Hydrogen bonded ferroelectric liquid crystal gels in freely suspended film geometry

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We study freely suspended films of smectic C* liquid crystalline gels by means of polarizing microscopy. The gel point of the system is determined from the suppression of flow in the films. The network of hydrogen bonds is mechanically fragile but stabilizes orientation patterns of the sample, in particular it stores the texture present during gelation. Electro-optical experiments are performed to study the dynamics of the sample reorientation under the influence of in-plane electric fields. Mesogen orientation and optical properties can be switched in electric fields of a few kV m⁻¹. After removal of electric fields, the network restores the ‘frozen-in’ texture. This texture can be erased by heating the films above the gelation temperature.

1 Introduction

Liquid crystal (LC) gels have attracted increasing interest over the past decade. This has been triggered not only by fundamental scientific questions but also by the potential for application, such as reflective displays based on the polymer network stabilized cholesteric texture or enhancement of the mechanical stability of ferroelectric liquid crystal displays. It has been shown that the formation of a network by chemical crosslinking of a few percent of photo-reactive additives in a low molecular mass mesogenic material can stabilize the orientation of mesogens. This leads to dramatic changes in the dynamics and the electro-optic characteristics. An alternative approach to produce LC gels makes use of hydrogen bonding additives. A physical network formed by such gelling agents can also stabilize the orientational state of LC phases. Moreover, in contrast to chemically cross linked gels, the network formation is completely thermo-reversible. At first, the promising perspective of such materials is for the storage of anisotropic, thermo-erasable states. However, there is comparably little known of the mechanical and electro-optical properties of hydrogen-bonded (‘physical’) LC gels. Together with an optimization of the chemical constituents of the system, there is a demand for a thorough physical characterization of the structure, mechanical, electrical and optical properties of these materials.

So far, experimental characterizations have been carried out in thin sandwich cells where the mesogens can be aligned by surface treatment and the layers may be oriented by some shearing techniques. Electric fields can be applied by means of transparent electrodes at the glass plates. While this geometry may be important from the applications aspect, it poses some problems during preparation, in particular the layer alignment is not easily achieved. Moreover, the evaluation of electro-optical data is quite complex because of the influence of cell boundaries.

In many types of layered liquid crystalline systems, freely suspended films have proven to be a powerful instrument for the investigation of structure and dynamics. The thickness of such films can vary from thousands down to two layers. One can often treat these systems as quasi two-dimensional, with a large experimentally accessible planar area. The orientation and dynamics of the LC director can be observed in samples with macroscopically well ordered layers.

This study is directed to the understanding of structure and physical properties of hydrogen bonded LC gels in freely suspended film geometry. The experiments include the structure assessment by means of polarizing microscopy, electro-optical investigations and some accompanying mechanical measurements. We will discuss the influences of the network formed in the gelling process on the mesophase properties of the material, i.e. the stabilization of orientational states and the dynamics of the reorientation in electric fields, and on the mechanical properties as shape distortions and the suppression of macroscopic flow in the films.

2 Materials, experimental setup and film preparation

The chemical structure of the gelling agent and the low molar mass ferroelectric liquid crystal (with the phase sequence K52°C SmC* 71°C SmA 81°C Iso) used in the experiments are presented in Fig. 1a. The synthesis of the gel former is described in ref. 4. When the gel former is added in small quantities of a few percent to the mesogen, it is completely solvable and the mesomorphism is preserved, except for slight changes of the phase transition temperatures. Above the gelling temperature, which turns out to be in the smectic C* phase close to the phase transition to SmA, the material behaves similarly to the pure LC.

The investigation of structure and electro-optics of the gels is performed in planar thin film geometry. Free-standing films are prepared in the smectic A phase, about 10 K above the geling point. A small amount of mesogenic material is drawn by means of a thin metal edge across a circular hole of about 1.0 mm diameter in a glass sheet. A pair of parallel copper foil...
slices mounted on the glass sheet at opposite sides of the hole serves as electrodes (Fig. 1b). They provide the driving electric fields in the film plane. We study the images of the films with a reflection microscope (NU2, Carl Zeiss Jena). All images and videos (maximum frame rate 25 frames per second) are recorded with a Nikon Coolpix 990 CCD camera. They are subsequently contrast amplified and processed digitally. The films are observed with crossed linear polarizers. However, since a number of optical elements are in the light path (e.g.: a prism that splits the incident and reflected beams), the polarization of the incident light is not perfectly linear but slightly elliptical. This has to be considered in the discussion of optical images (see below).

The mechanical resistivity of the gel to convective flow in the planar films gives a first estimate of the strength of the gel network. More quantitatively, the mechanical stability may be tested by the application of lateral stress on the gel film. In planar film geometry, the application and quantitative measurement of a well defined uniform stress is not straightforward. Therefore, these mechanical experiments are performed in spherical bubble geometry, where a uniform stress can be easily achieved by varying the bubble radius and the stress is easily determined from the inner excess bubble pressure. For the preparation of smectic bubbles from planar films, a technique described earlier\(^5,10\) is exploited. We use a tapered glass capillary with an opening of a few millimeters as support. A freely suspended film is drawn on the capillary opening in the smectic A phase at 80°C. The opposite end of the capillary is connected to a syringe and a sensitive difference pressure gauge. The film is inflated to a bubble by injecting air through the capillary. After the inflation, the smectic bubbles of a few millimeters in diameter are cooled into the gel state where the bubble shape and internal pressure are recorded in dependence of the contained air volume. The bubbles are enclosed in a sample container for temperature control (accuracy about 0.1°C) and protection against acoustic disturbances and ambient air flow. The samples are illuminated in parallel 546 nm monochromatic light, and transmission images for photometric evaluations are taken with a HAMAMATSU CCD camera and controller.

3 Results and discussions

3.1 Structure of the FLC gel films

After the preparation of the free standing film at a temperature within the smectic A phase above 80°C, the sample is cooled into the smectic C\(^*\) phase (to 60°C). In order to obtain uniform films, different cooling rates have been tested. During the gelation, the film is observed in reflection under normally incident polarized light. Because the tilted smectic C\(^*\) phase is optically anisotropic, the effective refractive index depends on the orientation of the polarization direction with respect to the \(c\)-director (the projection of tilt on the layer plane), light with different polarization directions experiences different optical path lengths. Interference effects lead to a dependence of the film reflectivity on the local \(c\)-director orientation. Hence, for a non-scattering material the optical reflectivity is sufficient to characterize the LC orientation in the film. Polarizers are crossed to keep the background from scattered ambient light small. However, the gel films themselves contribute a substantial amount of scattered depolarized light to the images. As will be demonstrated in the following, the film reflectivity is directly coupled to the local sample orientation, although the usual \(\alpha \cdot \sin^2 2\Phi\) dependence of the reflected intensity \(I\) on the angle \(\beta\) between polarizer and \(c\)-director is not reproduced.

The most obvious indication for the gelation is the suppression of flow in the film. During application, e.g. of DC electric fields, non-gelled free standing smectic films develop electrically driven convective flow. Coulomb forces on surface charges of the film produce flow patterns,\(^3,12\) in the circular films often manifested by one or a couple of irregular vortices. When the gel films are exposed to DC fields of moderate strength (<10\(^{-3}\) V m\(^{-1}\)), such flow effects are completely suppressed by the network of hydrogen bonds. Thus, the observation of free standing film in DC fields provides a direct approach to determine the gelling transition during the heating or cooling process.

If one cools the film quickly (at the rate \(\approx\,0.5\) K s\(^{-1}\)), non-uniform films can be prepared. Some parts of the film are in the gel state, while some other parts contain a non-gelled mixture of FLC and gelling agent\(^1\) as shown in Fig. 2. Gel regions appear darker in the reflection images as a consequence of light scattering. If a sufficiently strong DC field (3 \times 10\(^{-3}\) V/m) is applied to the film, it is often observed that electroconvective sets in within the liquid part, whereas the gel part is stable. Gel island are advected by the flow of surrounding liquid film. With increasing temperature, the liquid parts grow and at a certain temperature, the complete film becomes liquid. We define this temperature as the gelling point. In our experiments, this gelling point is at 70.5°C, slightly below the phase transition from the smectic C\(^*\) to the smectic A phase. It is almost independent of the concentration of gel former. Moreover, the thermo-reversibility of the gel network formation is proven by the observation of flow while the temperature is increased or decreased across the gelling point.

For the electro-optic experiments, we have chosen only such films that have been prepared at slower cooling rates, and where the whole film is in the gel state. Fig. 3 shows images of such homogeneous free standing FLC gel films in the smectic C\(^*\) phase. The reflective intensities of polarized light in different areas of the film represent domains of different orientation of the LC (indicated by arrows). An anisotropic network is separated from the LC environment. It is reflected in a texture of striations. In the absence of electric fields in the

\(^1\) This observation is somewhat counter-intuitive, since one would expect a better homogeneity in quickly cooled films and probably a diffusion limited phase separation in slowly cooled samples. An explanation could be that during rapid cooling, some flow in the films is caused by temperature gradients, which prevents the formation of a uniform gel.
film plane, the network is often hardly distinguishable from the LC background in the optical image. However, after application of an electric field, the liquid crystal domains reorient and change their reflectivity such that the network strands can be distinguished in the optical pattern. The percentage of film area covered by the visible network strands is much larger than the actual gel former content, therefore we have to conclude that the fibers contain a mixture of gel former and liquid crystal. We will discuss the nature of these strands in more detail in the final section. Within a domain of uniform film orientation, the network strands are preferentially aligned in one spatial direction. The reflectivity of the network strands in the field-free state is comparable to that of the surrounding LC area. This supports the conclusion that the birefringent strands themselves contain a considerable amount of oriented smectic liquid crystal material and the refractive index in the strands is essentially the same as that of the aligned smectic material. During application of electric fields, the orientation and the optical properties of the network fibers is largely preserved. Only at high fields, does a weak distortion of the network orientation itself occur (see next section). The behavior of the gel film can be best described by a structure of fixed network strands which define a preferential orientation of the enclosed liquid crystal director, with strong anchoring at the fibers and complete suppression of macroscopic flow. The electro-optic experiments in the gelated smectic C* samples show that the gel network stabilizes the orientation of the LC film within the domains. After electric fields applied to align the LC domains are switched off, the domains relax to the initial texture adopted after cooling into the gel state. Only after heating above the gelling point and subsequent cooling back into the gel state, can the domain pattern be erased and a new texture is created.

At domain boundaries, there is a sharp, discontinuous transition to the neighboring domains (see Fig. 3), in contrast to non-gelled smectic C* films with their continuous variations of the LC orientation in typical Schlieren textures. This is obviously related to the mechanism of network formation, which is dominated by an anisotropic growth of the fibers in the smectic matrix, and in turn, a feedback of the network growth on the orientation of the surrounding c-director. From different nucleation centers in the film, domains with random orientations of the respective local alignment grow simultaneously during cooling, until they cover the film plane. Since each domain follows a preferential growth direction, rather sharp discrete boundaries are formed. Within the domains of several hundred micrometers in diameter, the network structure is uniform and can be studied individually.

Attempts to prepare monodomain films by application of electric fields during cooling into the gel state have failed so far. The electric DC field strengths necessary to align the ferroelectric polarizations in the domains produce convective flow in the films during the gelation, which prevents the formation of an aligned network. In AC fields, such a convective flow can be avoided, but the anisotropic dielectric interactions are far too small to align the samples.

The lateral sizes of the network structures in the films depend on the concentration of the gelling agent. Fig. 4 shows the mean dimensions of the liquid crystal microdomains and the diameter of the network strands measured in the free standing films. The width of the striations of the network is relatively well defined and it is nearly uninfluenced by the gel former content in the concentration range between 1% and 5%. However, there is a broad distribution of the microdomain sizes (see other photographs in this paper) around the values indicated in Fig. 4 which represent averages of the width of a couple of films each. As a general trend, the size of individual LC microdomains decreases slightly with increasing amount of gelling agent in the sample. The thickness of all films considered here was below 1 μm, i.e. much smaller than the size of the observed structures. Thus one can assume that the strands of the network seen in the images extend through the complete free standing film from top to bottom.
The radius ing radius changes, similar to the pure smectic LC material. The spherical bubble shape is preserved during rupture. However, no such effects have been observed in bubbles, while the bubbles should no longer be inflatable without conservation of the film area. For this purpose, we use the bubble geometry described above. The spherical shape of the liquid bubbles is a consequence of the minimization of the film surface by the action of the surface tension $\sigma$ of the smectic fluid at the air/film interfaces. The film curvature (bubble radius $R$) is related to an inner excess pressure $P$ of the gas in the bubble by the well-known Laplace–Young relation $P = 4\sigma/R$.

The liquid bubbles are cooled to 60°C into the gel state, and afterwards we inflate and/or deflate the bubbles to test the mechanical properties. The inflation or deflation of gel bubbles involves macroscopic flow in the film plane. Thus, the experiment provides information on the mechanical resistivity of the hydrogen bonded network in thin films. If the gel network is strong enough to prevent flow, the gel film surface should be conserved, the films should wrinkle during deflation of the bubbles, while the bubbles should no longer be inflatable without rupture. However, no such effects have been observed in the experiments. The spherical bubble shape is preserved during radius changes, similar to the pure smectic LC material. The radius $R$ in dependence of the inner excess pressure $P$ of a uniformly gelled bubble with 5.0% gelling agent is presented in Fig. 5. The data can be fitted with the Laplace–Young equation in the liquid as well as in the gel state. The surface tension $\sigma$ extracted from the $R(P)$ graphs is comparable to that of common LC materials. This demonstrates the relatively low mechanical stability of the hydrogen bonded LC gels. During deflation, for example, the lateral stress in the film related to surface tension, $\sigma/d \approx 30$ kPa (with the film thickness $d$ of the order of 1 μm), must exceed the strength of the network of hydrogen bonds considerably, so that the value represents an estimate of the upper limit for the gel network resistivity to stress. On the other hand, it has been discussed above that in planar films exposed to moderate electric fields, the network sustains electroconvective flow in the film plane. This allows us to derive a lower estimate of the hydrogen bond related forces. Flow gradients normal to the film are negligible. The viscous stress in the fully developed convective flow field (in the liquid state) is of the order of $\eta v_{\text{max}}/r$, where $\eta$ (of the order of 1 Pa s) is some average shear viscosity of the LC material, $v_{\text{max}}$ is the largest local velocity and $r$ is the radius of the film. At field strengths of the order of a few kV m$^{-1}$, the velocity gradients in liquid films reach 10–100 s$^{-1}$, so that we find the lower limit of 10–100 Nm$^{-2}$ for the viscous torque that dissipates the electric power. In the convection-free gel films, we may assume that the interactions of the charges with the external field are of equal strength, the viscous torque is absent, hence the gel network must sustain at least comparable force per area. The actual value can therefore be estimated very crudely to be in the range of 0.1 to 30 kPa, it is presumably close to the lower limit given (a few hundred Pa). Summarizing, it can be stated that the strength of the hydrogen bond network is not efficient to stabilize self-supporting films against mechanical stress, but it is stable enough to suppress electrically or thermally driven flow in thin samples, and it stabilizes the mesogen orientation.

### 3.2 Mechanical stability

One of the properties of gel films that is interesting in connection with their perspectives for application is mechanical stability. It has become evident from the suppression of convective flow in the films that at least a weak mechanical stability is provided by the hydrogen bonded network. The fragility of this network is demonstrated, however, in an experiment where the film area is mechanically changed. For this purpose, we use the bubble geometry described above. The spherical shape of the liquid bubbles is a consequence of the minimization of the film surface by the action of the surface tension $\sigma$ of the smectic fluid at the air/film interfaces. The film curvature (bubble radius $R$) is related to an inner excess pressure $P$ of the gas in the bubble by the well-known Laplace–Young relation $P = 4\sigma/R$.

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### 3.3 Electro-optical characterization

The domain structure of the LC gel film is fixed during the gelation, but the orientational state can be reversibly influenced by means of electric fields applied in the cell plane. In SmC*, the electric field $E$ couples to the local spontaneous polarization $P$ and creates a torque on the $c$-director. It causes a reorientation of the mesogenic tilt plane and thus of the optic axis in the individual domains. The electro-optic response of the gel film is investigated by recording the change of reflection intensity in polarized light under lateral electric fields. Fig. 6 contains images of a 3% gel film in different electric fields. Fig. 6b represents the field-free (off) state where the network structure itself is hardly distinguished from the LC microdomains. The picture shows the boundary region of two well distinguishable domains with different orientations of the network. It is evident that the easy axis of mesogenic tilt follows the preferred direction of the network strands, although the sense of the $c$-director orientation cannot be determined from the reflection images. Presumably, the spontaneous polarization is initially perpendicular to network striations, i.e. in both domains it differs from the vertical axis along which the electric field is applied. Fig. 6a shows that after a DC field (‘positive’) is switched on, one of the film regions remains nearly uninfluenced while the other (top of the image) shows a pronounced change of the reflectivity. Since the network structure itself is not affected and the reflectivity of the network strands remains constant, the LC microdomains appear clearly visible as dark areas on bright background. A reversal of the electric field causes the upper domain in the image to return into a state where the reflectivity of the LC regions is close to that of the easy orientation. The second (bottom) area shows the opposite behaviour. Its reflectivity increases in the...
second electric field state (‘negative’) while the network remains unchanged, thus the microdomains appear bright on dark background. Obviously, the preferred alignment of the bottom domain in Fig. 6a is close to the $E_+$ state while that of the top domain is closer to the $E_-$ state. In general, all films decompose into a couple of domains with arbitrary orientations, and for the detailed investigation of the switching dynamics we will have to select representative individual domains. When a square wave voltage is applied, the periodic switching can be observed and reproducibility of the dynamic response can be verified. A cut through film reflectivity profiles for two representative domains is shown in Figs. 7a and b. Fig. 7a shows a space–time plot of a cut perpendicular to the network stripes during the first four cycles after a field ($5 \text{ kV m}^{-1}$, $0.5 \text{ Hz}$) is switched on. The time axis runs from bottom to top. One acknowledges that the initial film profile is uniform, and after application of the field the network fibers are unchanged in brightness and position. The LC domains change their reflectivity synchronous to the applied electric field. In Fig. 7b, another film is shown during exposure to a $9 \text{ kV m}^{-1}$ field. The strands of the network still keep their reflectivity, but the network itself is reversibly distorted by the field, the positions of the fibers shift by several micrometers during the switching. If the electric field strength is further increased by approximately one order of magnitude, the strong distortions lead to the rupture of the network structure and convective flow sets in. We will disregard the lateral deformation of the network and study the switching dynamics of the LC inside the microdomains.

Fig. 6 Images of a 3.0% gel film show switched states (a,c) under electric fields of opposite polarities, (b) field-free state.

Fig. 7 (a,b) Cross-sections of the reflection profiles of 3% gel films presented as space–time plots, the time axis runs vertically from bottom to top, the horizontal axis is a cut nearly perpendicular to the local network stripes. (a) Shows a domain which appears bright in the field-free state, then, four cycles of the electric square-wave field are seen where the reflectivity of the microdomains is periodically modulated and the stripes of the network remain at fixed positions with unchanged reflectivity, $E = 5 \text{ kV m}^{-1}$, $f = 0.5 \text{ Hz}$. Note that during one half cycle of the field, the optical state is nearly equivalent to the field-free texture. (b) Shows another (dark) domain in an electric field of $9 \text{ kV m}^{-1}$, $f = 0.5 \text{ Hz}$. Here, the strong electric field leads to a periodic distortion of the network, seen in the lateral shift of the dark stripes in the space–time plot.

Fig. 8a shows the reflective intensity change in an individual LC microdomain of a 3.0% gel film in different electric fields. The electric field was periodically reversed at a frequency of 0.5 Hz for all field strengths. In the particular domain, the field-free, off-state reflectivity (dark) is very close to that of the $E_-$ state, whereas the on-state $E_+$, shows a field strength dependent reflectivity. A certain saturation value of the intensity is reached at electric field strengths exceeding $\approx 7 \text{ kV m}^{-1}$. The existence of a saturation value indicates that at fields above $7 \text{ kV m}^{-1}$, the reorientation into the field aligned state is almost complete, i.e. the spontaneous polarization is almost aligned to $E$. At lower electric field strengths, the reorientation into the aligned on-state remains incomplete at the chosen AC excitation frequency. At electric fields below $2 \text{ kV m}^{-1}$, electro-optic switching effects are practically not observable.

Other domain orientations lead to qualitatively different electro-optic reflectivity changes. Fig. 8b shows a domain in another 3% film and its corresponding switching curves. Here, the bright state is near to the preferred one (cf. the reflectivity of the network in the insert), and the switching into the electric field forced dark state is strongly field dependent. In general, domains with other preferred alignment axes can have more complex switching characteristics and in special cases, the optical reflectivities of the electrical on and off states may coincide.

The above results clearly indicate that the reorientation behavior of LC in electric fields is qualitatively different from the switching of the pure ferroelectric liquid crystal film. The network does not only induce a preferential alignment but also imposes elastic torques that counteract the reorientation of the $c$-director. In order to determine the strength of this influence quantitatively, we consider the field dependence of the switching dynamics in detail. Before we analyse these curves, a remark on the optical properties of the system is necessary. Unlike in pure smectic C films (e.g. ref. 13), the optical characteristics of the gel films in the reflection microscope are very complex, and it is not possible to establish a direct unique relation between reflectivity and orientation of the $c$-director.
During switching, the local optical axis as well as the scattering efficiency of the inhomogeneous texture are both influenced in a complex way. (The scattered light by the inhomogeneous film structure makes quantitative statements from transmission microscopic images of thin gel films practically impossible.) When the field-free film is rotated stepwise in the reflection microscope, and the local intensity profile of each individual domain is recorded as a function of the rotation angle, one reflectivity maximum is found for each domain within a full sample rotation.

For a quantitative evaluation of the reorientation dynamics without prerequisite knowledge of the exact optical characteristics, we apply the following procedure: it is assumed that the reorientation rate in the vicinity of the ground state is proportional to the effective torque on the c-director, and the variation of that torque with the electric field can be compensated by a proper scaling of the time axis. We consider first the transition into the on-state in Fig. 8b and scale the time coordinates of all curves with a phenomenological parameter \( t' = t/\tau(E) \) such that the initial switching characteristics scale to a master plot. The 8 kV m\(^{-1}\) curve is taken as reference. The result is shown in Fig. 9a. The individual scaling factors \( \tau(E) \) can be considered as a measure for the ratio of mechanical and electrical vs. viscous torques. This will be discussed below, and it can be exploited for a semi-quantitative evaluation of the involved mechanical and electrical terms.

Since the excitation frequency of 0.5 s\(^{-1}\) is faster than the total switching time at low fields, electric field reversal in the first three curves of Figs. 8 and 9 takes place before the switching is complete, i.e. before a saturation of the reorientation angle is reached. With increasing field strength (at 6 to 7 kV m\(^{-1}\)), the orientation reaches a certain plateau during the field cycle and deviates from the master curve at large switching angles. Within the cycle of the applied field, the sample reaches a certain equilibrium of electric and elastic (network related) torques. At still higher fields (above 8 kV m\(^{-1}\)) the plateau value saturates, indicating that the field aligned state of the spontaneous polarization is nearly reached.

Likewise, the relaxation of the switching curves into the off-state can be plotted in a master graph with another set of scaling factors \( t'' \). This is shown in Fig. 9b. The scaling factors are chosen such that the curves coincide near the off-state, irrespective of the magnitude of the initial deviation. Fig. 10 shows a plot of the scaling factors used to create the graphs in Figs. 9a and 9b.

**Fig. 8** Electro-optic switching behavior of 3.0% gel films under different electric fields. The insert shows the corresponding reflection images (64.5 x 47.7 um) in the on-state, i.e. electric field in the phase of maximum contrast between gel network and LC domain, (a) and (b) correspond to domains in different films. The reflectivities in the graphs have been determined in the LC compartments of the texture.

**Fig. 9** The re-scaled switching curves of the 3.0% gel film taken from Fig. 8b. Graph (a) shows the switching into the on-state, from the preferential (bright) state to the elastically unfavorable (dark) state, (b) gives the switching off graphs.

**Fig. 10** The scaling factors used to produce Fig. 9, reflecting the inverse dependence of the switching time on the applied electric field of different gel films with the fitting curve. Open and solid symbols correspond to the graphs of Figs. 8a and b, respectively (see text).
and b. The scaling factors of switching-on curves (into the non-favoured state) are plotted on the positive E-axis while the scaling factors for the relaxation toward the easy alignment are plotted with negative sign on the negative E-axis. In addition to the values extracted from Figs. 9a and b (Fig. 10 solid squares) the graph contains the scaling factors obtained from a different film (that of Fig. 8a), which agree fairly well with those obtained from Fig. 8b. For low electric fields, we can extrapolate a linear slope connecting the scaling factors. When the torques on the c-director are considered, it is expected that the reorientation rate (inverse reorientation time) should depend upon the ferroelectric torque per volume \( \Gamma_p = \vec{P} \times \vec{E} \) on the spontaneous polarization, the elastic torque density \( \Gamma_{\text{elast}} \) exerted on the c-director by the hydrogen-bonded gel network, and the viscous torque per volume \( \Gamma_{\text{visc}} \), viz. \( \vec{y} \theta \) on the c-director. Here, \( \gamma \) denotes a rotational viscosity for reorientations of the c-director, \( \theta \) is the azimuthal angle of the mesogenic tilt. All torques are normal to the film plane, therefore the vector signs will be omitted. From the torque balance \( \Gamma_{\text{visc}} + \Gamma_p + \Gamma_{\text{elast}} = 0 \) we expect that the reorientation rate is proportional to the effective torque density \( \Gamma_p + \Gamma_{\text{elast}} \) for relaxation into the off-state and to \( \Gamma_p - \Gamma_{\text{elast}} \) for the switching onto the on-state. The fact that the curves corresponding to different field strengths are scalable at least in the small deformation part to a master plot justifies the assumption that the elastic and electric torques have roughly the same dependence. When the reduced relaxation rates \( \tau(E) \) (scaled with the value of the 8 kV m\(^{-1}\) switching-on curves) are plotted as a function of the electric field strength (Fig. 10), a linear curve is obtained which intersects the abscissa at \( \Gamma_p = \Gamma_{\text{elast}} \). With \( \Gamma_{\text{visc}} = \gamma \theta \), the quite linear relation between the reorientation rates and \( E \) allows us to assume a linear dependence of \( \Gamma_p + \Gamma_{\text{elast}} \) on \( \theta \) for small deflections. This intersection of the 1/\( \tau \) curve in Fig. 10 with the abscissa yields \( E_c = 2.0 \) kV m\(^{-1}\) for both data sets. With the known value for the spontaneous polarization, \( P = 125 \) nC cm\(^{-2}\) we obtain \( \Gamma_{\text{elast}}/ \theta = 2.5 \) Nm\(^{-3}\) as a rather good estimate for the torque per volume exerted by the gel network on the c-director.

The determination of absolute switching times, which could be used to obtain the rotational viscosity, is more problematic, since the complex optical characteristics do not allow us to map the optical transmission unambiguously to a well-defined c-director orientation angle. In domains that switch in the electric field from a dark to a bright state and vice versa (as those presented in Figs. 8), one may define the switching time phenomenologically as the interval of optical reflectivity change between 10% and 90% of the total difference of on and off states. Such a definition yields a value \( \tau_{\text{opt}} \) of about 400 ms for the 3% sample at 8 kV m\(^{-1}\) (average of on and off switching curves), and \( \tau_{\text{opt}} (PE) \approx 4 \) ps. From the torque balance, by comparison with the definition of \( \Gamma_{\text{visc}} \), we can take this value as a crude estimate for the rotational viscosity. This quantity should be field strength independent but might depend upon the sample composition, i.e. the gel former content (see below).

4 Conclusions

The experiments indicate that the free standing films of the hydrogen-bonded gel are inhomogeneous on a mesoscopic scale. It is found that during the gelation an anisotropic network of thin birefringent strands phase-separates from the surrounding LC material. This network is visible in polarized light in the reflection microscope. We note that the physical nature of this network found in the free standing films is not identical with the structures observed by scanning electron microscopy (STM). The latter (discovered in a disordered bulk sample on a glass plate) appear on a much smaller length scale. Rather, the elongated crystallites of the gelator observed in STM are formed during the gelation. They separate from the liquid crystal into macroscopic bundles that are observed in the polarizing microscope. We expect that the same structure is present in sandwich cells. In previous investigations of such cells, the macroscopic optical appearance of the sample was not studied, it is natural to assume that the same microphase separation happens in these samples too. It is much more difficult to resolve the network structure in sandwich cells by optical methods because the network will form in three dimensions there. We predict, however, that the sandwich cell samples will still show increased light scattering due to the local inhomogeneities when they are exposed to sufficiently large electric fields.

The study of the free standing films shows that the size of individual phase-separated LC microdomains decreases with higher content of gelling agent in the sample. However, the width of the striations is nearly the same for all sample compositions studied here (1% to 5% gel former content). Thermally or electrically driven convective flow in the films is efficiently suppressed by the network, and the forces per area that hold the network structure together are estimated to be in the range of several hundred N m\(^{-2}\), but definitely not larger that a few thousand N m\(^{-2}\).

During gelation, the network stabilizes the texture of the tilted smectic phase. This texture can repeatedly be erased by heating the system above the gel point near 70.5 °C. The network creates a memory of the ‘frozen-in’ texture and influences the switching behavior of the ferroelectric phase considerably. Under the application of electric fields of several kV m\(^{-1}\), the sample orientation can be switched in the LC microdomains, and after removal of the electric field, the elastic forces restore the memorized local alignment. The dynamic reflectivity curve reaches a saturation value at electric fields above \( \approx 7 \) kV m\(^{-1}\), suggesting that such field strengths are sufficient to align the c-director in the gel phase. When the reorientation rates for different electric field strengths are compared, one finds a value of an electric ‘retardation field’ of about 2.0 kV m\(^{-1}\) in the 3% gel former samples. This value provides a measure of the aligning torques of the hydrogen bonded network on the c-director. Within a simple Fredericksz-model, which is certainly a rather crude approximation for the complex system studied here, one can assume that the sample orientation is pinned at the network strands with rigid anchoring and the c-director field is deflected across the microdomains. The estimated value of \( \Gamma_{\text{elast}}/ \theta = 2.5 \) N m\(^{-3}\) (from the value of the retardation field) can be explained in such a model by an elastic torque \( K \theta \), with a mean elastic constant \( K \) for in-plane deformations of the c-director field and an average wave number \( q \) of the distortions. With reasonable values of \( K \approx 10^{-11} \) N and \( q \approx \pi / l (l \approx 10 \) µm representing the mean distance between adjacent fibers of the network), the experimental value is in the expected order of magnitude.

By means of FTIR measurements in thin sandwich cells, the switching characteristics of the same compounds as used here (with maximum gel former contents below 2%) has been measured earlier. The sample geometry, in particular the observation direction, was somewhat different in the FTIR experiment: in the bookshelf geometry, a full 180° reorientation of the c-director corresponds to an angular reorientation of the IR absorption maxima by twice the tilt angle.) The FTIR experiments were performed in electric fields of several MV m\(^{-1}\), three orders of magnitude larger than the fields in our study, and thus the switching times are of the order of microseconds. An exact quantitative comparison of the switching dynamics with the electro-optical observations in free standing films is not possible, since a definition of the switching times has not been given in ref. 5 but from the order of magnitude, both results are consistent: at field strengths of 10.9 MV m\(^{-1}\) and 21.7 MV m\(^{-1}\), respectively, the mesogen reorientation in a 0.75% sample occurs on a time scale between 20 and 100 ms (Fig. 6 in ref. 5), i.e. the product \( \tau_{\text{opt}} (PE) \) is of the order of
0.5–1.5 Pa s. This gives, again, an estimate for the rotational viscosity $\gamma$. It is of the same order of magnitude as the value of 4 Pa s from the electro-optic measurements of 3% samples. The larger gel former content in our mixtures may explain a somewhat higher viscosity.

One of the conclusions from the FTIR experiments has been that the switching angle drops rapidly in electric fields lower than $10^7$ V m$^{-1}$. However, this is not in contradiction with the measurements presented here, but is simply the consequence of the fast AC frequency (4 kHz) in the FTIR curves. An equilibrium balance of elastic and electric torques is not reached during the short field cycles. The conclusion that can be drawn from the FTIR curves is only that switching of the gel samples with fields below $10^7$ V m$^{-1}$ requires longer times than 250 $\mu$s. If the excitation frequency is lowered, the $c$-director will switch in much lower electric fields, as our electro-optic measurements have clearly shown. In the free standing films, a few kV m$^{-1}$ are sufficient to reorient the $c$-director, although with correspondingly long reorientation times (increasing proportional to the inverse electric field strength). We cannot exclude, however, that the preparation conditions of bulk samples in the FTIR experiments (for example, the cells are sheared to achieve uniform layer alignment) lead to other topologies and mechanical properties of the hydrogen bonded network.

Whereas the free standing gel films, due to the fragility of the network, may not have the potential for application in switching or display elements, it has been demonstrated here that they can be used to extract quantitative data on smectic hydrogen bonded gels. In particular, the transition into the gel state can be easily observed from the onset/disappearance of convective flow in the film plane. The problems to prepare free standing films with uniform director orientation by means of gelation in DC electric fields can be avoided in sandwich cells. In thin cells, sufficiently strong DC fields can be applied during the gel formation without excitation of flow in the sample, and it seems possible that defined textures are written and stored into the gel phase during gelation. The electro-optical experiments have demonstrated that hydrogen bonded gels may successfully replace chemically bonded gels for the stabilization of director textures, with the advantage that the network is reversible and the textures are erasable thermally.

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References


5. J. Prigann, C. Tolksdorf, H. Skupin, R. Zentel and F. Kremer, Macromolecules, 2002, 35, 4150. We note that this paper contains a misprint in the phase sequence of the gel mixture, the smectic A phase is missing.


