

## Thin crystalline film retarders for LCD

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### ABSTRACT

We have studied a new class of materials for LCD retarders produced by Cascade crystallization method. Advanced materials comprise the amphiphilic compounds and include salts of carboxylic and sulfonic acids with conjugated aromatic cores, which do not absorb light in visible range of light spectra. The Cascade crystallization method of manufacturing of the thin crystalline films (TCF) is based on printing from aqueous solution of lyotropic liquid crystal phase. We have produced and examined a series of retardation films that exhibit properties of negative A-plates. As compared to conventional retardation materials, new retardation films produced with the Cascade crystallization method are strikingly thinner (thickness range is 100 - 1000 nm), whereas birefringence is typically much higher ( $\Delta n$  varies from 0.05 to 0.40). Such a broad range of available thickness and retardation values makes feasible tailoring of LCD designs for customer needs. Viewing angle performance of the crossed polarizers is significantly improved in the presence of TCF retardation films, so that the light leakage at oblique incidence decreases several times. Formation of the new coatable stretchless retardation coatings by a roll-to-roll process can be easily incorporated into the techniques widely used in the LCD industry. The TCF retarders are aimed for LCD HTV application and open up opportunities for the manufacturing cost reduction.

**Keywords:** retardation film, compensating film, birefringence, thin crystalline film

### 1. INTRODUCTION

Motivation for development of coatable high-birefringence thin layer optical components is created by rapidly growing Home TV LCD market segment. Home TV LCD is winning market over CRT on the basis of form factor and performance characteristics and now market development is entering in new stage – cost reduction stage that will ensure the home TV LCD segment of the market expansion. Cost reduction process requires increase of function efficiency from all optical components and elimination of dysfunctional structural elements like inert substrates that have only supporting function. It calls for components that can be coated directly on another functional components and/or on existing structural components like glass envelope.

Development of reflective interference polarizers will eliminate conventional dichroic polarizers while providing an increase of the light efficiency for LCD. Currently, dichroic polarizers are responsible for light-to-heat conversion of more than 50% of light generated by backlight. Development of interference polarizers (I-polar<sup>TM</sup>) requires high birefringence (0.8 – 1.0) and low thickness (60 – 120 nm). Obviously, these specifications can be made available only in coating technology processes.

Home TV market requirements for viewing angle qualities of the LCD device create need in retarders for LC cell and polarizers compensation [1-3]. Thin and birefringent coatable films promise cost reduction by eliminating expensive stretching processes and by eliminating structural supporting films.

Present paper is devoted to development of highly birefringent coatable films that would serve as retarders and materials for I-polar.

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## 2. MATERIALS AND METHOD

### 2.1 Molecular design

Coating materials for TCF retarder manufacturing are based on water-soluble heterocyclic compounds based on the aromatic molecular core I (Fig. 1) [4]. Compounds C001 and C002 are both products of sulfonation of acenaphtho[1,2-b]quinoxaline carboxylic derivatives and differ in location and character of functional groups.

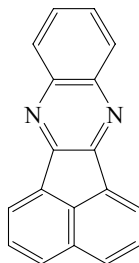


Fig. 1. Structure I: Acenaphtho[1,2-b]quinoxaline molecule.

### 2.2 Coating material formulation

Coating solutions of materials were prepared with different counterions:  $\text{NH}_4^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  [4]. The  $\text{H}^+$ -forms of the core compound, i.e. sulfo- or carboxy- acids of C001 and C002 were dissolved in DI water containing  $\text{NH}_4\text{OH}$ ,  $\text{LiOH}$ ,  $\text{NaOH}$ , or  $\text{KOH}$  and concentrated on rotary evaporator. Typical pH of concentrated LLC is close to neutral. Optical textures corresponding to nematic Lyotropic Liquid Crystal (LLC) phase formation were observed on Nikon Eclipse E400 microscope with a polarizer and an analyzer, fitted with a Mettler FP82 heating stage. Complete transition into nematic LLC phase occurred above 18-20 wt% of solids for C001 material at normal conditions. A typical optical texture of the C=20% w/w,  $\text{Li}^+$  counterion material in nematic phase is shown in Fig. 2.

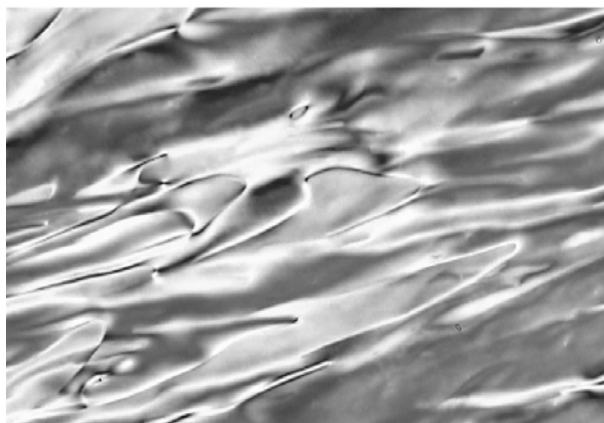


Fig. 2. A typical texture of LLC phase in water of C001 compound, C=20% w/w,  $\text{Li}^+$  counterion.

A typical working concentration for the coating solution is in the range of C=18-20% w/w.

### 2.3 TCF retarder coating

Samples of TCF retardation films were produced by direct deposition of LLC coating solution on glass and on cellulose triacetate (TAC) film substrates. We used Buschman® microgrooved stainless steel rod for coating. The rod has microgrooves with the depth of microgroove depending on the required thickness of the retarder film. A uniform wet coating of 5 to 15  $\mu\text{m}$  thick [4-9] allows producing TCFs from 100 to 1100 nm thick. Shear field imposes flow alignment on the supramolecular structures of the LLC material. The necessary alignment can be achieved under high shear rates ( $\sim 10^6 \text{ s}^{-1}$ ). Microgrooved rod's ridged surface produces even thickness of the liquid layer on the substrate surface and creates shear force during distribution of material on the substrate, which aligns supramolecular structures of the LLC material.

## 2.4 Optical characterization of TCF coating material

LCD optical applications require colorless materials for optical compensation films. We define a material as a colorless, if its extinction coefficients are less than  $10^{-3}$  in visible spectral range.

A typical absorbance UV-VIS spectrum of a diluted solution of compound C001 is presented in Fig. 3.

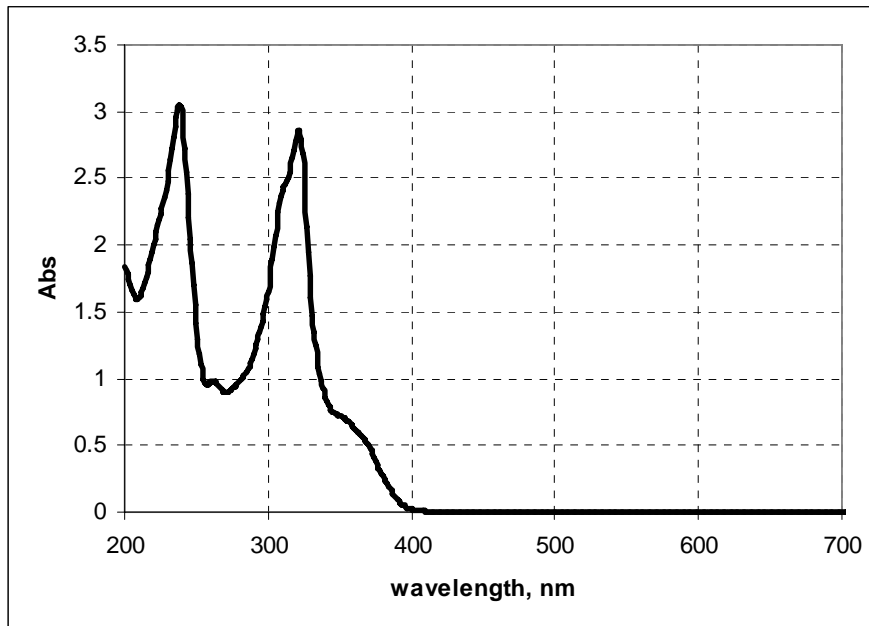


Fig. 3. Absorbance spectrum of compound C001 water solution with concentration  $C \sim 5 \times 10^{-4} M$ .

## 2.5 Optical properties of TCF retarders. Refractive indices measurement methodology

Combined measuring and calculation technique was used to determine all three refractive indices.

First, the values of one of the refraction indices and thickness of the anisotropic film were determined from spectral measurements using Varian Cary-500 spectrophotometer (400-750 nm spectra of transmittance at normal incidence and reflectance for 12 degree incidence). The spectral data were processed by the Multilayer software specially designed for inverse problem solving, producing  $n_x$  spectra and thickness  $\delta$  as the output data.

Secondly, we used, Axometrics' ® Mueller Matrix Polarimeter (MMP, Fig. 4) equipped with visible range wavelength light source to determine all three refractive indices.

We needed information about at least one refraction index and thickness of anisotropic film that have been obtained from intensity-based calculations (Inverse problem, Multilayer software). In the calculations,  $n_x$  index was taken as an input parameter. TCF thickness value was calculated by using Inverse problem optimization, and also independently measured with Veeco ® Dectak S3T surface profilometer.

In plane and out of plane retardance is measured with Axometrics MMP using Brewster's angle sample holder. TCF coated on  $60 \times 60$  mm display glass was fixed in holder; film was coated on side of the glass oriented to beam. Firstly, sample was rotated around coating direction  $x$  (fast axis). Fast axis was oriented horizontally (perpendicularly to the beam). Retardance  $\delta\varphi_{\text{par}}(\lambda, \theta)$  was recorded for 400 – 750 nm spectral region with the step of 10 nm and with 10 times averaging for each measurement. Measurements were performed for the sample inclined by the angles  $\theta$  varied from -65 to 65 degrees with the 5-degree step. Secondly, the sample was fixed such as it could be rotated around the  $y$ -axis, which is perpendicular to coating direction (slow axes). Slow axis was oriented horizontally (perpendicularly to the beam). Measurements of  $\delta\varphi_{\text{per}}(\lambda, \theta)$  were performed in a same way.

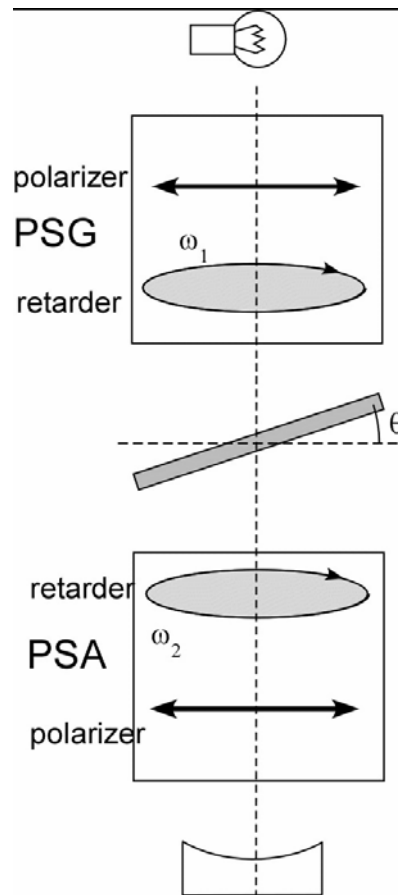


Fig. 4. General scheme of Axometrics ® Mueller Matrix Polarimeter used in MMP technique for out-of-plane indexes determination.

$n_y$  was calculated from  $n_x$  and average in-plane retardation  $\delta\varphi(\lambda,0) = (\delta\varphi_{par}(\lambda,0) + \delta\varphi_{per}(\lambda,0))/2$  (which is given in degrees):

$$n_y(\lambda) = n_x(\lambda) + \frac{\delta\varphi(\lambda,0)}{360d} \lambda \quad (1)$$

Formally  $n_z$  could be calculated independently from each angular measurement using trigonometric equations linking  $n_z$  with  $n_x$ ,  $n_y$  and incidence angle  $\theta$ .

$n_z(\lambda)$  was calculated from averaging of obtained values of  $n_z(\lambda,\theta)$  for  $30^\circ \leq \theta \leq 65^\circ$  and  $-30^\circ \leq \theta \leq -65^\circ$  (Fig. 5):

$$n_z(\lambda) = \frac{\left[ \sum_{\theta=30}^{65} n_z(\lambda,\theta) + \sum_{\theta=-30}^{-65} n_z(\lambda,\theta) \right]_{per} + \left[ \sum_{\theta=30}^{65} n_z(\lambda,\theta) + \sum_{\theta=-30}^{-65} n_z(\lambda,\theta) \right]_{par}}{32} \quad (2)$$

It could be done by fitting of  $n_z(\lambda)$  with one of the analytical functions.

$n_z(\lambda)$  function could be smoothed to remove oscillations (Fig. 5). Amount of  $\delta\varphi(\lambda,\theta)$  measurements needed for  $n_z$  determination could be reduced without influence on final  $n_z$  value (Fig. 6).

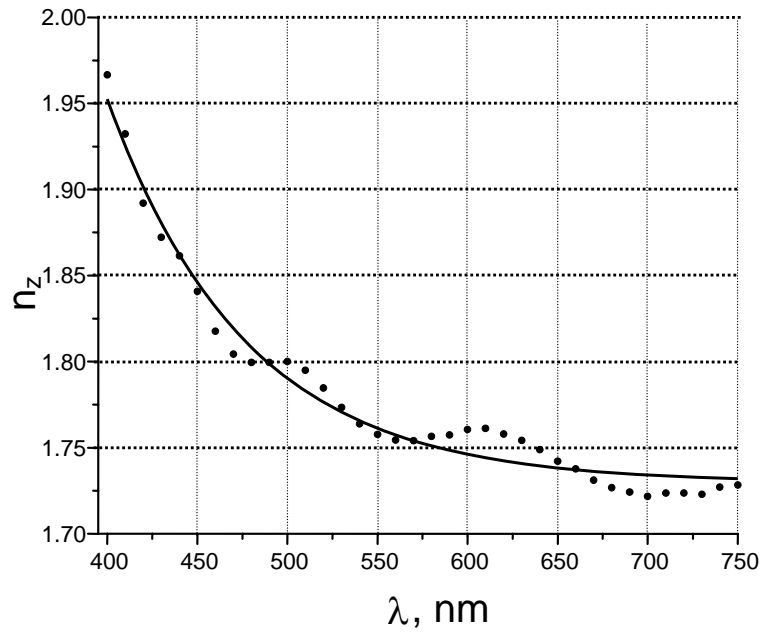


Fig. 5. General  $n_z(\lambda)$  smoothed with first order exponential decay.

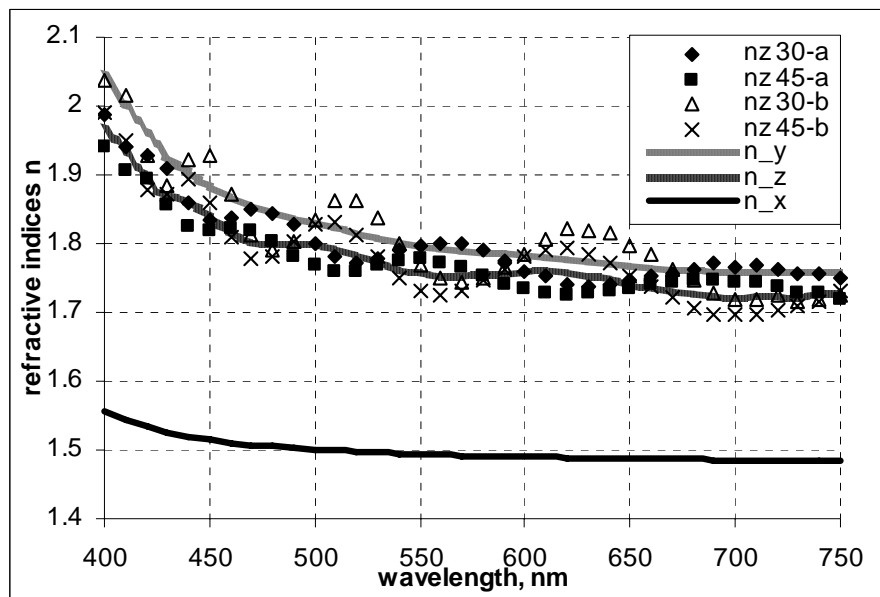


Fig. 6. Calculated refractive indices of TCF C001 ( $\text{NH}_4^+$  based) on glass substrate.  $n_x$  and  $d$  are obtained from “Multilayer” calculations.  $n_z$  calculated from  $\delta\phi_{\text{par}}(\lambda,30)$ ,  $\delta\phi_{\text{par}}(\lambda,45)$ ,  $\delta\phi_{\text{par}}(\lambda,60)$ ,  $\delta\phi_{\text{per}}(\lambda,30)$ ,  $\delta\phi_{\text{per}}(\lambda,45)$ ,  $\delta\phi_{\text{per}}(\lambda,60)$ .

## 2.6 Environmental stability of TCF retarders

Material of the optical film has to be water-insoluble in its TCF form. From the stage of molecular design of the future material, certain considerations are needed. For example it is possible to design a molecule containing less functional groups capable of “holding” crystallization water ( $-\text{SO}_3^-$  groups). Also, materials C001 and C002 have the capability of converting into water-insoluble form. Material of the optical film (TCF) usually has to be post-treated (stabilized) to become fully water-insoluble [4-8]. Post-treatment converts TCF material from its initial ionic (usually  $\text{Na}^+$  or  $\text{NH}_4^+$ )

form into water-insoluble (bivalent heavy metal  $Me^{2+}$ ) cationic form. This ion-exchange reaction is performed via dipping of TCF sample on polymer film or glass substrate into  $Me^{2+}$  salt solution for very short time. Rinsing with water is applied after dipping. In case of line production, coated film “slides over” the tank containing post-treatment solution. 2 or 3 rinsing tanks with DI water follow the main tank, which produces the stable TCF.

After 1000 hour-cycle environmental test under high humidity (60°C/90%RH) we performed measurement of optical indices and haze/depolarization. Over the sample area of  $\sim 5 \text{ cm}^2$ , both depolarization index and refraction differ from initial values for not more than  $\pm 5.0\%$ .

### 3. RESULTS AND DISCUSSION

#### 3.1. Molecular structure, liquid crystal arrangement and refraction indices

One of fundamental results of present study is demonstration of molecular structure that has strong enough  $\pi - \pi$ -stacking interaction in order to produce stacks in the water and form kinetic units long enough to be ordered by hydrodynamic flow in coating technique and, at the same time, is still colorless. It is well known that heterocyclic conjugated compounds are mostly colored and it limits their potential in producing useful retarder materials. Achievement of LLC phase state at relatively low concentration of solids that allows a production of thin retarders proves viability of this direction of molecular engineering.

Rod-like molecular stacks are aligned in the coating process along coating direction with molecules positioned with their plane perpendicular to the surface of substrate. Polarizability of  $\pi - \pi$ -bond is relatively low and it results in the relatively low refraction coefficient along the coating axis.

Refraction in two other directions depends upon polarizability of molecule in its plane and position of the molecules in stacks as well as position of stacks relative to each other.

Refractive indices are presented in Fig 7. Indices for X and Z directions are practically equal and in conventional nomenclature it corresponds to negative A-plate retarder (Fig. 8). Relative values of refraction coefficients allow assuming that molecules have libration freedom inside stack and/or stacks are randomly oriented relative to each other. In any way, birefringence of the resulting A-plate is about 0.39, which is much higher than birefringence of stretched polymeric materials and conventional liquid crystals. High values of birefringence create opportunity to produce retarders with sub-micron thickness, which are useful in practical applications and, on other side, it creates stringent requirements on accuracy thickness that limits applicable coating processes.

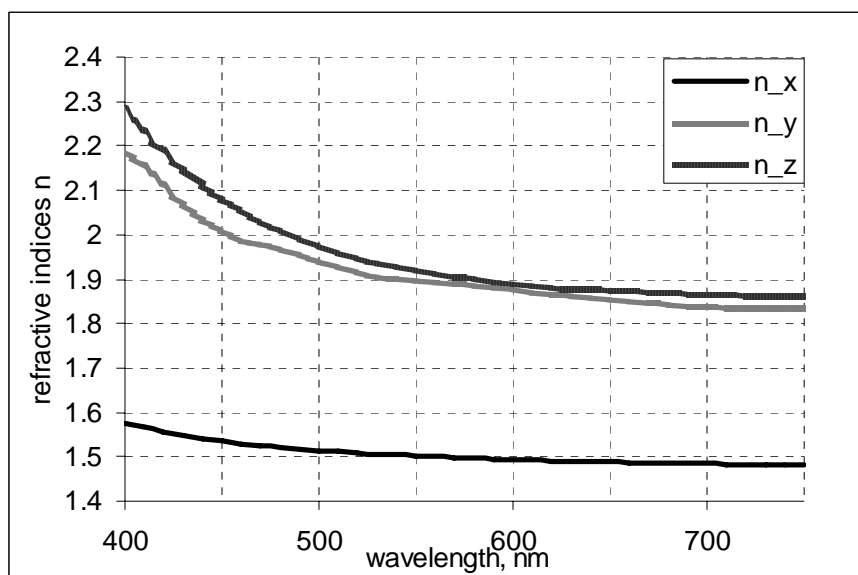


Fig. 7. Refractive indices of TCF C002 ( $NH_4^+$  based) on glass substrate.  $n_x$  and  $d$  are obtained from “Multilayer” calculations.  $n_z$  is measured with Axometrics MMP technique.

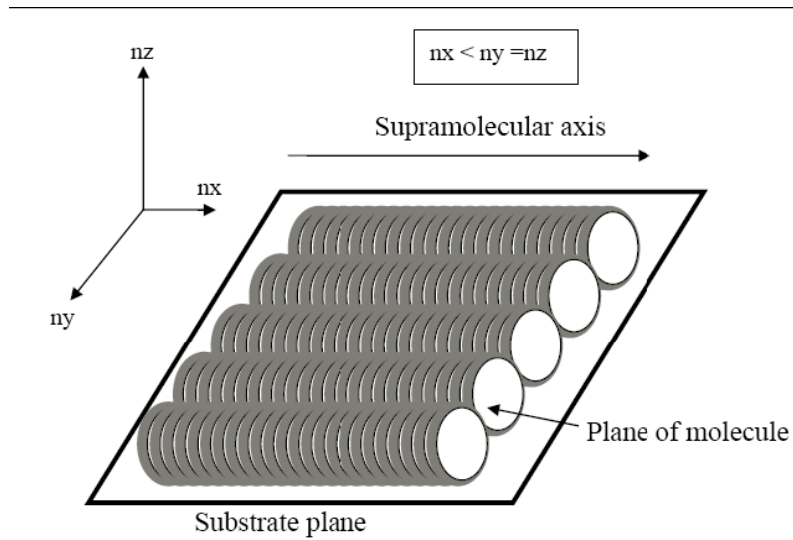


Fig. 8. C002 packing to form close to uniaxial negative A-plate.

By prototyping LCD cell compensated by new retarders, we have shown that coating might be in required tolerances.

### 3.2. Coatable retarder application for LCD optical compensation

We present the results of LCD cell simulation with new coatable retarders below [10]. For value  $\Delta n_{xy} \sim 0.39$  ( $\lambda = 550nm$ ) (negative A-plate retarder) in coated TCF layer with thickness  $\delta = 640$  nm, in-plane retardance is equal to  $R_A = 250nm$ . Using this characteristics, computer simulation of VA compensation LCD design performance was made (optical stack is presented in Fig. 9, and contrast ratio contour plot is shown in Fig. 10).

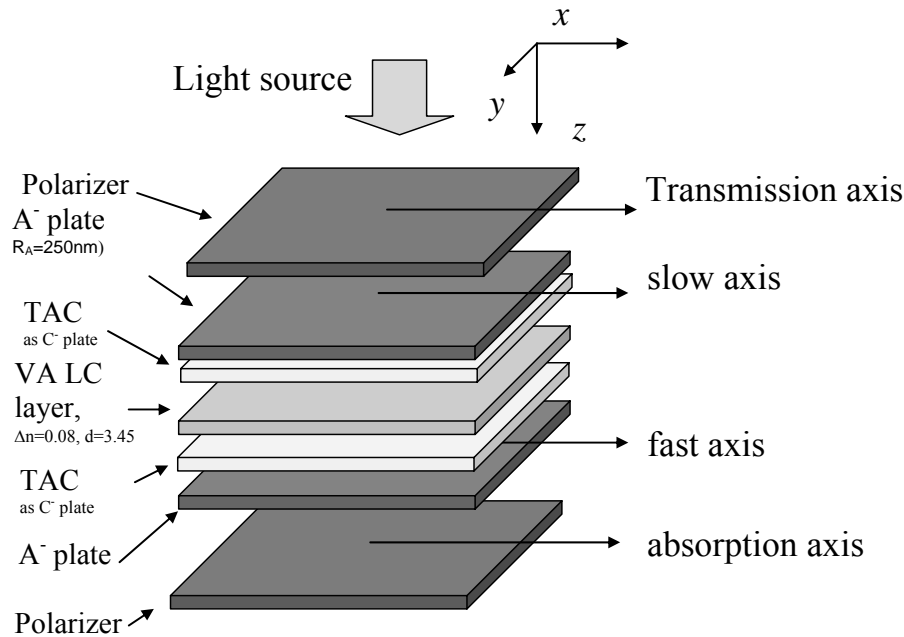


Fig. . VA LCD design optically compensated with TCF C002 retarder; simulation is based on measured optical parameters of TCF C002 coated from LLC on TAC substrate: TCF thickness  $\delta = 640$  nm, TCF retardance  $R_A = 250nm$ , TAC film retardance  $R_{TAC} = 130nm$ .

To realize this VA LCD design we have chosen commercially available TAC film of certain retardation and thickness. One of commercially available types of TAC film exhibiting properties of C-plate provides retardation value  $R_{TAC}=130\text{nm}$  at a film thickness  $d_{TAC} = 120\mu\text{m}$ . The following contrast plots demonstrate what level of compensation can be reached by using such a TAC film (Fig. 10).

**Contrast ratio at 550 nm.**

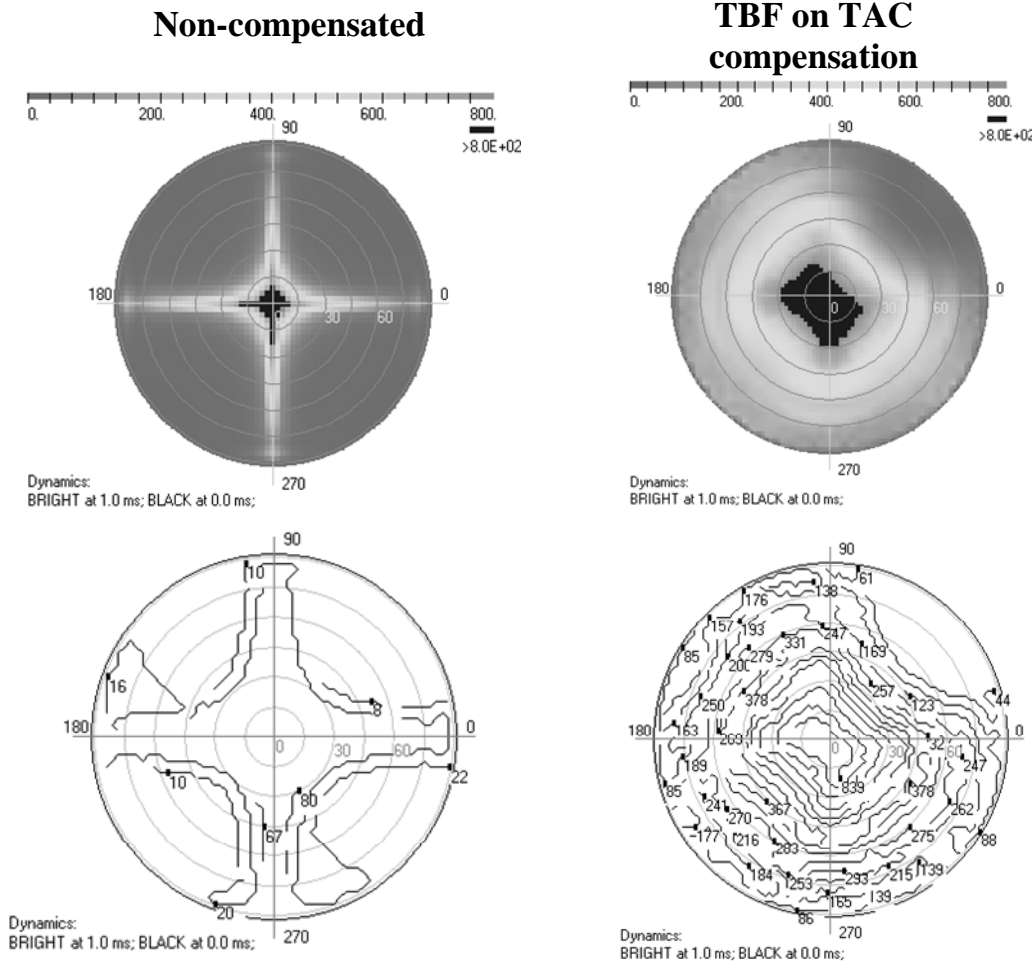


Fig. . Comparison of non-compensated and TCF-on-TAC compensated VA LCD design performance: Contrast ratio viewing angle dependence at 550nm (results calculated using TCF C002 characteristics: TCF retardance  $R_A=250\text{nm}$ , TAC substrate film retardance  $R_{TAC}=130\text{nm}$ ).

Results of simulation and prototyping have shown feasibility of new coatable A-plate retarder applications for optical compensation of VA cell LCD. We developed new design of VA cell and polarizer compensation that is based on conventional negative C-plate TAC and new coatable negative A-plate.

#### **4. CONCLUSIONS**

Summing up the results and discussion points above, we would like to state that:

Molecular engineering can produce colorless molecular materials with rod-like stacks of molecules.

Rod-like stacks form Lyotropic Liquid Crystal phase that allow to order molecules in coating process.

After drying, coated film exhibits properties of negative A-plate.

Negative A-plate coated on TAC provides sufficient birefringence for VA cell LCD compensation.

Coated layer of new birefringent material is environmentally stable and passes standard LCD industry tests.

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