Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Light diffraction studies on director arrangement in the polymer-pinned striped pattern obtained via the electric field-induced Fréedericksz transition of nematics

Ken-Ichi Izumi[a]; Toshihiko Nagamura[a]; Hirotsugu Kikuchi[b]
[a] Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan [b] Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga-Koen, Kasuga 816-8580, Japan

To cite this Article Izumi, Ken-Ichi , Nagamura, Toshihiko and Kikuchi, Hirotsugu(2006) 'Light diffraction studies on director arrangement in the polymer-pinned striped pattern obtained via the electric field-induced Fréedericksz transition of nematics', Liquid Crystals, 33: 6, 665 — 670

To link to this Article: DOI: 10.1080/02678290600647485

URL: http://dx.doi.org/10.1080/02678290600647485

Liquid Crystals, Vol. 33, No. 6, June 2006, 665–670

Taylor & Francis
Taylor & Francis Group

Light diffraction studies on director arrangement in the polymer-pinned striped pattern obtained via the electric field-induced Fréedericksz transition of nematics

KEN-ICHI IZUMI†, TOSHIHIKO NAGAMURA† and HIROTSUGU KIKUCHI*‡

†Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

‡Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga-Koen, Kasuga 816-8580, Japan

(*Received 24 October 2005; accepted 12 January 2006*)

We have observed an anomalous pattern forming phenomenon in which a striped pattern in a nematic liquid crystal appeared after removing an electric field following a Fréedericksz transition, and this pattern was preserved even in the equilibrium state in zero-electric field. The nematic director arrangement in the striped pattern was investigated by light diffraction measurements. The stripes are proposed to consist of a periodic distortion of the nematic directors, specifically, tilted directors with the same absolute value of tilt angle but of opposite sign are alternately arrayed. The proposed model of the stripes is in good accord with the experimental results of light diffraction dependence on polarizing direction and light incidence angle.

1. Introduction

The study of nonlinear non-equilibria on pattern-forming phenomena has been a very active area in materials science. In particular, in the field of liquid crystals, the spontaneous appearance of dissipative periodic patterns is widely seen. These dissipative patterns are generally observed during the application of appropriate external fields such as an electric or magnetic field, oscillating shear, etc. It is known that two kinds of process generate dissipative patterns on the application of external fields: stationary pattern forming [1, 2] and transient pattern forming [3–12]. Stationary patterns are generally induced by electro-hydrodynamic instabilities of the nematics. For example, when an a.c. electric field of low frequency is applied to a uniformly oriented nematic liquid crystal, roll convections of the nematic director are generated through a balance between an electric field effect and a current effect, resulting in the appearance of a periodic striped pattern. The roll domains are referred to as 'Williams domains' [1]. The Williams domains appears stationary while applying an electric field and disappear after removing it.

The formation of transient dissipative patterns occurs on moving from a non-equilibrium state to an equilibrium state. Periodic patterns emerge transiently during the director reorientation in the Fréedericksz transition when a sufficiently high magnetic or electric field, beyond the threshold value, is suddenly applied to a uniformly aligned nematic liquid crystal. This phenomenon has been observed in low molar mass liquid crystal systems [3–6], lyotropic systems [7], and liquid crystalline polymer systems [8–12]. As a matter of course, the periodic patterns disappear after reaching an equilibrium state. Although, the formation mechanism of this periodic structure has been well discussed in theoretical studies [7, 9, 10], experimental results on the director arrangement in the periodic pattern are rarely reported because of the technical difficulty in observing the transient phenomenon.

The stabilization effect on liquid crystal directors by polymer dispersed in a liquid crystal have been well investigated in the last 20 years [13–17]. In general, the polymer produced by *in situ* polymerization of monomers dispersed in a liquid crystal stabilizes the director arrangement formed during the polymerization. The micro-patterns which occur in polymerizable liquid crystalline monomers due to electrohydrodynamic convection were recently demonstrated to be frozen-in by *in situ* photopolymerization [18, 19].

In this study, we observed an anomalous pattern-forming phenomenon in which the striped pattern of the nematic appeared 'after' removing an electric field, and

*Corresponding author. Email: kikuchi@cm.kyushu-u.ac.jp

Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290600647485

was preserved even in the equilibrium state in the zero-electric field. The director arrangement in the striped pattern was experimentally investigated by optical texture observation and light diffraction measurements. The polymer with mesogenic side groups that was initially dispersed in the nematic liquid crystal should play a key role in developing and memorizing the striped pattern. We discuss the molecular pinning effect of the dispersed polymer.

2. Experimental

Figure 1 shows the chemical structures and physical properties of materials used in this study. A photo-polymerizable monomer, 4-cyanophenyl 4-acryloyloxy-benzoate (CPAOB) was synthesized by a standard method [20]. CPAOB and a photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPAP) (Aldrich) were dissolved in E7, a eutectic mixture of cyanobiphenyl-type low molar mass nematics (Fuji pigment Co., Ltd). The weight ratio of CPAOB/DMPAP/E7 was $x/0.2x/100\text{-}1.2x$. The fraction of CPAOB, x was varied between 0 and 7 wt %. The mixture solution was injected into a cell consisting of a pair of indium/tin oxide (ITO) coated glass plates in an optically isotropic state at 353 K. The ITO glass plate surfaces were coated with polyimide and then rubbed in anti-parallel directions to provide planar orientation of the nematic directors. The cell gap was maintained at 13 μm with a spacer. The cell with the mixture solution was cooled to a nematic state at 303 K, and then irradiated with non-polarized and non-holographic UV light (λ=365 nm) from a metal halide lamp. The composite system after curing with UV was subjected to an a.c. electric field perpendicular to the cell plane.

The optical textures of the composite system were observed by polarizing optical microscope (POM) (OPTPHOT2, Nikon, Co., Ltd), perpendicular to the cell plane. Photographs of the textures were taken with a CCD camera. The polarizing directions of the polarizers were parallel to each other.

To evaluate the periodicity of the pattern structure, linearly polarised He-Ne laser light (λ=632.8 nm) was directed perpendicular to the cell plane (angle of incidence of laser beam=0°). The measurement geometry of the light diffraction is shown in figure 2. The diffracted light passing through the cell was projected onto a screen through an analyser. The directions of light polarization are denoted by H (parallel to the rubbing direction) and V (perpendicular to the rubbing direction). The term 'H_H' means that both the incident light and the diffracted light had H polarization, and 'V_V' means that both had V polarization. The dependence of the diffraction pattern on angle of incidence was also observed.

The electric capacitance C of the cell was calculated from:

$$C = \frac{I \sin\delta}{2\pi f V} \tag{1}$$

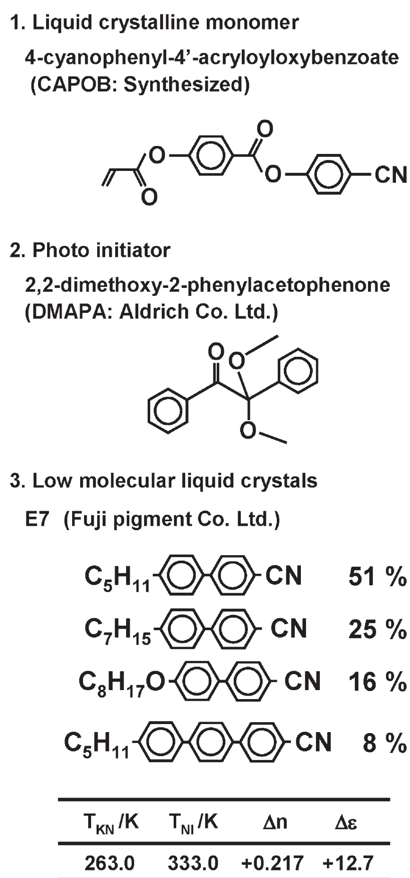

Figure 1. Chemical structures and physical properties of the materials used in this study.

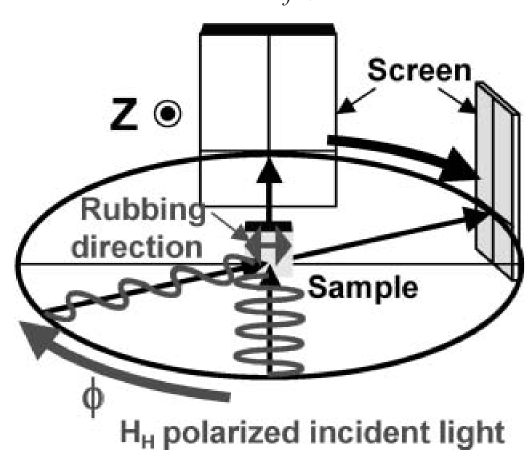

Figure 2. Experimental geometry of the polarized light diffraction measurement.

where V and f are the amplitude and frequency of the applied electric voltage, respectively; I is the amplitude of current measured with a current amplifier, (Model 428, Keithley Instruments, Inc.), and δ is the phase shift angle between the electric voltage and current. To generate the Fréedericksz transition in the cell, an a.c. electric field of frequency 1 kHz was applied perpendicular to the cell plane.

3. Results and discussion

The optical textures of samples filled in unidirectionally rubbed cells were observed by POM before and after photopolymerization of CPAOB in the solutions CPAOB/DMPAP/E7 (x/0.2x/100-1.2x; x=0, 0.5, 1, 2, 3, 5, 7 wt%). Before photopolymerization, all the solutions in the nematic phase showed homogeneous orientation of the director along the rubbing direction in each cell. After photopolymerization, the homogeneous orientation remained for the composites where x=0.5, 1, 2, 3, 5 wt%. In the case of the composite where x=7 wt%, however, a heterogeneous texture due to phase separation was observed.

Because the mixtures in the nematic phase have a positive dielectric anisotropy, the directors tend to reorient parallel to the electric field on its application; that is, a splay–bend Fréedericksz transition occurs. On application of a 6 V a.c. voltage at 298 K perpendicular to the cell plane, the brightness of the textures decreased under crossed polarizers, indicating that the directors moved to homeotropic orientation from the initial homogeneous orientation. The observation field did not become completely dark and a vague sand-like texture, implying poly-domains, was observed. In order to evaluate the average tilt angle of the director in the cell, its electric capacitance was measured. Completely homeotropic and homogeneous orientations are expected to give a capacitance of 1.04 nF ($=C_{//}$) and 0.29 nF ($=C_{\perp}$), respectively, which were obtained from measurement of the electric capacitance of E7 in directions parallel and perpendicular to the director. The average tilt angle θ of the director with respect to the cell plane can be calculated from:

$$C=C_{//}\sin^2\theta+C_{\perp}\cos^2\theta. \qquad (2)$$

The electric capacitance of an as-polymerized sample was 0.29 nF, indicating that the initial director alignment was nearly homogeneous, $\theta=0^\circ$. When the voltage of 6 V was applied the electric capacitance of the cell (x=2 wt%) became 0.82 nF, indicating $\theta=58^\circ$. Since the directors near the substrate surface cannot be reoriented because of an anchoring effect, the directors in the middle region should be tilted on average more than 58°. Therefore, highly tilted poly-domains were formed in the cell during application of the 6 V voltage.

After removing the electric field, a unique texture appeared for the cell (x=2 wt%) as shown in figure 3, obtained under parallel Nicol polarizers. The appearance of the unique pattern, however, depended on the value of x. In the case of x=0, 0.5, 3, and 5 wt%, no unique texture was observed and only the homogeneous texture remained after removing the electric field. Although a weakly striped pattern was obtained for x=1 wt%, it was mechanically weak and easily destroyed by external shock. Interestingly x=2 wt% is a special concentration for the generation of a striped pattern. The electric capacitance of the cell after removing the 6 V was 0.50 nF in the case of x=2 wt%, indicating that the average tilt angle θ of the director with respect to the cell plane was about 32°, based on equation (2). The directions of the stripes were tilted in plane by $\alpha=\pm 21^\circ$ with respect to the rubbing direction. The spacing of typical stripes was about 3.7 μm.

The contrast of the striped pattern in the POM observation was strongly dependent on the polarizing direction of the light source. When the polarizing directions of the polarizer and analyser were parallel to the rubbing direction, the striped pattern was observed most clearly. On the other hand, when both polarizing directions were perpendicular to the rubbing direction, the striped pattern was invisible, as shown in figure 3 (*b*). Although it is uncertain at present why the striped pattern was observed only the case of x=2 wt%, the pattern forming was highly reproducible. Unlike conventional pattern evolution phenomena in liquid crystal, which appear during the application of a reorienting electric field, the striped patterns in our study existed for zero-electric field after application and removal of an external electric field. The pattern formed has been kept at least one year without change. Furthermore, the striped pattern was switched to uniform texture upon application of an electric field and returned reversibly to the striped pattern after its removal, because the molecules were not fixed permanently.

A sample-filled cell with a striped pattern exhibits light diffraction because of the periodic modulation of refractive index. Figure 3 (*c*) shows the diffraction pattern of a laser beam passed through a cell with angle of incidence zero, normal to the cell surface, and both polarizers sandwiching the cell parallel to the rubbing direction (H_H light polarization). The azimuthal angles α of the main diffraction spots were about $\pm 21^\circ$ with respect to the meridian, and the spacing calculated by the Bragg formula was about 3.7 μm. The values obtained agreed well with those of

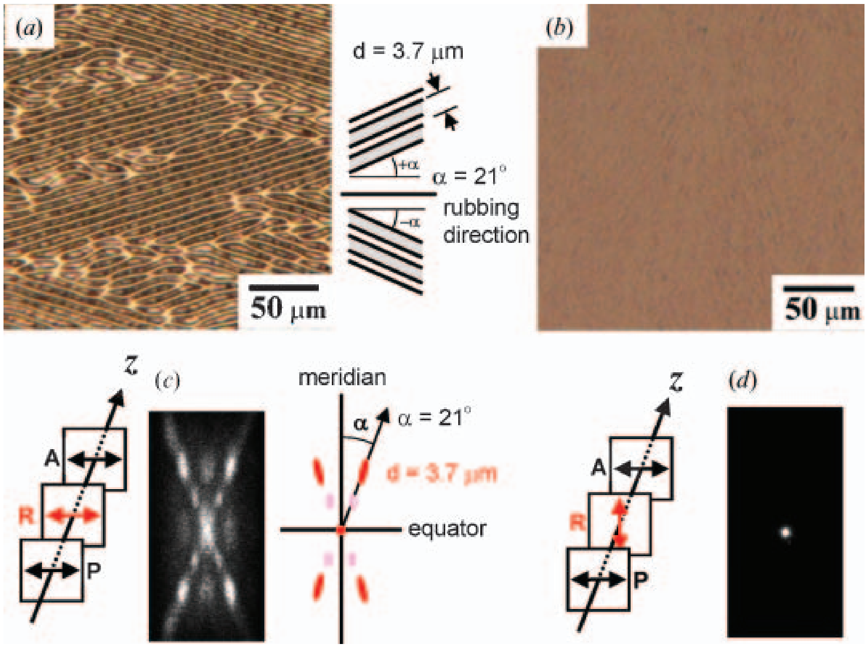

Figure 3. (*a*), (*b*) POM micrographs and (*c*), (*d*) projections of diffracted light for (CPAOB/E7:2/98 wt/wt) composite system. Black arrows indicate the direction of polarizer (P) and analyser (A). Colour fig. arrows indicate the direction of rubbing (R).

the striped pattern observed by POM. Therefore, the main diffraction spots originate from the striped pattern shown in figure 3 (*a*). The diffraction pattern was also dependent on the light polarization. When the directions of the polarizers sandwiching the cell were perpendicular to the rubbing direction (V_V light polarization), no diffraction occurred, as shown in figure 3 (*d*), which agreed well with POM observations.

Since a transient pattern was sufficiently preserved at zero-field in our study, the diffracted spot dependence on angle of incidence could be easily and accurately evaluated in an identical sample cell. The diffraction pattern also depended on the angle of incidence (ϕ) of the laser beam. The upper part of figure 4 shows the dependence of the diffraction pattern on ϕ for H_H polarization, where the *z*-axis is normal to the cell surface. The diffraction spots corresponding to 3.7 μm spacing weakened as ϕ shifted from 0°, it disappeared at about 23°. Interestingly, other diffraction spots corresponding to 7.3 μm, which is nearly twice the 3.7 μm

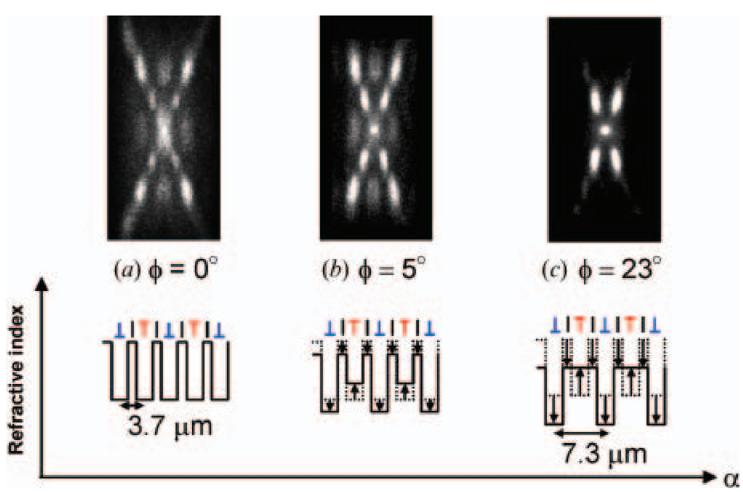

Figure 4. The angular dependence of the projections of diffracted light (upper part); and schematic drawing of the angular dependence of the spatial periodic structure of refractive index of the sample (lower part). Signs (⊥) indicate the projection of the orientation of nematic directors, with the bar indicating the nearest point to the reader.

spacing corresponding to the main spot at 0°, became stronger.

The angular dependence of the diffraction intensity of the spots along the α-axis, which is at an angle of 21° with respect to the meridian in the projected plane, should correlate with the angular dependence of the spatial periodic structure of the refractive index of the sample, as schematically shown in the lower part of figure 4, along an axis tilted in-plane from the rubbing direction at an angle of 21°. The application of an electric field to the cell perpendicular to the cell substrate surface, tilts the director out of the cell plane to which the initial direction was parallel. Therefore, it is reasonable to consider that the resultant stripe is composed of domains in which the directors are tilted out of plane. Figure 5 is a schematic illustration of a possible structure of the directors in the striped pattern; that is, the two types of domain, having tilted directors with angle $\theta=+\theta_z$ and $-\theta_z$ with respect to the cell plane, are adjacent to each other and arrayed alternately. The directors at the boundaries between domains might be merged with twist deformation, and $\theta=0°$ at the centre of the boundary as in the Bloch wall. Therefore, the stripe is possibly composed of three kinds of layer with tilt angle of $+\theta_z$, $-\theta_z$ and the boundary region. When light polarized parallel to the rubbing direction is incident perpendicular to the cell plane, the refractive index depends on the tilt angle θ of the director; that is, the refractive indices of the regions with $\theta=+\theta_z$ and $-\theta_z$, $n(+\theta_z)$ and $n(-\theta_z)$, respectively, are equivalent because the absolute value of the tilt angles are equal, but the refractive index of the boundary region is larger than $n(+\theta_z)$ and $n(-\theta_z)$. Therefore the distance between neighbouring layers at the boundary region, about 3.7 µm, is the fundamental periodic spacing of the stripes. Thus a phase grating is formed due to periodic mismatching of the refractive indices. On the other hand, in the case of incident light polarized perpendicular to the rubbing direction, the refractive indices in the whole region are almost constant because only the ordinary refractive index of the liquid crystal interacts with the light, resulting in an apparent optical structure that is almost uniform. The experimental results shown in figure 3 are well explained by the proposed model shown in figure 5.

When the viewing angle of the proposed model is changed from the normal (z-axis) by rotating around the meridian perpendicular to the rubbing direction in the cell plane, $n(+\theta_z)$ and $n(-\theta_z)$ are no longer equivalent because their angles with respect to the viewing axis are different. Then, another periodic structure appears, whose periodic spacing is twice that of the stripe spacing. Since the refractive index of the boundary region also changes with the viewing angle, the periodicity of the boundary region disappears when the refractive index of the boundary region and $n(+\theta_z$ or $-\theta_z)$ are close to each other. Such a model can also explain the experimental results of figure 4, if the viewing axis is replaced by the laser beam axis.

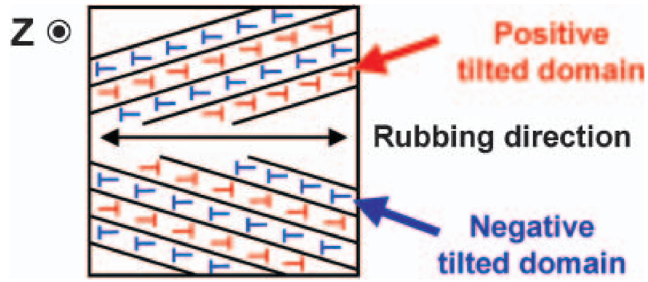

Figure 5. Illustration of proposed orienrational model for retained periodic structure.

The distinguishing feature of the observations in this study is that the striped structure appears at the moment of removing an electric field, and remains under zero-electric field. The striped structure might be formed transiently during the rise process, upon application of the field. In the steady state during application, no striped structure was seen. The polymer probably memorizes the transient striped pattern during the rise process by changing its structure, and then the memory is maintained during application of the electric field and even after its removal. We term the effect the 'polymer-pinning effect'. It is important to know the role of the polymer at the molecular level and to observe the morphology or microstructure of the polymer in the composite. We attempted to observe the polymer structure with a scanning electron microscope. However, the real structure could not be observed because the polymer collapsed after extraction of the low moar mass liquid crystals.

The liquid crystal pattern preserved by the polymer-pinning effect responds to an external field such as an electric field because molecular mobility is not lost. We believe that the polymer-pinning effect will open the door for applications of liquid crystal pattern formation to optical devices.

4. Conclusion

To summarize the main result of this study: the director arrangement in the unique striped pattern induced via Fréedericksz transition was investigated. A pattern was formed in a nematic composite (in which 2 wt% of polymer with mesogenic side groups was produced by photopolymerizing the monomer) by applying an electric field to cause a Fréedericksz transition; the field was then removed. A stripe is proposed to be composed of periodic distortion of the nematic directors; that is, tilted directors with the same absolute value of tilt angle but opposite sign are arrayed alternately. The proposed stripe model is in good agreement with the experimental results on the dependence of light diffraction on polarizing direction and light incidence angle. The polymer plays an important role in developing and memorizing the striped pattern of nematic directors. The striped pattern thus formed could be reversibly switched to a uniform state by an electric field.

References

[1] R. Williams. *J. chem. Phys.*, **39**, 384 (1963).
[2] J.-H. Huh, Y. Hidaka, S. Kai. *J. phys. Soc. Jpn.*, **68**, 1567 (1999).
[3] A. Buka, B. Dressel, L. Kramer, W. Pesch. *Phys. Rev. Lett.*, 044502-1 (2004).
[4] M.R. Kuzma. *Phys. Rev. Lett.*, **57**, 349 (1986).
[5] A. Buka, M.T. Juarez, L. Kramer, I. Rehberg. *Phys. Rev. A*, **40**, 7427 (1989).
[6] B.L. Winkler, H. Richter, I. Rehberg, W. Zimmerman, L. Kramer, A. Buka. *Phys. Rev. A*, **43**, 1940 (1991).
[7] A.J. Hurd, S. Franden, F. Lonberg, R.B. Meyer. *J. Physique*, **46**, 905 (1985).
[8] F. Lonberg, R.B. Meyer. *Phys. Rev. Lett.*, **55**, 718 (1985).
[9] N. Schwenk, H.W. Spiess. *J. Physique II*, **3**, 865 (1993).
[10] E.E. Pashkovsky, T.G. Litvina. *Macromolecules*, **28**, 1818 (1995).
[11] M. Grigutsch, R. Stanarius. *Eur. Phys. J. E*, **8**, 365 (2002).
[12] M. Srinivasaro, J.O. Park. *Polymer*, **42**, 9187 (2001).
[13] R.A.M. Hikmet. *J. appl, Phys.*, **68**, 1 (1990).
[14] D.K. Yang, L.C. Chien, J.W. Doane. *Appl. Phy. Lett.*, **60**, 3102 (1992).
[15] H.Y. Yang, H.T. Kikuchi, T. Kajiyama. *Liq. Cryst.*, **29**, 1141 (2002).
[16] H. Kikuchi, M. Yokota, Y. Hisakado, H. Yang, T. Kajiyama. *Nat. Mater.*, **1**, 64 (2002).
[17] Y. Hisakado, H. Kikuchi, T. Nagamura, T. Kajiyama. *Adv. Mater.*, **17**, 96 (2005).
[18] N. Mießen, J. Strauß, A. Hoischen, K. Kürschner, H.-S. Kitzerow. *ChemPhysChem*, **7**, 691 (2001).
[19] N. Stich, H.-S. Kitzerow. *J. appl. Phys.*, **97**, 033519-1 (2005).
[20] D. Braun, G. Frick, M. Kilmes, J.H. Wendorff. *Macromol. Chem. Phys.*, **196**, 3905 (1995).