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Effect of UV-light irradiation on phase diagram of lyotropic chromonic liquid crystal

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ABSTRACT

We demonstrate that the phase diagram of a Lyotropic Chromonic Liquid Crystal (LCLC) is affected by ultraviolet (UV) light irradiation. UV-irradiation induces a phase transition from the nematic (*N*) to isotropic (*I*) state at a fixed temperature. Birefringence measured *in-situ* decreases under irradiation, until the moment when the isotropic phase starts to nucleate and the initial homogeneous nematic transforms into a biphasic state. On further irradiation the birefringence of the *N* fraction of the biphasic *I-N* state increases revealing redistribution of the composition components between the two coexisting phases. The efficiency of the irradiation-induced changes depends on the orientation of the chromonic aggregates *w.r.t.* the polarization of UV light. Changes of the birefringence are noticeably higher for light polarization perpendicular to the nematic director. The effect can be understood as a photo-induced weakening of the face-to-face molecular attraction within the chromonic aggregates and the resulting shortening of these aggregates.

1. Introduction

Twenty years ago John Lydon [1] drew attention of the liquid crystal community to the family of lyotropic liquid crystals (LLCs) formed by plank-like aromatic molecules. These molecules, otherwise recognized as dyes, drugs and nucleotides, tend to aggregate face-to-face with each other, forming elongated aggregates, when dissolved in water. In certain temperature-concentration range the aggregates form LLC phases. Exciting possibilities for applications of these liquid crystals have been reported in recent years [2 and references herein,3,4].

Lydon introduced the term “chromonics”, which now appears to be a shorthand for the Lyotropic Chromonic Liquid Crystals (LCLCs), that have to be considered as a separate class of lyotropics, distinctively different from their surfactant-based counterparts, or Lyotropic Surfactant Liquid Crystals (LSLCs) formed by solutions of amphiphilic rod-like molecules [1–7]. Because of non-surfactant nature of the constituent molecules, the LCLCs are non-toxic [8] and can be interfaced with biological systems, enabling new applications such as real-time detection of microbes [9] and command of dynamic behavior of swimming bacteria [10].

The building units in both LCLCs and LSLCs are molecular aggregates, but the nature of these aggregates is different. The aggregates of surfactant molecules, called micelles, are either closed spheroids (spheres or ellipsoids) or infinitely long objects (worm-like cylinders or highly flexible bilayer membranes). The molecules can migrate within the micelles; there is no well-defined repetitive distance between them. In contrast, in the chromonic aggregates, the molecules are stacked on top of each other with a well-defined period of about 3.4 Å [11,12]. The one-dimensional order is imperfect though, not only in the sense of Landau-Pieirls effect, but also because of possible lateral displacements of molecular planes [13]. It is often assumed that the energy needed for splitting an aggregate into two (called the scission energy) does not depend on the length of the aggregate nor on the location of the break; such type of aggregation is called isodesmic [14,15]. Isodesmic aggregation implies no critical micellar concentration (*cmc*). Instead, it leads to polydispersity of the aggregates' lengths. Absence of *cmc* and polydispersity of aggregates are among the key properties distinguishing LCLCs from LSLCs. In chromonics the aggregate length distribution shows a broad maximum corresponding to some finite aggregation number, which is controlled by factors such as concentration,

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temperature, presence of ions, *etc.* [16–18]. Chromonic aggregation is stabilized by hydrophobic attractions of molecular planes which are much weaker than chemical bonding. As a result the aggregation number in chromonic assemblies can be strongly affected by the temperature.

The average length of aggregates, estimated as $l \propto \sqrt{\phi}\ \ln\left(\frac{E}{k_B T}\right)$ for dilute isotropic dispersions [19] depends on temperature *T*, volume fraction ϕ, and the scission energy $E \approx (4 - 12)k_B T \approx (1.6 - 5) \times 10^{-20} J$ [13,20–24]. Simple estimation shows that the energy carried by a single light photon of the UV–vis light wavelengths between $0.3 - 0.6\mu m$ is in the range of $(1 - 2) \times 10^{-19}$J being about one order of magnitude higher than the scission energy *E*. The latter implies that in principle, the adsorbed light energy might be enough for breaking the aggregate into shorter pieces, which might result in the change of the orientationally ordered state of the LCLCs. In this paper, we demonstrate that the effect of UV irradiation on the phase diagram of LCLCs could be indeed profound.

2. Experimental

We study disodium cromoglycate (DSCG) [6], $C_{23}H_{14}O_{11}Na_2$ (Spectrum Inc., purity 98%), dissolved in water with the concentrations $12 - 15$wt. %, showing the nematic phase at room temperature. The solutions were filled into flat glass capillaries of the gap thickness $d = 50\mu m$ or confined in sandwich type cells of the thickness $d = 19.5\mu m$ formed by two glass substrates covered with unidirectionally rubbed polyimide SE-7511. At most of substrates, including clean glass and polyimide SE-7511, the studied LCLC aligns its director parallel to the substrates [25]. Rubbing of the polyimide layer provides unidirectional alignment of the director along the rubbing direction. At the walls of the flat capillary, the azimuthal degeneracy of tangential director orientation is lifted by unidirectional flow of the material during the filling of the capillary. Unidirectional alignment along the long axis of the capillary was confirmed by polarization microscopy observations.

In contrast to many LCLC materials that are dyes, DSCG dispersions in water are transparent in the visible part of spectrum, absorbing mostly in the UV [25]. The UV-source represented a lamp PL-S9W/08 2P (Philips) with the consuming electrical power 9 W, and the maximum intensity at the wavelength $\lambda = 365$nm. Intensity of the irradiating light at the sample surface, illuminated at an angle 30° by the UV lamp mounted 15 cm above the sample plane, was estimated to be on the order of 0.5 mW/cm^2. The thicknesses of the capillary wall and of the glass substrate were 35 μm and 1 mm, respectively. Estimated light losses due to absorption in and reflection at glass were on the order of 5% percent for the capillary and about 30% for the cell substrate in the spectral range around the wavelength of the maximum UV intensity from the lamp. Birefringence was measured with the accuracy ± 0.0001 at the wavelength of 632.8 nm using an ellipsometer equipped with a He-Ne laser.

3. Results

The sample filled into a $d = 50\mu m$ flat capillary at room temperature showing uniform alignment of the nematic director along the capillary long axis was placed on the microscope stage with the director $\overleftrightarrow{n}$ at 45° *w.r.t.* to the crossed polarizers. The UV-lamp was mounted 15 cm above the microscope stage such that the UV-light obliquely incidences on the sample at about 30° *w.r.t.* the cell normal. *In-situ* observations during the irradiation show that the birefringence interference color of the sample changes with the exposition time as shown in Fig.1.

Birefringence values for this LCLC, reported in [25] for room temperatures and concentrations $c = 12$–15 wt% range from 0.012 to 0.02. Yellow-greenish color of the sample observed before the UV-exposition between crossed polarizers indeed corresponds to the phase retardation of about $R = 800$ nm; the birefringence estimated for this value is $\Delta n = R/d = 0.016$, which agrees well with data in reference [25]. Changes of the interference colors shown in Fig.1 reveal that the birefringence decreases with the exposition time until the moment $t = 72$min (counted from the beginning of irradiation), when droplets of the isotropic phase (seen as round inclusions in the microscope photographs in Fig. 1) appear. After this moment the change of interference colors reverses, indicating that the birefringence of the nematic fraction increases on further UV-exposition (Fig.1 below the polarization microscope photographs).

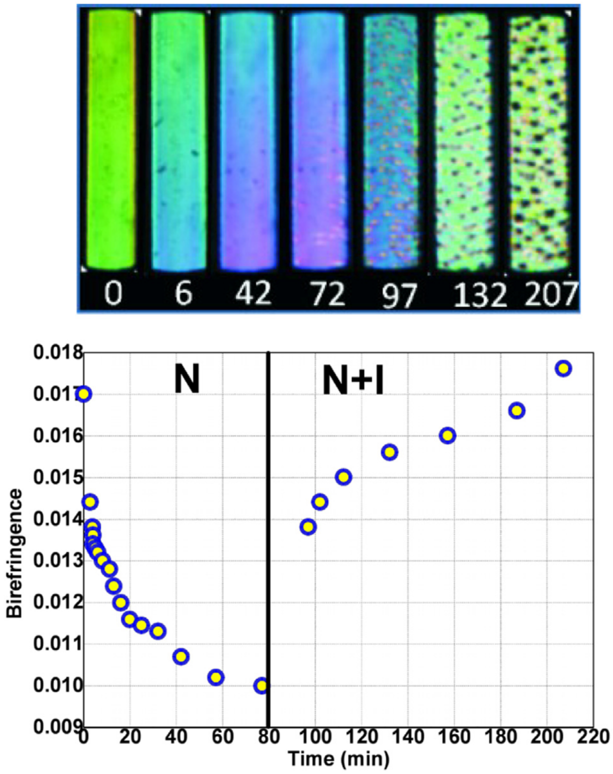


Fig. 1. (Color online) Optical retardation interference colors observed for 50 μm capillary in the diagonal position between crossed polarizer as a function the irradiation time indicated below each picture in minutes and evolution of the birefringence measured *in situ* during the UV-irradiation.

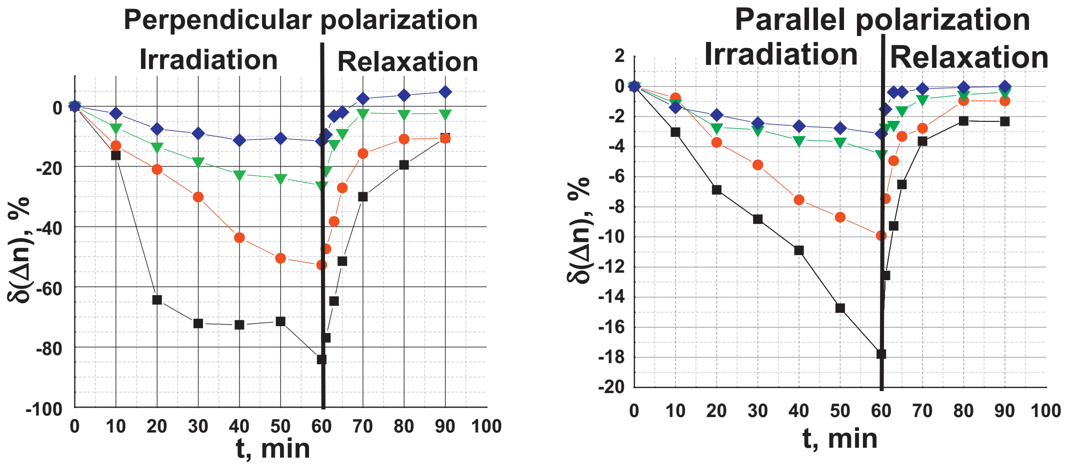
Time evolution of the relative birefringence change $\delta\Delta n = \{(\Delta n|_t - \Delta n|_{t=0})/\Delta n|_{t=0}\} \times 100\%$ measured in the time moment *t* for polarizations of the irradiating UV-light being perpendicular and parallel to the nematic director in the cell of the thickness $d = 19.5\mu m$ is shown in Fig.2.

The relative change of birefringence $\delta\Delta n$ measured for perpendicular (*w.r.t.* $\overleftrightarrow{n}$) polarization is significantly higher (Fig. 2a) than for parallel polarization (Fig. 2b). This is in agreement with UV light absorption spectra (Fig. 3), which show higher absorption (thick red line in Fig.3) for the light polarization perpendicular to the nematic director, *i.e.* parallel to the molecular planes.

We have performed similar experiments for three different concentrations and found that the values of relative decrease $\delta\Delta n$ are higher for lower concentrations. Exposure for 1 h leads to the following results: $\delta\Delta n(12,14,15\%) = -93, -84, -55\%$ for $\overrightarrow{P} \perp \overleftrightarrow{n}$ and $-39, -18, -14\%$ for $\overrightarrow{P} \parallel \overleftrightarrow{n}$.

4. Discussion

Increase of the birefringence (Fig. 1) of the nematic in the biphasic $I + N$ state created by the UV irradiation suggests that the corresponding *N* phase is more concentrated as compared to the homogeneous *N*



(a) **(b)**

Fig. 2. (Color online) Evolution of the birefringence for a cell ($d = 19.5$ μm, $c = 14\%$) during UV-irradiation ($t < 60$ min) and relaxation ($t > 60$ min), *in-situ* measured for different irradiation intensities (in arb. units): 0.15 (blue diamonds), 0.3 (green triangles), 0.5 (red circles), 1 (black squares).

phase of the sample prior to the nucleation of the *I* phase. Therefore, the UV irradiation causes redistribution of the aggregates between the isotropic and nematic regions of the biphasic state. The nematic fraction is more concentrated and contains aggregates that are on average longer than those in the isotropic fraction and those in the homogeneous nematic sample prior to the nucleation of the isotropic phase. Longer aggregates show higher orientational order, which implies higher birefringence. Similar increase of the birefringence was observed in Ref. [25] for the nematic fraction of the biphasic $N + I$ state produced by heating.

Relaxation of the isotropic phase back to the nematic phase after UV-irradiation is a slow process. Fig. 2 shows that at least tens of minutes are needed for the cell with $d = 19.5$ μm and $c = 14\%$ to recover the birefringence of the initial homogeneous nematic prior to irradiation. Visual inspection of the sample between crossed polarizers shows that a prolonged irradiation for >12 h of a weakly concentrated solution ($c = 12.5\%$) placed in thick rectangular capillaries ($d > 100$ μm) causes such a strong modifications of the structure that the system requires a very long time, between several hours to several days, to relax to the original homogeneous nematic state.

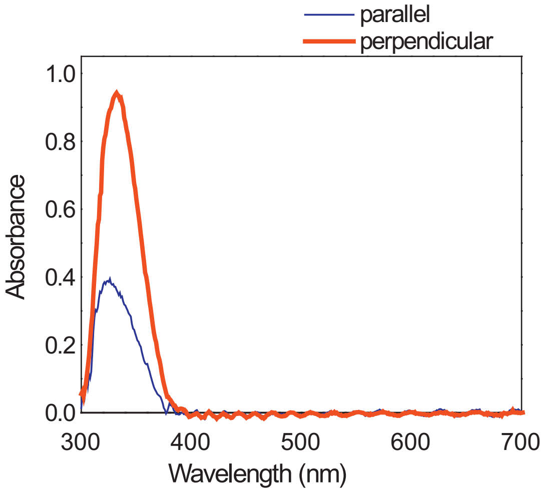


Fig. 3. (Color online) Absorption spectra for a 2 μm planar cell of 15% cromolyn in water solution for light polarization parallel and perpendicular to the director.

On cooling under ambient conditions, the *I*-*N* transition shows a hysteresis (up to several degrees). Thus one might suggest that the observed UV-induced phase transformation results from the absorption-triggered heating. However, our experiments show that after a direct heating (no UV) of the samples to the temperature that is ten degrees above the *N*-*I* transition, the system needs a much shorter time, a few minutes, to relax back to the homogeneous nematic phase. Moreover, if the solutions are kept at the elevated temperatures (again in absence of the UV irradiation) for several hours in the homogeneous isotropic phase at 20° above the start of the *N*-*I* transition, and then the heating is stopped, the system again relaxes to the homogeneous nematic within minutes. It is thus unlikely that the UV-induced changes that require hours and even days to relax could be explained solely by the light-induced heating of the cell.

Taking into account that (1) the energy of a light photon is about one order of magnitude higher than the chromonic scission energy; (2) UV-light induced decrease of birefringence of the homogeneous nematic is higher for perpendicular polarization, for which absorption is higher [26]; (3) relaxation time of the UV-induced isotropic phase to the nematic state is much longer than the time of thermal relaxation, we suggest that the UV-triggered changes are associated with the modification of molecular interactions within the aggregates and a corresponding change in the length distribution of these aggregates. Several mechanisms can be responsible for this effect, besides the direct light-induced heating.

Excitation of the chromonic molecules to their higher energy levels most likely weakens attractive hydrophobic interactions within the aggregates and thus implies a reduction of the scission energy and shortening of the aggregates. A direct scission of aggregates into pieces by excited molecules kicked out of the aggregate by high-energy photons might also take place. Although it is clear that the observed effect of UV irradiation on the phase diagram of the LCLC is associated with the modification of the aggregates' length distribution, the exact molecular mechanisms of it require further studies.

5. Conclusions

We have demonstrated that the phase state of the Lyotropic Chromonic Liquid Crystal (LCLC) can be affected by UV light irradiation. The irradiation induces the phase transition from the nematic (*N*) to isotropic (*I*) state at a fixed temperature and concentration. Optical phase retardation measured *in-situ* during the UV-irradiation decreases until the moment of the *I* phase appearance. On further irradiation the birefringence of the *N* fraction of the biphasic *I-N* state increases revealing the redistribution of the chromonic molecules between the two coexisting phases. The data suggest that the nematic fraction contains aggregates that are on average longer than those in the coexisting isotropic phase. They are also longer and thus better aligned than the aggregates in the homogeneous nematic prior to the nucleation of the *I* phase.

Efficiency of the irradiation-induced changes depends on the orientation of the chromonic aggregates with respect to the polarization of UV light. Changes of the birefringence are noticeably higher for light polarization perpendicular to the nematic director. Several molecular mechanisms might be responsible for the observed effect of UV irradiation, the details of which needs to be elucidated by future experiments.

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