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PAPER

Homogeneous and homeotropic alignment of bent-core uniaxial and biaxial nematic liquid crystals

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The effect of well-established homeotropically and homogeneously aligning polyimides, developed for calamitic liquid crystals, on the alignment of the nematic phases of bent-core mesogens was investigated using polarizing optical microscopy and conoscopy. Two polyimides, the homogeneously aligning SE7792 and the homeotropically aligning S659, were used to align three bent-core mesogens. Two of the mesogens, with an azo group in one of their arms, are found to align in a manner similar to the calamitic mesogens, while a fluorenone core based mesogen counter-intuitively aligns homogeneously on S659 coated surface and homeotropically on SE7792. Attractive interactions between unidirectionally oriented polyimide side-chains and the alkyl chains of mesogens determine the direction of alignment of the nematic director.

Introduction

Nematic liquid crystals (NLCs) are used in basic scientific research as well as in applications such as liquid crystal (LC) displays.[1] Both situations require the symmetry/optic axis of NLC to be well aligned in a predetermined spatial direction(s). Specifically, two types of alignment,[2] known as homeotropic and homogeneous, are most commonly needed and several methods have been developed to achieve the two configurations.[3] In a *homogeneously* aligned cell, the molecules and, consequently, the director *n* of the uniaxial NLC are parallel to the bounding surfaces, *e.g.*, glass substrates, of the cell and point in a specific in-plane direction defined by the rubbing process, see Fig. 1(a). In the *homeotropically* aligned state, the director is perpendicular to the substrates, as shown in Fig. 1(b). Special polymers have been developed to anchor the director in these two configurations. These include several polyimides (PIs) which align *n* homogeneously when coated on a substrate and mechanically buffed unidirectionally. Other PIs align *n* homeotropically, and they are rubbed to offer an azimuthal bias to the molecules of dielectrically negative NLC when an external field is applied to the cell.

There are two factors at play in aligning an NLC on *treated* surfaces such as rubbed PI films. One of the factors is purely physical (or, geometrical) in origin and relates to the surface morphology and anisotropic elastic properties of NLCs.[4] For example, the rubbing process creates linear micro-grooves and increases[5] the vertical rms roughness of a substrate/film surface. However, one of the substrate's in-plane directions becomes rougher than the orthogonal direction, thus giving rise to morphological (or, roughness) anisotropy. It has been found that NLC always aligns *n* parallel to the *smoother* direction,[5] because it costs the least amount of elastic energy.[4] This is true for rubbed plain glass surfaces, rubbed PI[5] and other polymeric alignment layers,[6] as well as for polymer surfaces exposed to linearly polarized UV light (which also causes surface roughness anisotropy).[7] The second factor is the nature and strength of intermolecular interactions between the polymer film and the LC molecules, which evidently determines the magnitude of anchoring energy.[8] In some cases, anisotropic orientation of,

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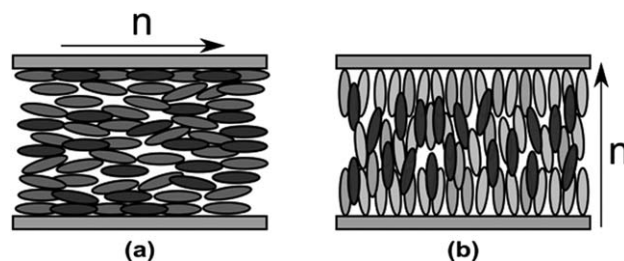
Fig. 1 Schematic representation of NLC alignment in cells with (a) homogeneous and (b) homeotropic boundary conditions. The ellipses represent calamitic molecules.

say, polymer chains in alignment layer may reinforce the effect of the morphological anisotropy. The anchoring energy of one NLC is usually different from that of another chemically different NLC on the same alignment layer. While a surface's morphological anisotropy determines the anchoring direction of the NLC director and the anchoring energy, chemical interactions amplify the anchoring energy and may influence the alignment direction dictated by elastic considerations and surface structure.

An applied external electric or magnetic field can override the default director orientation determined by the boundary conditions. The control of the director's alignment in a cell using a combination of surface anchoring and applied electric fields forms the basis of all electrooptical and display devices. In LC industry, different alignments make it possible to design devices with various switching modes, such as the vertical alignment (VA), in-plane switching (IPS), hybrid aligned nematic (HAN), *etc.* Evidently, understanding of NLC alignment is very important.

One may achieve homogeneous alignment of a dielectrically positive NLC in a cell. A sufficiently high external field applied perpendicularly to the two substrates can temporarily change the director orientation to homeotropic. Conversely, homeotropic alignment of the director of a dielectrically negative NLC can be rendered homogeneous with the help of a *vertically* applied electric field. This and other possible geometrically different anchoring conditions, combined with the freedom to apply external fields in different directions, allow one to measure different physical properties such as components of the dielectric tensor and refractive index ellipsoid of an NLC.

In general, surfactants, such as hexadecyltrimethylammonium bromide (HTAB),[9] lecithin, and polymers, are used for homeotropic alignment. The polar head of a surfactant chemically attaches to the substrate and the hydrocarbon tails point perpendicular to its surface. Intermolecular interaction between the surfactant and the liquid crystal molecules promotes perpendicular anchoring of the NLC director. However, surfactant based homeotropic alignment is not stable against heat and humidity. On the other hand, specially formulated PI materials provide stable and strong homeotropic alignment.[10] Rubbed PI films have predominantly been used as the alignment layers of choice in liquid crystal displays (LCD) industry. Polyimides offer not only good alignment characteristics but also desirable electrical properties such as resistivity and chemical stability.

Until now, it is only the uniaxial nematic phase out of nearly 40 different thermotropic LC phases, that has been used in practically all commercial products. With the recent discovery of the biaxial nematic phase[11–15] in bent-core mesogens, the hope of realizing the long anticipated biaxial nematic display technology begins to appear realistic in the near future. However, before the work on biaxial electrooptical devices can commence, it is imperative to learn how these materials interact with and anchor on different surfaces. This paper reports the results of our investigation of the alignment properties of three achiral bent-core mesogens on rubbed surfaces of two different PIs developed to affect homogeneous and homeotropic anchoring for calamitic liquid crystals. These bent-core mesogens exhibit the uniaxial and biaxial nematic phases.

Experimental details

Three bent-core mesogens, two azo-substituted bent-core mesogens, A131 and A103,[12] and the third with fluorenone core,[16] were used in this investigation. Fig. 2 shows the chemical structures of these molecules along with their phase sequence and transition temperatures. The difference between A131 and A103 resides in the end chains attached to the rigid bent-core. One of the end chains of A103 is octyloxy, while A131 has an octyl chain. Compounds A131 and A103 exhibit[12] the uniaxial and the biaxial nematic phases and an underlying smectic phase. The nematic phase of fluorenone core mesogen is rather viscous and has two nematic regions, where the lower temperature nematic is biaxial. Its nematic phase slowly freezes into a nematic glass near room temperature.[16]

Optical textures are observed with a polarizing microscope (Olympus BX-5) in cells with thick (10–15 μm) and thin (5 μm) gaps prepared with ITO-coated glass plates. The glass plates were covered with thin layers of polyimide SE7792 (Nissan Chemical Corporation), and polyimide S659 received from Samsung Electronics Company, and mechanically rubbed with a cloth. Rubbed layers of SE7792 and S659 align the calamitic NLC phase homogeneously and homeotropically, respectively. Sample temperature is controlled with a hot-stage (Mettler-Toledo FP82HT) with an accuracy of ±0.1 °C. A long working distance ×50 objective lens with a numerical aperture (NA) of 0.5 and a condenser with NA = 0.65 are used for conoscopy observations of A131. Textures of A131 and A103 are observed at low intensity illumination to minimize the effect of photo-isomerization of the N=N bond.[17] On the other hand, conoscopy requires a higher level of illumination; so a high-quality optical green filter (Andover Co., 550FS40-50, with 1% bandwidth of
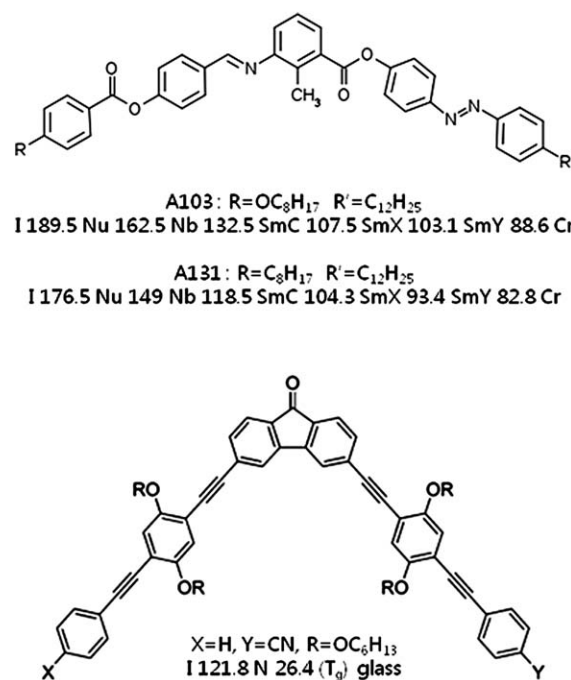

A103 : R=OC₈H₁₇ R'=C₁₂H₂₅
I 189.5 Nu 162.5 Nb 132.5 SmC 107.5 SmX 103.1 SmY 88.6 Cr

A131 : R=C₈H₁₇ R'=C₁₂H₂₅
I 176.5 Nu 149 Nb 118.5 SmC 104.3 SmX 93.4 SmY 82.8 Cr

X=H, Y=CN, R=OC₆H₁₃
I 121.8 N 26.4 (Tg) glass

Fig. 2 Chemical structures of azo substituted achiral bent core mesogens (top) and bent core mesogen with hexyloxy chains and fluorenone core (bottom). Phase sequences are also denoted.

~87 nm) is used to prevent photoisomerization of azo-benzene.[18] Narrow bandwidth optical filter eliminates much of photo-isomerization by transmitting only a narrow band of the visible spectrum while blocking UV and near-IR wavelengths. For the fluorenone core mesogen, a Zeiss Axioscope 40 with a Linkam THMS600 hot stage was used for conoscopy with 10–15 μm thick cell.

Results and discussion

Cells containing A131 and A103 show well-aligned homogeneous texture in the uniaxial nematic (N_u) phase at higher temperature, and in the lower temperature biaxial nematic (N_b) phase. Optical transmission through these cells is highest when the rubbing direction R is at 45° with respect to the easy axis of the polarizer P (or, analyzer A) and minimum at 0° (and 90°), as shown in Fig. 3. There are three parameters which determine the measured refractive indices of a nematic phase, namely, the orientational order parameter(s), molecular shape, and the degree of macroscopic alignment of the director(s).[19] If it is assumed that liquid crystals have a similar molecular shape and the degree of alignment, then measured birefringence in the NLC phase is also comparable. For example, the homologs of classical calamitic mesogens nCB and nOCB (where, n ranges from 5 to 8) have comparable physical properties, such as, refractive indices and exhibit the same phase sequence.[20] The difference in their birefringence is also quite small. In similarly prepared 5 μm gap cells, A131 and A103 are also expected to have a small difference in their birefringence. Birefringence colors observed between cross-polarizers at high and low nematic temperatures are indeed the same. Furthermore, since both azo compounds yield similar results, we will present in this paper only the results on A131.

Normally, electro-optic techniques permit one to observe any unusual and abrupt changes/differences in birefringence (or color of uniform texture) as sample temperature is changed, indicating transition to a different phase. Compound A131 shows discrete changes at 162.5 °C and 149 °C in positional order correlation
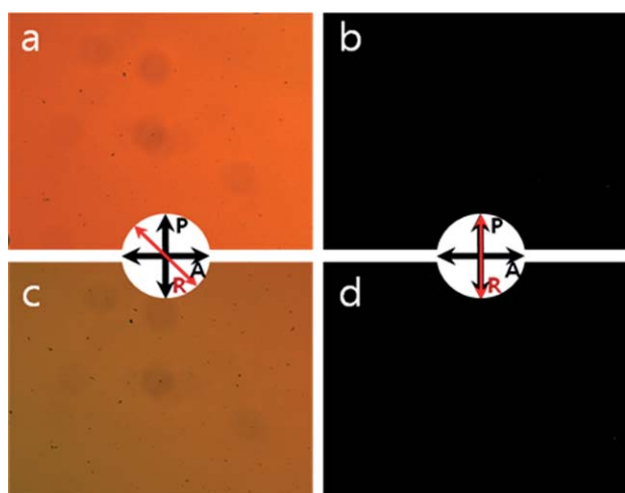
length and d-spacing measured by X-ray diffraction.[12] Compound A131 has positive/negative $\Delta\varepsilon$ at low/high frequency electric fields. Its dielectric anisotropy changes sign at a temperature-dependent *crossover frequency*.[18] Temperature dependence of the crossover frequency changes at the N_u–N_b transition. NMR and Raman measurements are consistent with these results.[14,15] However, due to very small optical variation at the N_u–N_b transition, their planar texture do not show appreciable changes.

The dual frequency behavior of $\Delta\varepsilon$ is very useful to quickly determine the director alignment in a cell. For example, a negative $\Delta\varepsilon$ nematic in a homogeneously aligned cell does not change director orientation in response to an electric field applied perpendicular to the cell walls. On the other hand, the director of a homeotropically aligned positive $\Delta\varepsilon$ nematic phase does not change its orientation when a field is applied normal to the cell. For these compounds, the director in a cell with homogeneous boundary conditions reorients to become parallel to a low frequency electric field. At higher frequencies, no major change in the effective optical retardation of a homogeneously aligned cell is observed.

A 6.4 μm thick cell with homeotropic boundary conditions was filled with A131 in the isotropic phase. The cell appears dark upon cooling below the clearing temperature as the optic axis (∥ n) orients perpendicular to the cell, Fig. 4, left. Rotation of the sample about microscope axis does not alter the intensity of transmitted light. Below the N_u–N_b transition, the dark texture gradually becomes grayish as the second birefringence of the N_b phase develops making the background locally bright, Fig. 4, middle and right. The background gradually becomes brighter at lower temperatures. In the N_b phase, the *entire* cell never becomes completely dark or as bright as unaligned uniaxial NLC phase. The cell shows *local* intensity modulation when rotated between crossed polarizers. This suggests that n remains predominantly perpendicular to the cell walls and orientational order in the direction of a secondary director m develops. The direction of m lies in the plane of the cell but its direction varies from region to region. Apparently, the homeotropic condition at the substrates is unable to offer directional anchoring to m. The two indices of refraction in the plane perpendicular to n are different in the N_b phase causing the optical transmission to gradually increase.

Conoscopy has traditionally been used to investigate the orientation of optic axes in crystalline samples such as minerals. When the optic axis of an uniaxial medium is parallel to the light's path (or, microscope axis), it forms a Maltese's cross in the
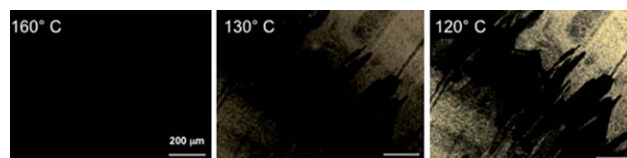

Fig. 3 POM texture of A131 in a cell with homogeneous boundary conditions at: (a) and (b) a high temperature (175 °C) in the N_u phase; (c) and (d) low temperature (127 °C) in the N_b phase. For (a) and (c): rubbing direction (R) is at 45° to the polarizer axis (P). R is parallel to polarizer or analyzer (A) in (b) and (d).

Fig. 4 POM textures of a homeotropically aligned nematic phases of A131: (left) below the clearing point in the N_u at 160 °C, (middle) in the N_b phase at 130 °C, and (right) the N_b phase at 120 °C. The cell gradually changes from dark to grayish color across the N_u–N_b transition at 149 °C. Images were taken with a 10× objective lens with 0.3 NA. Scale bars represent 200 μm.

center, as shown in Fig. 5(a). The cross is symmetrically split into two arcs when the two optic axes of a biaxial medium subtend an angle with respect to the direction of light's propagation, except when the optic axes are positioned along the direction of analyzer's (or, polarizer's) easy axis. In a cell with perfect homeotropic alignment of n achieved with polyimide S659, the optic axis is oriented normal to the substrate surface as confirmed by the Maltese cross at 165 °C in Fig. 5(a) and (b), and its invariance under rotation. A new symmetry direction m emerges when the N_u phase transitions to the N_b phase. In the N_b phase also n remains perpendicular to the cell, but its two optic axes are tilted at the same angle with respect to n. When the sample is rotated by 45°, the cross changes into two arc shaped isogyres as shown in Fig. 5(c) and (d) and the separation between them is proportional to the degree of biaxiality. These results clearly show that the major director n of A131 remains homeotropic in both the phases while the secondary director m of the biaxial phase adopts a planar configuration on surfaces coated by S659.

The fluorenone core based mesogen exhibits very interesting and counter intuitive alignment. It aligns homogeneously under homeotropic surface condition obtained with the use of S659. In cells with homogeneous boundary conditions produced by rubbed polyimide SE7792, textural observations shown in Fig. 6 confirm that director n aligns homeotropically at temperatures below the clearing point in the N_u phase. This is evident from the appearance of a dark region in the lower right-hand corner of Fig. 6(a) where the system has reached the N_u phase. Bright areas in the top left part of this figure are transient nematic textures seen during the I–N_u transition. In the N_u phase, the cell becomes completely dark and light transmission does not vary upon rotation of the cell between crossed polarizers. It should be pointed out that when an electric field is applied perpendicular to the cell, the director reorients and adopts a homogeneous configuration. This confirms that the N_u phase of this mesogen is dielectrically negative.
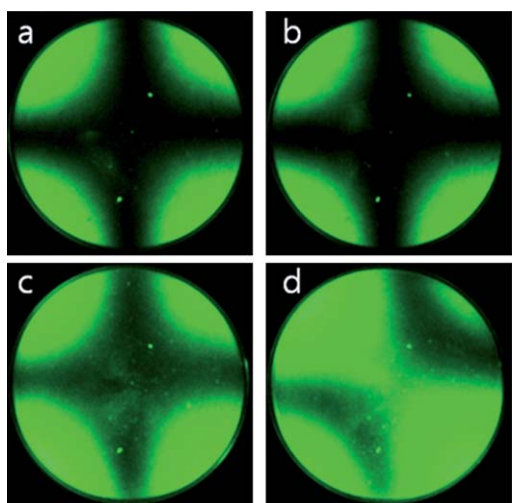

Fig. 5 Conoscopic images of A131 with homeotropic alignment: (a and b) at higher temperature (165 °C) in the N_u phase; (c and d) at lower temperature (120 °C), in the N_b phase; (b and d) the images are obtained after 45° rotation from (a) and (c). High quality optical green filter provides the green background color.
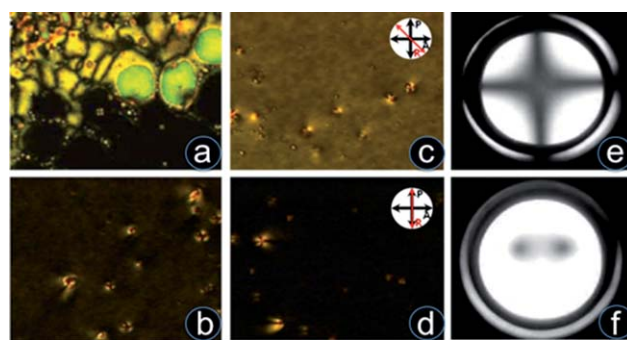

Fig. 6 (a–d): POM textures of fluorenone core mesogen under homogeneous boundary condition for calamitic mesogens offered by a rubbed SE7792 film. (a) Schlieren texture of unaligned nematic (~118 °C) changes to homeotropic alignment (lower right); (b) at lower (50 °C) temperatures, dark homeotropic texture becomes brighter as the N_b phase develops secondary birefringence; (c) cell transmission (shown at 25 °C) is high when the rubbing direction (red arrow, R) is at 45° to polarizer (P)/analyzer (A), but (d) zero when R is parallel to P/A. Conoscopic images in (e) the N_u phase and (f) the N_b phase with Benford plates. The two dots mark the locations where two optic axes of the biaxial phase pass through the field of view.

Upon further cooling, the dark texture gradually becomes brighter but remains faint with the growth of biaxiality in the N_b phase, Fig. 6(b). The cell becomes more birefringent after reaching 25 °C, Fig. 6(c), and transmits most light when the rubbing direction R is at 45° to the direction of polarizers. Clearly, the *secondary* birefringence becomes non-zero in the plane perpendicular to n with the onset of the N_b phase as the secondary director m aligns parallel to the rubbing direction. Consequently, the cell becomes completely dark, Fig. 6(d), when rotated so that m becomes parallel to the polarizer/analyzer directions. Conoscopic observations discussed below confirm that n remains parallel to the cell normal. Evidently, in the N_b phase, n and m align homeotropically and homogeneously, respectively on a rubbed film of SE7792.

Conoscopy is performed to confirm homeotropic alignment of n in cells with homogeneous boundary conditions on rubbed films of SE7792. Fig. 6(e) shows a Maltese's cross in the N_u phase. With a λ-compensator it becomes evident, that the nematic phase is optically negative,[16] consistent with the response to an applied field mentioned above. In the N_b phase, two arc like isogyres were observed upon 45° rotation, just as for A131. Benford plates were introduced, one after and the second one before the sample, to help visualize the two optic axes of the N_b phase. The two dark spots in Fig. 6(f) mark the positions of the two optic axes located symmetrically relative to the center.

Based on the alignment of the three types of mesogens on treated films of the two polyimides, it is possible to draw inferences about the factors/interactions that determine the direction of the director in the systems investigated. It is concluded that interactions of the molecular alkyl chains with the chains of the coated polyimide determine the direction of alignment of n. For example, as shown in the top panel of Fig. 7, the chains of (*homeotropically orienting*) polyimide S659 point in the direction normal to the substrate. These side chains interact and interdigitate with the chemically similar terminal chains of calamitic and azo-incorporated bent-core mesogens
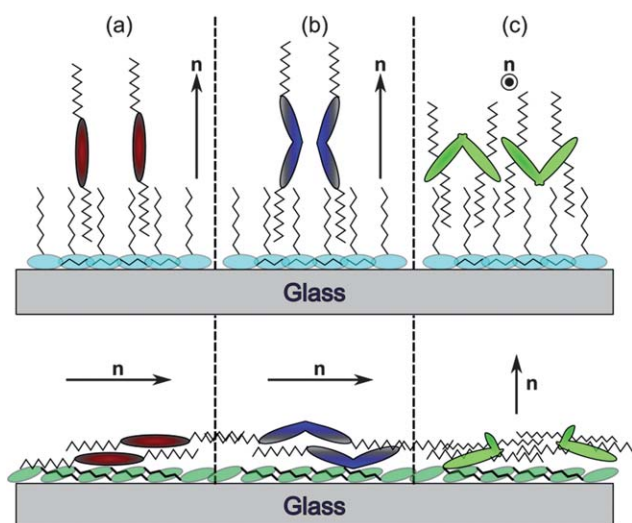
Fig. 7 Schematic depiction of how alkyl chains of (a) calamitic and (b) bent-core mesogens having nearly longitudinal terminal alkyl chains, and (c) alkyl chains transverse to the fluorenone core interact and interdigitate with the side chains of (top panel) homeotropically (S659) and (bottom panel) homogeneously (SE7792) aligning polyimides.

and orient them, on average, homeotropically as expected. This is in agreement with the trend seen in the anchoring of uniaxial nematics at the surface of polyacrylates with alkyl side chains,[21] where an (enthalpic) interaction has been postulated for the observed homeotropic alignment. Quite interestingly, although the same mechanism causes the chains of the fluorenone molecules to orient perpendicular to the substrate, their rigid bent-cores lie in a plane parallel to the substrate, *i.e.*, in a planar configuration. This obviously arises from the preorganization of the lateral chains.[16] However, since the films of S659 were gently rubbed, the rubbing direction provides a bias for *n* and orients the bent core parallel to the rubbing direction, thus giving rise to an overall homogeneous alignment. Conversely, the chains in a rubbed film of the (*homogeneously orienting*) polymer SE7792 are parallel to the rubbing direction and lie in substrate's plane. The calamitic and azo substituted bent-core molecules align homogeneously as required by terminal chains which prefer to be parallel to the side chains of PI, and thus adopt homogeneous configuration. Again, the alkyl chains of the fluorenone molecules become parallel to the side chains of polyimide offering vertical direction as lower energy state to the core of these molecules, essentially affecting a (counter intuitive) homeotropic alignment of *n*.

Summary

Three bent core liquid crystals were investigated under different surface anchoring conditions using commercial polyimides. Bent core liquid crystals align well just as conventional calamitic liquid crystals do, but with significant differences. Mesogens A131 and A103 show good homogeneous alignment for major director *n* in both the N_u and the N_b phases. On the other hand, homeotropic boundary condition causes nearly perfect homeotropic alignment in the N_u phase. But in the N_b phase, two

different types of domains, partially aligned and misaligned, were observed. The polyimides only align the primary director, and the secondary director aligns perpendicularly. In rubbed polyimide cells that align *n* homeotropically, the direction of *m* is determined by the rubbing direction. Fluorenone core mesogen shows quite the opposite behavior hitherto known. It aligns homeotropically on homogeneous (for calamitic mesogens) boundary condition and homogeneously on homeotropic boundaries. At the core of this difference in alignment properties of the two types of bent-core mesogens may be the location of hexyloxy chains, *i.e.*, the middle of each arm of fluorenone core. The alignment appears to be dominated by interactions between hexyloxy chains and the side chains of polyimides in the alignment layer, essentially resulting in a behavior opposite to that of calamitic mesogens. However, homeotropic alignment of *n* in the N_b phase of fluorenone mesogen is rather uniform pointing to stronger interactions between these molecules and the polyimide layer. This work is continuing to further develop effective alignment protocols for bent-core mesogens which exhibit the biaxial nematic phase.

Acknowledgements

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