Uniform textures of smectic liquid-crystal phase formed by bent-core molecules

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Smectic liquid crystals consisting of achiral bent-core molecules may be polar due to asymmetric packing of the molecules. Recently it was proposed that the planes of the molecules are tilted with respect to the smectic layers and the structure is chiral. The ground state is antiferroelectric and the majority of the films are racemic with the same tilt direction in the subsequent layers. Basically the tilt directions are equivalent, and stripes with oppositely tilted molecules exist. In this paper we show that it is possible to suppress the formation of the stripes, and to obtain a uniform texture in thin films. In uniform racemic textures, weak quadratic electro-optical switching can be observed. Voltage dependences of the switching are measured and the switching mechanisms are discussed. [S1063-651X(98)05806-1]

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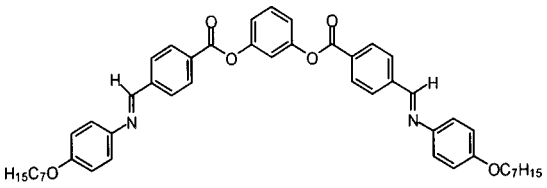
I. INTRODUCTION

It has been known since 1975 [1] that chiral liquid crystals of C_2 symmetry may be ferroelectric. Theoretically it is also possible to achieve ferroelectric states even from nonchiral liquid crystals by appropriately decreasing the symmetry [2]. Candidates for nonchiral polar phases include certain main chain liquid crystal polymers [3], bowl-shaped columnar phases [4,5], the tilted smectic phase of polyphilic compounds [6], and the orthogonal smectic phase of perflurinated swallow tailed compounds [7]. Recently, achiral bent-core molecules were synthesized [8,9], and switching of the electric polarization without any electro-optical effect was observed [10]. It was suggested that this phase has a smectic *A* structure with C_{2v} symmetry (there is a twofold symmetry axis in the direction along the kink of the molecules, and there are two mirror planes perpendicular to the twofold axis). Because of the absence of the mirror plane normal to the twofold axis, the material can be polar and termed Sm-A_P or Sm-A_b emphasizing either the polar [2] or biaxial [11] nature of the phase, respectively. In Ref. [12] several homologs of the same moiety with alkyl and alkyloxy side chains were synthesized. It was found that the phase where switching took place in the external electric field, has a Sm-*C*-like texture, but no miscibility with a Sm-*C* phase of rodlike molecules was observed [12]. Similar substances were synthesized and studied by Weissflog *et al.* [13,14], who suggested that the ground state has an antiferroelectric arrangement. Link *et al.* [15] proposed that the planes of the bent-core molecules are tilted with respect to the smectic layers and each layer is chiral having C_2 symmetry. In freely standing films they found that the ground state is antiferroelectric, leading them to suggest that the nomenclature ''Sm-CP_A'' be adopted for this novel phase. In both Ref. [13] and Ref. [14] observed the spontaneous formation of a fringe pattern parallel to the smectic layers. Their explanations for this texture, however, are different. Reference [13] assumes a Sm-*A* structure and suggests that the fringes indicate a spontaneous helix formation due to two-dimensional escape from a macroscopic polarization [16]. According to Link *et al.* [15] the stripes are due to domains in which the uniform tilt directions are opposite.

In the present paper we describe textural and electro-optical studies on a substance synthesized in Ref. [12]. Our results confirm the smectic layer structure proposed by Link *et al.* [15]. We will show that the formation of the fringe pattern can be suppressed, and that there is weak quadratic reversible electro-optical switching in the racemic state.

II. EXPERIMENT

The substance studied is part of a homologous series of bent-core molecules that were synthesized at the Technical University of Berlin [12]. The structure of the molecule is given below.



The molecules of our substance differ from those of Niori *et al.* [10] only in the alkoxy side chain (shorter by one methyl group). Based on DSC and polarizing microscope investigations the phase sequence of the material can be given as [17]

$$B_4 \underset{144.0^\circ C}{\overset{157.4^\circ C}{\rightleftarrows}} B_3 \underset{153.6^\circ C}{\overset{165.3^\circ C}{\rightleftarrows}} B_2 \underset{170.2^\circ C}{\overset{172.7^\circ C}{\rightleftarrows}} Iso$$

In the B_4 phase the material is solid and has a bright blue reflection. The B_3 phase seems to be a highly ordered tilted smectic phase. Here we concentrate on the behavior of the B_2 phase, where electro-optical switching is observed. We prepared unsealed 3 μm and 6 μm films where the material was sandwiched between clean ITO coated substrates. We also used sealed 10 μm, so-called EHC cells whose inner surfaces were treated with uni-directionally rubbed polya-

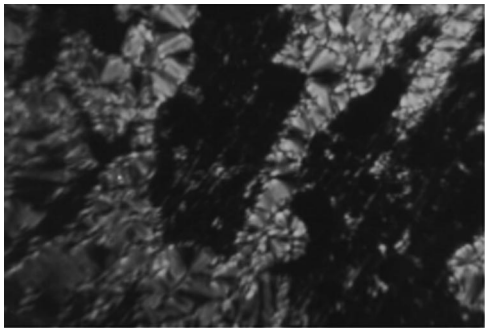


FIG. 1. Polarizing microscopic picture of the texture partially transformed from homeotropic (dark) to planar (bright) texture after 1 min application of $U=30$ V, $f=2$ Hz triangular wave form. ($T=162.7$ °C, $d=3$ μm, clean ITO coated substrates.) The picture represents 1.4 mm$\times$1.0 mm area.

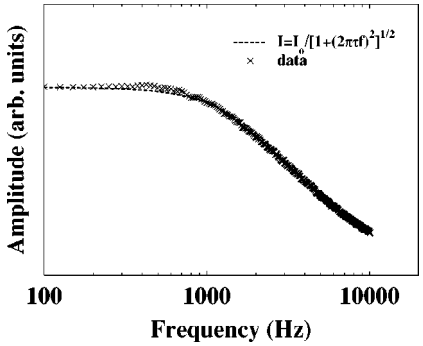


FIG. 2. Frequency dependence of the second Fourier component of He-Ne laser light intensity transmitted through 3-μm film between crossed polarizers ($U_{\text{eff}}=4.85$ V, $T=165.5$ °C).

mide. In the B_2 phase the film could be easily sheared. After displacing the upper plate parallel to the lower one by about 0.2 mm a dark gray, almost uniform texture formed. We assume that this is a homeotropic texture (layers parallel to the substrates). The dark gray texture could be transformed into a colored one under application of a low frequency field of 5 V/μm. Figure 1 shows the texture of a 3 μm film during transformation. The process is similar to the reformation of homeotropic ferroelectric Sm-C^* textures into bookshelf configuration [18].

The textures appearing after realignment depend on the film thickness.

(i) In the 3 μm film all domains behaved uniformly under electric fields. During the application of the field the extinction directions indicated a smectic-A type structure. After removing the field the optical axis rotated by about 5°, and the birefringence increased (the color changed from purple to reddish, yellowish). This texture remained stable after turning off the field, and only a few isolated stripes appeared.

Provided that the reformation from the homeotropic texture was slow (taking at least 10 min) the resulting domains were large enough (~ 1 mm^2) for optical studies. The small periodic modulation of the extinction direction (about 5°) under the application of ac fields resulted in weak electrooptical switching. We measured the first and second harmonic components of the optical signal as a function of frequency by a lock-in amplifier. The frequency of the transmitted light intensity consisted mainly of second harmonic components. Typical responses of the second harmonic signals are shown in Fig. 2.

The frequency dependences could be fitted by the equation $\Delta I=\Delta I_0/\sqrt{1+(2\pi\tau f)^2}$. The switching time τ was determined by the frequency where $\Delta I(2\pi/\tau)=\Delta I(0)/2$. The voltage dependence of the switching time is shown in Fig. 3 at $T=165.5$ °C. In the figure we also plotted the voltage dependence of the amplitude of the optical modulation (switching strength). It is seen that at low fields the switching time is roughly constant, and the switching strength increases. At higher fields the strength becomes constant and the time decreases roughly as $1/(E^2-E_0^2)$. The time dependence of the transmitted light intensity under various wave forms was also studied. For bipolar voltages the optics was not sensitive to the sign of the electric field. Under the effect of sinusoidal and triangular field waves, and between crossed polarizers parallel and perpendicular to the smectic layers, the transmitted intensity was maximum at zero fields. For rectangular voltages no change in the transmittance was observed except for a small transient decrease due to light scattering during switching. In case of unipolar square wave driving the periodicity of the optical signal was equal to that of the electric field. Maximum contrasts were reached in the directions parallel to the smectic layer normal and about 5° away. In the middle of these two directions there was no contrast between the field ON and field OFF states. The switching was not bistable: after field removal the texture relaxed back (in about 100 μs) to the equilibrium orientation.

(ii) In the 6 μm film two types of texture formed [Fig. 4(a)] similar to the observations of Link *et al.* [15]. In the ground state the majority regions had a grainy texture consisting of stripes running parallel to the smectic layers whereas in the minority areas the texture was smooth. Under the effect of electric fields the two types of textures behaved differently. (a) In the grainy texture the fringes disappeared above a threshold of 3 V/μm, and a uniform texture appeared. When we reversed the polarity of the rectangular fields the extinction direction remained unchanged, on decreasing the magnitude of the field the fringe pattern reformed. (b) In the uniform areas the extinction direction followed the polarity of the field and rotated by $\pm 25°$. As in each case this behavior is analogous to the observations of Link *et al.* [15], we assign the grainy texture to a racemic

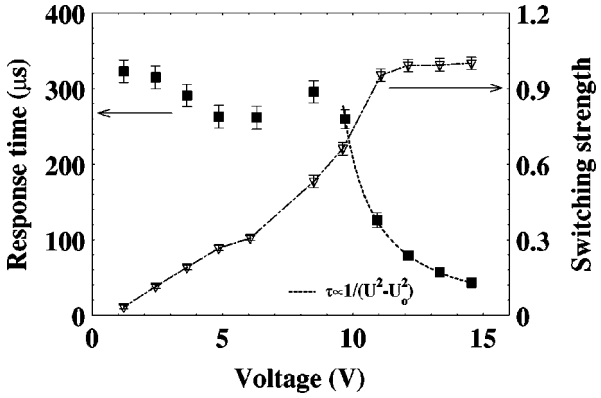


FIG. 3. Switching time (τ), and switching strength ($I_{\max}-I_{\min}$) as a function of applied voltage (V). $T=165.5$ °C, $d=3$ μm, clean ITO-coated substrates.

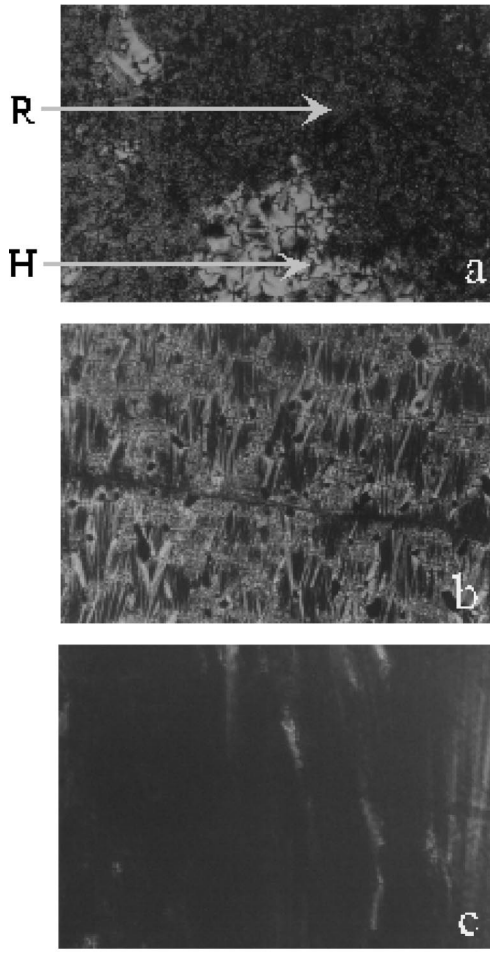


FIG. 4. 1.4 mm×1.0 mm area of the 6-μm film at $T=168\,^{\circ}\mathrm{C}$ between crossed polarizers. (a) Freshly realigned film. (b) After rectangular voltage ($U=15$ V; $f=0.6$ Hz) and a horizontal periodic shear with amplitude of 50 μm and frequency of 1 Hz is applied for 1 min. (c) After application of the above treatment for 15 min.

(R) structure. As was shown [15], in this texture the ground state is antiferroelectric and synclinic, i.e., the polarization in the subsequent layers is antiparallel, and the plane of the bent molecules tilts in the same direction. The fringes correspond to domains of oppositely tilted molecules. Under high fields R has a ferroelectric anticlinic structure with the extinction direction parallel and perpendicular to the smectic layer normal. The minority regions are homogeneously chiral (H); the ground state of the H structure has an antiferroelectric anticlinic arrangement which, under sufficiently high fields, switches to synclinic ferroelectric states.

We observed that with low frequency ($\sim 1-10$ Hz) electric fields of amplitude in the range of 3 V/μm, the texture changed gradually. The size of the grainy domains increased whereas the H domains slowly disappeared [Fig. 4(b)] until, after about 15 min, a uniform texture formed [Fig. 4(c)]. This texture behaved in exactly the same way as that observed in the 3 μm film. In that it formed gradually from the grainy racemic regions, hereafter we will call it a racemic uniform (RU) state.

(iii) In the 10 μm EHC cells we observed only grainy texture, which, under electric fields, showed the same behavior as that of the texture R in the 6 μm film.

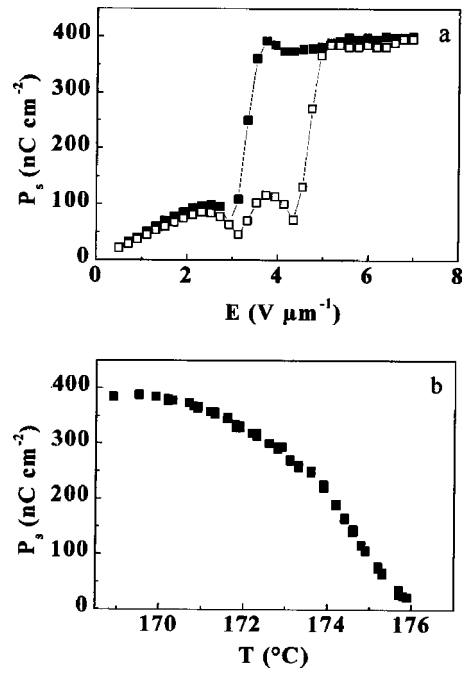


FIG. 5. Polarization measurements on the 10-μm-thick EHC cell. (a) Field dependence of the magnitude of the polarization ($f=110$ Hz, $T=169.1\,^{\circ}\mathrm{C}$). (b) Temperature dependence of the polarization at an electric field strength of 7.1 V/μm.

We measured the polarization currents under triangular wave voltages for all the films that were studied by polarizing microscopy. The time dependence of the electric current showed no polarization switching in the homeotropic textures. In the RU textures, where no fringes appear in the

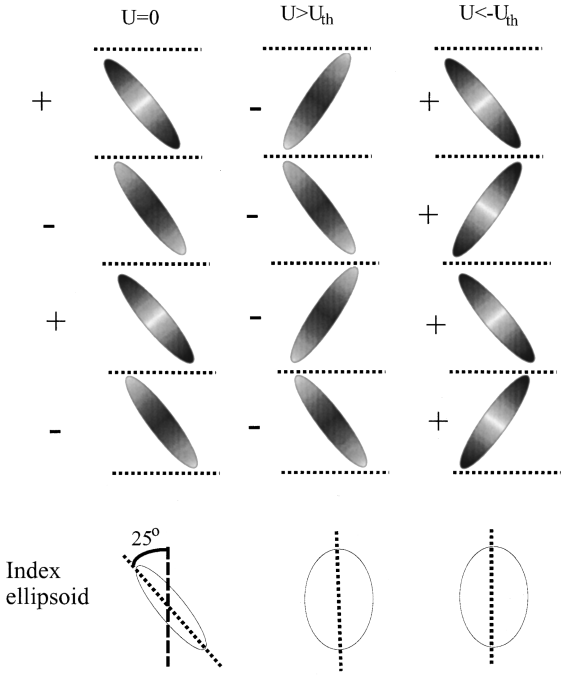


FIG. 6. Model of the switching of the bent-core molecules supposing bookshelf texture of a racemic Sm-CP_A phase. Top view: smectic layers are vertical. Brighter areas are closer to the observer. + and − signs indicate the direction of polarization.

ground state, the polarization current had only one peak in each half period (ferroelectric type behavior). For textures with stripes in the ground state we observed antiferroelectric-type switching characterized by two peaks of the electric current in each half period of the triangular voltage. The field dependence of the polarization of the 10 μm EHC cell is seen in Fig. 5(a), where the arrows indicate increasing and decreasing field strengths. The figure shows hysteresis. The sudden increase of the polarization probably corresponds to an antiferroelectric-ferroelectric transition. The temperature dependence of the polarization is represented in Fig. 5(b).

III. DISCUSSION

Our observations are consistent with the model of Link *et al.* [15]. Accordingly, the B_2 phase has a tilted smectic structure with an alternating polarization direction in the subsequent layers. In this phase both racemic (R) and homogeneously chiral (H) structures may coexist. In the ground state the H areas are uniform whereas the R regions usually consist of fringes running parallel to the smectic layers. We observed that, with appropriate electric field treatment, the grainy texture might gradually be replaced by a uniform texture (RU), which is stable even in absence of the electric field. This type of textural transformation takes place more easily in thinner films, thereby indicating the importance of surface effects. The stripe formation is due to the equivalence of the tilt directions [15]. Accordingly, their absence indicates that one of the tilt directions became preferred under the effect of the electric field. Textures in RU show reversible quadratic electro-optical switching characterized by only a few degrees of modulation of the extinction direction. With the constraints of keeping the racemic structure [15] and the magnitude of polarization the switching should take place by rotation of a molecule about the smectic layer normal (Goldstone mode). Using this model, and supposing bookshelf texture (smectic layers are vertical), we sketched the structures under different fields (see Fig. 6). As may be seen from the projection of the optical axis on the film surface, the extinction direction would rotate by the director tilt angle (25°, as estimated from the switching angle observed in the H state). This is much larger than the experimentally observed $\sim 5°$ modulation of the optical axis.

Our view is that both the suppression of stripes and the small optical modulation could be explained by assuming that the layers are not vertical, but are tilted with respect to the film surface. However, additional studies are needed to prove this and to explore the physical mechanism for the suppression of the stripes.

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