P-138: Plasma Beam Alignment of Lyotropic Chromonic Liquid Crystals

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Abstract
We have successfully extended the plasma beam alignment technique to the class of lyotropic chromonic liquid crystals (LCLCs). High quality alignment of these materials was obtained in sandwich cells and in dried films coated on a solid substrate. The plasma beam alignment of LCLCs facilitates practical applications of these materials.

1. Introduction
Most of liquid crystal (LC) devices use uniformly aligned LCs. The most widely used method of LC alignment is based on mechanical rubbing of a relatively soft polymer substrate. Well-known shortcomings of this method stimulated development of new techniques. One of the most promising is the so-called ion/plasma beam alignment [1,2]. The essence of this method is that the aligning ability of the substrate is achieved by an oblique irradiation with an ion or plasma beam. The treatment generates an anisotropic surface profile through a selective and orientation-dependent destruction of molecular bonds. In contrast to the traditional rubbing technique, the ion/plasma beam method yields an excellent microscopic homogeneity, compatibility with alignment pattering, and is applicable for curved and flexible substrates. Furthermore, the unique feature of this technique is that presence of the special alignment layer is optional, as the LC can be aligned directly by treated bare substrates such as glass, silicon, plastic, *etc.* [3].

As previously reported, the ion/plasma alignment is suitable for various types of LCs, including thermotropic nematic [1-3], cholesteric and ferroelectric smectic LCs [4]. The ion/plasma aligned LCs can be used in passive optical elements such as anisotropic optical films (retarders and polarizers) and surface electronic devices [5]. In contrast to the electrooptic LC cells used in displays, many other applications of LCs do not require the LC to be repeatedly realigned by an external field, thus the alignment-related problems such as image sticking, alignment aging, etc., do not appear. The applications of these "passive LCs" are based on non-traditional LC materials such as reactive mesogens (RMs), lyotropic LCs, and glassy LCs (GLCs).

Our general goal is to extend the ion/plasma beam alignment method to different classes of passive LCs. In [5] we have already reported high efficiency of this method for RMs and GLC. In this report we study the capabilities of the method for lyotropic chromonic LCs (LCLCs) [6-8], alignment of which is rather difficult in both the dry film form [7] and in the form of mesomorphic aqueous solutions [8]. Material flow and shear play quite an important role in alignment of the LCLCs. The aligning abilities of these factors can be enhanced by the anisotropic treatment of the substrates. In this work we demonstrate that the ion/plasma beam method results in good surface alignment of LCLCs, both in the form of water solutions with mesomorphic phases and in the form of dried films.

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2. Experimental
2.1. Lyotropic LC
Nematic aqueous solutions of Disodium Cromoglycate (DSCG) and neutral gray dye NO15 from Optiva were used as LCLC materials. The nematic aqueous solution of DSCG was prepared by dissolving 1.4 g of DSCG in 8.6 g of de-ionized water. The aqueous mixture of neutral dye NO15 was used as obtained from Optiva.

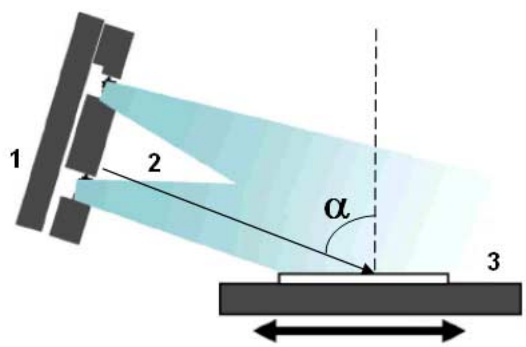

Figure 1. Scheme of alignment treatment with a sheet-like plasma beams generated with anode layer source. 1 – source; 2 – two "sheets" of accelerated plasma; 3 – substrate on moving platform.

2.2. Substrates and alignment process
We used glass slides coated by thin layers of polyimide (PI) AL3046 from JSR. These substrates were treated with the oblique beam of Ar plasma produced with an anode layer source as described in our previous papers [2,3]. The processing scheme is presented in Fig. 1. The beam of accelerated particles was directed onto the substrate at an angle $\alpha=65^o$ with respect to the normal to the substrate. During the exposure, the glass slides were periodically shifted back and forth with a speed ~ 2 cm/min, to ensure multiple exposures of the sample and to achieve a better homogeneity of surface treatment. The working pressure was (6-8) 10^{-4} torr and the anode potential was 600 V that corresponded to the current density in the plasma beam of about 6 $\mu A/cm^2$. The exposure time was set at 4 and 15 min, which produced the so-called 1st and the 2nd alignment modes, respectively. In the 1st mode, the alignment direction is towards the propagation direction

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of the plasma beam and in the 2nd mode, it is perpendicular to this beam. The quality of LC alignment on the processed substrates was preliminarily tested in the cells filled with a thermotropic nematic LC.
In addition to the treated PI substrates, we used the same substrates coated with thin (~50 nm) layer of reactive mesogen RMM256C (Merck) designed for planar alignment. This layer was spin coated on the substrates from the toluene solution and subsequently irradiated with unpolarized UV light to polymerize. In this case, the plasma treated PI surface served as an aligning layer for RM, and the RM layer was an aligning layer for LCLC. Finally, as reference substrates we used untreated bare glass and PI substrates, as well as unidirectionally rubbed PI substrates.

2.3. Samples

2.3.1. *Sandwich cells*

The alignment of LCLC in the liquid crystalline state, *i.e.*, in the water solution, was tested in sandwich cells. For this purpose, pairs of similar substrates were used to assemble the LC cells. Each cell was assembled in an anti-parallel fashion (*i.e.*, with the antiparallel alignment of the directionally plasma beam treated substrates). The gap of each cell was fixed by using glass fibers mixed with optical adhesive Norland NOA-71. This mixture was deposited on the edge of the substrate along its perimeter and, after assembilng the cell, cured with UV light. The prepared cells were filled with LCLC solutions by using suction force of a vacuum pump. The cells were sealed with an epoxy glue.

2.3.2. *Dry films*

To produce dry films, the plasma beam processed aligning substrates were covered with aqueous solutions of DSCG and NO15. The LCLC was then sheared along the easy alignment direction induced by the plasma treatment. A glass bar and a metal doctor blade were used as shearing tools. After the shear, the films were dried at the room temperature.

2.4. Alignment characterization

The samples were observed between a pair of crossed polarizers with the naked eye and in Nikon polarizing optical microscope. The corresponding textures were captured by CCD camera. Angular distortions of molecular alignment in transparent DSCG samples were characterized by mapping the optical phase retardation with Abrio Polscope.

3. Results

3.1. Alignment in sandwich cells

For both LCLC materials, highly uniform alignment was achieved in sandwich cells. Fig. 2 shows the textures of cells filled with DSCG solution. The cells (a) and (b) use the PI and PI/RM aligning layers, respectively. The photographs in parts (1) and (2) are taken under the polarizing microscope with the alignment direction and the polarizer axis making an angle 0^o and 45^o, respectively. Part (3) presents a pseudo color map of angular orientation of DSCG director as viewed in Polscope. The markers with two numbers represent optical retardation (in nanometers) and azimuth angle measured in randomly chosen points. One can see that the bare PI films produce rather good alignment with the alignment direction varying in the azimuthal plane by about 3^o. The quality of this alignment was markedly better than in the case of rubbed PI films. In the cells with untreated substrates, the alignment induced by flow was very poor.

The alignment further improved if the PI aligning films were covered with the RM layers. The alignment direction variations in this case were only 1^o, indicating high alignment uniformity. The effect of improving the LCLC alignment using auxiliary layers of RM is similar to that previously described for thermotropic LCs [9-11].

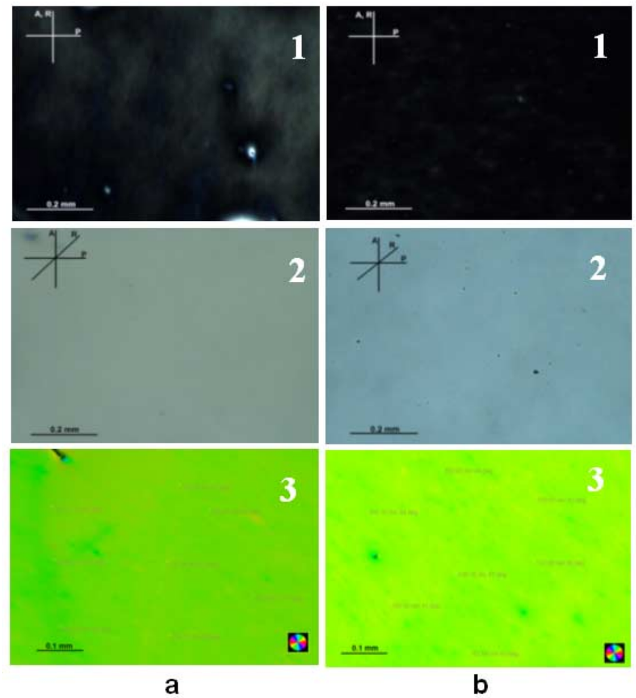
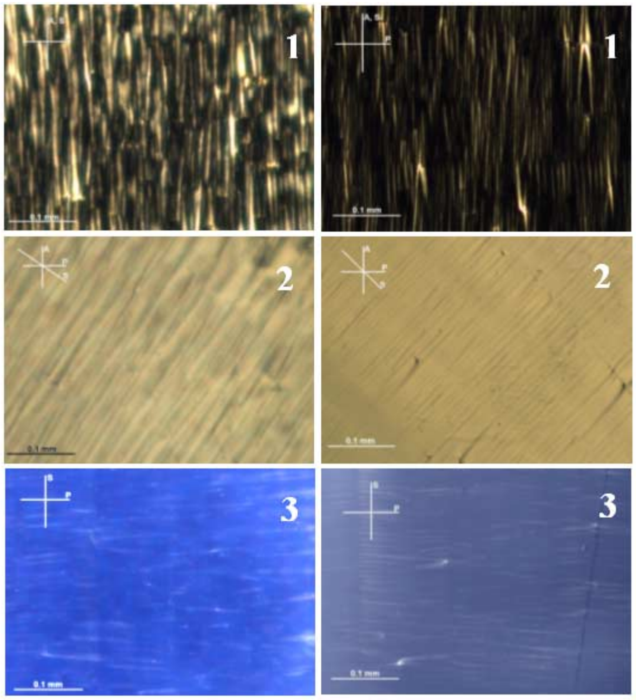


Figure 2. (1a), (2a), (1b), (2b): Microphotographs of sandwich cells based on plasma beam treated PI aligning films non-coated (a) and coated (b) with the layer of RMM 256C. The cells are filled with LCLC DSCG. Figures 3a and 3b present the pseudo-color map of angular orientation of DSCG molecules processed in Polscope.

3.2. Alignment in dry films

Similarly to the sandwich cells, highly uniform alignment was achieved in the dried LCLC films deposited on plasma treated single substrates. Fig. 3 presents results for the films of neutral gray dye NO15 deposited on an untreated bare glass (a) and plasma beam treated PI film (b). The microphotographs are taken under the polarizing microscope with the polarizer and alignment axes making the angle 90^o (1), 45^o (2) and 0^o (3).
It is clear that the untreated substrate provides the worst alignment with a typical "tiger stripe" texture caused by director undulations in the range of 0-15^o. The alignment of NO15 on the untreated PI film was of similar quality. In the case of plasma processed PI films, the quality of alignment is markedly improved, but the deviation angle is still large (about 6^o). Nevertheless, these films showed considerably better alignment that the rubbed films of the same PI. The plasma treatment also improved wettability of PI with LCLC.
Alignment of the dry films greatly improves in samples with the RM layers placed on top of the beam-treated PI layers (Fig. 4). These samples are highly uniform with the alignment deviation angle being only about 1^o. Apparently, the RM layer with a "frozen" orientational order interacts strongly with a layer of LCLC



a b

Figure 3. Microphotographs of the dry films of neutral dye NO15 taken under a polarizing microscope with crossed polarizer and analyzer. The films are coated on bare glass (a) and plasma beam processed PI films (b). The alignment axis of the film and the polarizer direction form an angle 90°, 45° and 0° in cases 1, 2 and 3, respectively.

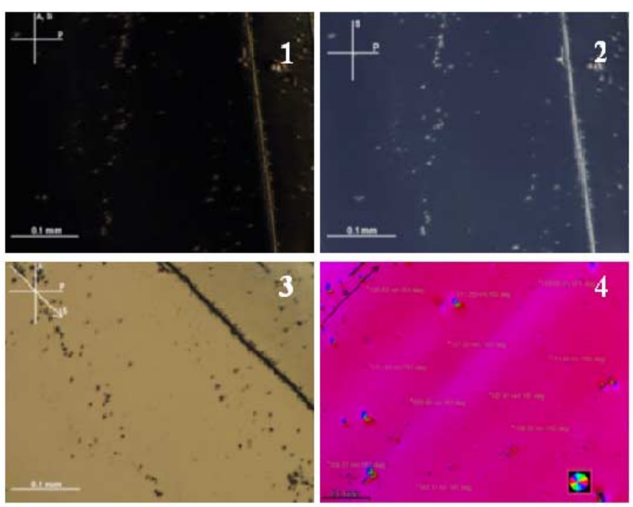


Figure 4. Microphotographs of the dry film of neutral dye NO15 taken under a polarizing microscope with crossed polarizer and analyzer. The film is coated on plasma beam processed PI films cover by a thin layer of RM. The alignment axis of the film and the polarizer direction form an angle 90°, 45° and 0° in cases 1, 2 and 3, respectively. Picture 4 presents the pseudo-color map of angular orientation of NO15 molecules processed in Polscope.

projecting its own alignment into the one of LCLC. It would be of interest to verify whether the RM auxiliary layers can also improve alignment of LCLC films on rubbed and photoaligned surfaces, as is the case of thermotropic LCs [9-11].

4. Conclusions

We demonstrated that the ion/plasma beam treatment is highly effective for alignment of LCLCs in the form of mesomorphic aqueous solutions and in the form of dry films. The best alignment is achieved when the plasma treated PI layer is additionally covered with a layer of reactive mesogen, whose orientational order was fixed by photopolymerization. In this case, the angular deviations of the alignment direction are small, on the order of about 1°. The possibility of high-quality alignment of LCLCs opens up good prospects for using this method in preparation of retardation films, dichroic polarizers and semiconducting anisotropic films [12] based on LCLCs. We believe that a similar technique can also be effectively used for alignment of other water-based systems with orientational order. Finally, new results [13,14] offer hope to move the process of plasma treatment in atmospheric pressure range, which makes it even more attractive for practical applications.

5. Acknowledgements

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