Lyotropic chromonic liquid crystals (LCLCs) represent a special class of
lyotropic mesophases markedly different from conventional amphiphilic mesogens.
Materials forming LCLCs are composed of plank-like molecules with a polyaromatic
central core and hydrophilic ionic groups at the periphery. The individual molecules
tend to assemble into rodlike aggregates that form the $N$ phase once the concentration
exceeds about $0.1M$.

The LCLC materials show a tremendous potential for applications in optics as
self-assembling polarizing and compensating films and in the area of real-time
biological sensing. The emerging applications require an understanding of basic
properties of LCLC. This work addresses these needs by providing the optical
characterization of LCLC.

We studied in detail the optical anisotropic properties of three different nematic
LCLCs: disodium cromoglycate (DSCG), Blue 27, and Violet 20. We determined the
birefringence of these three materials as the function of the temperature $T$ and
wavelength $\lambda$ and the corresponding dependencies of the absorption coefficients for Blue 27 and Violet 20. The birefringence is negative and significantly lower in the absolute value as compared to the birefringence of typical thermotropic N materials.

We determined the scalar order parameter of the nematic phase of Blue 27 and its temperature dependence. The scalar order parameter is close to the one predicted by the classic Onsager theory for solutions of rigid rods. However, this similarity is not complete, as the measured scalar order parameter depends on temperature.

The $I$-$N$ pretransitional fluctuations in an aqueous solution of DSCG were studied by light scattering. We obtained the correlation length of the orientational order-parameter fluctuations of isotropic DSCG solution. The pretransitional behavior of light scattering does not completely follow the classic Landau-de Gennes model. This feature is explained by the variable length of DSCG aggregates as a function of temperature.
OPTICAL CHARACTERIZATION OF LYOTROPIC CHROMONIC LIQUID CRYSTALS

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Chapter I

Introduction

Liquid crystals (LCs) are the intermediate state of matter between crystalline solids and the liquids. Crystalline solids generally possess both positional and orientational order, meaning that the centers of mass of the molecules occupy specific locations and the molecular axes point in certain directions. In liquid state there is no positional or orientational order. In a liquid crystalline phase (also called mesophase) the building units show an orientational order, with no or partial positional order [1].

There are two main classes of liquid crystals, thermotropic and lyotropic, which are distinguished by the mechanisms that drive their self-organization. Thermotropic liquid crystals are induced mainly by changing the temperature, while lyotropic liquid crystals are induced by changing the concentration of a solute material in an appropriate solvent [2].

1.1 Thermotropic liquid crystals

Thermotropic liquid crystalline state can exist in a certain temperature range.
Upon heating, thermotropic LCs will eventually transform into a conventional liquid state characterized by random and isotropic molecular ordering and fluid-like flow behavior. The building blocks (molecules or groups of molecules) of a thermotropic liquid crystal are generally anisometric, elongated (calamitic molecules) or disk-like (discotic molecules) [4].

Thermotropic LCs can be further divided into the following categories by the type of ordering of the system: nematic with no long range positional order, smectic with a 1-D long-range positional order, columnar with a 2-D long-range positional order, and 3-D correlated structures.

1.1.1 Nematic phase

Nematic liquid crystals have a long-range orientational order of the molecules but no long-range translational order. The simplest LC is the uniaxial nematic phase. The molecular axes of neighboring molecules on average point in a certain direction, called the director $\mathbf{n}$, $\mathbf{n}^2 = 1$.

While most of nematic LCs are uniaxial, some of them are biaxial, meaning that their molecules, in addition to orienting one of their axes, also align their secondary axes. The biaxial nematic phase was first identified by Yu and Saupe [88] for a lyotropic system, namely, in a ternary mixture composed of potassium laurate, 1-decanol and D$_2$O. Biaxial nematics can be expected with building blocks shaped in
the form of rectangular boxes.

When the building blocks are chiral (i.e. different from their mirror image), or a chiral dopant is dissolved in a nematic LC, the nematic LC will show a helical structure. The helical distortion is often unidirectional and the director $n$ rotates around a single axis in space. This helical phase is called cholesteric because the first materials identified as cholesteric LCs were derivatives of cholesterol [2].

1.1.1.1 Order parameter

The director of LCs only specifies the direction of average orientation but not the degree of orientational order [4]. LCs have a lower symmetry than the high-temperature isotropic liquid. We express this qualitatively by saying that the nematic phase is ‘more ordered’. To put this ordering on a quantitative basis, we need to define an order parameter that is non-zero in the liquid crystal phase but vanishes, for symmetry reasons, in the isotropic phase [2].

One can define the order parameter based on average of the second order Legendre polynomial [2]:

$$S = \langle \frac{3\cos^2 \theta - 1}{2} \rangle,$$

where $\theta$ is the angle between the axis of an individual molecule (or building unit) and the director, and $\langle \ldots \rangle$ means an average over molecular orientations. $S$ is often called
the ‘scalar order parameter’ [4].

For a regular isotropic liquid, one would expect \( \langle \cos^2 \theta \rangle = \frac{1}{3} \), thus \( S = 0 \), which means that there is no orientational order present. For a perfect crystal, all the molecules rigidly aligned parallel to each other, one would expect \( \langle \cos^2 \theta \rangle = 1 \), so \( S = 1 \). For a system with all the molecules orienting randomly in a plane, \( \langle \cos^2 \theta \rangle = 0 \), thus, we would have \( S = -1/2 \).

1.1.1.2 Onsager theory

Onsager [44] had proposed a model of solutions of hard-rod molecules with well defined length \( L \) and diameter \( D \) and discussed the statistics of such system. He assumed that the long rods \((L >> D)\) cannot interpenetrate each other and the volume fraction of the rods is very small.

The free energy is given by [2]

\[
F = F_0 + k_BT \left( \int f_a \log(4\pi f_a c) d\Omega + \frac{1}{2} c \iint f_a f_{a'} \beta_1(aa') d\Omega d\Omega' \right),
\]  

(1.2)

where \( c \) is the concentration of rods; \( \beta_1(aa') \) is the excluded volume of one rod in the direction \( a \) as seen by another rod in direction \( a' \), and \( \beta_1 = 2L^2D|\sin \gamma| \); \( \gamma \) is the angle between \( a \) and \( a' \); \( f_a \) is the probability of a rod pointing to the unit vector \( a \); \( \Omega \) is the solid angle; and \( \int f_a d\Omega = 1 \).

The second term in Eq. (1.2) describes the loss of orientational entropy with
increasing molecular alignment. The third term addresses the contribution of the free energy due to the excluded volume effect on the entropy.

It is not easy to solve Eq. (1.2) with \(f_a\) that satisfies Eq. (1.3) exactly. Onsager used a variational method, based on a trial function of the form

\[
f_a = \frac{A \cosh(\alpha \cos \theta)}{\sinh(\alpha \cos \theta)},
\]

(1.4)

where \(\alpha\) is a variational parameter, and \(\theta\) is the angle between \(a\) and the nematic axis; \(A\) is chosen to normalize \(f\) according to Eq. (1.3). The order parameter is

\[
S = \left\langle \frac{1}{2} (3 \cos^2 \theta - 1) \right\rangle = \int \frac{1}{2} (3 \cos^2 \theta - 1) f(\theta) d\Omega,
\]

(1.5)

Minimizing free energy \(F\) (Eq. (1.2)) with respect to \(\alpha\), one could obtains a function \(F(c)\) showing a first order phase-transition from isotropic \((\alpha = 0)\) to nematic \((\alpha \geq 18.6)\) [2].

Putting the volume fraction of rods \(\Phi = \frac{c \pi LD^2}{4}\), we can have isotropic phase when \(\Phi < 3.34 \, D/L\), where the order parameter \(S = 0\); nematic phase for \(\Phi > 4.49 \, D/L\), the order parameter \(S = 0.84\), and a biphasic region for \(3.34D/L < \Phi < 4.49D/L\).

Note that \(\Phi\) is a temperature independent parameter in this model: hard rods are an ‘athermal’ system. Order parameter \(S\) is also independent of temperature.
1.1.1.3 Maier-Saupe theory

Maier and Saupe developed a statistical theory of the nematic state including contributions from an attractive intermolecular potential.

The free energy density can be written as

\[
\int \Omega - \int \frac{1}{\rho} \ln \left( \frac{\rho^{2}US^{2}}{\rho kT} \right) d\Omega, \tag{1.6}
\]

where \( U \) is a measure of the strength of the interaction, \( \rho = V/N \), \( V \) is the total volume of the system, \( N \) is the number of molecules, \( S \) is the order parameter, \( P_{2}(\cos \theta) \) is the second Legendre polynomial.

To determine the order parameter \( S \), we minimize the free energy \( f(S) \) with respect to \( S \) and setting \( \frac{\partial f}{\partial S} = 0 \) gives

\[
S = \frac{\int \rho^{2}US^{2} e^{\frac{\rho^{2}US^{2}P_{2}(\cos \theta)}{kT}} d\Omega}{\int e^{\frac{\rho^{2}US^{2}P_{2}(\cos \theta)}{kT}} d\Omega}. \tag{1.6}
\]

Eq. (1.6) is a self-consistent equation for the order parameter \( S \). Eq. (1.6) can be solved graphically [2].

The phase transition at \( T = T_{c} \) is first order transition, and the order parameter just below the transition \( T_{c} \) is [2]

\[
S = S(T_{c}) = 0.44. \tag{1.7}
\]

At high temperature, the isotropic fluid is stable, \( S = 0 \). At low temperature, there
are two additional solutions which correspond to nematic and isotropic phase respectively. For a typical nematic LC, $S$ decreases as the temperature increases, and drops from 0.44 to 0 when the LC transforms into isotropic phase, where $T > T_c$.

1.1.2 Smectic phase

The *smectic* phase is the one where in addition to orientational order, the building blocks also show long-range positional order, usually of a one-dimensional nature, by forming a stack of equidistant layers. Thus, the smectic phase is more ordered than the nematic phase. From a structural point of view, all smectics are layered structures with a well defined interlayer spacing [2]. Smectic layers are flexible and can slide over each other. Within the layers, molecules move as in a liquid.

The smectic phase can be further divided into many sub-phases, called A, B, C, D, etc. In the smectic A phase, the system is optically uniaxial with the director normal to the layers. In the smectic C phase, the molecules are tilted with respect to the layer normal [3].

1.1.3 Columnar Phase

The *columnar* phase exhibits orientational order and 2-D positional order. The columnar phase in its simplest form consists of discs stacked one on top of the other
to form liquid-like columns. The columns arrange into a 2-D periodic lattice [3]. Most frequently, the columns are packed hexagonally. Note that there is no positional order of molecules along the columnar axes.

1.1.4 Blue Phase

Blue phases occur in a very narrow temperature range (on the order of 1K) between the chiral nematic and isotropic phases [3]. In blue phases, the director forms double twisted structures. The double twist can not expand through the entire volume of the material and must be accompanied by a 3-D periodic lattice of defects.

1.2 Lyotropic liquid Crystal

_Lyotropic liquid crystals_ are formed by dissolving a material in a suitable solvent and by changing its concentration [2]. Thus lyotropic LCs are made of two or more components. Generally one of them is amphiphilic molecules (soaps, phospholipids, etc.) and another one is a solvent, such as water or oil. Amphiphiles have two distinct parts: (polar) hydrophilic part and (non-polar) hydrophobic, oleophilic part (generally aliphatic) [5]. The building blocks of the lyotropic liquid crystal phase are aggregates of molecules rather than single molecules.

Lyotropic liquid crystals may be subdivided even further into surfactant-based liquid crystals and chromonic liquid crystals [6].
1.2.1 Surfactant-based liquid crystals

Surfactant type lyotropic liquid crystals are generally composed of a hydrophilic head and a hydrophobic tail. A familiar example of such a system is soap (sodium dodecyl sulphate). When dissolved into water, the hydrophilic head is attracted to water, and the hydrophobic tail is repelled by water. The surfactant molecules tend to arrange themselves so that the polar heads are in contact with a polar solvent and the non-polar tails are in contact with a non-polar solvent. As the surfactant concentration increases, several phases can be observed, such as (isotropic) micellar phase, nematic micellar phase, columnar phase, lamellar phase, and inverted phase.

1.2.1.1 Micellar phase

At a very low concentration, the surfactant molecules are distributed randomly throughout water without any ordering. For concentration above the critical micellar concentration (CMC), the molecules begin to arrange themselves into aggregates (Fig 1). The simplest configuration would be a spherical *micelle* (Fig. 1(a)), whose size scales with the size of the molecules, usually between 2 nm and 5 nm [5]. The surface of a micelle is a layer of polar heads facing water, while the inner portion consists of hydrophobic tails screened from the water by the hydrophilic heads. Mixing different amphiphilic substances might result in the formation of anisometric micelles.
1.2.1.2 Hexagonal columnar phase

As the concentration of the surfactants increases, the molecules can arrange into cylindrical micelles (Fig. 1(b)). The hydrophobic tails are located inside the micelle. The cylindrical units are arranged parallel to each other in a hexagonal array (Fig. 1(c)) [3]. But the distances of inter-cylindrical units are not regular.

1.2.1.3 Lamellar phase

At even higher concentrations the amphiphilic molecules can arrange into bilayer membranes and form a lamellar phase (Fig. 1(d)). If the solvent is water, water is sandwiched between the polar heads of adjacent bilayers, while the hydrocarbon tails, which are disordered or in a liquid-like configuration, are in a non-polar environment [3]. This pattern is similar to that of smectic liquid crystals in the thermotropic category. The sheet-like layers can slide easily past each other.

1.2.1.4 Inverted Micelles

Inverted micelles can occur in the hydrophobe-dominated compositions. In this phase, the hydrophobic tails point outwards the hydrophobic medium, while the solvent (such as water) is trapped inside [7].

Two or more phases may overlap to create biphasic or triple point regions in the
phase diagram. All phases can be inverted in lyotropic systems.

1.2.2 Lyotropic Chromonic Liquid Crystals

Another class of lyotropic mesomorphism is presented by the so-called lyotropic chromonic liquid crystals (LCLC) [6, 8]. The family embraces a range of dyes, drugs, nucleic acids, antibiotics, carcinogens, and anticancer agents [5]. In this thesis we will focus our effort on these materials. Structurally, the lyotropic chromonic liquid crystal molecules are plank-like or disc-like, and consist of a hydrophobic aromatic core with polar solubilizing hydrophilic periphery. When dissolved in water, the molecules tend to aggregate face-to-face to form nano-structured 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 micelles formed by rod-like surfactant type lyotropic liquid crystals. In contrast to spherical micelles, LCLC aggregates do not have a clearly defined size (length), because there are no geometrical restrictions to prevent another molecule adding to the existing aggregates. At high enough concentration, the aggregates can order themselves and form two basic mesomorphic phases, labeled $N$ and $M$ [6].
Fig. 1. Structural organization of surfactant molecules in water: (a) a spherical micelle, (b) a worm-like micelle, (c) hexagonal columnar phase formed by worm-like micelles, (d) bilayer membrane.
In the $N$ phase, the columnar aggregates align parallel to each other but show no long-range positional correlation, similar to a regular nematic phase in thermotropic materials. The variety of possible geometries of aggregation is enriched by the fact that the molecular planes can adopt different orientation with respect to the aggregates axes. In the so-called $H$-aggregates the molecular planes are perpendicular to the columnar axis, i.e., the molecules are stacked on the top of each other, while in the so-called $J$-aggregate, the molecules are shifted with respect to each other and thus their planes are strongly tilted with respect to the aggregate’s axis [6, 8, 9, 10, 11]. These two types of aggregation differ significantly in their spectroscopic properties, because the molecular interactions within the aggregates alter the absorption properties of the system as compared to individual molecules [10, 11, 12, 13]. Although it is plausible that the aggregates in LCLCs are formed by the attraction between the central core of plank-like molecules, there is no clear understanding of how exactly the molecules are arranged within the aggregates. Different models can be found in literature, including simple columns with one molecule in the cross-section, columns with hollow center (chimney type) and others [6, 8, 9].

Because of the polyaromatic molecular core, many LCLC absorb light in the range from the ultra-violet part to the near infrared part. The absorption is also anisotropic, i.e., it depends highly on the orientation of the LCLC aggregates’ axis with respect to the incident light polarization.
In the LCLC systems, there is a wide temperature range (generally about 2-3 °C), in which two phases, such as a nematic and isotropic phase, can coexist.

1.3 Motivation for this work

Despite a lack of complete understanding of supramolecular self-organization in LCLCs, it has recently become evident that some of these materials can be of practical use precisely because of their mesomorphic properties. Among the potential applications of LCLCs, the most actively pursued is the idea to use dried dye-based LCLCs films as light polarizing elements [75-85] in liquid crystal displays (LCD), especially in flexible plastic LCDs [76-85]. LCLCs could also be used as compensating films in LCDs [86] when the corresponding materials do not have significant absorption in the visible range of spectrum.

Other emerging applications of LCLCs are in biological sensors as a medium to amplify the antibody-antigen binding and visualize the growth of immune complex through director distortions [15, 91] and in formation of nanostructured monolayers with long-range in-plane orientational order [25]. In the latter case, one can directly visualize the bundles of LCLC rodlike molecular aggregates at nanometer scales with an atomic force microscope, after depositing the molecular monolayers of LCLCs onto a suitably charged substrate [25].

The LCLC materials show a tremendous potential for applications in optics as
self-assembling polarizing and compensating films and in the area of real-time biological sensing. The emerging applications require complete and detailed characterization of the LCLC properties and understanding of physical mechanism of their self-organization, especially of their optical properties and structural features, such as optical birefringence, absorption anisotropy, size of the aggregates, etc. This work addresses these needs by providing the first optical characterization of LCLC.

1.4 Summary and outline of this work

The goal of this work was to characterize the basic optical properties of a number of LCLCs. Because of previous difficulties of aligning LCLC, research in this area has been hindered. In most research articles, LCLCs are characterized spectroscopically for non-aligned samples, but not much attention is paid to their optical anisotropic properties [6, 9].

In this work, using a newly developed technique of uniform alignment of LCLCs based on rubbed polyimide alignment layers [29], we perform the first comprehensive study of the optical anisotropic properties of three different nematic LCLC materials: DSCG, Blue 27, and Violet 20. We determine the optical birefringence $\Delta n = n_e - n_o$ ($n_e$ and $n_o$ are the extraordinary and ordinary refractive indices, respectively) as a function of temperature $T$, weight concentration $c$, and wavelength $\lambda$, and the corresponding dependencies for the coefficients of absorption for Blue 27 and Violet.
20. We characterized the anisotropic light absorption of Blue 27 and Violet 20 and the absorption data are used to determine the scalar order parameter $S$ for the $N$ phase of Blue 27 and its temperature dependence.

By combining light-scattering and viscosity measurements on pretransitional fluctuations in the isotropic phase of the DSCG aqueous solutions we have been able to obtain the correlation length of the orientational fluctuations. We found that the pretransitional behavior of the DSCG aqueous solution cannot be fully described by the classic Landau-de Gennes model, but can be explained by the temperature dependence of the length of the DSCG aggregates. The increased length of aggregates upon cooling of the sample can explain a dramatic increase of the shear viscosity near the transition into the nematic phase.

This thesis is organized as follows: In chapter II, we described the materials and sample preparation techniques. Chapter III describes the result on optical birefringence, light absorption and scalar order parameter. Chapter IV describes the light scattering experiments, probing the pretransitional fluctuations. Conclusions and outline of future work are summarized in chapter V.
Chapter II

Materials and sample preparation

2.1 Materials

The lyotropic chromonic liquid crystals we studied are (Fig. 2) disodium chromoglycate (DSCG or cromolyn); 6,15-Disulfonicacid-7,16-dichloro-6,15 – dihydro - dinaptho[2, 3-a; 2', 3'-h]phenazine-5, 9, 14, 18-tetraone diammonium salt (also called blue 27); and 2,5-disulfonic acid diammonium salt-peryleno[3'', 4'':3, 4,5; 10'', 9''-3', 4', 5'] dipyridino [1, 2-a:1', 2'-a'] bisbenzimidazol-6, 11-diol (also called Violet 20).

2.1.1 Disodium Chromoglycate

Chemical formula: $C_{23}H_{14}O_{11}Na_2$

Disodium Chromoglycate (DSCG), also known as Cromolyn or Intal, was obtained from Spectrum Chemical Mfg. Corp. (Gardena, CA, CAS No. 15826-37-6). Although it is one of the most studied LCLCs overall [6, 8, 13-15] overall, the available data on it refer only to one concentration [14, 15]. The DSCG molecule is formed by two rigid heterocycles connected by a flexible bridge that allows the
molecule to assume many energetically similar conformations. One of the possible conformations of a free and isolated DSCG molecule, obtained through energy minimization in the Hartree-Fock approximation (PC SPARTAN PRO), is shown in Fig. 2; the two sodium cations at the opposite ends of the molecule appear blue in the figure.

The liquid crystalline phases of DSCG, namely, the (uniaxial) $N$ phase and a more highly ordered columnar phase (also called an $M$-phase) have been reported in 1970’s [16, 17]. The $N$ phase is formed by aggregates of stacked molecules. The aromatic cores of the molecules are on average perpendicular to the aggregate’s axis [18, 19]. The detailed phase diagram of DSCG aqueous solutions can be found in [6]. At room temperature (23 °C), the aqueous solution of DSCG is in the isotropic ($I$) phase for the (weight) concentration $c < 10$ wt %. In the range $10 < c < 12$ wt %, the solution demonstrates a wide biphasic region in which $N$ and $I$ phases coexist. The $N$ phase is observed in the range $12 < c < 17$ wt %, another biphasic region with coexisting $N$ and $M$ phases at $17 < c < 21$ wt %, and $M$ phase at $21 < c < 35$ wt %.

As demonstrated by X-ray diffraction [17], the molecular stacking distances along the axis of aggregates are about 0.34 nm, and the average distance between the aggregates scales approximately as $1/\sqrt{c}$ and decreases when the temperature is increased toward the isotropic phase. The scalar order parameter $S$ has been estimated in deuterium NMR experiments by Goldfarb et al. [19]. $S$ was found to be surprisingly high, ranging from $0.76 \pm 0.08$ to $0.97 \pm 0.1$ [19]; one of the possible reasons is that the studied range of concentrations spans through both the $N$ and $M$ phases.
Fig. 2. Structural formulas and molecular models for DSCG.
2.1.2 Blue 27 (B27) and Violet 20 (V20)

Chemical formula:

Blue 27: C$_{28}$H$_{18}$O$_{10}$N$_4$Cl$_2$

Violet 20: C$_{36}$H$_{22}$S$_2$O$_8$N$_6$

Blue 27 and Violet 20 were obtained from Optiva, Inc. (San Francisco, CA).

Figures 3 and 4 show the corresponding molecular configurations as calculated by PC SPARTAN PRO using the semiempirical module and an Hartree-Fock approximation in the dissociated state (the two ammonium cations $NH_4^+$ have been omitted). The phase diagrams of aqueous solutions of Blue 27 and Violet 20 are measured by Yuriy A Nastishin and Tod Schneider shown in figure 5 [70]. The accuracy of the data on the transition temperature is ± 0.5 °C; the accuracy of the concentration data is better than ±0.1 wt %. Both phase diagrams feature relatively wide biphasic regions of coexisting $N$ and $I$ phases, which is common also for DSCG. This broadening of the $N$-$I$ coexisting region is generally attributed to the length polydispersity of the nematogenic building units [20-24].

The light absorption in aligned samples of both $N$ materials is anisotropic with the maximum absorption for light polarized perpendicularly to the rubbing direction of the aligning layers, which is consistent with the $H$-aggregation, as the absorption direction is in the plane of the molecule. Studies of molecular monolayers of both Violet 20 [25, 26] and Blue 27 [70] assembled by an electrostatic layer-by-layer deposition technique, also demonstrate that the absorption axis is perpendicular to the shear direction during deposition. Note, however, that the geometry of aggregates
bounded by a charged substrate might be generally different from the geometry of aggregates in the bulk [25].
Blue 27

Fig. 3. Structural formulas and molecular models for Blue 27.
Fig. 4. Structural formulas and molecular models for Violet 20.
Fig. 5. Phase diagrams of aqueous solutions of DSCG (a), Blue 27 (b) and Violet 20 (c) (by Yu. A. Nastishin and Tod Schneider) [70].
2.2 Sample preparation

When aqueous solutions of the LCLC materials (DSCG, blue 27, violet 20) are made, deionized water with an initial resistivity of 18 MΩ cm (Barnstead/ThermolyNANOpure Ultrapure water system, model: 04741) is used. The mixture is properly sealed in the vial and heated about 20 °C above the clearing point (which is the temperature above which the solution is completely isotropic) of the specific concentration of the LCLCs, and stirred on a vibrating stage (Fisher Scientific Vortex Genie 2, model: G560) for about 20 minutes. This process is repeated several times to ensure that the solute (DSCG, Blue 27, or Violet 20) is completely dissolved in water. The mixture is then placed in the centrifuge machine (International Equipment Co., model: MP4R) at 2500 RPM to drive out the air bubbles in the solution.

For an accurate measurement of the physical properties such as the order parameter $S$ by optical means, the LCLCs need to be well aligned. Uniform alignment of DSCG is hard to achieve. Ichimura’s group [27-28] had reported that DSCG and the dye direct blue 67 (4-([4-[(6-Anilino-1-hydroxy-3-sulfo-2-naphthyl)diazenyl]-5-methoxy-2-methylphenyl]diazenyl)-5-hydroxynaphthalene-2,7-disulfonic acid) can be aligned by irradiating a photosensitive polymer azo compound with linearly polarized light, when the material is doped with a non-ionic surfactant. Oleg D. Lavrentovich’s group had demonstrated that LCLCs could be aligned by certain rubbed polyimide films and by obliquely deposited SiO layers; the technique does not require any surfactant (amphiphilic) additives [29]. We take advantage of the high-quality alignment achieved for LCLCs and use this technique in sample characterization.
In this work, we used the spin-coated and rubbed films of polyimide SE-7511 (Nissan Chemical Industries, Ltd.) to align the nematic phase of LCLCs in planar fashion, along a single direction in the plane of the bounding substrate determined by the direction of rubbing. Glass substrates were washed in an ultrasonic bath of Alconox detergent and water for 10 minutes at 60 °C, removed and dried. The polyimide SE-7511 Sunever, grade 7511L and the solvent Sunever, both from Nissan Chemical Industries, Ltd. (Japan) were mixed in the proportion 1:1. The solution was coated onto the glass substrates by a spincoater at 1500 rpm. The coating was dried at 100 °C for 2 minutes and then baked at 180 °C for one hour. The polyimide-coated substrates were rubbed using an aluminium block covered with felt.

After the aligning process, the substrate is cut and assembled into cells with the rubbing directions being antiparallel to each other. The pretilt angle (detected between the director and the substrate using magnetic null technique) was less than 1°. Figure 6 demonstrates a drastic difference in alignment quality of 12.5 wt % DSCG solution between the regular glass cell with flow-induced alignment [Fig. 6(a)] and the cell with rubbed SE-7511 alignment layers [Figs. 6(b) and 6(c)].

The thickness of the gap between the glass plates in LCLC cells was controlled by powder spacers and was measured by the interference technique prior to the filling of cells.

Because of water evaporation, the LCLC solutions cannot be filled into the cell in vacuum chamber as the case for the thermotropic LCs. To minimize the effect of evaporation, we designed a device that can produce negative pressure on one of the two open sides of the cell and fill the LCLC solutions into the cell by capillary flow.
smoothly and quickly (3-5 seconds).

This device is composed of three parts: a soft pipe connecting the copper tube and a vacuum pump, a copper tube, and a pipette rubber head that is cut to put the cell in, as seen in Fig. 7.

The direction of flow and the pressure gradient were parallel to the rubbing direction of the polyimide layers. To facilitate the capillary flow, the LCLC solution was heated to \( I \) phase (about 10 °C above the clearing point), and the empty cell as well as the pipette are also heated before the filling process begins. After the process, turn off the vacuum slowly to prevent the flow of the LCLC solutions. The cell was promptly sealed by water-proof epoxy (ITW Devcon, Part No.: 1233) after filling.

The samples were heated to about 10 °C above the \( N-I \) transition prior to each measurement, to mitigate the prehistory effects mentioned in Ref. [9]. The measurements were performed 2 hours after cooling to the \( N \) phase for the LCLCs to stabilize.
Fig. 6. Polarizing microscope textures of 12.5 wt% DSCG solutions aligned in cells by: (a) untreated glass plates with flow-induced alignment; (b), (c) rubbed SE-7511 coated glass plates; (b) shows the image when the director (as well as the rubbing direction) is parallel to the polarizer, (c) shows the image when the director is not strictly parallel to the polarizer or the analyzer direction. The arrows in (c) point to the spacers.
Fig. 7. Scheme of the vacuum assisted filling system for LCLC solutions.
Chapter III

Optical properties of LCLCs

3.1 Birefringence and anisotropic absorption of N phase in planar samples

To characterize optical anisotropy of the $N$ phase, we used LCLC samples with planar alignment, and studied them under the polarizing microscope Nikon Optiphot2-POL, equipped with a computer-controlled Nikon microspectrophotometer comprised of a Photometry system P100S, Monochromator G70, and Photometer P102. The spectra were measured for a circular area of the sample (restricted by the microscope’s pinhole) of the diameter 10 $\mu$m. The sample was placed on the microscope stage between a pair of parallel polarizers.

The optical transmittance $T$ of the cells was calculated as

$$T = \frac{I}{I_0},$$

where $I$ was the transmitted light intensity through the two parallel polarizers and the sample cell, and $I_0$ was the reference light intensity transmitted through a cell that was identical to the sample cell but filled with water instead of the LCLC, namely, $I_0$ was measured as the intensity of light passed through this water-filled cell. The scheme of the experimental setup is shown in Fig. 8.
3.1.1 Optical birefringence of DSCG

DSCG aqueous solutions are transparent in the visible part of the spectrum. We can determine the optical birefringence $\Delta n = n_e - n_o$ of the $N$ phase by measuring the phase retardation $\Delta \varphi = 2\pi \Delta n d / \lambda$ between the ordinary wave and the extraordinary wave. Here $n_e$ and $n_o$ are the extraordinary and ordinary refractive indices, $d$ is the thickness of the cell gap, and $\lambda$ is the incident light wavelength. The director was oriented at $45^\circ$ with respect to the parallel polarizers. We used parallel polarizers because the signal could be detected by photometer even when the director is perpendicular to the polarizers, while there is no signal detected when the director is parallel or perpendicular to the crossed polarizers. Using the data for normal incident light, $\Delta n$ is calculated from the expression [Eq. (A10) in appendix]:

$$T_{45} = \cos^2(\Delta \varphi / 2),$$

$$|\Delta n| = \lambda \left( \arccos \left( \sqrt{T_{45}} \right) + 2m\pi \right) / (\pi d), \quad (m \text{ is an integer})$$

Analyzing the transmission data for cells with different thickness and different incident angles, we concluded that $\Delta \varphi$ was less than $2\pi$ in the cells with cell gap $d \leq 15 \mu m$ in the visible wavelength range (400-700 nm), and thus $m = 0$.

To illustrate the procedure, we show $T(\lambda)$ for three different concentrations, $c = 12, 15, \text{ and } 17 \text{ wt } \%$ in Fig. 9(a). All the minima correspond to $\Delta \varphi = \pi$. As expected, the minima are shifted towards shorter wavelengths for lower concentrations indicating a smaller birefringence. The curves in Fig. 9(b) show dispersion of birefringence as calculated from Fig. 9(a).
Fig. 8. Scheme of the optical characterization setup of LCLC. We used parallel polarizers. The planar LCLC sample was rotated on the microscope stage.
There are no anomalies in the observed wavelength range; $\Delta n$ slowly decreases with $\lambda$ and increases with $c$. We also measured $\Delta n$ for tilted geometry: the sample was rotated around the rubbing direction by 30° with respect to the direction of incident light. We obtained the same $\Delta n$ values within the accuracy range. This result implies that the $N$ phase is optically uniaxial.

We verified the negative sign of $\Delta n$ in two separate experiments using a violet $\lambda$ plate and a quartz wedge. The quartz wedge allows one to determine $\Delta n$ independently, by compensating the birefringence of LCLC with the birefringence of the wedge. For example, the optical retardation of the 15-$\mu$m-thick DSCG cell can be compensated by the portion of the wedge in which the optical retardation is about 300 nm, i.e., $\Delta n \approx -0.02$.

The temperature dependence of the birefringence was also measured for $c = 15$ wt % using the microspectrophotometer and a hot-stage with temperature control. Figs. 10(a) and 10(b) show the results of $\Delta n(T)$ for two wavelengths, $\lambda = 633$ and 546 nm, respectively. Experimental points in the biphasic region correspond to the $N$ phase coexisting with the islands of the $I$ phase. To select the region of measurements, we inserted an opaque screen with a calibrated pinhole that allowed us to analyze the texture in a circular spot of about 10 $\mu$m diameter. Note that the absolute value $|\Delta n|$ of the nematic phase might increase with temperature in the biphasic region, as clearly seen in the Fig. 10(b). The reason is that the $N$ phase in the biphasic region becomes more concentrated, as discussed in the next section.
Fig. 9. (a) Transmittance $T = \cos^2(\frac{\Delta \phi}{2})$ and (b) birefringence $\Delta n$ of DSCG as measured for a planar cell at $T = 20^\circ C$ for concentrations $c = 12$ wt % ($d = 13.5 \ \mu m$), 15 wt % ($d = 14.0 \ \mu m$), and 17 wt % ($d = 13.4 \ \mu m$).
Fig. 10. $\Delta n(T)$ of DSCG, $c = 15$ wt % for two wavelengths $\lambda = 633$ (a) and 546 nm (b), respectively. Circles correspond to the $N$ phase, triangle to the $I$ phase. Points above the $N$-$I$ phase transition were obtained for the nematic and isotropic part of the biphasic region using a pinhole.
3.1.2 Birefringence and absorption of Blue 27

Blue 27 is a light absorbing material, so the birefringence can not be calculated as in the DSCG sample. The transmission for an absorbing crystal plate with its optical axis oriented at the angle $\alpha$ with respect to the two parallel polarizers is of the form [30], see Eq. (A8) in appendix:

$$T = T_0 \cos^4 \alpha + T_{90} \sin^4 \alpha + \left(\sqrt{\frac{T_0 T_{90}}{2}}\right) \cos \Delta \varphi \sin^2 (2\alpha),$$  \hspace{1cm} (3.4)

where $\Delta \varphi = 2\pi \Delta n d / \lambda$ (same as in the case of transparent materials), $T_0 = \exp(-4\pi k_\parallel d / \lambda)$ and $T_{90} = \exp(-4\pi k_\perp d / \lambda)$ are transmittances at $\alpha = 0$ and $90^\circ$, respectively; $k_\parallel$ and $k_\perp$ are the absorption indices of Blue 27 for light polarized parallel and perpendicular to the director; $d$ is the thickness of the sample; $\lambda$ is the incident light wavelength.

We used the transmission spectra $T_0(\lambda)$ and $T_{90}(\lambda)$ to determine absorption indices $k_\parallel$ and $k_\perp$:

$$k_\parallel = -\frac{\lambda}{4\pi} \ln T_0 \left(\frac{4\pi d}{\lambda}\right)$$ \hspace{1cm} (3.5)

$$k_\perp = -\frac{\lambda}{4\pi} \ln T_{90} \left(\frac{4\pi d}{\lambda}\right).$$ \hspace{1cm} (3.6)

To determine $\Delta \varphi$ and $\Delta n$, one needs an additional measurement at $\alpha$ different from 0 and $90^\circ$. As follows from Eq. (3.4), the best accuracy of $\Delta \varphi$ can be achieved for $\alpha = 45^\circ$. We thus calculated $\Delta \varphi$ and $\Delta n$ by additionally measuring the transmittance $T_{45}$ at $\alpha = 45^\circ$.

From Eq. (3.4) we can find that:

$$\cos \Delta \varphi = \left(4T_{45} - (T_0 + T_{90})\right) / \left(2\sqrt{T_0 T_{90}}\right).$$ \hspace{1cm} (3.7)
Using Eq. (3.5-3.7), one can simultaneously determine the optical birefringence $\Delta n$, absorption indices $k_{//}$ and $k_{\perp}$, and absorption anisotropy $\Delta k$ ($= k_{//} - k_{\perp}$).

To determine $\Delta n$ from the spectroscopic data, we plotted $\cos \Delta \phi$ in Eq. (3.7) as a function of $\lambda$ for a planar Blue 27 cell of thickness $d = 15 \ \mu m$ and normal light incidence [Fig. 11(a)].

Note that an uncertainty term emerges that needs to be determined separately for phase retardation:

$$|\Delta \phi| = \arccos\left(\frac{4T_{45} - (T_0 + T_{90})}{2\sqrt{T_0 T_{90}}}\right) + 2m\pi, \ (m \ is \ an \ integer).$$ \hspace{1cm} (3.8)

In order to determine $m$, we prepared a planar wedge cell with director perpendicular to the thickness gradient. A Mylar spacer of thickness 75 $\mu m$ was placed parallel to the rubbing direction at one side of the wedge; the thin side had no spacer. The wedge demonstrated only one set of interference colors somewhat modified by the dichroism of the material. It allowed us to conclude that $m = 0$, as for $m \geq 1$ one would observe multiple sets of interference colors.

The values of $\Delta n$ were first determined from the spectroscopic data. The dependency $\cos \Delta \phi$ vs $\lambda$ was measured for $d = 15 \ \mu m$ at normal incidence.

Another method to determine the sign and approximate value of $\Delta n$ was performed on a wedge cell filled with nematic Blue 27. The results confirmed the conclusion of $m = 0$. The experiments also showed that the sign of $\Delta n$ is negative.

To measure the optical birefringence of Blue 27, 4.5 wt % Blue 27 solution was prepared and filled into planar nematic cells. A cell with thickness $d = 15\mu m$ is chosen. Fig. 11(a) shows the dependence of $\cos \Delta \phi$ as a function of $\lambda$ at $T = 20 \ ^\circ C$.
Fig. 11. Birefringence of 4.5 wt % Blue 27: (a) $\cos\Delta\phi$ vs. $\lambda$, for cells with $d = 15\, \mu$m at normal incidence; (b) dispersion of birefringence for above sample at $T = 20$ °C, obtained from Fig. 11(a) and equation (3.7).
for the normal light incidence. The dependencies $\cos \Delta \varphi \ vs \ \lambda$ are rather unusual as compared to similar plots in regular materials, in which $\Delta n$ depends only slightly on $\lambda$.

In our case, $\cos \Delta \varphi \ vs \ \lambda$ plots often feature maxima with amplitude less than 1 [Fig. 11 (a)]. This behavior can be attributed to the fact that near the maxima, in addition to $\Delta \varphi \approx 0$ and $m = 0$, the function $\Delta n(\lambda)$ is nonmonotonic, approaching almost zero values near $\lambda = 575$ nm.

The dispersion of birefringence $\Delta n(\lambda)$ for 4.5 wt % Blue 27, calculated using Eq. (3.7) and shown in Fig. 11(b), is clearly nonmonotonic; $\Delta n$ is negative and approaches almost a zero value ($\Delta n \approx -0.001 \pm 0.001$) near $\lambda = 575$ nm.

In order to verify whether $\Delta n$ remains negative and does not change its sign around $\lambda = 575$ nm, we used a quartz wedge cell. The wedge cell is 15 $\mu$m thick in one end and filled with 4.5 wt % Blue 27 solution. The cell of thickness 15 $\mu$m filled with 4.5 wt % Blue 27 solution was tested under the polarizing microscope in a monochromatic mode with a quartz wedge. The optic axis of the wedge was perpendicular to the director $\hat{n}$. From the shift of the extinction bands of first order we determined that $\Delta n$ remains negative.

The temperature dependencies of birefringence of 4.5 wt % Blue 27 solution were measured at $\lambda = 633$nm (squares) and $\lambda = 546$nm (circles), and the results were shown in Fig. 12.

From Fig. 12, we can clearly see that the birefringence of the $N$ phase region increases after the cell went into the $N-I$ biphasic region, just as what we observed in DSCG solution.
The absorption indices could be calculated from the transmission data using Eq. (3.5) and (3.6). For a better accuracy, we used a thinner planar cell with thickness $d = 5\mu m$ and measured the absorption at two different temperatures, 20 and 27°C, for $\alpha = 0$ and 90°, as shown in Fig. 13. The absorption band for 4.5 wt % Blue 27 is around $\lambda = 649$ nm, as seen from the Fig. 13.

The light absorption in the aligned samples of $N$ phase of Blue 27 shows a pronounced anisotropy with the maximum absorption for light polarized perpendicularly to the rubbing direction of the polyimide aligning layers, which is consistent with the $H$-type of aggregation in both materials, as the absorption direction is in the plane of the molecule.

Detailed temperature dependencies of absorption indices of $k_{\parallel}$ and $k_{\perp}$ were also measured at $\lambda = 633$ nm (which is very close to the absorption band for Blue 27), as seen in Fig. 14.

3.1.3 Birefringence and absorption of Violet 20

The absorption anisotropy and birefringence for Violet 20 (5 wt % aqueous solution) were shown in Fig. 15. One can see that the behaviors for Violet 20 are very similar to those of Blue 27 solution. As in Blue 27, $\Delta n$ and $\Delta k (= k_{\parallel} - k_{\perp})$ are both negative in the visible wavelength range; the dispersion of $\Delta n$ is nonmonotonic.
Fig. 12. Temperature dependence of birefringence of 4.5 wt% Blue 27 aqueous solution measured at two different wavelengths: $\lambda = 633$ nm (Solid square) and $\lambda = 546$ nm (solid circle).
Fig. 13. Spectra dependencies of the absorption coefficients for 4.5 wt % Blue 27, calculated from the transmission data measured for a planar N cell for parallel and perpendicular polarizations of the incident light with respect to the director for $T = 20^\circ C$ (solid line) and $27^\circ C$ (dashed lines).
Fig. 14. The temperature dependencies of $k_{//}$ and $k_{\perp}$ for 4.5 wt % Blue 27 measured at $\lambda = 633$ nm.
Fig. 15. Absorption spectra (a) and dispersion of the birefringence (b) for 5 wt % Violet 20, calculated from the transmission data measured for a planar nematic cell: absorption coefficient $k_{||}$ corresponds to $\vec{n} // \vec{P}$ ($\vec{P}$ is the direction of the incident light polarization) whereas $k_{\perp}$ corresponds to $\vec{n} \perp \vec{P}$ and $\Delta k = k_{||} - k_{\perp}$. 

Violet 20, $c = 5 \text{ wt } \%$, $T = 20 \degree \text{C}$
3.2 Order parameter measurements

The order parameter is very important for the liquid crystal system to quantify just how much order is present in the material. The nematic scalar order parameter $S$ can be deduced from the absorption anisotropy (linear dichroism) [31, 32]:

$$S = \frac{2(gN - 1)}{(gN + 2)(3\cos^2 \beta - 1)},$$

(3.9)

where $N = \frac{k_{\parallel}}{k_{\perp}}$ is the dichroic ratio, $\beta$ is an angle between the molecular symmetry axis and the dipole moment of the transition that is responsible for absorption, $g$ is a correction factor accounting for the anisotropy of refractive indices and a local field (exciton) effects.

Analysis based on the Green function formalism [33] shows that $S$ can be recovered more properly from the ratio of the integral absorption moments $M_{\parallel(\perp)}$ rather than from the dichroic ratio at a single wavelength. Thus Eq. (3.9) holds but with the integrated dichroic ratio determined as:

$$N = N_M = \frac{M_{\parallel}}{M_{\perp}},$$

(3.10)

where $M_{\parallel}$ and $M_{\perp}$ are the integral absorption moments for the polarizations parallel and perpendicular to the director, respectively:

$$M_{\parallel(\perp)} = \int \text{Im}(\varepsilon_{\parallel(\perp)}) d\omega = 2\int n_{\parallel(\perp)} \kappa_{\parallel(\perp)} d\omega,$$

(3.11)

The integration is performed over the frequency region of the absorption band; and the correction factor $g$ is also modified as $g = g_M$.

The calculation of $S$ from the standard dichroic ratio $N = \frac{k_{\parallel}}{k_{\perp}}$ would be
valid only when the absorption bands have the same shape for two orthogonal polarizations and when the dispersion of refractive indices within the absorption band is small. If these conditions are satisfied, the standard and the integral approach would match each other, provided one takes into account the relationship between the two correction factors, \( g = g_M n_\parallel / n_\perp \).

The effect of orientational order on the spectral properties of LCLCs is different as compared to the case for thermotropic LCs, because an individual molecule of LCLC finds itself in the environment of the aggregate. On the other hand, the birefringence of LCLCs is rather small, so \( g_M \approx 1 \). As a result, the integral absorption moments in \( N \) phase can be expressed through the individual integral absorption moments \( M_{\parallel(\perp)}^{\text{C}} \) of a column oriented parallel (perpendicular) to the director (derived by Sergij Shiyanovskii):

\[
M_{\parallel} = \frac{C_c}{3} \left[ (2S + 1)M_{\parallel}^{\text{C}} + 2(1 - S)M_{\perp}^{\text{C}} \right],
\]

\[
M_{\perp} = \frac{C_c}{3} \left[ (2 + S)M_{\perp}^{\text{C}} + (1 - S)M_{\parallel}^{\text{C}} \right],
\]

(3.12)

where \( C_c \) is the column concentration. The values of \( C_c \) is difficult to determine without knowing how many molecules form an aggregate. Fortunately, \( C_c \) drops out of the expression for \( S \):

\[
S = \frac{1 + \alpha_M / 2}{1 - \alpha_M / 2} \frac{1 - N_M}{1 + N_M / 2}.
\]

(3.13)

Here \( \alpha_M = M_{\parallel}^{\text{C}} / M_{\perp}^{\text{C}} \) is an integral dichroic ratio of the LCLC aggregate that depends on the orientation of the dipole transition moment with respect to the
aggregate axis. For Blue 27 the dipole transition moment is in the plane of the molecule. Furthermore, the molecular planes are apparently perpendicular to the aggregate axis. The later is supported by (1) simulations of the mutual orientation of molecular pairs using Spartan software and (2) measurements of the dichroic ratio for a dry film of Blue 27 well aligned by using a block copolymer additive as described in Ref. [34]; the measurement yields a very low value $N < 0.05$. Therefore, one can simplify the consideration by putting $M_{1}^{C} = 0$ and $\alpha_{M} = 0$, and Eq. (3.13) reduces to:

$$S = \frac{1 - N_{M}}{1 + N_{M}/2}. \quad (3.14)$$

Fig. 13 shows that the absorption band extends beyond the long-wave limit of the spectral region accessible for measurements. Therefore we used three methods to calculate $S$ [Fig. 16]. First, we estimate $N_{M}$ by integrating $M_{//L}$ (Eq. (3.11)) through the accessible range of absorption band (480-700 nm); the corresponding values of $S$ are represented with crosses.

In the second technique, we approximate the absorption bands with Gaussian peaks and determine $N_{M}$ and $S$ (solid triangles) from this fitting. In the third approach, we follow the approximate but widely used procedure and estimate $N_{M}$ as the ratio of amplitudes of the absorption peaks for two orthogonal polarizations, the corresponding values of $S$ are represented with open circles. Fig. 16 shows that the Gaussian approximation method yields the values of $S$ somewhat higher than the other two. Although we can offer the possible explanation of this fact (associated with the red-shift of the absorption peak for the polarization parallel to the transition
Fig. 16. Temperature dependencies of the order parameter of 4.5 wt % Blue 27 determined (1) by integrating Eq. (3.11) through the accessible range of the absorption band 480 - 700 nm (crosses); (2) by approximating the absorption bands with Gaussian peaks (solid triangles); (3) from the ratio of amplitudes of the absorption peaks for two orthogonal polarizations (open circles).
dipoles as compared to the peak for the orthogonal polarization, the effect similar to
the Davydov splitting in the molecular crystals [35]), the difference in the values of
S is not significant, only about 0.03.

3.3 Discussion and Implications

3.3.1 Birefringence

The optical characterization procedure described in section 3.1 to characterize the
anisotropic absorption and birefringence of LCLCs is based on the approach
developed for absorbing crystals [30]. The approach is justified when the LCLC is
well aligned within the area probed by the light beam.

The measured $\Delta n$ are small (from about -0.02 for DSCG to about -0.001 or less
for Blue 27 and Violet 20) which is natural as these aqueous solutions are highly
diluted. These data are not influenced much by a nonzero birefringence of the buffed
polymer layers used to align the LCLC. The thickness of the LCLC layers (10-100 $\mu$m)
in all the experiments was orders of magnitude larger than the thickness of the
polymer layers (100 nm). Direct measurements show that the optical retardation
caused by the buffed polyimide aligning layers is of the order of 2 nm [38]. The
optical retardation caused by the birefringence of LCLCs in cells of thickness 15 $\mu$m
is significantly larger, ranging from 300 nm for DSCG to the lowest value of 15 nm as
measured for Blue 27 in the spectral region 550-600 nm, Fig. 11(b). Therefore, the
finite birefringence of polyimide layers is lower than the accuracy of our $\Delta n$
measurements, $\pm 0.001$. The data for $I$ phase (Fig. 10) also support this conclusion.
The birefringence of Blue 27 $c = 4.5$ wt % solution is much smaller than that of DSCG at $c = 15$ wt %. The feature of almost zero birefringence of Blue 27 near $\lambda = 575$ nm can be attributed to the effect of the absorption band and anomalous dispersion. For the Blue 27 solutions, absorption is most efficient for polarization in the plane of the molecules, i.e. perpendicular to the director. Therefore, one should expect that the ordinary refractive index $n_o = n_\perp$ (the subscript refers to polarization perpendicular to the director) would reach a minimum at a wavelength that is somewhat shorter than the maximum of the absorption band (650 nm). The extraordinary index of refraction $n_e = n_\parallel$ should not experience this dispersion effect as the absorption along the director is much weaker, Fig.12. This difference in the behavior of $n_o$ and $n_e$ explains the non-monotonous $\Delta n(\lambda)$ ($= n_e - n_o$) with a minimum near $\lambda = 575$ nm that is somewhat smaller than the absorption maximum of Blue 27 at 650 nm. In this spectral region, Blue 27 can be considered as a dichroic but nonbirefringent LCLC. A similar non-monotonous $\Delta n(\lambda)$ trend is observed in the absorbing solutions of Violet 20, Fig. 15.

In lyotropic LCs formed by molecular aggregates there might be at least two mechanisms for birefringence. The first is caused by the molecular anisotropy, while the second one, the so-called form birefringence [39], is caused by the anisotropy of the molecular aggregates. The interplay between the molecular anisotropy and form birefringence was documented by Nallet and Barois [40] for the surfactant lamellar $L_\alpha$ phase in which the rod-like molecules (positive $\Delta n$) are arranged into lamellae (negative $\Delta n$) [40, 41]; the two contributions can cancel each other at a particular wavelength, which depends on specific composition.
In the $N$ phase of the studied LCLC materials, we have the opposite situation: the plank-like LCLC molecules (negative $\Delta n$) are stacked into rods (positive $\Delta n$). In our case, $\Delta n$ remains negative (although small) in the studied spectral range, i.e. the form birefringence is not as significant as the molecular anisotropy contribution to the total birefringence.

The wide biphasic region allows one to determine $\Delta n$ in the $N$ phase in coexistence with the $I$ phase. The $N$ phase is more concentrated than the $I$ phase, which is verified by direct observation of the biphasic sample in a test tube: the $I$ part is floating above the higher density $N$ phase. The increase of $|\Delta n|$ with temperature observed in the biphasic region suggests that the corresponding $N$ phase is more concentrated not only as compared to the $I$ phase but also as compared to the $N$ phase at temperatures just below the biphasic region; therefore, its order parameter and $|\Delta n|$ might be higher. This conclusion is supported by the enhancement of deuteron quadrupole splitting observed by Yu and Saupe [42] in the $N$-part of the biphasic region for DSCG in D$_2$O; the latter result means that $S$ increases in the biphasic region.

3.3.2 Absorption anisotropy and scalar order parameter

Blue 27 and Violet 20 in the $N$ phase show negative absorption anisotropy around the absorption band with the maximum approximately at $\lambda = 650$ nm (Fig. 13) and $\lambda = 570$ nm (Fig. 15(a)), respectively: light polarized parallel to the molecular plane is absorbed most strongly. The $N$ phase of both materials is uniaxial, as verified in the experiments with cells tilted with respect to the incident light by an angle up to
within the accuracy of the experiment, the values for $\Delta k$, $\Delta n$ and the positions of absorption maxima remained the same in the spectral region (400-700 nm).

The anisotropy of absorption allowed us to determine the scalar order parameter for the $N$ phase of Blue 27 and its temperature dependence, Fig. 16. The data clearly demonstrate a decrease in $S$ as the system approaches the $N$-$I$ transition; this decrease is small, about 5%-7% over the range of about 10 °C. At the transition point, $S_c = 0.73 \pm 0.01$.

The measured values of $S$ are much higher that those in the regular thermotropic nematic liquid crystals and in the Maier-Saupe theory (in which $S_c = 0.44$) [2], but are close to the predictions of the Onsager theory ($S_c = 0.84$) for the $N$ phase formed by rigid rods [44].

The Onsager model has been developed to describe the occurrence of orientational order in the system of thin long rods. The rods are supposed to be rigid and not interacting with each other (except through the effect of "excluded volume"). Above some concentration that depends on the length-to-diameter ratio $L/D >> 1$, the system phase separates into a more concentrated and ordered $N$ phase and a less concentrated $I$ phase.

The Onsager model predicts a high value of the order parameter in the $N$ phase, as compared to the values found in typical thermotropic low-molecular-weight nematic materials. The original result based on the trial function produced $S = S_c = 0.84$ [44]. More accurate (numerical) solutions resulted in somewhat lower values [45, 46], $S = S_c = 0.79$, very close to our results. The Onsager model describes satisfactory many polymer liquid crystalline systems, since in these systems it is easy to achieve
the condition $L/D > 10$ for which the accuracy of solution is acceptable. The LCLCs seem to satisfy the condition $L/D > 10$, even in the $I$ phase close to the $I-N$ transition. First of all, as determined by light scattering technique for the $I$ phase of DSCG at temperatures just above the $N-I$ transition, $L/D \geq 10$ [47]. Second, atomic force microscopy of aggregate bundles in dried films of Violet 20 and Blue 27 at solid substrates also suggests that $L/D > 10$.

Despite a close match between the Onsager model and the data above, the correspondence is not complete. The most obvious difference is that the Onsager model predicts no temperature dependence of $S$. The experimentally observed decrease of $S$ with temperature can be considered as the evidence of aggregate interactions (other than pure steric excluded volume repulsion) and/or the effect of temperature dependence of the aggregate length [47]. As the aggregates are formed by molecules with ionic groups at the periphery (that make them water soluble), multi-body Coulomb interactions (aggregate-aggregate, aggregate-counterions, and counterions-counterions) might play an important role in stability and ordering of LCLCs, as suggested by a number of recent models developed for similar systems such as polyelectrolytes [48-51]. The length polydispersity of LCLC aggregates [20, 24, 50] and their finite flexibility [90] should also be taken into account in the description of LCLCs.

As already indicated, the scalar order parameter for water solutions of DSCG has been estimated by Goldfarb et al. to range from 0.76 in 4 wt % solution (at low temperatures) to 0.97 in 29 wt % solution (which probably corresponded to the $M$ phase) [19]. Lower values of the order parameter have been observed recently by
Horowitz et al. [52] in the LCLC material Sunset Yellow FCF: $S$ decreases from $S = 0.76$ at room temperature to about $S_c = 0.6$ at the $N$-$I$ transition ($\approx 72 \, ^\circ C$). The difference in the values of $S_c$ measured for Blue 27 and Sunset Yellow FCF might be attributed to a much larger temperature interval of the nematic phase in the latter material.
Chapter 4

Pretransitional Fluctuation in LCLC

4.1 Introduction

The details of molecular packing within the LCLC aggregates, including cromolyn, are still being debated [13, 53]. Originally, Hartshorne and Woodard [17] assumed that there is one molecule per circular cross-section of the cylinder in cromolyn aggregates. 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. 2(a)). Later, Lydon et al. [54] proposed that the aggregate has a hollow square chimney shape formed by four molecules linked by electrostatic salt bridges. Hui and Labes [55] argued that the structure is similar to that of regular micelles. Namely, they claimed that 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.

To expand the characterization of LCLCs and clarify the nature of the isotropic-nematic transition in such systems, we have performed dynamic and static light scattering on pretransitional fluctuations in the isotropic phase of the aqueous solution of cromolyn. As compared to NMR and X-ray techniques used in the past to
characterize the structural properties of LCLCs, the light scattering experiments enable one to gain an insight into the behavior of aggregates and mesoscopic fluctuations in the pre-transition region to directly test the applicability of phenomenological models such as the Landau-de Gennes model.

The concentration of cromolyn was chosen to be 14 wt %, in order to study the phase transformation from the isotropic to the nematic state. Previously Champion and Meeten [57] have performed light-scattering experiments for much more dilute (about 1 wt %) samples. Their studies indicated that the two ring systems of cromolyn are approximately coplanar; the configuration was though to be stabilized by multiple hydrogen bonds with the surrounding water molecules preserved even when the samples are dried [17].

4.2 Experiments

4.2.1 Sample and equipment preparation

The mixture studied in our light-scattering experiments was a 14 wt % aqueous solution of DSCG. The mixture was heated to a temperature $T$ of 55 °C and stirred on a vibrating stage until the cromolyn was dissolved completely. The sample was prepared in a transparent glass vial with a diameter of 1.5 cm, tightly closed with a plastic cap and wrapped with parafilm from Pechiney Plastic Packaging.

The light-scattering measurements were performed at the University of Maryland, College Park. To avoid possible time dependence of the solution properties [57], the sample was heated prior to each experiment to $T = 55$ °C, which is well
above the temperature of disappearance of the nematic phase upon heating; then aged
at 40 °C for 1 hour for it to stabilize. The sample was kept at each experimental
temperature for at least 20 minutes before measurements. To check the absence of
time dependence of the results, we repeated the experiment with the sample stored in
an oven at 55 °C for three days. We found complete reproducibility of the
light-scattering data and registered the same value $T_{NI} = 31.8 °C$ of the temperature, at
which the first nematic nuclei appear in the bottle on cooling.

The experimental setup can be found in Ref. [59] and the scheme is shown in Fig.

4.2.2 Light-scattering measurement procedure

We measured the light-scattering intensity as well as the dynamic correlation
function at each temperature $T$ for a given scattering angle $\theta$ with two settings of the
analyzer: VV and VH (where V and H denote the vertical and horizontal polarizations
of light, respectively; the first symbol corresponds to the incident light and the second
one to the scattered light).

The scattering plane is horizontal while the polarization of the incident light is
vertical, hence the measured intensity values $I_{VV}$ and $I_{VH}$ correspond to the settings
VV and VH as defined above. The measurements were conducted with ALV-5000/E
and PhotoCor correlators for four different angles: 19°, 45°, 90° and 135° at various
temperatures upon cooling. Two groups of data were obtained: static and dynamic
scattered light intensity. Static (intensity) and dynamic (dynamic correlation function)
data enabled us to obtain the information for the length scales and relaxation times of
Fig. 17. Scheme of experimental setup for light scattering experiments. Notice that there is a vertical polarizer in front of the focusing optics, and there is an analyzer in the receiving optics, which can be rotated to either vertical or horizontal position.
the inhomogeneities causing the light scattering.

At each temperature the light-scattering intensity, \( I(t) \), was measured as a function of the time \( t \) every several seconds. The intensity values used in subsequent analysis were obtained from averaging \( I(t) \) accumulated over time intervals of 10 minutes. Monitoring of \( I(t) \) enables one to detect stray light scattering from some submicron scatterers that may rarely appear in the scattering volume. This monitoring was useful in finding the temperature of the transition between isotropic-phase region and biphasic region where small drops of nematic phase appear. It helped us also to check whether or not dust particles appear in the scattering volume. The intensity of the incident laser beam was also measured and its variations were accounted for corrections of light-scattering intensity data.

In the isotropic phase of a dust-free sample, light is scattered by fluctuations of the refractive index associated with fluctuations of different variables. In a binary solution of anisotropic molecules or anisotropic supramolecular aggregates the main contribution to the light-scattering intensity is associated with fluctuations of concentration and fluctuations of anisotropy [58]. Near the isotropic-nematic phase transition, the fluctuations of anisotropy are the fluctuations of the orientational order parameter [2, 60], whereas the average value of the orientational order parameter is zero. The dynamics of these two types of fluctuations is different: concentration fluctuations (a conserved order parameter) relax to equilibrium by diffusion (the relaxation time depends on the length scale corresponding to the light-scattering wave number \( q \)), while fluctuations of anisotropy relax in first approximation independently of the length scale (non-conserved order parameter) [2, 60, 61].
The fluctuation modes can be independently identified from the static and dynamic light-scattering data. For the diffusive (isotropic) mode associated with isotropic fluctuations of concentration one can expect that $I_{VH} = 0$ and thus the only contribution to the depolarized scattering will be from the anisotropic fluctuations. Therefore, a nonzero $I_{VH}$ indicates the presence of orientational fluctuations that depolarize the scattered light. In addition to the orientational relaxation mode, in a solution of rod-shape scatterers, the depolarized component should contain a diffusion mode (dependent of $q$) associated with translational diffusion of rods [62, 63]. However, close to the isotropic-nematic transition, the anisotropic fluctuation effects are dominant and, therefore, the mode associated with them should prevail. This mode eventually becomes critical, being accompanied by the critical slowing down, although the first-order phase transition occurs before the stability limit is reached.

4.3 Data Analysis and Discussion

The vertically polarized component of the light-scattering intensity contains anisotropic and isotropic contributions:

$$I_{VV} = (I_{VV})_{an} + I_{iso},$$

(4.1)

The depolarization ratio for fluctuations of anisotropy is given by [58, 62, 64]:

$$I_{VH}/(I_{VV})_{an} = 3/4,$$

(4.2)

This is a rigorous result for fluctuations of the anisotropic part of the dielectric-permittivity tensor in the approximation of one single correlation length. In practice, this ratio does never reach 3/4 because of a contribution from the isotropic
light scattering associated with fluctuations of density and concentration.

Thus, the isotropic part of the polarized light scattering can be extracted from the total intensity of the vertically polarized component as:

$$I_{iso} = I_{VV} - \frac{4}{3} I_{VH}.$$  \[(4.3)\]

The temperature dependence of depolarization ratio \((I_{VH} / I_{VV})\) is shown in Fig. 18. The ratio increases upon approaching the temperature \(T_{NI}\), where the first nematic nuclei appear. However, \(I_{VH} / I_{VV}\) does not reach the limit 3/4 because of the significant contribution of isotropic scattering.

The anisotropic part of light scattering, \((I_{VV})_{an} = \frac{4}{3} I_{VH}\), is caused by the fluctuations of the orientational order parameter and can be deduced from the standard Landau-de Gennes model of the isotropic-to-nematic phase transition as [2, 64]

$$I_{an} = I_{VH} + (I_{VV})_{an} = \frac{7}{4} (I_{VV})_{an} = C \beta^2 \frac{k_B T}{A + L q^2},$$  \[(4.4)\]

where \(\beta\) is the optical anisotropy measure of the aggregates, namely, the proportionality coefficient relating the dielectric anisotropy to the orientational order parameter; \(A\) is the first coefficient in Landau-de Gennes expansion of the free energy in powers of the order parameter; \(L\) is the effective elastic constant of the spatial distortions of orientational order, \(q = (4\pi n / \lambda) \sin(\theta/2)\), \(\theta\) is the scattering angle, \(\lambda\) is the wavelength of light in vacuum, \(n\) is the refractive index, \(k_B\) is the Boltzmann constant, and \(C\) is an instrumental constant.
DSCG, $c = 14$ wt %

\[
\frac{I_{VH}}{(I_{VV})_{an}} = \frac{3}{4}
\]

Fig. 18. Depolarization ratio of light scattered in the aqueous solution of DSCG (14 wt %) measured at four different scattering angles ($19^\circ$, $45^\circ$, $90^\circ$, and $135^\circ$).
Fig. 19 shows that \( (I_{I_{IV}})_{an}^{-1} \) is indeed a linear function of \( q^2 \), in accordance with Eq. (4.4). By linear extrapolation to the limit of zero-angle scattering where \( q = 0 \), we introduce the quantity

\[
(I_0)_{an}^{-1} = I_{an}^{-1}(q = 0) = \frac{A}{C\beta^2 k_B T} = \frac{1}{C\beta^2 \chi},
\]

where \( \chi = \frac{k_B T}{A} \) is the susceptibility to the fluctuations of anisotropy \([2, 60]\).

Generally, in the vicinity of a weakly first-order transition

\[
\chi = \Gamma_0 e^{-\gamma},
\]

where \( \varepsilon = (T - T^*)/T \), \( \Gamma_0 \) is the susceptibility amplitude, \( \gamma \) is the susceptibility exponent. In the mean-field approximation \([2, 60]\) \( \gamma = 1 \) and

\[
A = a(T - T^*),
\]

where \( a = k_B / \Gamma_0 \), and \( T^* \) is the temperature of the absolute stability of the isotropic phase. The linear temperature dependence of \( A \) is well documented in the broad temperature range around the isotropic-to-nematic transition in thermotropic liquid crystals. Some deviations have been observed only in the close proximity of the transition \([65-69]\) and were later explained by a coupling between orientational (nematic) and translational (smectic) fluctuations \([64-66]\).

The case of cromolyn is very different. The experiment (Fig. 20) shows that the temperature dependence of \( (I_{I_{IV}})_{an}^{-1} \) is strongly nonlinear. This nonlinearity increases with increase of temperature and exhibits a concave shape, opposite to the convexity observed in thermotropic nematics very close to the transition temperature. The factor
Fig. 19. Ornstein-Zernike plots for the anisotropic part of the polarized light scattered in the aqueous solution of DSCG. The solid line represent a fit to Eq. (4.4).
$T$ in the denominator of Eq. (4.7) does not play a significant role as in our experimental domain the temperature $T$ differs from $T^*$ less than by 3\%. This nonlinear dependence of $(I_0)_{\text{an}}^{-1}$ on temperature might be interpreted in two different ways.

The first possibility would be that Eq. (4.8) rewrites as

$$A = a(T - T^*)^\gamma, \text{ where } \gamma > 1.$$  \hspace{1cm} (4.9)

However, the temperature dependence of $(I_0)_{\text{an}}^{-1}$ remains reasonably linear near the transition point and our data do not fit this modified expression for $A$ with a constant exponent $\gamma > 1$.

The second possibility is related to a peculiar nature of building blocks of the nematic phase, the rod-like aggregates. The aggregation number in these units should behave very differently from the aggregation number in micelle-based surfactant solutions where it is restricted by the closed geometry of micelles. A possibility that the aggregate length, $l$, increases as the temperature decreases is suggested by sharp increase of the shear viscosity when the temperature is reduced, as shown in Fig. 21.

The change in the aggregate length $l = l(T)$ implies that the temperature stability limit of the isotropic phase, $T^*$, is no longer a temperature-independent constant. We thus modify the classic temperature dependence of $A$ by including nonlinear terms and writing $A(T)$ in the form

$$A = a[T - T^*(T)];$$ \hspace{1cm} (4.10)

$$T^*(T) = T_0^* - \alpha_1(T - T_0^*) - \alpha_2(T - T_0^*)^2 - \alpha_3(T - T_0^*)^3,$$ \hspace{1cm} (4.11)
Fig. 20. Inverse intensity of the anisotropic light scattering in the aqueous solution of DSCG extrapolated to zero scattering angles. The symbols indicate experimental data. The solid curve is a fit with Eq. (4.11)
where $a$, $\alpha_{1,2,3}$, and $T_0^*$ are constants.

It is natural to expect that each value of the rod length $l=l(T)$ has its own value of $T^* = T^*(T)$ which would have been the temperature of the absolute stability of the isotropic phase if the rod lengths were "frozen". Obviously, the corresponding value of $T^*$ will be high when $l$ is large, while $T^* \to 0$ when $l$ becomes very small as the nematic phase does not form at all. The linear coefficient $\alpha_1$ does not change the temperature behavior of $A$, as it only renormalizes the coefficient $a$, i.e., $a \to a(1+\alpha_1)$. Therefore, in the first (linear) approximation the effect of the elongation of the rods on $T^*$ is absorbed by the coefficient $a$, which in turn cannot be separated from other prefactors in the equation and thus cannot be independently evaluated. Adopting $a/C\beta^2 = 1$, one can then use $\alpha_1$, $\alpha_2$, and $\alpha_3$ as adjustable parameters. Eq. (4.9) fits the experimental data presented in the Fig. 20 reasonably well with the following parameters: $T_0^* = 302.65$ K (29.4 °C), $\alpha_1 = 0.566$, $\alpha_2 = -0.294$ K$^{-1}$, $\alpha_3 = 0.042$ K$^{-2}$.

The aggregate elongation might lead to some increase of the optical anisotropy measure of the aggregates, $\beta$. Such a possibility is also in qualitative agreement with the experimental data. If one attributes the entire effect of nonlinearity in the temperature dependence of $(I_0)_0^{-1}$ to the change in $\beta$, this parameter can be empirically represented as

$$\beta = \beta^* (1 - b \varepsilon^2)^{1/2}$$  \hspace{1cm} (4.12)

where $\beta^*$ is the value of $\beta$ at $T = T^*$, with $b = 582$.

Therefore, the temperature dependence of the zero-angle intensity can be
Fig. 21. Shear viscosity of the aqueous solution of DSCG. The solid curve represents a fit to Eq. (4.20). The dashed line represents the viscosity of water.
approximated by

\[ I_0 = C(\beta^*)^2 \left(1 - b\varepsilon^2\right)(a\varepsilon)^{-1} \]  \hspace{1cm} (4.13)

The intercept of the extrapolated inverse intensity with the temperature axis yields \( T^* = 29.4 \, ^\circ\text{C} \), which is about 2.4 \(^\circ\text{C} \) lower than \( T_{NI} = 31.8 \, ^\circ\text{C} \) and equals to the value of \( T_0^* \) obtained with Eq. (4.11).

It is difficult to separate unambiguously the non-linear effects implied by Eq. (4.11) and Eq. (4.12), as qualitatively both mechanisms lead to the same unusual concave character of the temperature dependence of \( (I_0)_n \).

Finally, note that the elastic constant \( L \) is assumed to be temperature independent and possible increase in \( \beta \) caused by the elongation of rods could be compensated by the decrease in the number of rods (as the total number of the cromolyn molecules available for the construction of aggregates is constant).

The concentration fluctuations also play some role near the transition temperature \( T_{NI} \) as \( I_{iso} \) increases on cooling, as seen in Fig. 22. However, the intensity of the isotropic light-scattering does not diverge at \( T=T^* \).

We rewrite Eq. (4.4) in the form accessible for the estimation of the correlation length \( \xi = \sqrt{L/A} \):

\[ I_{nn} = I_{vv} = C\beta^2 \frac{\chi}{1 + \varepsilon^2 q^2} \]  \hspace{1cm} (4.14)

so that in the vicinity of the phase transition, where we can still use the approximation \( A \approx a(T - T^*) \) and \( \varepsilon \approx (T - T^*)/T^* \), one could have
\[
\xi = \frac{L}{A} = \sqrt{\frac{L}{a(T - T^*)}} = \sqrt{\frac{L}{aT^* \epsilon}} = \xi_0 \epsilon^{-1/2},
\]

where \( \xi_0 = \frac{L}{aT^*} \) (4.16)

is the amplitude of the correlation length. The correlation length as a function of temperature is shown in Fig. 23.

From these data and Eq. (4.15) we obtain \( \xi_0 = 2 \) nm. This value appears to be close to the larger dimension of the cromolyn molecule and to the diameter of aggregates [17, 70]. For comparison, in the thermotropic liquid crystal MBBA, \( \xi_0 = 0.6 \) nm [67, 68], which is close to the width of the MBBA molecule.

The term “chromonics” covers systems with very different types of aggregates. A common property, which all chromonics share, is a face-to-face stacking of the molecules forming aggregates, but the structure of the aggregates can be very different. Moreover, not all such systems are necessarily forming mesophases. Collings et al. [74] have deduced from a resonant light-scattering experiment that in the case of different apparently non-mesomorphic chromonic molecules (porphirin) the aggregates are about 0.8 \( \mu m \) long and 0.04 \( \mu m \) thick, which corresponds to about 20 molecules across the diameter of the aggregate. The length-thickness ratio of these rods is about 20, which is not much different from the ratio \( l/d \approx 10 \) that we estimated for the cromolyn aggregates above the \( N-I \) transition.
Fig. 22. Isotropic part (due to concentration fluctuations) of the light scattering intensities in the aqueous solution of DSCG.
Fig. 23. Correlation length of the orientational fluctuations in the aqueous solution of DSCG. The solid curve represents values calculated with Eq. (4.15).
Chapter V

Concluding Remarks

5.1 Conclusions

We have characterized the optical properties of the $N$ phase formed by aqueous solutions of three different materials: DSCG, Blue 27 and Violet 20. We also probed the pretransitional fluctuations in the isotropic phase of DSCG. The individual molecules in all these materials have plank-like polyaromatic cores and assemble into rod-like aggregates in water. According to the light absorption anisotropy data, the molecular planes are on average perpendicular to the aggregate axes and thus to the nematic director, indicating the $H$-type of aggregation.

We summarize our findings as follows.

1. We have determined the birefringence $\Delta n$ of these materials in the nematic and biphasic regions as the function of temperature $T$, wavelength $\lambda$ and concentration $c$ and found it to be negative and significantly lower in the absolute value as compared to the birefringence of the typical thermotropic $N$ materials.

2. In the light absorbing materials Blue 27 and Violet 20, the wavelength dependence $\Delta n(\lambda)$ is non-monotonic that can be attributed to the effect of anomalous dispersion near the absorption bands.

3. We determined the scalar order parameter of the $N$ phase of Blue 27 and found
it to be relatively high and weakly temperature dependent, which puts the findings into the domain of general validity of the Onsager model.

4. In the light scattering experiments, our results show that the main feature of the pretransitional fluctuations in the isotropic phase of lyotropic chromonic liquid crystal is similar to the phenomena observed in thermotropic liquid crystals. The growth of the orientational susceptibility and correlation length of the pretransitional fluctuations of anisotropy, are qualitatively in accordance with the Landau-de Gennes theory of isotropic-nematic transitions.

5. We found experimentally that the temperature dependence of the inverse intensity of the anisotropic light scattering shows a pronounced deviation from the linear Curie-Weiss law. We explained this phenomenon by the temperature dependence of the aggregates length. This temperature dependence may result in non-linear temperature dependence of the Landau-de Gennes coefficient $A$ and effective optical anisotropy $\beta$.

5.2 Publications


3. O.D. Lavrentovich, S.V. Shiyanovskii, H.Liu, Y. Yin, Y. Nastishin, I. Smalyukh, V. Nazarenko, M.A. Anisimov, A.F. Kostko, T. Schneider, C. Woolverton, Lyotropic Chromonic Liquid Crystals: Self-Assembly and emerging optical and


5, L. Tortora, H.S. Park, K. Antion, Hui Liu, D. Finotello, S.V. Shiyanovskii, C.J. Woolverton, O.D. Lavrentovich, Nanostructured Lyotropic Chromonic Liquid Crystals and effects of ions, Ohio Nanotechnology Summit, Columbus, OH, April 4-5, 2006

5.3 Future directions

We have explored the LCLC aqueous solutions without any additives. Some other work had shown that by adding some salt (like NaCl) to the LCLC solution, the phase diagram will change [71, 73, 89], because salt might change the way the molecules aggregate. The phase dependence on the amount of salt added would be of great importance because one could be able to change the phase behavior of the solutions.

In our research, we used primarily the planar cells. A homeotropic alignment that works for LCLCs might help us collect more information if we could find a way to align LCLC homeotropically in the cell. Our group had successfully aligned Violet 20
homeotropically, but further research needs to be done to expand to other LCLC materials.

Our current description of the pretransitional phenomena in aqueous solutions of cromolyn is intended to grasp only the most essential physical features. Further light scattering experiments can be done on a planar aligned DSCG nematic samples to find out the expected coupling between the orientational and translational dynamic modes, as well as a coupling between the nematic order parameter and supramolecular aggregation in LCLC.
Appendix

Derivation of Eq. (3.2) and (3.4)

We will derive the transmittance of a planar LCLC cell between two polarizers, using Jones matrix method [72].

We begin with an incident electric field polarized along the polarizer (Fig. 24) as

$$\vec{E}_0 = \begin{bmatrix} 1 \\ 0 \end{bmatrix},$$  \hspace{1cm} (A1)

The electric field before the LCLC cell is given by

$$\vec{E}_p = \vec{E}_0 [\cos \alpha_1 \quad \sin \alpha_1], \hspace{1cm} (A2)$$

where $\alpha_1$ is the angle between the polarizer and the director of the planar LCLC cell.

For an absorbing crystal, the matrix for the sample can be written as:

$$L = \begin{bmatrix} e^{\frac{2\pi d}{\lambda}} & e^{-\frac{2\pi d}{\lambda}} \\ 0 & e^{\frac{2\pi d}{\lambda}} \end{bmatrix} = e^{-\frac{2\pi d}{\lambda}} \begin{bmatrix} e^{\frac{2\pi d}{\lambda}} & 0 \\ 0 & e^{-\frac{2\pi d}{\lambda}} \end{bmatrix} e^{i\Delta \varphi}, \hspace{1cm} (A3)$$

where $\Delta n = n_e - n_o$ and $\Delta \varphi = \frac{2\pi \Delta n d}{\lambda}$; $k_{//}$ and $k_{\perp}$ are the absorption coefficient parallel and perpendicular to the director, respectively; $n_e$ and $n_o$ are the extraordinary and ordinary refractive indices; $d$ is the thickness of the cell gap.

The matrix for the analyzer is given by

$$A = \begin{bmatrix} \cos \alpha_2 \\ \sin \alpha_2 \end{bmatrix}, \hspace{1cm} (A4)$$

where $\alpha_2$ is the angle between the analyzer and the director of the sample.
Electric field of transmitted through the analyzer is obtained based on Eq. (A1) – (A4)

\[ \bar{E}_r = \bar{E}_\rho L A = e^{-\frac{2 \pi i d}{\lambda}} \bar{E}_0 \left[ \cos \alpha_1 \sin \alpha_1 \begin{bmatrix} e^{-\frac{2 \pi i d}{\lambda}} \\ 0 \end{bmatrix} + e^{\frac{2 \pi i d}{\lambda}} e^{i \Delta \varphi} \sin \alpha_2 \right] \sin \alpha_2 \]  

(A5)

The transmitted light intensity \( I \) is calculated as

\[ I = |\bar{E}_T|^2 = \left| e^{-\frac{2 \pi i d}{\lambda}} \cos \alpha_1 \cos \alpha_2 + e^{\frac{2 \pi i d}{\lambda}} e^{i \Delta \varphi} \sin \alpha_1 \sin \alpha_2 \right|^2, \]  

(A6)

Since the incident light intensity is \( I_0 = |\bar{E}_0|^2 = 1 \), we could conclude that the transmittance is:

\[ T = I/I_0 = e^{-\frac{4 \pi i d}{\lambda} \cos^4 \alpha + \frac{4 \pi i d}{\lambda} \sin^4 \alpha + \frac{2 \pi (k_{\perp} + k_{\parallel}) d}{\lambda} \cos^2 \alpha \sin^2 \alpha (e^{i \Delta \varphi} + e^{-i \Delta \varphi})} \]  

We chose parallel polarizers setup, which means that \( \alpha_1 = \alpha_2 = \alpha \), and we can get

\[ T = e^{-\frac{4 \pi i d}{\lambda} \cos^4 \alpha + \frac{4 \pi i d}{\lambda} \sin^4 \alpha + \frac{2 \pi (k_{\perp} + k_{\parallel}) d}{\lambda} \cos^2 \alpha \sin^2 \alpha \cos \Delta \varphi}, \]  

(A8)

When \( \alpha = 0^\circ \), we have \( T_0 = e^{-\frac{4 \pi i d}{\lambda}} \).

When \( \alpha = 90^\circ \), we have \( T_{90} = e^{-\frac{4 \pi i d}{\lambda}} \).

For an angle \( \alpha \) other than 0 and 90°, we have

\[ T = T_0 \cos^4 \alpha + T_{90} \sin^4 \alpha + \frac{1}{2} \sqrt{T_0 T_{90}} \cos \Delta \varphi \sin^2 (2 \alpha), \]  

(A9)

which is the case for Blue 27 solution, [Eq. (3.4)].
For the case of DSCG, the aqueous solution is almost transparent in the visible wavelength range, thus we could expect that $k_{//} \approx k_{\perp} \approx 0$:

$$T_{45} = \frac{1}{4} + \frac{1}{4} + \frac{1}{2} \cos \Delta \varphi = \frac{1}{2} (1 + \cos \Delta \varphi) = \cos^2(\Delta \varphi/2).$$
Fig. 24. Propagation of light through a polarizer, uniaxial absorbing material with thickness of $d$, and analyzer.
References


3380 (2002)


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