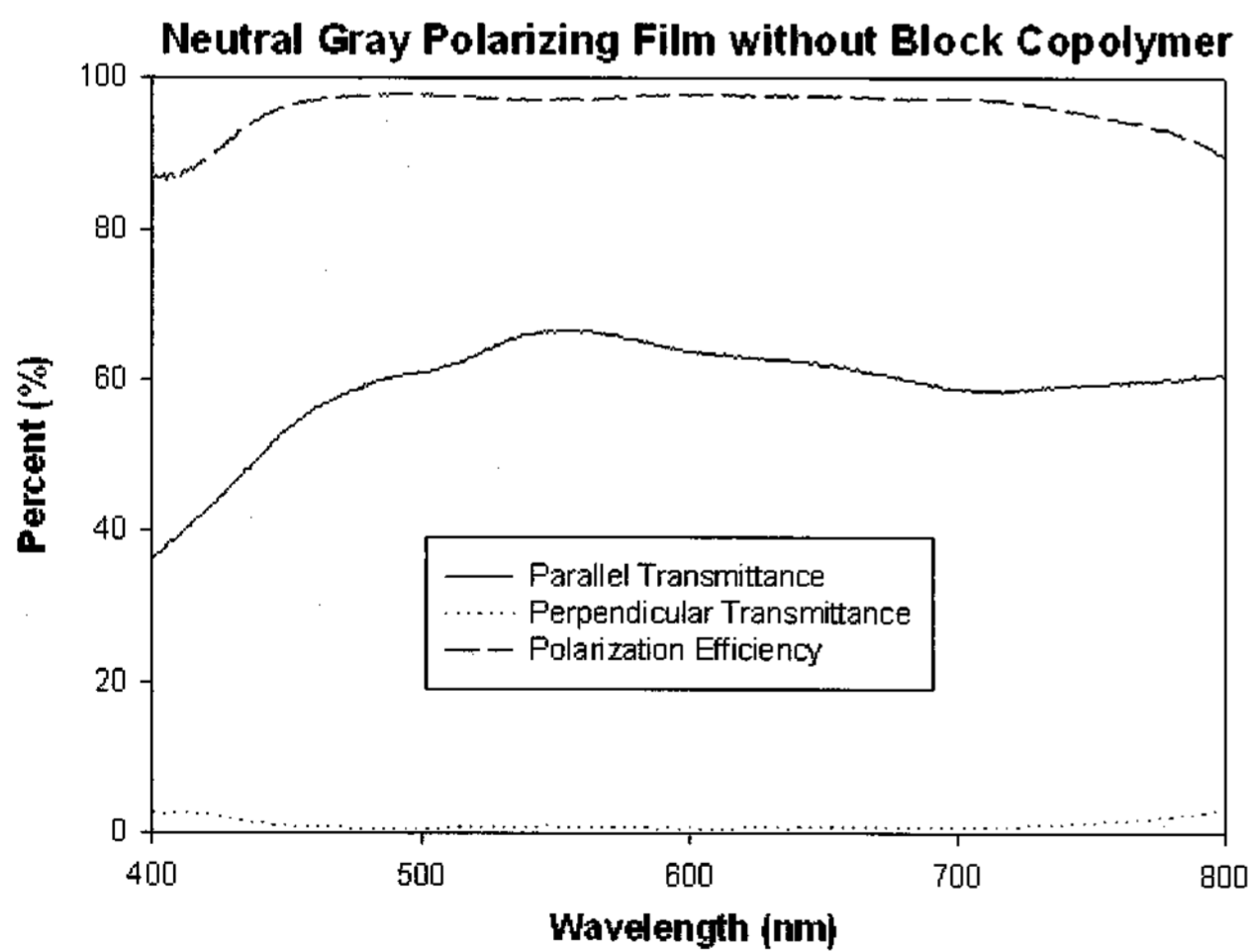
Neutral Gray (the mixture of different dyes producing a uniform absorption over the visible part of the spectrum), Blue 27, and Violet 20 dye films (with and without a 20:80, PDMS : PEO block co-polymer additive) were mixed as described above. The polarizing features of the resulting films were analyzed by "Lambda 18" spectrometer (Perkin-Elmer, Wellesley, MA). The transmittance and polarization properties exhibited by those films are presented in the graph form in Figs. 5a, 5b, 6a, 6b, 7a and 7b. In Fig. 5a, a lower perpendicular transmission is observed for a Neutral Gray film with the block co-polymer, indicating the



(a)

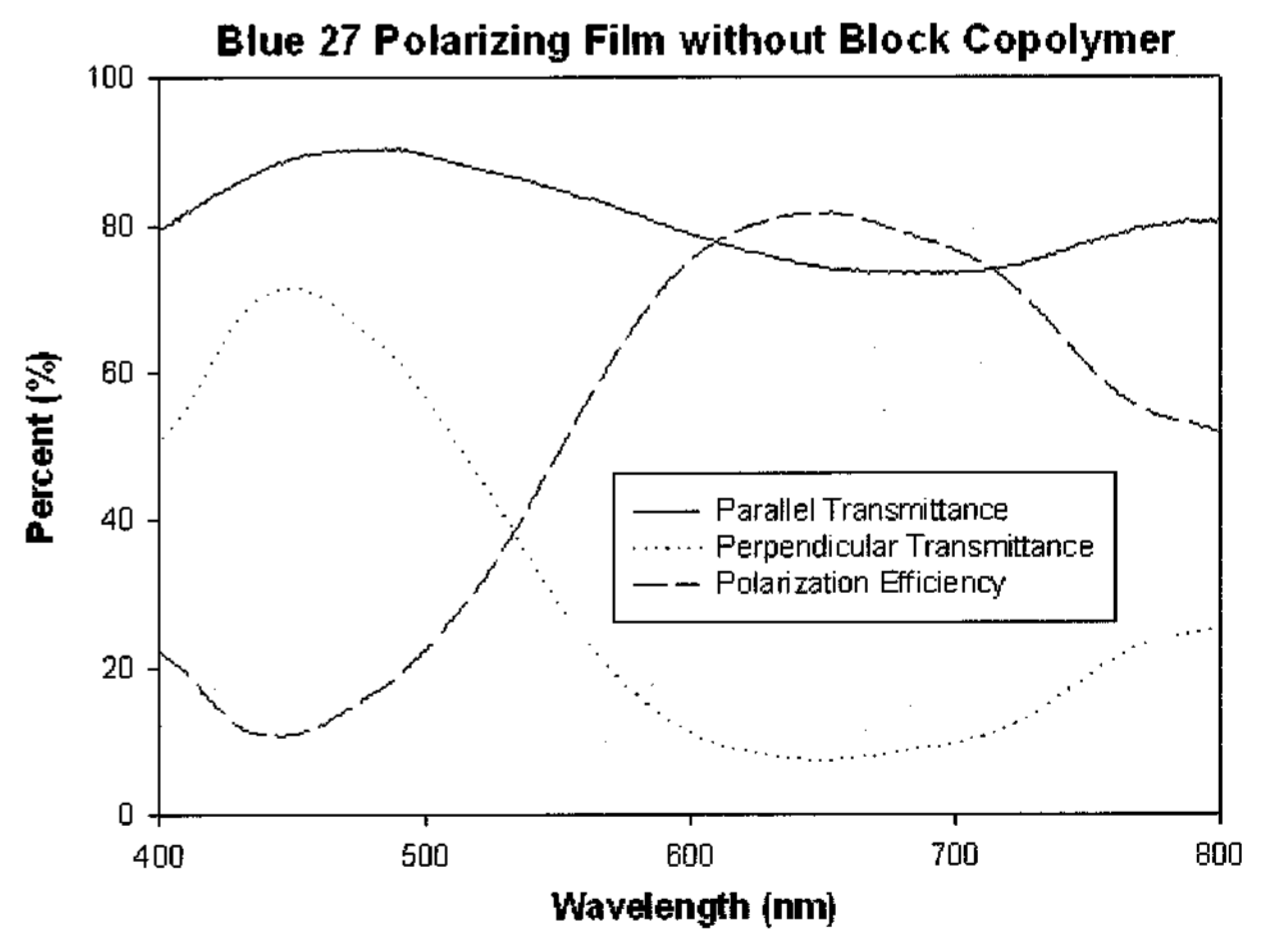


(a)



(b)

Fig. 5. Polarization efficiency of Neutral Gray as determined from the transmittance of light parallel to the director and perpendicular to the director for films (a) with PDMS-b-PEO and (b) without block copolymer.

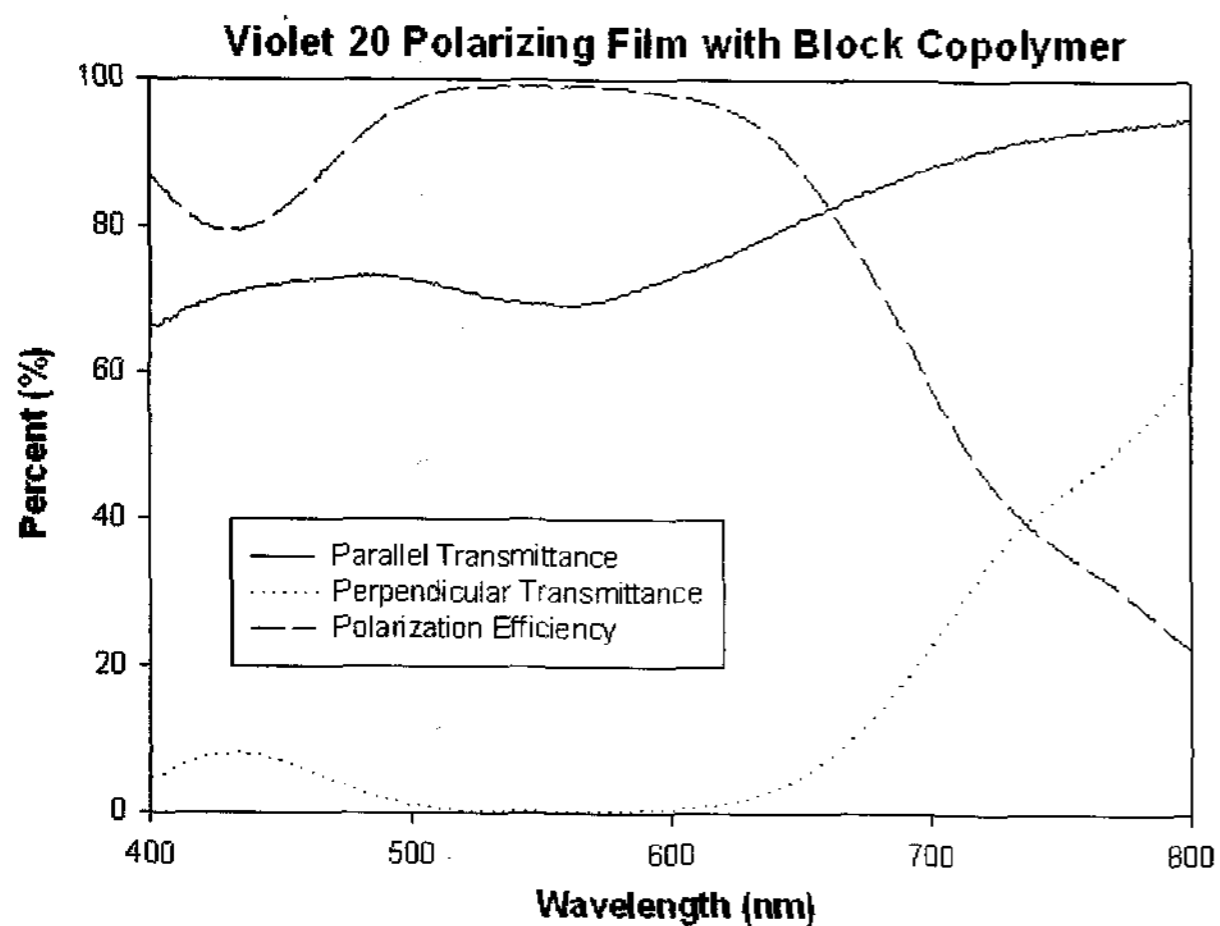


(b)

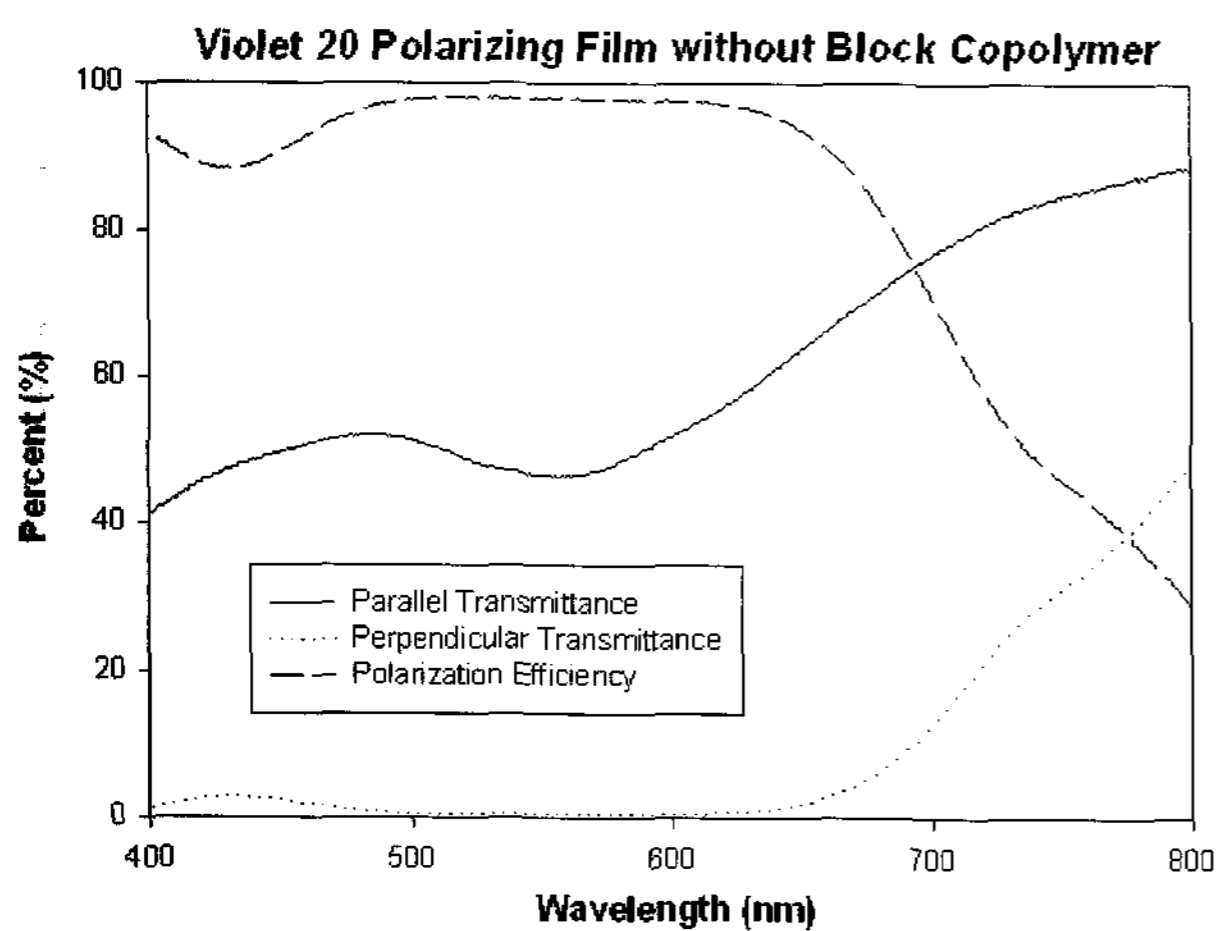
Fig. 6. Polarization efficiency of Blue 27 as determined from the transmittance of light parallel to the director and perpendicular to the director for films a.) with PDMS-b-PEO and b.) without block copolymer.

presence of a more uniform texture, compared to a Neutral Gray film without the co-polymer (Fig. 5b). In Figs. 6a and 6b, a higher polarization efficiency is observed for the Blue 27 film with the block-copolymer (Fig. 6a) compared to the Blue 27 film without co-polymer (Fig. 6b). In Figs. 7a and 7b, a higher parallel transmission is displayed by the Violet 20 film with the block co-polymer (Fig. 7a) than that displayed by the Violet 20 film alone (Fig. 7b).

By choosing the proper LCLC materials, one can create polarizing films that would perform as polarizers in one part of the spectrum, say, UV ($\lambda \approx 250\text{-}400\text{ nm}$) or IR, but be "invisible" or non-absorbing in the remaining part of



(a)



(b)

Fig. 7. Polarization efficiency of Violet 20 as determined from the transmittance of light parallel to the director and perpendicular to the director for films; (a) with PDMS-b-PEO and (b) without block copolymer.

the spectrum (say, in the visible region). One of the viable candidates for the UV polarizers is the DSCG (cromolyn) described in the Introduction. LCLC-based films were prepared from a 14 % (wt) aqueous solution of DSCG; at this concentration the material forms the N-phase [1]. The substrates were coated with a thin layer of this solution using a back edge of a razor blade. In this way, a layer of aqueous solution with LCLC director parallel to the shearing direction was formed. After drying, the LCLC layer became a solid film of thickness typically $0.8\text{-}1\ \mu\text{m}$.

Linearly polarized light in the UV range was obtained by transmitting partially polarized light through a fused silica multiple-plate polarizer known as a so-called "pile-of-plates." The optical properties were determined with a "Lambda 18" spectrometer (Perkin-Elmer, Wellesley, MA).

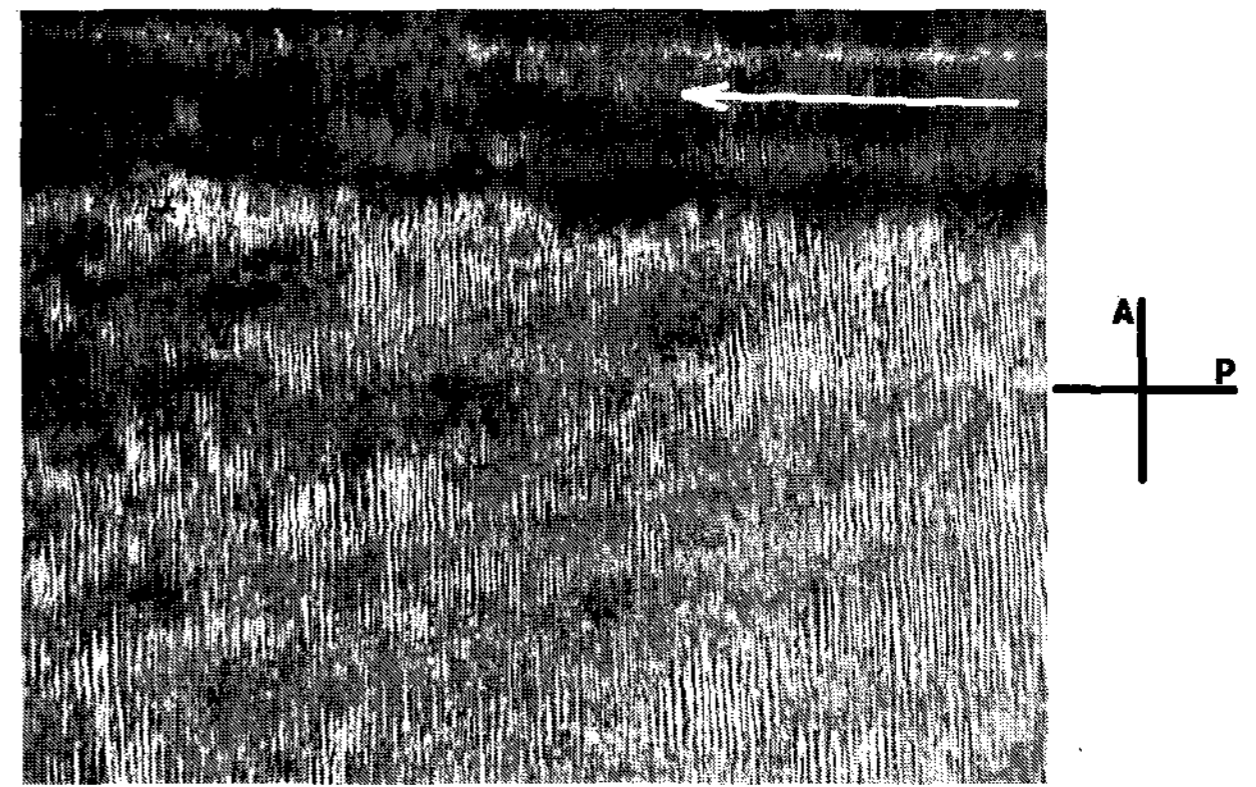


Fig. 8. Film of cromolyn sheared onto glass and dried. Notice the tiger-stripes perpendicular to the shearing direction (denoted by the white arrow).

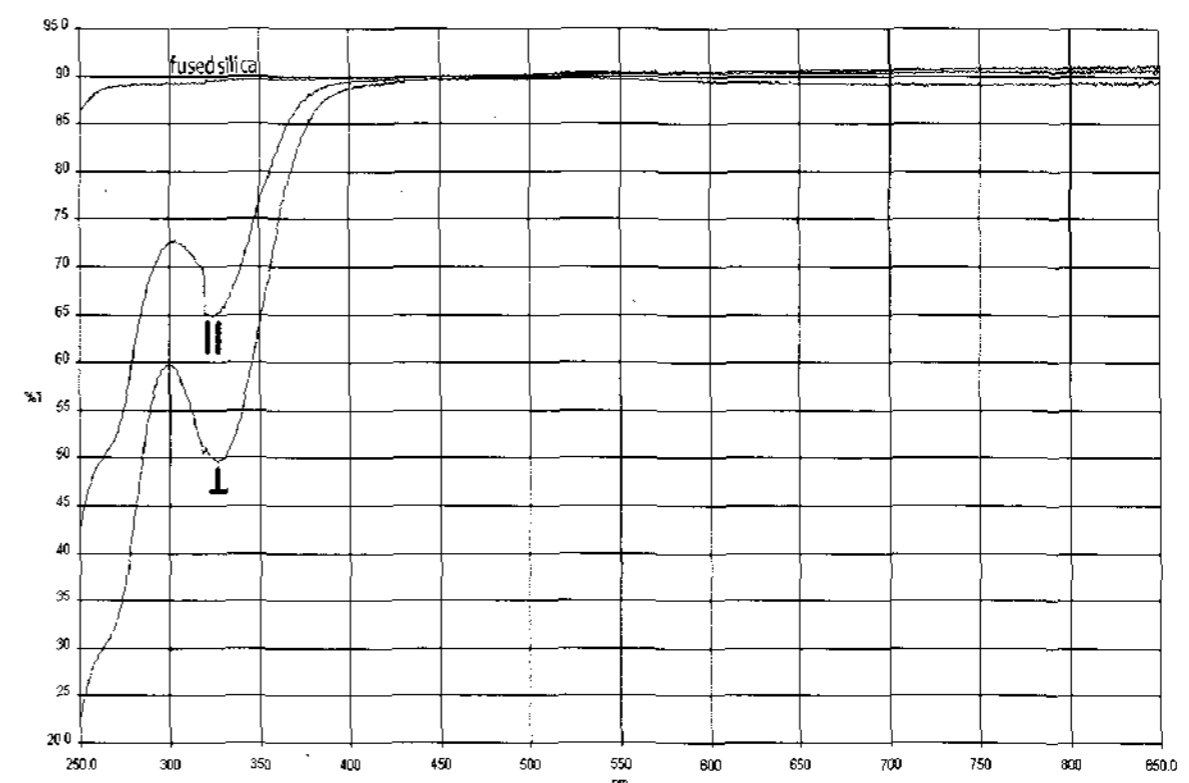


Fig. 9. Spectrum of the sheared cromolyn film showing parallel and perpendicular transmittance. Note the system only absorbs in the UV region as compared to the spectrum of fused silica (top curve).

The texture of the dry LCLC film is of a “tiger-stripe” type when the sample is placed between two crossed polarizers, Fig. 8. The arrow shows the shearing direction tilted at about 3 degrees with respect to the polarizer (P) axis. Fig. 9 shows the spectrum of a 0.8 μm thick film, obtained using linearly polarized light in the directions parallel and perpendicular to the shearing direction, and the transmittance of clean fused silica substrate. The dried film of LCLC demonstrates a significant difference in the transmittance of UV light (wavelength range 200-400 nm) linearly polarized along and perpendicular to the shearing direction. The film shows high transmittance ($\approx 99\%$) in the visible and near IR wavelength range 400-900 nm. The spectra clearly demonstrate that the film performs as light

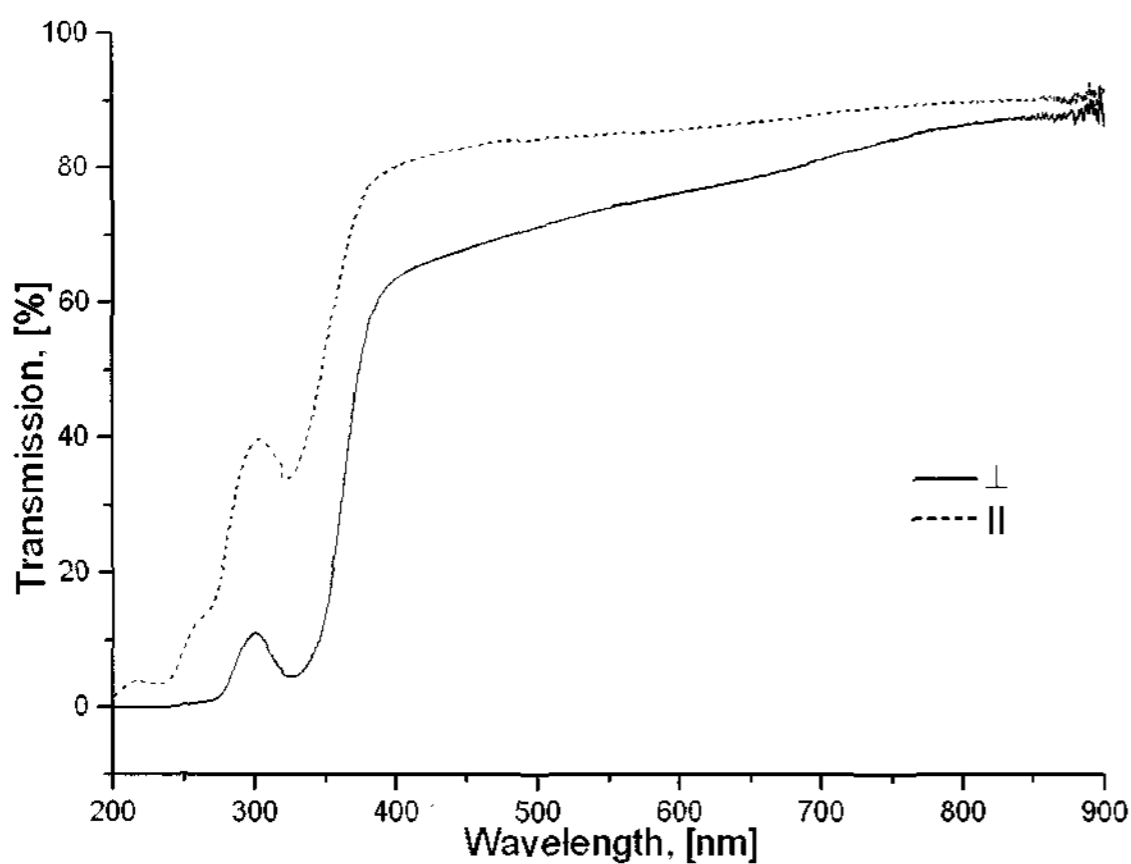


Fig. 10. The transmission spectrum of cromolyn with BC(b).

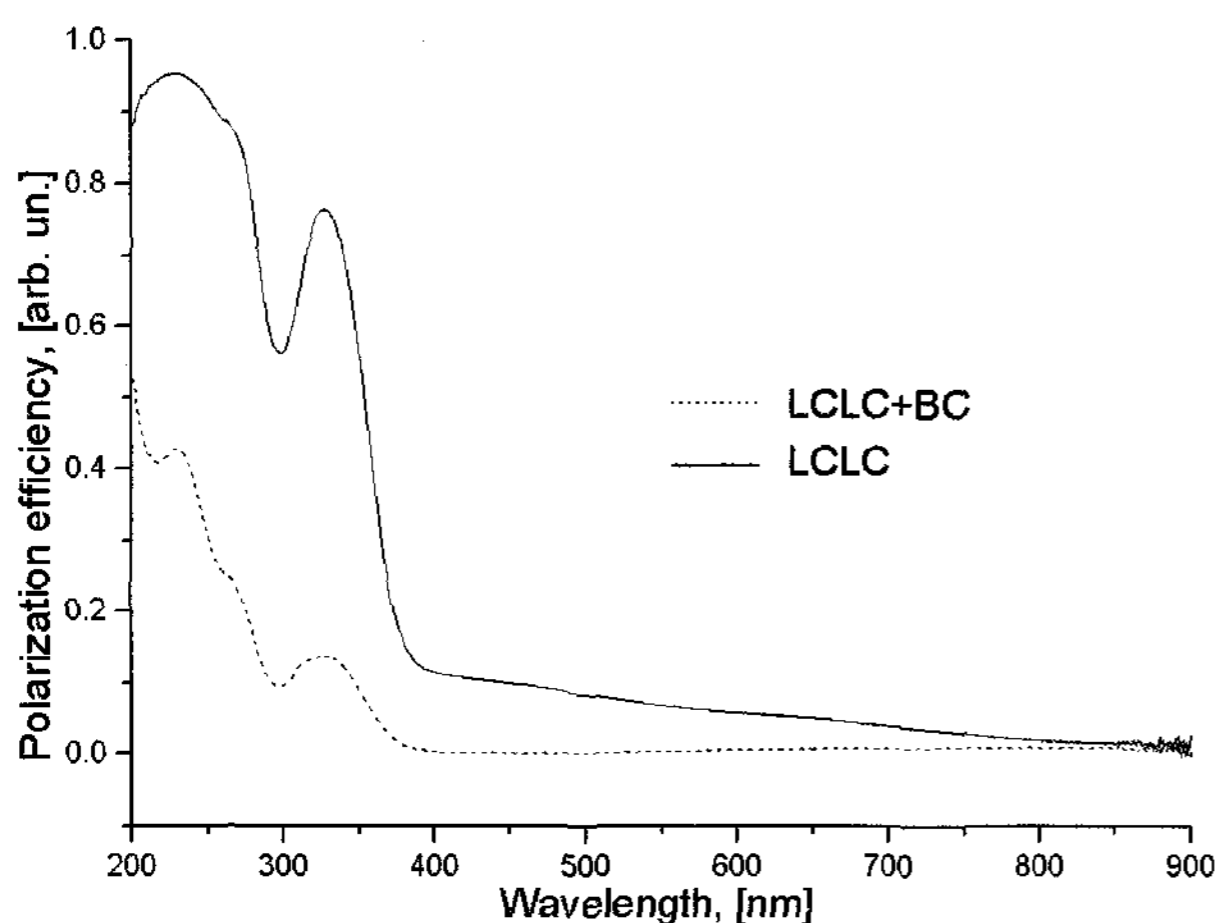


Fig. 11. The polarization efficiency of the film with cromolyn and BC(b). Notice the polarization efficiency is improved however, the block copolymer makes the material absorbing in the visible region.

polarizer at wavelengths below 400 nm. Above 400 nm, the film is essentially transparent for all directions of light polarization, although the residual scattering from the tiger stripe texture may make it “visible” to the naked eye.

To improve the efficiency of the LCLC-based thin film UV polarizer, a block copolymer (BC) was added to the cromolyn material. Two BCs of differing molecular weight were tested. The first (BC (a)) was a Poly(dimethylsiloxane-ethylene oxide) at a smaller MW = 1200 (purchased from Polysciences Inc, Warrington, PA). The second, (BC (b)), was Poly(dimethylsiloxane-b-ethylene oxide) at a larger MW = 3000 20 : 80 purchased from Polysciences, Inc (Warrington, PA). As above, both of the BCs contained 20 parts poly(dimethylsiloxane)[PDMS] 80 parts poly(ethylene oxide)[PEO] in their linear main-chain structure. Both BCs were tested by adding 0.005 g to 0.5 g of 14 % (wt) aqueous solution of cromolyn.

The film layer with BC (b) showed a significant improvement in polarization efficiency. Fig. 10 shows the transmission spectrum of a 0.5 μm thick dried film of sheared LCLC + BC (b). The transmittance of the film was determined using a beam with linear polarization parallel (∥) and perpendicular (\perp) to the shearing direction. The addition of block copolymer slightly increased the absorption of visible and near-IR polarized light ($\lambda \approx 400$ -900 nm) and significantly changed the transmission of UV-light. The polarization efficiency may be calculated as:

$$V_{pe} = \frac{T_{\parallel} - T_{\perp}}{T_{\parallel} + T_{\perp}}$$

Fig. 11 shows V_{pe} vs. wavelength for a

0.8 μm thick film of LCLC and a 0.5 μm thick film of LCLC + BC (b). The polarization efficiency is clearly improved with the block co-polymer, despite the fact that the thickness of the BC-containing film is somewhat lower than the thickness of the “pure” LCLC film.

The efficiency of “tiger stripe” reduction is somewhat different for BC (b) and BC (a). Fig. 12 demonstrates some remnant defects in the case of BC (b), whereas Fig. 13 shows a stripe-free texture when BC (a) is used. In Fig. 12, the arrow shows the shearing direction tilted at ≈ 10 degree with respect to the polarizer (P) axis; in Fig. 13, this angle is only ≈ 3 degree for better clarity. Figs. 12 and 13 demonstrate the possibility of controlling the optical appearance and optical efficiency of LCLC films doped with different types of BCs.

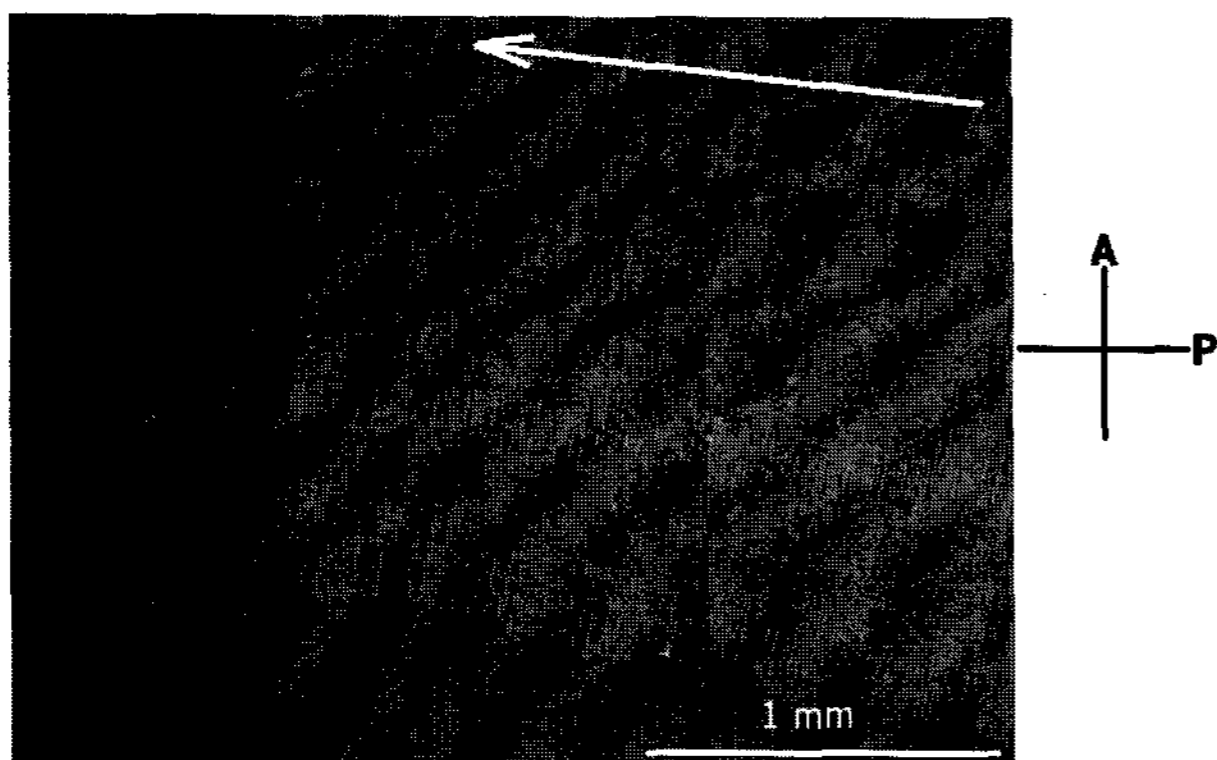


Fig. 12. Cromolyn with BC(b). Notice the presence of tiger stripes.

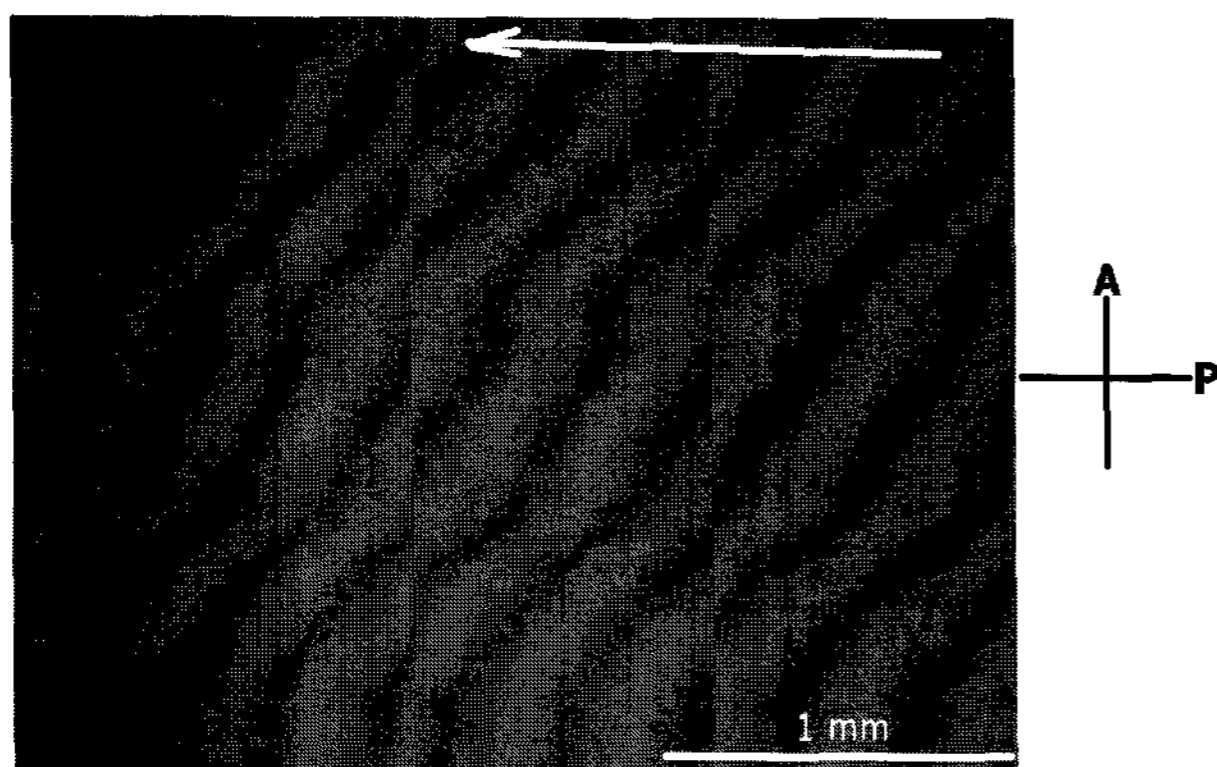


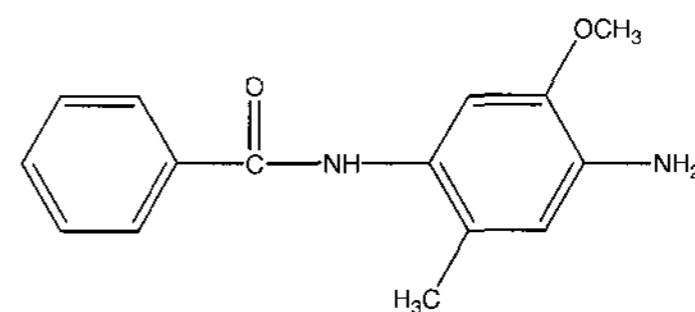
Fig. 13. Cromolyn with BC(a). Notice the suppression of tiger stripes.

3.3 Dye additives

When the dopant is a low molecular weight dye, it might intercalate into the LCLC aggregates, thereby stabilizing the aggregates and thus modifying the material parameters of the mesomorphic state. For example, if the dye interacts strongly with the host LCLC molecules, it will stabilize the rod-like aggregates, increasing the splay elastic constant in the liquid crystalline state and also increasing the scalar order parameter. It may be advantageous for the low molecular weight dye dopant to have an opposite electrostatic potential as compared to that of the LCLC, thereby stabilizing the intercalated dopant in the aggregates. For example, an LCLC material having tendency to give up a positive charge in an aqueous solution such as disodium cromoglycate (DSCG) or Blue 27 could be doped with an additive such as Fast Violet B (described below), which contains pendent groups that are likely to attract a positive charge. Alternatively, the guest molecule might intercalate into the rod like aggregate even if it is of the same electric

charge but of different chemical structure as compared to the host LCLC molecules.

The composition of the LCLC may also be varied by choosing other dopants for the purpose of improved alignment and elimination of defects such as tiger stripes, preferably dyes having a molecular weight of the same order of magnitude as the molecular weight of the LCLC molecules. Such molecules may be capable of intercalating in the LCLC aggregate structure and changing the pH. Dye additives can change the structural properties of the film such as the length or thickness of aggregates, elastic properties such as elastic constants, or viscosity coefficients such as shear viscosity coefficients, and the like, which often results in the improved alignment of the dried LCLC films. An example of such a dopant is the dye Fast Violet B, 4-Benzoylamino-2-methoxy-5-methylbenzeneamine, available from Sigma-Aldrich Corp. St. Louis, MO, USA, with the maximum of absorption at approximately 297 nm. The chemical structure is shown below.



The molecular weight of Fast Violet B is 256.39, somewhat lower but of the same order of magnitude as the molecular weight of the LCLC materials such as cromolyn (512.3) and Blue 27 (685.8) shown above in Fig. 1a,b. It may also be noted that the structure of the Fast Violet B molecule makes it likely to attract a proton or other positive charge, while DSCG and Blue-27 molecules are more likely to part with a proton or other positive charge in an aqueous solution. Therefore, electrostatic attraction may help to accommodate the molecules of Fast Violet B in the solutions of cromolyn, Blue 27 and similar LCLC materials and thus to alter the properties of the resulting LCLC phases such as the length of aggregates and their viscoelastic coefficient.

To prepare the DSCG-Fast Violet B mixtures, 0.0015 g of Fast Violet B dye powder was added to 0.9985 g of 14 % (wt) aqueous solution of DSCG. The mixture was sheared with a doctor blade and dried in the air, as described above. Fig. 14 shows the transmission spectrum of an 800 nm thick dried LCLC film containing Fast Violet B dye, with linear polarization of light parallel (II) and

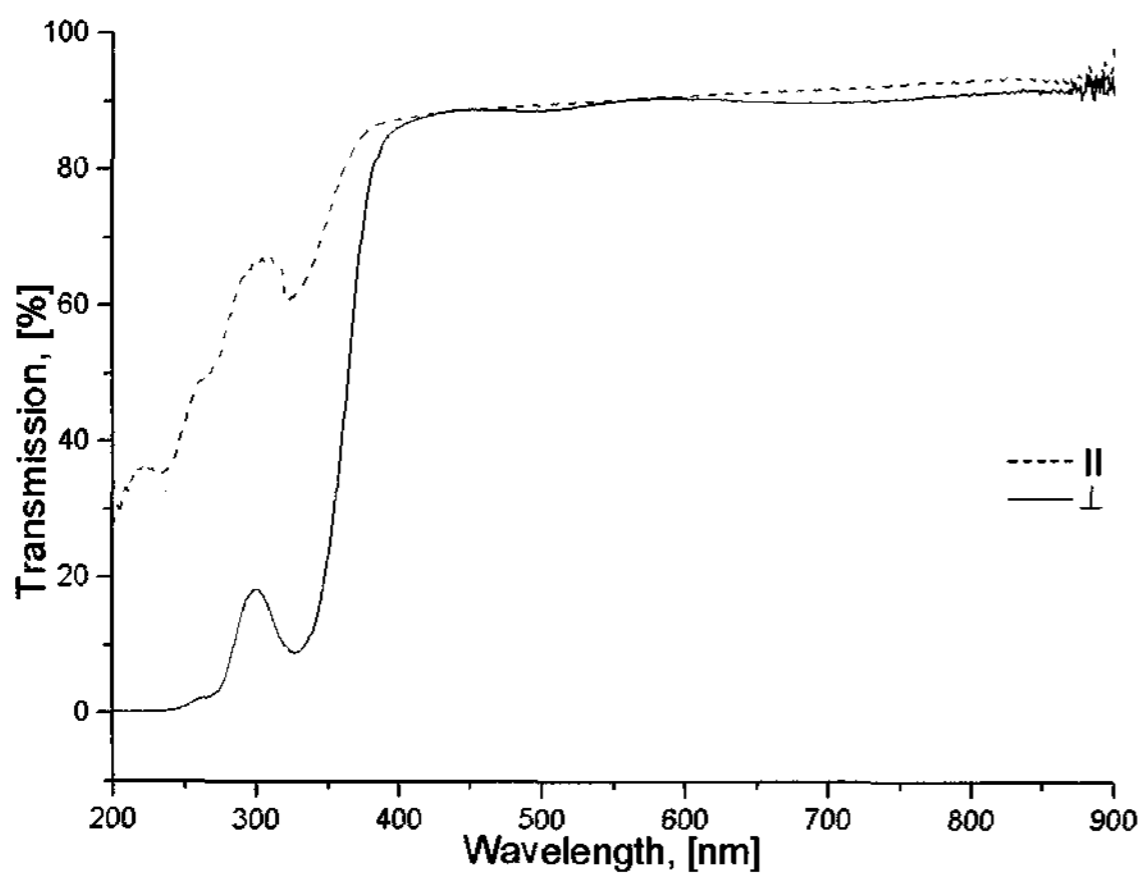


Fig. 14. The transmission spectrum of Cromolyn with Fast Violet B additive for light polarized parallel and perpendicular to the director.

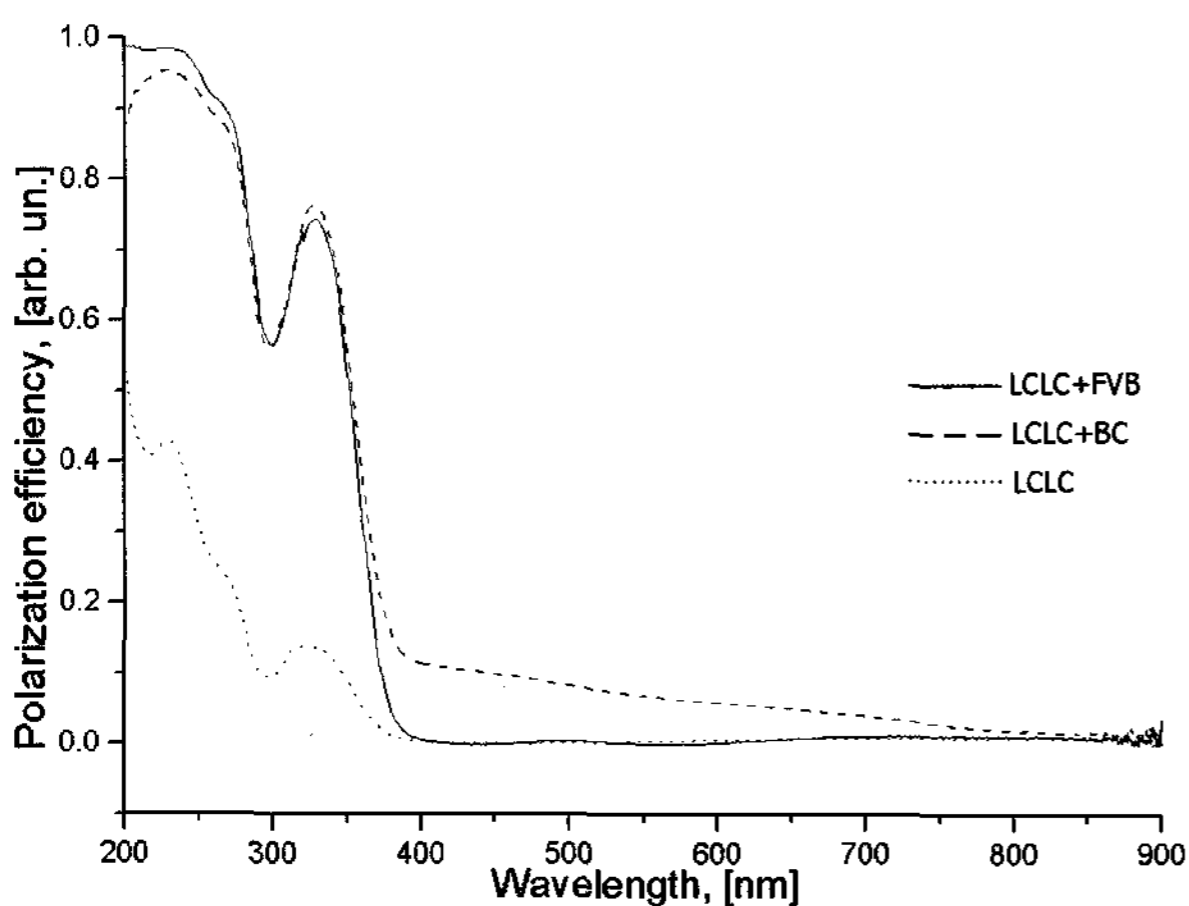


Fig. 15. The Polarization Efficiency of three films showing that cromolyn (LCLC) with Fast Violet B (FVB) is the best UV polarizer whereas the film with block copolymer (BC) is an effective UV polarizer but has some residual absorption in the visible region when compared with straight cromolyn.

perpendicular (\perp) to the shearing direction of dried film.

Fig. 15 shows the polarization efficiency of an 800 nm thick dried LCLC film with Fast Violet B dye in comparison to the polarization efficiency of dried films of pure LCLC, LCLC with block copolymer of the same thickness. The LCLC/Fast Violet B film shows the best polarization efficiency for UV range between 200 and 300 nm. Moreover, the film of LCLC with Fast Violet B shows a high transmittance ($\geq 90\%$) for visible and near-infrared light and no noticeable polarization capability in that wavelength range between 400 and 900 nm. The LCLC/Fast Violet B film also shows the minimum appearance

of “tiger stripes” texture, Fig. 16. The arrow shows the shearing direction tilted at ≈ 30 degree with respect to the polarizer (P). Fast Violet B dye also increases the absorption of UV light polarized normally to the shearing direction of the dried LCLC film.

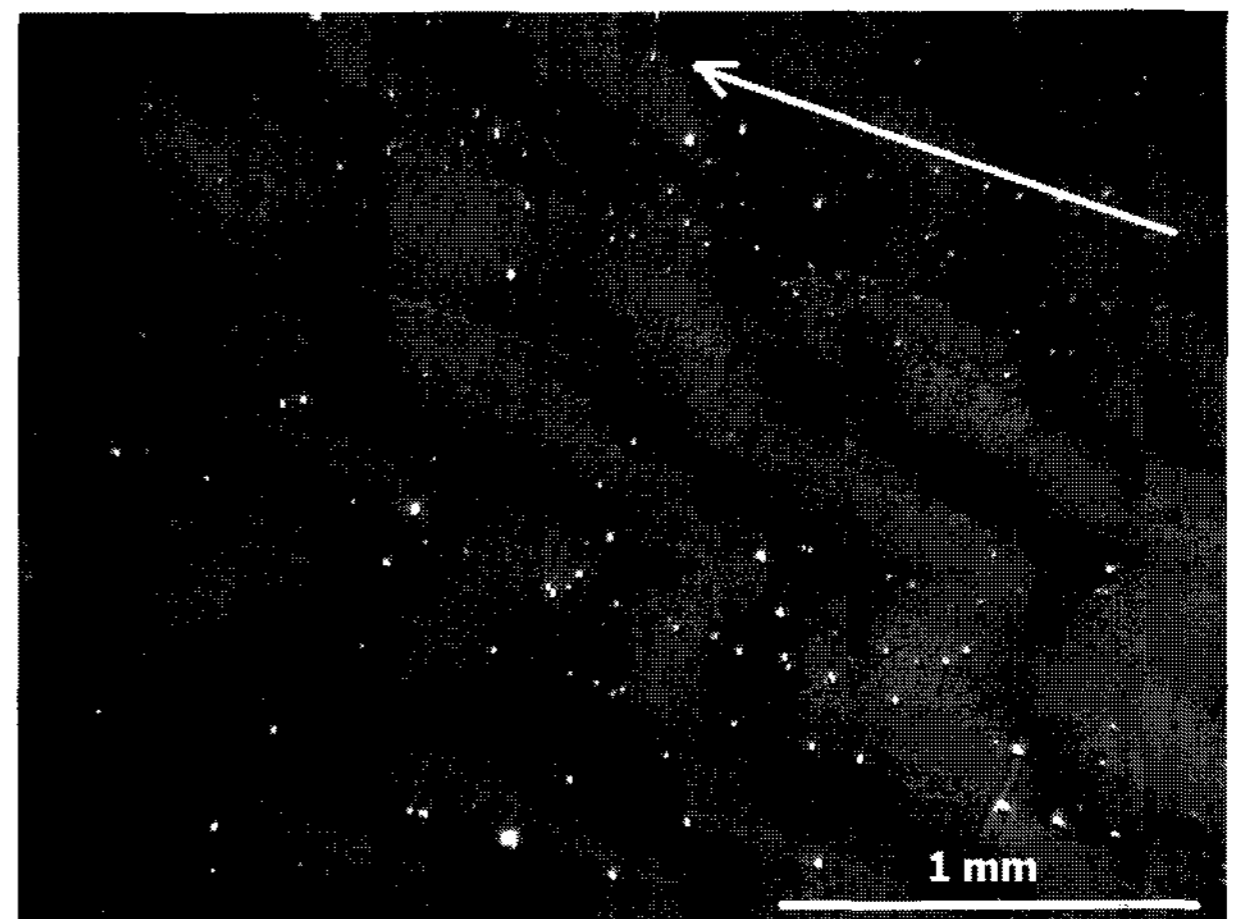


Fig. 16. Polarizing microphotograph showing the elimination of tiger stripes in the film with cromolyn and Fast Violet B.

It should be noted that concentrations of Fast Violet B dye greater than or equal to about 2 percent in the LCLC/dopant solution decrease the polarization efficiency of the resulting LCLC film. Moreover, a high concentration of additive decreases the film transmittance in visible and near-infrared wavelength range. The solution should contain no more than 4 percent dopant, and preferably less than about 2 percent dopant. Fig. 17 compares the

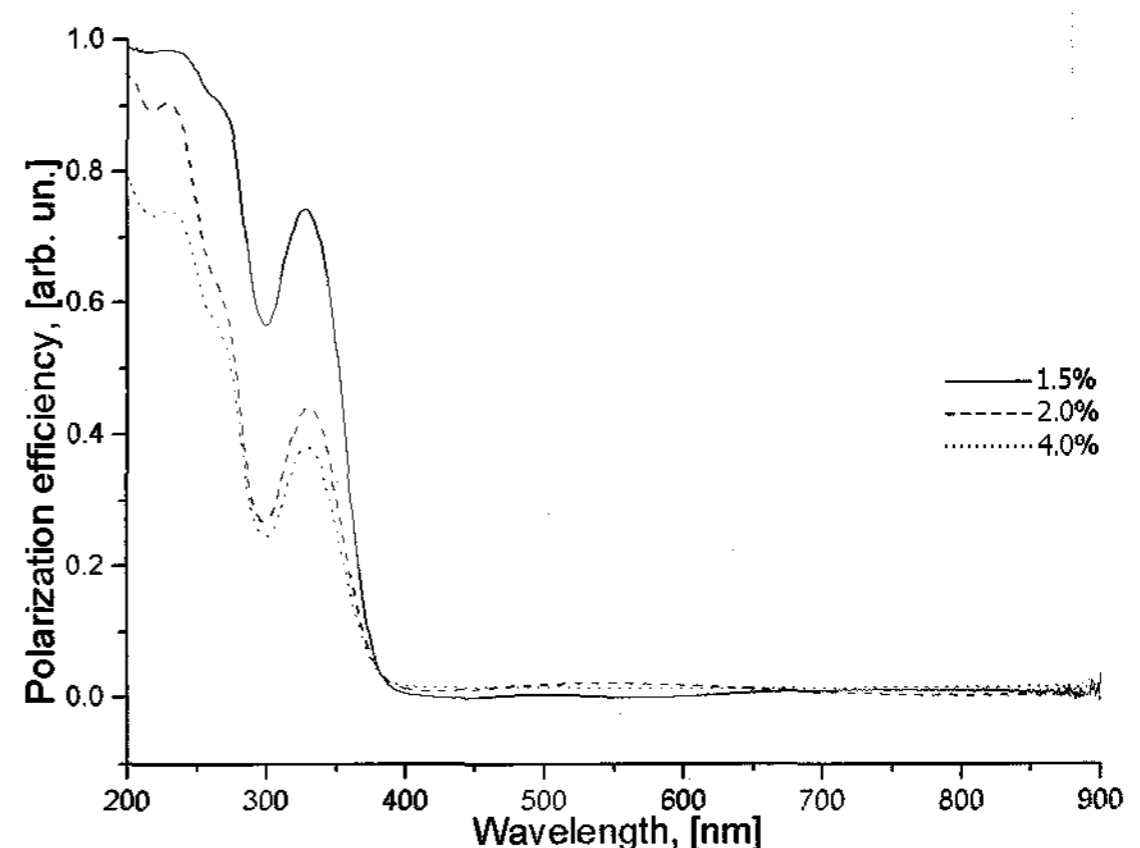


Fig. 17. Polarization Efficiency of films with cromolyn and an increasing amount of Fast Violet B. Note that the optimal concentration contains less Fast Violet B.

polarization efficiencies of dried LCLC films with different weight concentration of the Fast Violet B dye. A low concentration of about 1.5 % is optimum, as it provides an increased uniformity in director orientation and thus enhanced polarization efficiency.

The window of transmittance may be broadened in wavelength by the careful selection of particular UV dye additives. For example, using 2,2'-Dihydroxybenzophenone ($C_{13}H_{10}O_3$) dye, we enhanced the polarization efficiency for polarized UV light in the wavelength region of 300-400 nm. 2,2'-Dihydroxybenzophenone was purchased from Sigma-Aldrich (Corp. St. Louis, MO, USA), and has the following chemical structure:

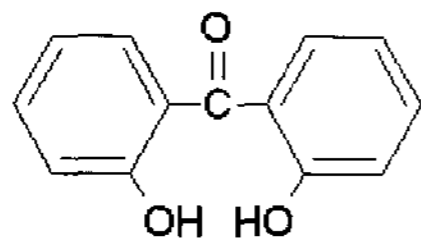


Fig. 18 compares the polarization efficiency of an 800 nm thick dried cromolyn film with 0.3 % weight concentration of 2,2'-Dihydroxybenzophenone dye to that of a cromolyn film with Fast Violet B dye (1.5 %) of the same thickness.

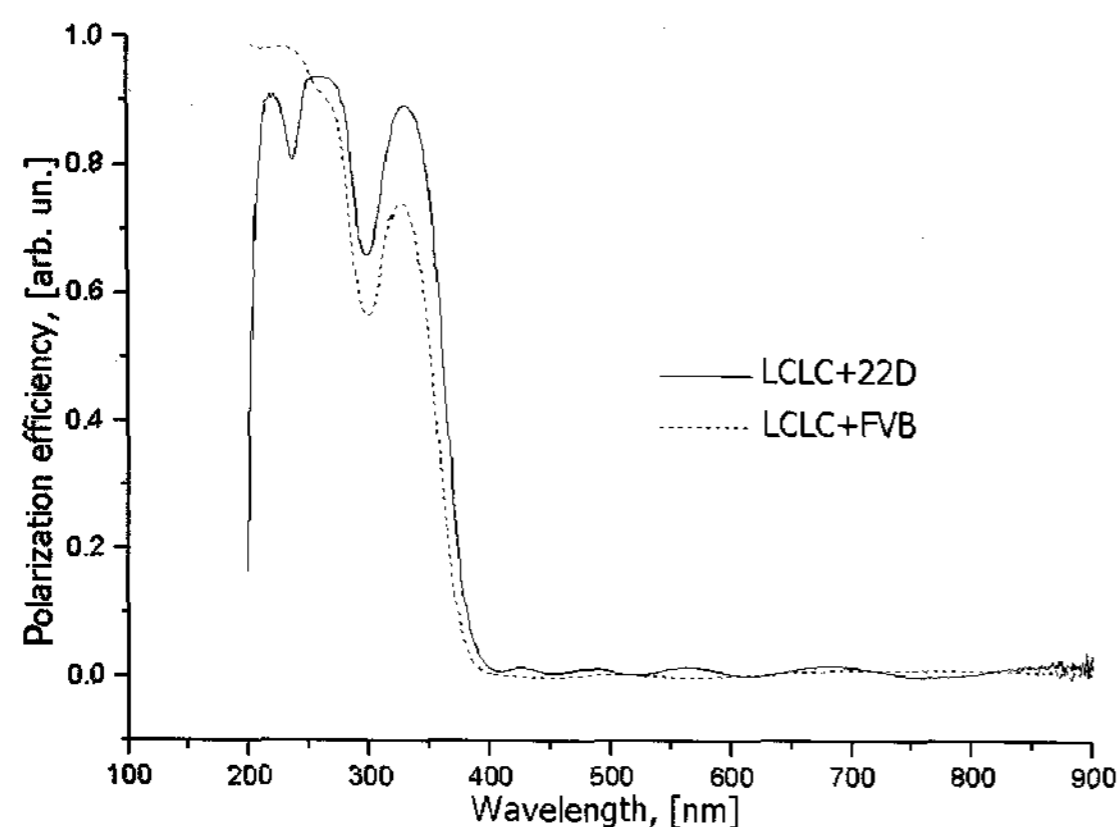


Fig.18. The polarization efficiency of two dried cromolyn films; cromolyn with 2,2'-Dihydroxybenzophenone (LCLC+22D) dye enhances the polarization efficiency of transmitted UV light in the region of 300 – 400 nm in comparison to a cromolyn film with Fast Violet B dye (LCLC+FVB) of the same thickness.

4. Conclusion

We demonstrated that the water solutions of the LCLC

materials can be used to produce aligned films with anisotropic optical properties that can be used in a variety of optical applications. One of the most attractive is

the fabrication of internal polarizers for flexible plastic displays. The advantage of placing the polarizer inside the cell, between the plastic substrate and the thermotropic electrically-switched liquid crystal is that the birefringence of the plastic does not play a major negative role in the performance of the device. We demonstrated that it is possible to improve the uniformity of LCLC alignment in the shear-deposition process, by using two different classes of materials as additives to the LCLC compositions. In both cases, the undesirable director distortions, the tiger stripes, are reduced (in terms of the amplitude of director distortions) or eliminated completely. The underlying mechanisms that control the director alignment in mixtures with different additives remain to be studied in a greater detail. We also demonstrated a UV polarizer formed from the mesomorphic water solutions of DSCG that does not adsorb in the visible region but polarizes light efficiently in the UV region.

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