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Growth dynamics of ferroelectric domains in chiral hexatic liquid crystals

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Abstract

The dynamics and anisotropy of ferroelectric domain growth was studied *in situ* for a tilted hexatic liquid crystal phase (SmI*) as a function of electric field amplitude, frequency and temperature. Domain growth proceeds parallel and perpendicular to the smectic layer plane (not the direction of uniform rubbing), with domain wall mobilities being several times larger in the direction parallel to the layers as compared to the perpendicular direction. Domain wall velocities were determined directly by digital image analysis of the wall displacement, as well as indirectly by determination of the fraction of switched sample area and analysis by a modified Avrami equation. Using a special smectic layer configuration known as horizontal chevrons, we additionally studied the effect of elastic anchoring interactions on the ferroelectric domain growth process, i.e. switching into the direction of preferred anchoring (rubbing direction) and out of it. The former process, which is elastically favoured, is one order of magnitude faster than the latter process, which is elastically hindered. This behaviour is confirmed by the estimation of an effective activation energy for the domain wall displacement for both switching processes.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Liquid crystals (LCs) are partially ordered, anisotropic fluids, thermodynamically located between the solid state crystal and the isotropic liquid. Depending on their degree of order, a variety of different phases can be distinguished. If only orientational order of the long molecular axis is observed, we speak of the nematic phase, while smectic phases exhibit additionally at least one-dimensional positional order of the molecular centres of mass. Meyer *et al* [1] have shown by symmetry arguments that every tilted smectic phase, composed of

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chiral molecules, can exhibit a macroscopic spontaneous polarization P_S , when the intrinsic helical superstructure is unwound either by electric fields or substrate interactions. The latter case is called the surface stabilized ferroelectric liquid crystal (SSFLC), discovered by Clark and Lagerwall [2]. Thus tilted chiral smectics show pyroelectric properties. If the direction of spontaneous polarization can be reoriented between two stable states by application and reversal of a sufficiently strong electric field, the LC exhibits ferroelectricity. This has been demonstrated for several LC phases (SmC^* , SmI^* and SmF^* [3–6]), where the SmC^* phase is the one which has been extensively investigated over the last 25 years [7, 8], also due to its promising potential for display applications.

The reorientation of the spontaneous polarization of ferroelectric materials after electric field reversal is generally accomplished via nucleation and growth of the energetically favoured domains at the expense of the unfavoured ones. This type of domain growth is well known for solid state ferroelectrics [9, 10], such as BaTiO_3 , and is achieved by a domain wall displacement. In the simplest model of ferroelectric domain wall motion [11], based on a treatment analogous to a rigid wall moving in a viscous liquid, the domain wall velocity v is linearly dependent on the field amplitude E :

$$v = \mu E \quad (1)$$

or

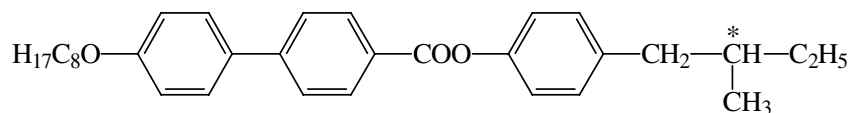
$$v = \mu(E - E_0) \quad (2)$$

if a critical field E_0 (threshold field) is observed.

Just like in solid state ferroelectrics, in SSFLCs domains with opposite directions of the spontaneous polarization are also formed to diminish the overall polarization of the sample. In LCs, these can be easily imaged by polarizing microscopy, due to optical anisotropy of the LC. The dynamics of the domain wall motion in ferroelectric liquid crystals has so far been largely disregarded in the study of macroscopically polar properties of FLCs; only spatially integrated response times are generally reported. To our knowledge, the only reports of FLC domain growth investigations have been given for a SmC^* material [12, 13], a tilted fluid smectic phase with only one-dimensional positional order (thus a two-dimensional liquid). In this study we present a detailed investigation of the ferroelectric domain wall dynamics for a tilted hexatic smectic phase, SmI^* , which exhibits additional short-range bond-orientational-order within the smectic layers [14], as demonstrated by x-ray [15] and electron diffraction [16]. This phase is observed as the low-temperature phase to SmC^* , separated by a first-order transition.

2. Experimental

The chiral LC used in the investigations is abbreviated as 8OSI and has the following molecular constitution:



Its phase sequence, as determined by polarizing microscopy on slow cooling of thin cells, was given by Iso. 170.2 N* 164.3 SmA^* 125.6 SmC^* 75.9 SmI^* 71.0 SmF^* 62 possible monotropic highly ordered phases (all temperatures in °C). The nature of the low-temperature phases does not seem to be completely resolved, with different phase designations reported in the literature [17–19]. They are presumably soft crystal phases with three-dimensional

translational long-range order. The transition temperatures determined are lowered by a few degrees compared to the values reported for bulk samples, which may be due to confinement of the LC to rather thin layers of $2\ \mu\text{m}$, but which is not of direct relevance to the reported results. Cells were prepared by capillary filling of the compound into commercially available LC sandwich cells (EHC, Japan) with uniform planar anchoring conditions (parallel rubbed). For the hexatic LC phases under investigation, this resulted in bookshelf alignment without any chevron structures present, as can be verified by the texture photographs presented below. For the reported investigations of the SmC^* phase [12, 13], a stroboscopic imaging technique had to be employed to follow the domain growth process, due to its fast response to an electric field (of the order of milliseconds). In contrast, the investigated domain growth process of SmI^* is comparatively slow (of the order of seconds), such that digital video recording at a frame rate of 25 Hz could be used. The sample was placed in a hot stage (Mettler FP82, for control of relative temperatures better than 0.1 K) between crossed polarizers of a polarizing microscope (Leitz Orthoplan). Ferroelectric switching was induced by electric field application with a function generator (HP33120A) and the domain growth process recorded with a Sony Hyper HAD model SSC-DC38P digital video camera in combination with imaging software (miroVIDEO Capture). The time resolution between images was 40 ms and the digital spatial resolution of images was 720×540 pixels, corresponding to a sample area of $650\ \mu\text{m} \times 490\ \mu\text{m}$. Digital image analysis was carried out by use of ImageTool2.0, developed at the University of Texas Health Science Center, San Antonio. General experimental conditions were as follows: LC cell gap $d = 2\ \mu\text{m}$, symmetric electric square wave field of amplitude $E = 5\ \text{MV m}^{-1}$, frequency $f = 0.1\ \text{Hz}$ and temperature $T = 75.0\ ^\circ\text{C}$. For the different measurement series presented below, only the one respective parameter was varied, leaving the others unchanged.

To be able to study not only the anisotropy of the domain wall velocity parallel and perpendicular to the smectic layer plane (subscript ‘par’ and ‘per’, respectively), a special smectic layer arrangement, known as rotated smectic layers, was induced in SmC^* , before cooling to SmI^* . By application of an asymmetric electric field, smectic layers may be reoriented in the plane of the substrate [20, 21], resulting in a layer configuration with the smectic layer normal being inclined to the rubbing direction by the amount of the molecular tilt angle θ . In this case one domain type ($+P_S$) has the director (which, at the same time, represents the optical axis) oriented parallel to the rubbing direction, while the director in the other domain type ($-P_S$) is inclined to the direction of rubbing by the amount 2θ . Thus, for a sample with rubbing direction along one of the polarizers the $+P_S$ state appears dark, while the $-P_S$ state is bright. A typical texture photograph, together with a schematic illustration of the respective layer and director configuration, is depicted in figure 1. This arrangement allows us to additionally study the influences of surface anchoring, as the switching process of the director into the rubbing direction is elastically more favourable than out of it (subscript ‘in’ and ‘out’, respectively).

3. Experimental results and discussion

Figure 2 shows an exemplary time series of texture images taken during the ferroelectric domain growth process. Starting in the optically dark $+P_S$ state (figure 2(a)) the electric field direction is reversed and optically bright $-P_S$ domains nucleate and grow (figures 2(b)–(k)) until after approximately 2 s the switching process is completed (figure 2(l)). From the image series it can readily be seen that domain growth proceeds in directions parallel and perpendicular to the smectic layers, not to the rubbing direction, which is parallel to the short edge of the photographs. Following the spatial positions of domain walls as a function of time, we can determine the domain wall velocity from the slope of the $d(t)$ – d_0 lines, as well

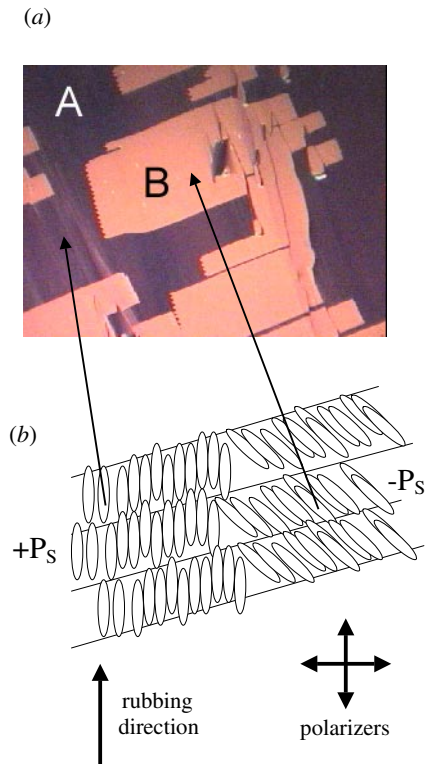


Figure 1. (a) Texture illustration of ferroelectric SmI* domains and (b) schematic smectic layer configuration used for the *in situ* investigations of the ferroelectric domain growth dynamics.

as its anisotropy, as illustrated in figure 3. Ferroelectric domains are growing several times faster in a direction parallel (squares) to the smectic layers than perpendicular (triangles) to them ($v_{\text{out,par}} = 142 \mu\text{m s}^{-1}$ as compared to $v_{\text{out,per}} = 20 \mu\text{m s}^{-1}$). The switching process into the direction of rubbing (open symbols) is clearly faster than out of it (full symbols). This behaviour can be understood qualitatively if we consider the smectic layer and cell geometry used: the elastic energy due to the interaction between the LC and the substrate has a minimum when the director is parallel to the rubbing direction. Thus the free energy of the $+P_S$ state is lowered by the amount of the elastic energy as compared to the $-P_S$ state. This means that switching out of rubbing (dark to bright), we have to overcome the elastic potential, which reduces the domain wall velocity, while switching into rubbing, the state of minimum free energy is reached, enhancing the domain wall velocity. Nevertheless, the same anisotropic domain growth behaviour is observed: domain growth parallel to the smectic layers proceeds much faster than in the perpendicular direction ($v_{\text{in,par}} = 434 \mu\text{m s}^{-1}$ as compared to $v_{\text{in,per}} = 39 \mu\text{m s}^{-1}$). It should be noted that care was taken during the analysis of the images to avoid pinning effects of the domain walls due to impurities within the liquid crystal or substrate roughness, which can readily be observed, as the domain wall motion was followed *in situ* by polarizing microscopy.

3.1. Dependence on electric field amplitude

Applying the above procedure to a variety of digital image series taken at different electric field amplitudes, we obtain the field dependence of the domain wall velocity $v(E)$, as shown in figure 4. Again, the general anisotropic behaviour is observed, with the domain wall motion

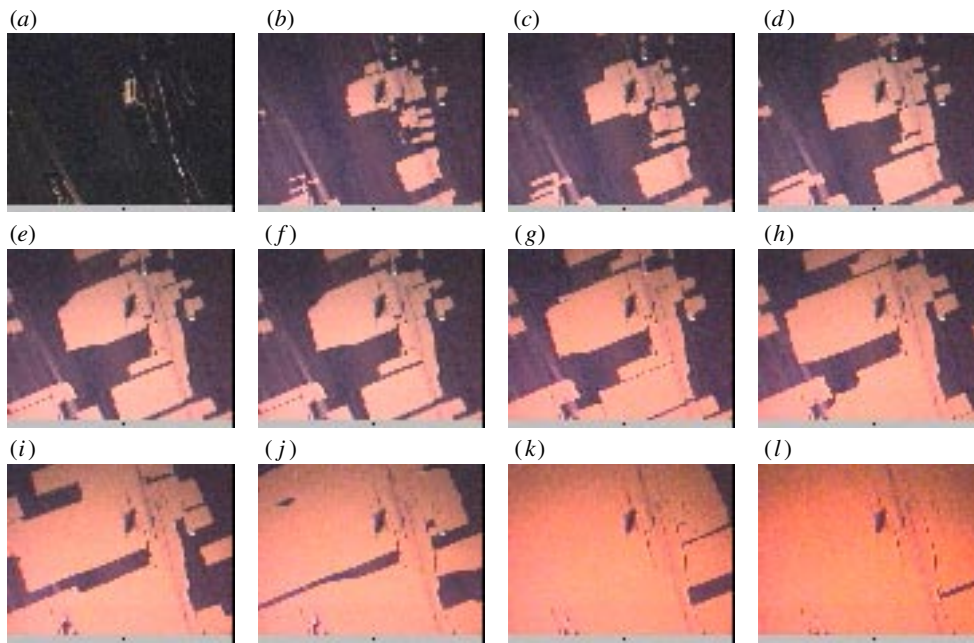


Figure 2. Exemplary time series of textures observed during the switching process from $+P_S$ ((a), dark) to $-P_S$ ((l), bright). Note that the ferroelectric domain growth proceeds parallel and perpendicular to the smectic layer plane (configuration as in figure 1(b)) and not along the rubbing direction, which is parallel to the short edge of the photographs. The image size is $650 \mu\text{m} \times 490 \mu\text{m}$.

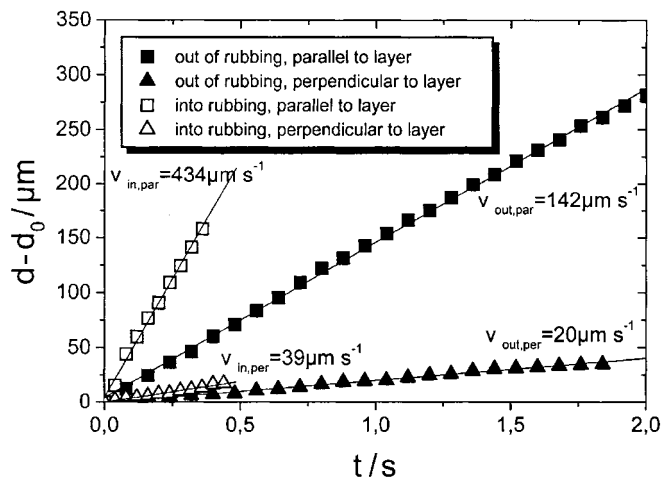


Figure 3. Domain wall position as a function of time after reversal of the electric field direction. Full symbols refer to the switching process out of the rubbing direction, open symbols to switching into the direction of rubbing. The domain wall velocities are larger parallel (squares) than perpendicular (triangles) to the layer plane, illustrating the anisotropy of ferroelectric domain growth.

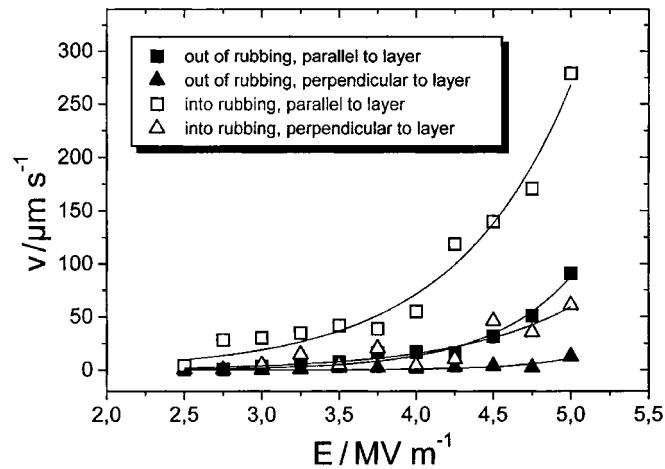


Figure 4. Domain wall velocity v as a function of applied electric field amplitude E for $f = 0.1$ Hz at $T = 75$ °C. Full symbols refer to switching out of the direction of rubbing and open symbols refer to switching into the direction of rubbing. The domain wall velocities are larger parallel (squares) than perpendicular (triangles) to the layer plane. For moderate field amplitudes $E < 4$ MV m⁻¹ above the threshold field of $E_0 = 2$ MV m⁻¹ a linear relation $v(E)$ is observed, which allows an estimation of the domain wall mobilities (see table 1).

Table 1. Experimentally determined domain wall mobilities μ for the different switching processes.

Domain wall motion	μ (cm ² V ⁻¹ s ⁻¹)
Out of rubbing, parallel to layer	$(1.2 \pm 0.17) \times 10^{-7}$
Out of rubbing, perpendicular to layer	$(1.19 \pm 0.39) \times 10^{-8}$
Into rubbing, parallel to layer	$(2.63 \pm 0.51) \times 10^{-7}$
Into rubbing, perpendicular to layer	$(1.15 \pm 0.27) \times 10^{-7}$

proceeding more quickly parallel to the smectic layer plane than perpendicular to it (compare squares to triangles). Also the expected behaviour of a faster domain growth for switching into, as compared to out of, the rubbing direction is again confirmed (compare open to closed symbols). We note that the observed field dependence of the domain wall velocity only follows the simple behaviour predicted by equation (2) for small electric field amplitudes above the threshold field of $E_0 \approx 2$ MV m⁻¹ up to approximately $E = 4$ MV m⁻¹. Over this range we can estimate domain wall mobilities μ as listed in table 1. The values are very small compared to those of solid state ferroelectrics, which are of the order of $1\text{--}10^{-3}$ cm² V⁻¹ s⁻¹ for BaTiO₃ and Rochelle salt, respectively [9]. This is understandable if we take into consideration that the spontaneous polarization of the LC is also a factor of $10^4\text{--}10^5$ smaller than that of solid state ferroelectrics: in the case of 8OSI it is $P_S \approx 5$ nC cm⁻².

Once the switching process has proceeded to a point where different domains begin to coalesce, a suitable measure to further characterize the switching process is the fraction of switched sample area $A(t)/A_0$ as a function of time [13], first introduced by Orihara and Ishibashi [22], based on the Avrami theory of phase ordering for homogeneous nucleation. They obtained a relationship:

$$\frac{A(t)}{A_0} = 1 - \exp(-\beta(t - t_0)^2) \quad (3)$$

with β being a constant proportional to v^2 and t_0 the time between field reversal and domain nucleation. We find that equation (3) (full curves) well describes the data obtained for the

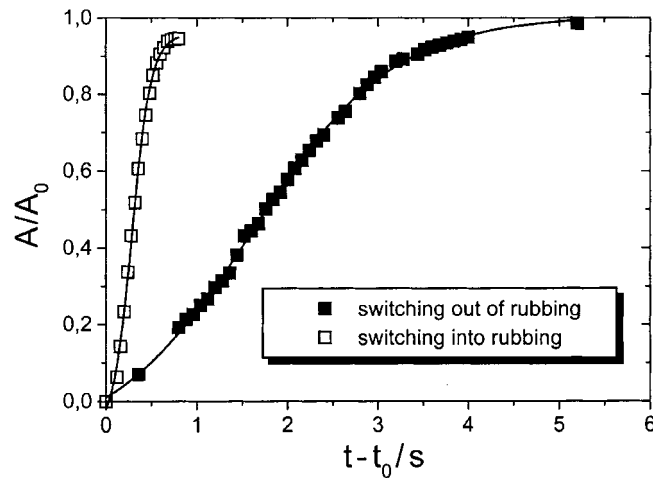


Figure 5. Time dependence of the switched area fraction for director reorientation out of (full squares) and into (open squares) the direction of rubbing. The data can be well fitted by a modified Avrami equation (equation (3), full curves).

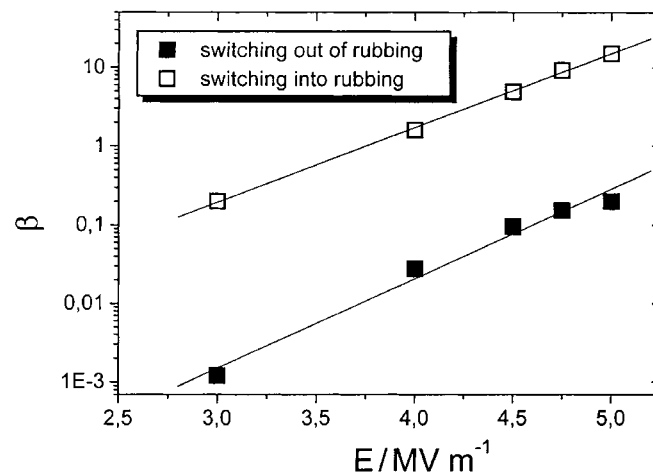


Figure 6. Electric field dependence of the constant β from equation (3). Values obtained for switching into the direction of rubbing (open squares) are two orders of magnitude larger than for the reverse process (full squares).

switching process out of rubbing (full squares), as well as into rubbing (open squares), as is demonstrated in figure 5. Fitting such data obtained from several texture series, we derive the electric field amplitude dependence of the constant β , which indicates a strongly increasing domain wall velocity for increasing electric field (figure 6). The evolution of β is equal for switching into (open symbols) and out of (full symbols) the direction of rubbing, while β is approximately one to two orders of magnitude larger for the former process as compared to the latter.

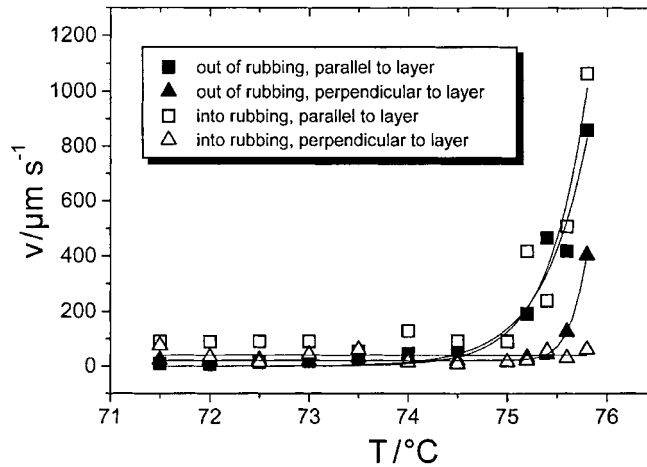


Figure 7. Temperature dependence of the domain wall velocity for $E = 5 \text{ MV m}^{-1}$ at $f = 0.1 \text{ Hz}$. A steep increase is observed on approaching the transition to SmC^* ($T_C = 75.9^\circ\text{C}$), attributed to a strong pre-transitional decrease in the viscosity.

3.2. Temperature dependence

The temperature dependence of the domain wall velocity and its anisotropy parallel and perpendicular to the smectic layer plane is depicted in figure 7 for switching into (open symbols) as well as out of (full symbols) the rubbing direction. Within the close vicinity of the transition into SmC^* ($T > 75.2^\circ\text{C}$) the domain wall velocity strongly increases, which is in accordance with the fact that the optical response time in smectic C^* is much faster than that of smectic I^* . This is attributed to a strong decrease in the viscosity at the $\text{SmI}^*-\text{SmC}^*$ transition, as has been reported previously for other materials [5, 6]. Disregarding the temperature interval in the close vicinity to the phase transition, the temperature dependence of the viscosity $\eta(T)$ can often be described by an Arrhenius-like behaviour [23]:

$$\eta = \eta_0 \exp\left(-\frac{E_A}{k_B T}\right). \quad (4)$$

As the domain wall velocity is inversely proportional to the viscosity, a plot of $\ln(1/v)$ versus $1/T$ allows the estimation of an activation energy E_A for the domain wall displacement. From the respective plot of figure 8 we estimate the activation energy for switching out of the rubbing direction as $E_A = 12 \text{ kJ mol}^{-1}$, while $E_A = 0.5 \text{ kJ mol}^{-1}$ is obtained for switching into the direction of rubbing. This result is in accordance with the discussion above, relating to the elastic energy for the specific layer configuration used.

The switched area fraction can again be well described by equation (3), which yields the temperature dependence of the constant β . This increases with increasing temperature and is again approximately one to two orders of magnitude larger for switching into, as compared to out of, the direction of rubbing (figure 9). In the pre-transitional regime, approaching the transition to SmC^* , β strongly increases with values for switching into and out of rubbing approaching each other, i.e. the influence of elasticity becomes less pronounced.

3.3. Dependence on applied frequency

Using a square wave electric driving field of low frequency, one would intuitively not expect any dependence of the domain wall motion on frequency. This is, in fact, the case, as depicted

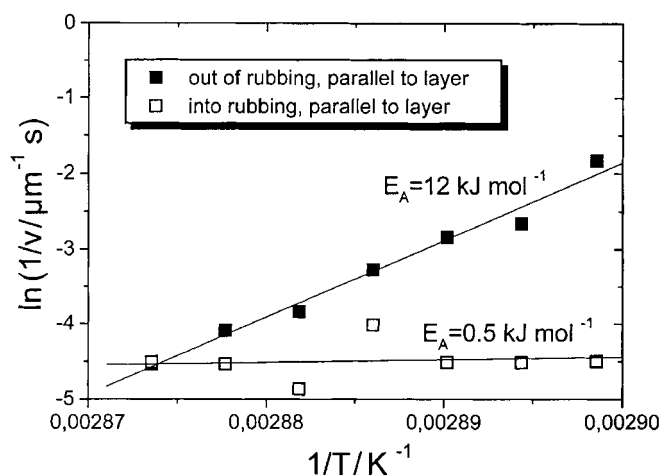


Figure 8. Arrhenius-like representation of $\ln(v^{-1})$ versus T^{-1} for temperatures below the pre-translational regime, which allows the estimation of an activation energy E_A for the domain wall displacement for switching out of (full squares) and into (open squares) the direction of rubbing.

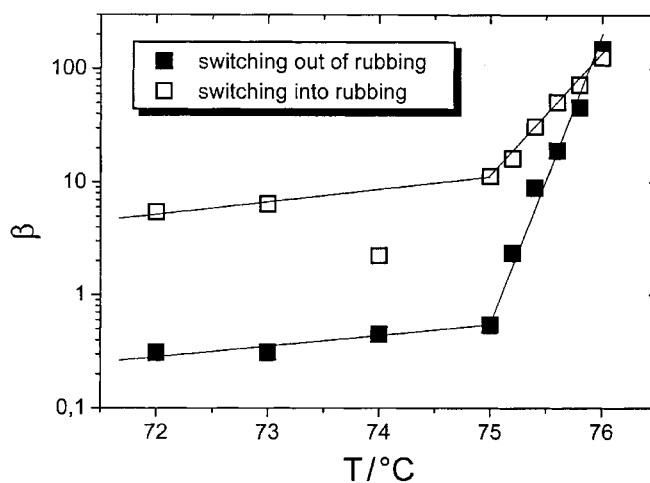


Figure 9. Temperature dependence of the constant β in equation (3). Values obtained for switching into the direction of rubbing (open squares) are one to two orders of magnitude larger than for the reverse process (full squares).

in figure 10, showing the domain wall velocity and its anisotropy as a function of frequency for the different switching processes. As pointed out before, we also observe here the domain wall velocity to be larger in the direction parallel to the smectic layer plane than perpendicular to it. The switched area fraction is again well described by the Avrami-like behaviour of equation (3) and shows no dependence on frequency. This behaviour is clearly illustrated by the frequency dependence of β , which is constant within the frequency range of saturated switching (figure 11). As before, the constant β for switching out of the direction of rubbing is approximately one to two orders of magnitude smaller than for the reverse process.

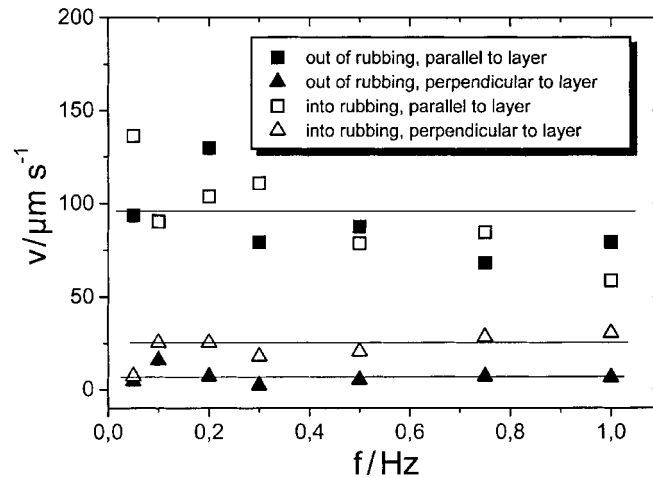


Figure 10. Dependence of the domain wall velocity on frequency of the applied square wave electric field of amplitude $E = 5 \text{ MV m}^{-1}$ at $T = 75^\circ\text{C}$. As expected, $v(f)$ is basically constant in the frequency range of saturated director switching.

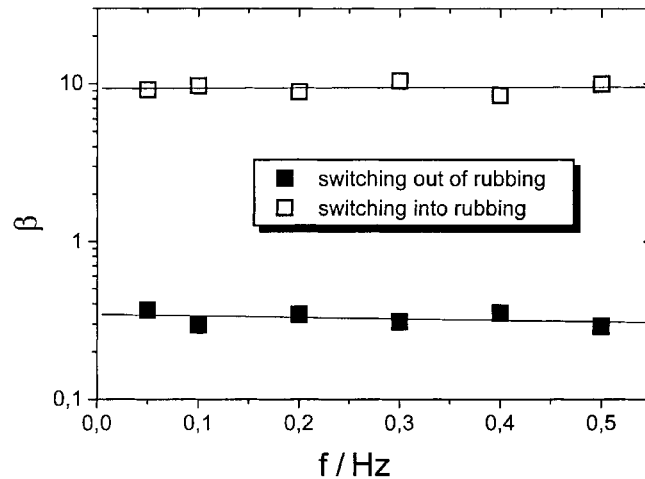


Figure 11. Frequency dependence of the constant β in equation (3). Values obtained for switching into the direction of rubbing (open squares) are one to two orders of magnitude larger than for the reverse process (full squares), but constant for both processes.

4. Conclusions

The growth of ferroelectric domains after electric field reversal was studied for a tilted hexatic SmI^* ferroelectric LC phase. Domain growth occurs in the directions parallel and perpendicular to the smectic layer plane and not along the rubbing direction. The domain wall displacement proceeds linearly with time. The observed domain wall velocities are anisotropic, being several times larger parallel to the smectic layers than in the perpendicular direction. From domain wall velocity measurements as a function of applied electric field amplitude, domain wall mobilities were estimated, which are several orders of magnitude smaller compared to solid state ferroelectrics. This behaviour is accounted for by the spontaneous polarization

also being several orders of magnitude smaller. The ferroelectric domain growth dynamics is independent of the frequency of the applied electric field, and the domain wall velocities increase with increasing temperature. This is attributed to the temperature dependence of the viscosity. Following an Arrhenius-like behaviour, activation energies for the domain wall displacement were estimated, which are in qualitative agreement with the behaviour observed. Using a rotated smectic layer configuration, the effect of elastic hindrance and enhancement on ferroelectric domain growth was studied for switching the director out of and into the rubbing direction, respectively. It is found that the latter process is approximately one order of magnitude faster than the former, with a greatly reduced activation energy.

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