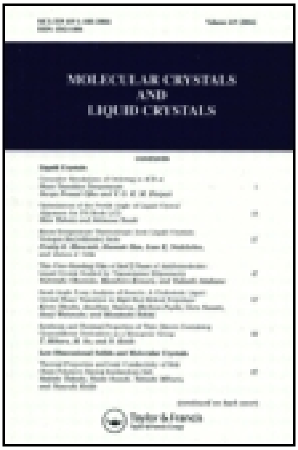

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Thin Ferroelectric Liquid Crystal Cells with Surface-Induced Alignment: Optical Characterization and Electro-Optic Performance

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Thin Ferroelectric Liquid Crystal Cells with Surface-Induced Alignment: Optical Characterization and Electro-Optic Performance†

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Different surface treatments commonly used for nematics have been tested for alignment effect on ferroelectric smectic C* liquid crystals. Thin samples of thickness around 2 μm are used in order to elastically unwind the helix present in the chiral smectic materials. Electro-optic measurements are made as a function of temperature and the viscosities are deduced. Response times and frequency cut-offs are presented for four different ferroelectric compounds. For some conditions bistability is observed. Different methods for obtaining good alignment are discussed in view of the reported observations.

INTRODUCTION

Surface-stabilized ferroelectric liquid crystal (SSFLC) cells, i.e. chiral tilted smectics in thin "book-shelf geometry" cells (see below), have achieved incomparably much faster switching than previous liquid crystal technologies.[1–15] However, device R & D is still in its infancy and further rapid progress is presently linked to two major factors: synthesis of new ferroelectric smectic substances and control of alignment methods for making large enough smectic C* monocrystalline samples. The work reported here is concerned with the latter point. Moreover, we report on measurements of response times for thin electro-optic cells that are surface-treated with a polyimide resin.

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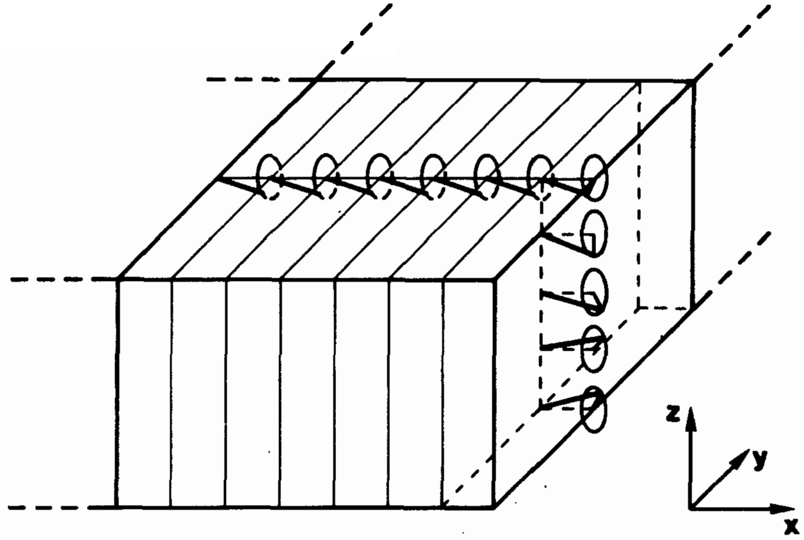
The original work on the SSFLC devices used an unconventional alignment method (shear in the smectic A phase), described for instance in references 1 and 5. This method gives high performance in homogeneity, bistability and speed, but complicated manufacturing and will probably put some restrictive limits on the obtainable size of the device. Conventional "nematic" alignment methods are much easier to work with but seem less adequate for smectics and, as described below, were found to give only moderate performance in some respects. We want to point out that only some "classic" compounds and some "classic" alignment procedures are reported in this study. In particular no experiments with "mixed" or "weak" surface conditions (different coatings or different treatments on the two sides) are included. With ferroelectric substances having the phase transition sequence N*-A-C* (so far hardly available), some of the conventional methods may be adapted[11] to the smectic case, such that the director is aligned in the (unwound) chiral nematic phase, then the layers locked at the N-A transition, and finally, the director unlocked at the A-C transition. Syntheses under way will soon allow us to extend the studies to this important case. Also, new alignment methods dedicated to the smectic C phase will be developed as documented by some recent results.[16]

The studies of different alignment layers were made with the model for smectic layer configuration shown in Figure 1 in mind. We refer to this as the "book-shelf geometry," where the books are the smectic layers. From now on we consider only cells thin enough, so that the spontaneous helix structure is not present in the samples. With the smectic layers confined in the book-shelf geometry there still exist several possible configurations for the $\hat{c}$ director through the sample, depending on the nature of the boundary conditions. For instance, with the very special boundary condition of freely rotatable director constrained to be in the plane of the glass plates, only two director states are possible:[1,2] molecules tilted $+\theta$ or $-\theta$ relative to the smectic layer normal (θ being the tilt angle). These states correspond to up and down directions for the spontaneous polarization $\vec{P}$ and make the cell operate in a bistable way. A short electric pulse of 10 volts and 10 microsecond duration is sufficient to switch between the up and down states. By further raising the voltage, sub-microsecond operation is possible.

The surface treatments used in the present work only weakly promote monodomain book-shelf geometry and they also give strong anchoring rather than a freely rotatable director. Finally, with several



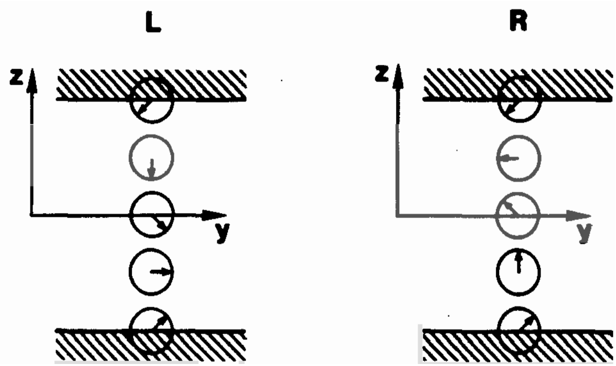


FIGURE 1 Smectic C* phase in the book-shelf geometry. The layers are perpendicular to the horizontal glass plates confining the sample. Along horizontal planes the director orientation is supposed to be homogeneous (helix unwound). This condition is less easy to obtain the more pronounced the spontaneous helix of the material (supposed to be chiral). Many different director configurations across the sample (within each layer) are possible. These depend primarily on the boundary conditions, especially if they are polar or not. A twisted configuration, with a planar boundary condition, is shown in the top drawing. Two director states obtained with tilted boundary conditions for the director are shown below (states R and L). The arrows shown for these states are the local ĉ directors. For the common minus type material (e.g. all materials used in this work) the direction of the local polarization is everywhere obtained by following the ĉ arrow and making a 90° right turn.

cases of strong anchoring, the boundaries may dominate the bulk even in the sense that the condition for the director is equivalent at both surfaces whereas the director configuration between the plates is distorted rather than corresponding to a minimum of bulk elastic energy. This will markedly affect (essentially in a negative way) the electro-optic switching properties of the cell. One of the many possible cases (with pre-tilt at the boundary) is exemplified in Figure 1.

Because the book-shelf geometry is rather hard to realize in practice, using the conventional aligning methods, most investigations of smectic C*-materials in this geometry had to be carried out only on small aligned domains. One aim of the work reported here is to see to what extent fast switching is observed also in such cells with boundary surfaces characterized by a more or less uniform layer and director orientation.

The other methods of obtaining the required book-shelf geometry can presently be listed as: strong magnetic field,[17] electric field,[18] shear flow,[5] spacer edges[19] and cooling in a temperature gradient.[20]

With a magnetic field, the alignment of the smectic is carried out in the phase transition region of coexisting isotropic and smectic A phases. This region is broad for smectic mixtures, making the alignment effect of the magnetic field more efficient. For a mixture where the phase transition region is spread out over 10°C, as is commonly the case, a field strength of 10–20 kGauss may be sufficient to obtain a homogeneous orientation, even in rather thin (2–3 μm) cells.[17]

The use of an electric field alone is the least effective method for alignment although it can be very powerful in combination with shear. It can also be used to improve orientation obtained by other methods, the major effect being to heal out defects. An obvious drawback of this method in applications is that the area outside the electrode pattern is not orientationally affected by the field, making it difficult to obtain an optically uniform background (cf. Figure 4).

Mechanical shear flow has a very strong alignment effect on the smectic layers,[5] making it possible to produce cells with the book-shelf geometry rather easily. Also, in this method the surfaces can be chosen to have very weak anchoring effects for the liquid crystal molecules, permitting the required in-plane motion in the switching process. However, as hinted at earlier, there may be practical difficulties when applying this alignment method of making switching devices of larger area. Finally it should be pointed out that different chemical classes of liquid crystal ferroelectrics behave very differently in their ability to align by shear, and also by other methods.

CELL PREPARATION

The influence of different boundary surfaces on the alignment of ferroelectric liquid crystals was compared with DOBAMBC and a ferroelectric mixture as test substances. In the comparative electro-optic studies additional substances were used. The molecular structure and thermal phase sequence for all liquid crystals used are given in Figure 2.

The different surface-treatments are applied on two ITO- (transparent conducting indium tin oxide) coated glass plates. The plates are held together by two stripes of aluminium tape to form a sandwich-cell of approximately 0.5 cm^2 area. The liquid crystal (being in the isotropic phase on filling) is sucked into the space between the glass plates by capillary force, and acts itself as spacer in the filled cell. Before assembling the cell the glass plates are carefully washed in a cleaning process consisting of ultrasonic agitation in methylene chloride to remove particles and organic contaminants. This step is followed by ultrasonic agitation in a Deconex detergent. The plates are then carefully rinsed in 18 MΩ DI-water and dried in a gas jet of clean nitrogen. The different surface treatments that were tested for DOBAMBC and mixture 1 are summarized in table I.

Every surface treatment was tested several times to check for reproducibility. Not all surface coating materials could be tested for DOBAMBC, since around the clearing point 117°C the aligning properties are lost for some materials, e.g. the silanes.

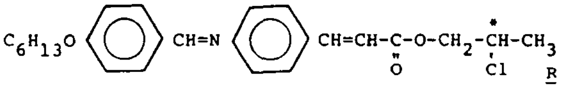
ALIGNMENT PROPERTIES OF DIFFERENT SURFACES

In the literature there are some reports on different methods for surface-induced alignment in the chiral smectic C phase, such as SiO evaporated obliquely,[21] rubbed polymeric coatings[22,23] and inorganic metal-oxides.[23] However, there is so far no classification of cell quality reported for the coatings.

The surface-treated samples in the present work were examined under a polarizing microscope. For comparison samples filled with a nematic reference substance were also prepared. In all cases a parallel director orientation of excellent homogeneity resulted for the nematic liquid crystal.

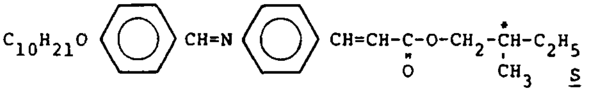
To obtain a smectic C single crystal is more complicated, since apart from the director orientation also the orientation of the smectic layers has to be controlled. One way to deal with this is to start with

MOLECULAR STRUCTURE THERMAL PHASE DIAGRAM



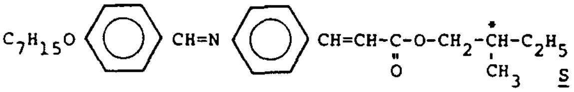
$X\ 60^{\circ}J^{*}\ 67.5^{\circ}I^{*}\ 73.5^{\circ}C^{*}\ 80$
$A\ 136^{\circ}L$

p-HEXYLOXYBENZYLIDENE-p'-AMINO-2-CHLORO-PROPYL-CINNAMATE
(HOBACPC)



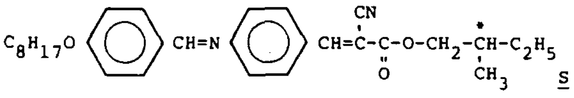
$X\ 76^{\circ}C^{*}\ 95^{\circ}A\ 117^{\circ}L$ (A)
$I^{*}\ 63^{\circ}$

p-DECYLOXYBENZYLIDENE-p'-AMINO-2-METHYL-BUTYL-CINNAMATE
(DOBAMBC)



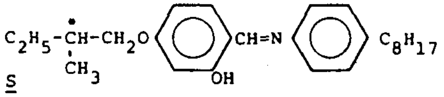
$X\ 75^{\circ}C^{*}\ 93^{\circ}A\ 119^{\circ}L$
$I^{*}\ 71^{\circ}$

p-HEPYLOXYBENZYLIDENE-p'-AMINO-2-METHYL-BUTYL-CINNAMATE
(HOBAMBC)



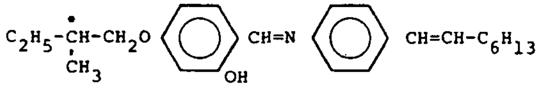
$X\ 89.4^{\circ}A\ 98.7^{\circ}L$ (B)
$C^{*}\ 73.5^{\circ}$

p-OCTYLOXYBENZYLIDENE-p'-AMINO-2-METHYL-BUTYL-CYANO-CINNAMATE
(OOBAMBCC)



$X\ 36^{\circ}C^{*}\ 50^{\circ}A\ 57^{\circ}L$ (C)

2-HYDROXY-4-(2-METHYL-BUTYLOXY)-BENZYLIDENE-4-pn-OCTYL-ANILINE
(MBRA 8)



(D)

2-HYDROXY-4-(2-METHYL-BUTYLOXY)-BENZYLIDENE-4-pn-OCTENYL-ANILINE

Mixture 1: 25 Mole % of D in C $X\ 28^{\circ}C^{*}\ 57^{\circ}A\ 64^{\circ}L$

Mixture 2: 15 weight % of B in the antipode of A

FIGURE 2 Molecular structures and liquid crystal phases of substances used in this work. Our phase designations are X, I, C, A, N and L for crystalline, smectic I, C, A, nematic and isotropic liquid phases respectively.

TABLE I

Surface coating scheme

Surface layer	DOBAMBC	Mixture 1	Solvent	Applying method for surface layer	Curing temp.	Curing time	Mechanical treat-ment	Supplier
PIQ[a]	T	—	N-methyl-2-pyrolidone	Spin-coated	350°C	30 min	rubbed[h]	HITACHI
SP510[b]	T	—	dimethyl-acetamide	Spin-coated	350°C	30 min	rubbed	TORAY
NYLON 11	T	T	m-cresol	Spin-coated	150°C	20 min	rubbed	COMMERCIAL
NYLON 6.6	T	T	m-cresol	Spin-coated	150°C	20 min	rubbed	COMMERCIAL
SiO (rubbed)	T	T	—	Evaporated	—	—	rubbed	—
SiO (evap.)	T	T	—	Obliquely evap.	—	—	—	—
TiO_2	—	T	toluene	Spin-coated	350°C	10 min	rubbed	MERCK
SiO_2	—	T	toluene	Spin-coated	350°C	10 min	rubbed	MERCK
SA72[c]	—	T	DI-water	Spin-coated	120°C	20 min	rubbed	AMERICAN LIQUID XTAL
SA73[d]	—	T	DI-water	Spin-coated	220°C	10 min	rubbed	AMERICAN LIQUID XTAL
SA74[e]	—	T	DI-water	Spin-coated	220°C	10 min	rubbed	AMERICAN LIQUID XTAL
Silan 133	—	T	DI-water	Spin-coated	120°C	20 min	rubbed	DOW CORNING
MAP[f]	—	T	DI-water	Spin-coated	120°C	20 min	rubbed	DOW CORNING
Parylene[g]	—	T	—	Plasma polymerization	—	—	rubbed	PHILIPS

T:tested, [a]PIQ-polyimide isoindroquinazoline-dione, [b]SP510-polymide resin, [c]SA72-polyvinylalcohol, [d]SA73-polyester resin, [e]SA74-polyimide resin, [f]MAP n-methyl-aminopropyltrimethoxy-silan, [g]Parylene-poly-para-xylene, [h]with conventional buffing machine (American Liquid Xtal No7, 9").

an already oriented texture in a phase of higher symmetry. For instance, the ferroelectric smectic phase may be entered via a nematic-smectic A phase change, or even an isotropic-smectic A phase change, where the A phase is "weak" in the sense that there "almost" exists a nematic phase (at a slightly different composition in the phase diagram, or in an adjacent homolog). It should be easier for the surface to affect the director orientation if the smectic layer structure is not so prominent. This is the case near the isotropic-smectic A transition, where smectic batonnets float in the isotropic liquid. One conclusion of this is that a mixture with a broad transition region should need an orientationally less "stiff" surface than a pure substance with a narrow transition region in order to show a homogeneous orientation in the smectic phase.

This is one of the observations that can be made from table II, where the results for the different cells are summarized. The textures in the smectic A phase are used for characterization: (1) Aligned texture, (2) Ordered fan-shaped texture and (3) Random fan-shaped texture. We can see that mixture 1 gives an aligned texture for a greater number of different surfaces than does pure DOBAMBC. In order to study the broadness of the transition peak, samples of DOBAMBC and mixture 1 were examined in a Mettler TA3000 DSC equipment. The transition peak at the isotropic-smectic A transition was approximately 1°C for DOBAMBC and 10–12°C for mixture 1.

TABLE II

Alignment properties for different surfaces

Surface layer	Alignment of the Nematic reference	Alignment for DOBAMBC	Alignment for mixture 1
PIQ	//	2	—
SP 510	//	1[a]	—
NYLON 11	//	2	1
NYLON 6.6	//	2	1
SiO (rubbed)	//	2[a]	2
SiO (evap.)	//	3[a]	2
TiO_2	//	—	3
SiO_2	//	—	2
SA 72	//	—	1
SA 73	//	—	1
SA 74	//	—	1
Silan 133	//	—	3
MAP	//	—	3
Parylene	//	—	1

[a] microphotographs shown in Figure 3, // parallel alignment.

It is sometimes helpful to look upon a surface interaction as being equivalent to the effect of an externally applied field. Keeping in mind the previously mentioned alignment effects of a magnetic field, we may introduce a surface index S_i giving the magnetic field strength required to obtain the same alignment effect as a certain surface coating. To make this kind of quantitative comparison of different surfaces, we need to characterize the resulting textures. There are several ways to do this. We can look at the batonnets at the isotropic-smectic A transition, or we may look at the texture in the smectic A phase or look at the texture in the smectic C phase. It turns out that there is a good correspondence, such that good batonnet alignment implies good alignment in the smectic phases and vice versa.

In Figure 3 are shown microphotographs of textures for three typical examples. The surface coatings are polyimide SP 510, rubbed SiO and obliquely evaporated SiO; the liquid crystal is DOBAMBC. Based on these observations for DOBAMBC, we might say that surfaces giving textures belonging to group 1 have $S_i \approx 50$ kG, corresponding to this very high magnetic field necessary when aligning pure DOBAMBC.[24] If next we compare the aligning effect of Nylon 11 for mixture 1 and DOBAMBC, we see that this gives texture (1) for the mixture but texture (2) for DOBAMBC. Since it has been found that a field of around 25 kG was sufficient to obtain good batonnet alignment in a thin sample of a ferroelectric smectic mixture,[17] it is appropriate to assign this value to surfaces giving textures of type (2). Finally, type (3) textures are obtained at low fields ($S_i \approx 10$ kG), the influence of the field being mainly to avoid the formation of homeotropic alignment. Comparing Figure 3a in this work with Figure 6 of reference 17 gives an illustration of the close similarity in surface-induced and magnetic-field-induced batonnet alignment, supporting our notion of surface index S_i. The classification scheme and surface index introduced here is to be seen merely as one step towards a more detailed description of smectic alignment on different surfaces.

Before continuing to discuss the consequences for the electro-optic switching behaviour of the cells, it is of interest to compare the difference in texture between a surface-aligned and a shear-aligned sample. In Figure 4 (a through f) is shown a shear-aligned 2 μm thick MBRA 8 cell as used for measurement of spontaneous polarization.[25] The smectic C* is very free of focal conic distortions and other large-scale defects and essentially shows no texture in the active area, even at very high magnification. The red and black states in Figure 4a and e are the extreme states (under applied field) corresponding to $+\theta$ and $-\theta$ tilt angles, or equivalently, to a homogeneous up and down

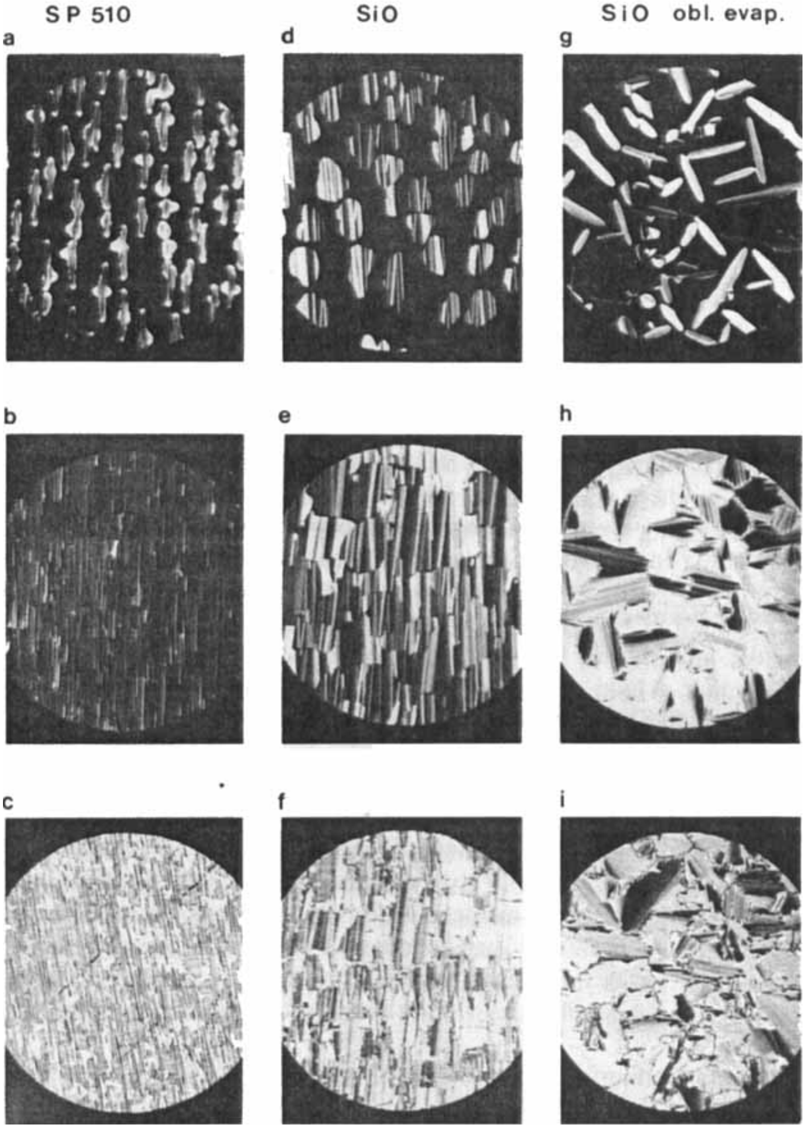


FIGURE 3 Textures obtained with DOBAMBC in cells with three different surface treatments: a-c polyimide SP 510, d-f SiO, rubbed, g-i SiO, obliquely evaporated. Smectic A batonnets in isotropic liquid are seen in a, d, g; smectic A textures in b, e, h and smectic C^* textures in c, f, i. The difference in batonnet alignment between a and g is clearly seen. The sample was rotated in c to show the two types of domain obtained in the C^* phase. The diameter of the sample area shown is 0.6 mm. Relation to classification (1,2,3) of smectic A textures in table II:b, aligned texture (1); e, ordered fan-shaped texture (2); h, random fan-shaped texture (3).

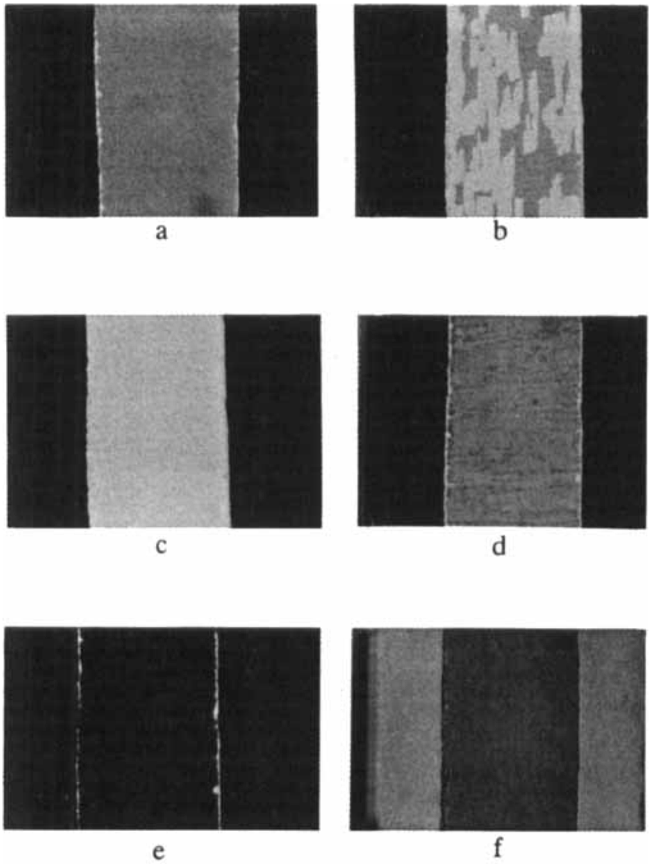


FIGURE 4 Photomicrographs of a portion of a shear-aligned cell of thickness $2\ \mu m$. The liquid crystal is MBRA 8 in the C^* phase at 35°C. The width of the activated electrode is 1 mm, and the active area seen is about $2\ mm^2$ out of a total aligned area of $20\ mm.^2$ a. The cell is connected to a DC voltage of $+10$ volts. The director is uniformly aligned in the sample at the tilt angle θ to the smectic layer normal, giving the red-violet birefringence colour between crossed polarizers. (Smectic layers are aligned parallel to the electrode edge.) b. The cell at a DC voltage of a few volts. In this situation coexisting domains of the extreme (homogeneous) state in a and the low-voltage (probably twisted) state in c is found. c. Low-voltage state, also found to be the field-free state. No extinction position is found between crossed polarizers in this case, suggesting a twisted director as discussed in the text. d. When reversing polarity compared to a-c, this bluish state is found at a few volts. Zig-zag walls[9] are here visible, becoming more prominent on raising the voltage and preceding the switching to the extinction state in e. e. At a DC voltage of -10 volts the opposite homogeneous extreme state $(-\theta)$ compared to a is found. f. Cell between parallel polarizers, showing SiO spacers (yellow absorption colour) and the green colour complementary to red-violet in a. See Color Plate IV, Volume 131, nos. 3-4.

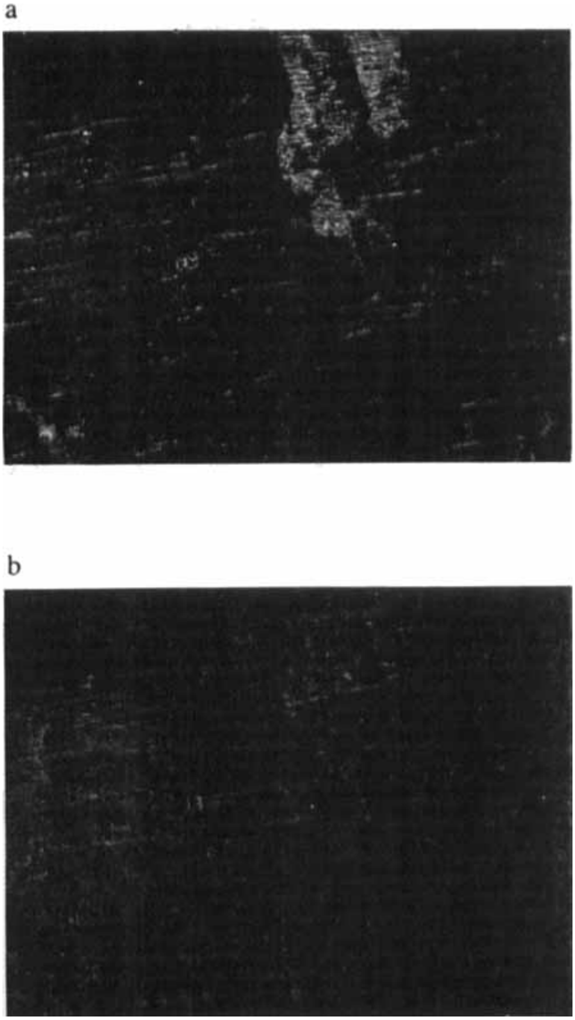


FIGURE 5 Two field-free states of mixture 2 in a cell with polyimide coating. Cross section of micrographs around 0.6 mm. Both states seem to be twisted and different structures are consistent with the switching behaviour, e.g. the ones described in references 27, 6 and 9, or the one in Figure 1. In all cases the director turns, from top to bottom, 180° around the tilt cone, and its xy projection turns clockwise or anti-clockwise by an angle less than 2θ. This will wave-guide the polarization plane of the traversing light in an incomplete manner, leading to elliptical polarization and incomplete extinction between crossed polarizers, and still incomplete but better extinction between some state of non-crossed polarizers. The wave-guiding has been especially well observed in reference 27, corresponding to the thick sample used in that work. See Color Plate V, Vol. 131, nos. 3-4.

polarization. In Figure 4b is shown the sample at an intermediate state between the extreme state in 4a and the field-free state in 4c. Changing polarity of the field results in state 4d, which at higher field changes into the other state 4e. Finally, Figure 4f shows the sample in the initial state but now with polarizers parallel. The sequence a to e demonstrates the possibility of ferroelectric colour switching, e.g. between black and white in addition to two colours.

In Figure 5(a,b) are shown for comparison two field-free optical states obtained with a polyimide-coated cell filled with mixture 2. (The switching between the states is discussed below.) The appearance of a marked texture in the sample is typical of surface-aligned cells, illustrating the difficulty to obtain a monodomain cell with such techniques. Often a macroscopically good orientation is found, but a microscopic study reveals a very distinct texture.

The book-shelf geometry is more or less obtainable with surface-induced alignment as indicated in table II. (A slight layer tilt is hard to detect unambiguously in textures containing a large number of defects and will here be left out of discussion.) However, it does not seem possible to obtain both a free rotation of the molecules near the boundary and a book-shelf geometry with the use of a nematic or A phase as preligned phase to the C phase. If an entrance from the nematic phase directly to the C phase takes place, alignment of the director is possible, but a twofold degeneracy of the orientation of the smectic layers will result.[26] If instead an entrance from the A phase is used, the book-shelf geometry may be obtained with a fair homogeneity, but the director orientation obtained for the A phase may not be compatible with the molecular tilt in the C phase. The result in this case will be a non-homogeneous director configuration through the sample. This is consistent with the experimental observation that in most cases no extinction is found between crossed polarizers in the C* phase, when there is no electric field applied across the sample.

As an example we may discuss the switching behaviour of the sample with the texture shown in Figure 5(a,b). It is not possible to analyze uniquely the direction of the coupled $\hat{n}$-$\vec{P}$ vectors across the sample, but one of the possibilities is the L and R pair of configurations with twist in $\hat{n}$ (and splay in $\vec{P}$) from Figure 1. Although the polarization is inhomogeneous in each state, there is a net upward component for L and a corresponding downward component for R. If the sample is assumed to be in L at zero voltage, corresponding to the green state in Figure 5a, a downward electric field ($-z$ direction) of about 10 volts will switch the colour to pink, corresponding to the major part of the molecules being forced to the west direction (with $\vec{P}$ down) by the electric field. On diminishing the applied field to zero the sample now relaxes to the R state corresponding to the brown texture of Figure 5b. If an upward field (+ z direction) is then applied the sample switches to a greyish state with fair extinction corresponding to an eastward majority $\hat{c}$ director and finally relaxes back to the green state (4a) when the field goes to zero. Although the definition is not as good as for a shear-aligned sample, in principle we find four differentiable states, two on-states and two off-states. Thus, by using pulses of opposite sign, we can switch between the two "memory" states of Figure 5a and b. The switching process probably involves both the field-induced transition from a twisted state to one of the extreme states and the subsequent relaxation back to the other twisted state. This accounts for the longer switching times needed to produce a switching compared to the original SSFLC-cell with shear alignment.

Another observation that should be made from table II is that not only the orientational anisotropy of the polymer chains (oriented by rubbing), or for oxide layers the microscopic grooves, are responsible for the aligning properties, but that also the chemical interactions between the surface material and the liquid crystal molecules are of importance. For instance polyimide and parylene surfaces have been found to give strong anchoring in the case of nematics.[28] Even for unrubbed surfaces of these materials strong (but random) anisotropic orientational effect was found, indicating that there is a strong chemical interaction between the polyimide layer and the liquid crystal molecules. The two polyimides PIQ and SP 510, which can be assumed to form very similar grooves when rubbed, produce different textures on DOBAMBC. The surface material having the best alignment effect on DOBAMBC is the polyimide SP 510 from Toray. Since this surface coating material also gives an aligned texture for the HOBACPC, HOBAMBC and MBRA 8 ferroelectric liquid crystals (see Figure 2), it was used to prepare cells for the test of bistability and the electro-optic measurements described in the next sections.

During the preparation of this article the authors were informed about the extensive work of Patel, Leslie and Goodby[29] concerning smectic alignment by polymers. For the products used in both studies, such as PVA and some nylons, our results seem to be consistent with theirs.

BISTABLE SWITCHING

Cells coated with the SP 510 polyimide resin were used to test bistable behaviour. To ensure that the observed memory effects are not a simple charged-capacitor effect, the cells were short-circuited and grounded.

In accordance with the previous discussion it is still experimentally difficult to control and analyze the director configuration across the sample for a surface-aligned smectic C phase. In most cases the homogeneous director configuration found in the smectic A phase does not remain in the C phase and it is not nearly as easy to obtain good extinction between crossed polarizers in the non-activated state as in shear-aligned non-twisted samples. As illustrated in Figure 1 there are many pairs of possible twisted director configurations consistent with the boundary conditions having nearly the same elastic energy. By passing through the sample, we can seen that the twist handedness can be right or left. It might then be possible to switch between the two states by applying an electric field across the sample as exemplified in the foregoing discussion. Thus a kind of bistable behaviour may be obtained even with boundary conditions giving strong anchoring for the director.[12] However, because the $\nabla \cdot \vec{P}$ field is completely different in the two configurations, the states may really differ appreciably in energy, depending both on bulk properties but, more important, on the polar nature of the boundary conditions. The switching will generally be asymmetric, and in most cases slow, incomplete and inefficient because only a small component (if any) of the applied field will be favourably directed to drive one state to the other.

The bistable behaviour was reproducible for the C* phase only at sample thicknesses below approximately 2 μm in DOBAMBC, HOBACPC and a mixture of DOBAMBC (the less common antipode) and OOBAMBCC (p-octyloxybenzylidene-p'-amino-2-methyl-butyl-α cyano-cinnamate). In the similar but more ordered smectic I* phase below the C* phase in HOBACPC and DOBAMBC, bistability is also seen in cells of around 4 to 5 μm thickness. To investigate if the critical thickness d_c of around 2 μm for bistability in the C* phase is related to the helical pitch, a mixture was prepared (mixture 2) of R-DOBAMBC and S-OOBAMBCC which have opposite helical handedness. By mixing in 15 weight % of OOBAMBC a helical pitch of the order 20 μm is achieved as compared to 1.5–3 μm for pure DOBAMBC. However, d_c does not change; the mixture still showed bistable behaviour only in cells below approximately 2 μm. These results show that d_c, not unexpectedly, is different for different smectic phases and confirms the interpretation[13] that d_c is rather a critical thickness for uniform polarization across the sample.

ELECTRO-OPTIC MEASUREMENTS

We now continue to study the difference in electro-optic response of four different ferroelectric liquid crystals: DOBAMBC, HOBAMBC, HOBACPC and MBRA 8. As indicated above, it was possible to obtain aligned samples with these materials. The spontaneous polarization $\vec{P}$ is lowest for MBRA 8 and highest for HOBACPC, with a factor of about 5, at the relevant temperatures, between the two.

Measurement cells were prepared from two ITO-coated glass plates that were sealed with UV-sealant, which was screen-printed onto one of the plates. This method makes it possible to expose the glue when the glass plates are observed to be parallel in monochromatic light from a Hg-lamp. In this way very thin cells of around two micrometers with good uniformity in layer thickness are obtained. The cell thickness is measured by polychromatic interference in a Shimadzu UV-240 spectrophotometer. The active area of the cells is about 1 cm^2.

The main measurement concerned cell response to a 100 Hz square wave of amplitude varying between 2 and 11 volts. In the optical response two characteristic times τ_{on} and τ_{off} are measured between 10% and 90% transmission (cell placed between crossed polarizers). In Figure 6 are shown the measured response times for the four investigated liquid crystals as a function of applied voltage at different temperatures in their smectic C* range. The samples were temperature-controlled to within ± 0.2°C in a Mettler hot stage. The measurements were made with a He Ne laser as light source (wavelength 632.8 nm) and a photodiode as detector. The signal from the diode was fed into an operational amplifier with a rise time of less than 1 μs. The area of the expanded laser light beam crossing the sample is about 4 mm^2 (this is the area of the sample used in the optical response measurements).

In most cases τ_{on} and τ_{off} are observed to be almost the same. Therefore, we show only $\tau \equiv \tau_{on}$ in Figure 6. Asymmetric response ($\tau_{on} \neq \tau_{off}$) was found especially for MBRA 8 at temperatures below 42°C, and in the supercooled smectic C* phase of DOBAMBC. The asymmetry is more pronounced at lower voltages.

The experimental points may be fitted to a straight line in a log τ − log V diagram for voltages above 6V. For HOBACPC this fitting is also possible at lower voltages, presumably as a result of the higher polarization in that material. From Figure 6 we see that one single exponential relation is not sufficient to describe the behaviour of τ as a function of voltage. Also, the curves for MBRA 8 tend to show an irregular behaviour at lower temperatures.

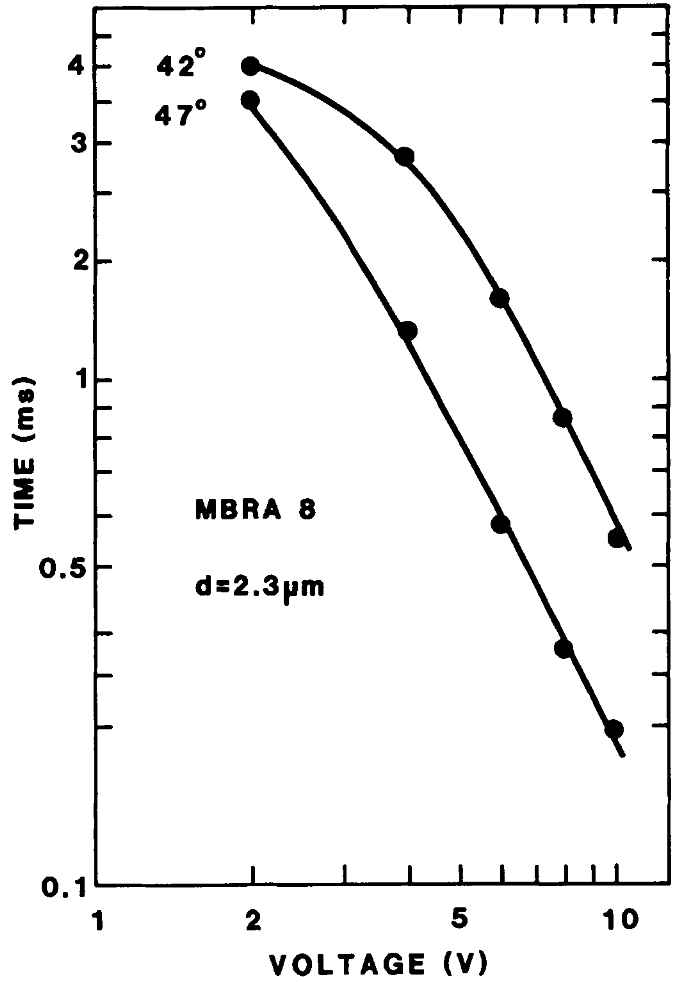


FIGURE 6 (a) Curves showing log τ versus log V for MBRA 8. The corresponding curves for HOBAMBC, DOBAMBC and HOBACPC at different temperatures are shown in figures (b), (c) and (d) respectively. Measuring square wave frequency 100 Hz in all cases.

A simple estimate for the response time τ for high field switching in the bulk of the sample is[5]

$$\tau = \frac{\eta}{P \cdot E}$$

where η is a rotational viscosity. It is found that τ may be fitted to

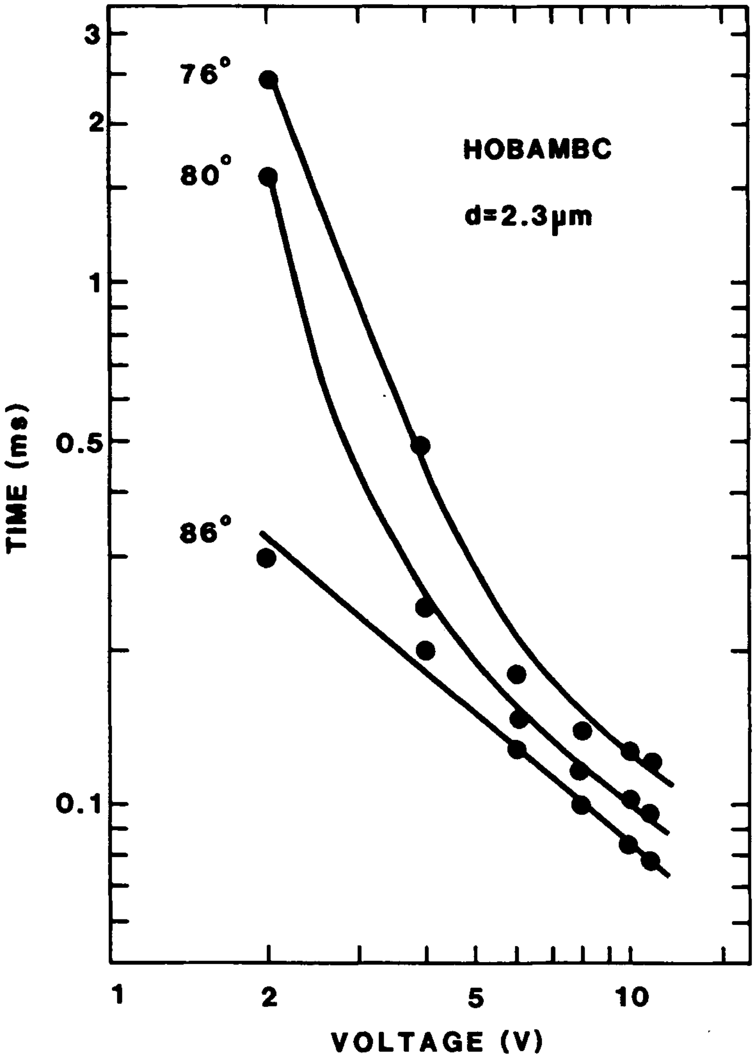


FIGURE 6 (b) *Continued*

this relation for voltages above 6V, that is $\tau \sim 1/V$, since $E = V/d$, where d is the sample thickness. A plot of τ versus $1/V$ is shown in Figure 7 for the different liquid crystals. From the slopes of the straight lines, fitted to the expression for τ by the least-squares method, we get the ratios η/P. Based on the literature values for the polari-

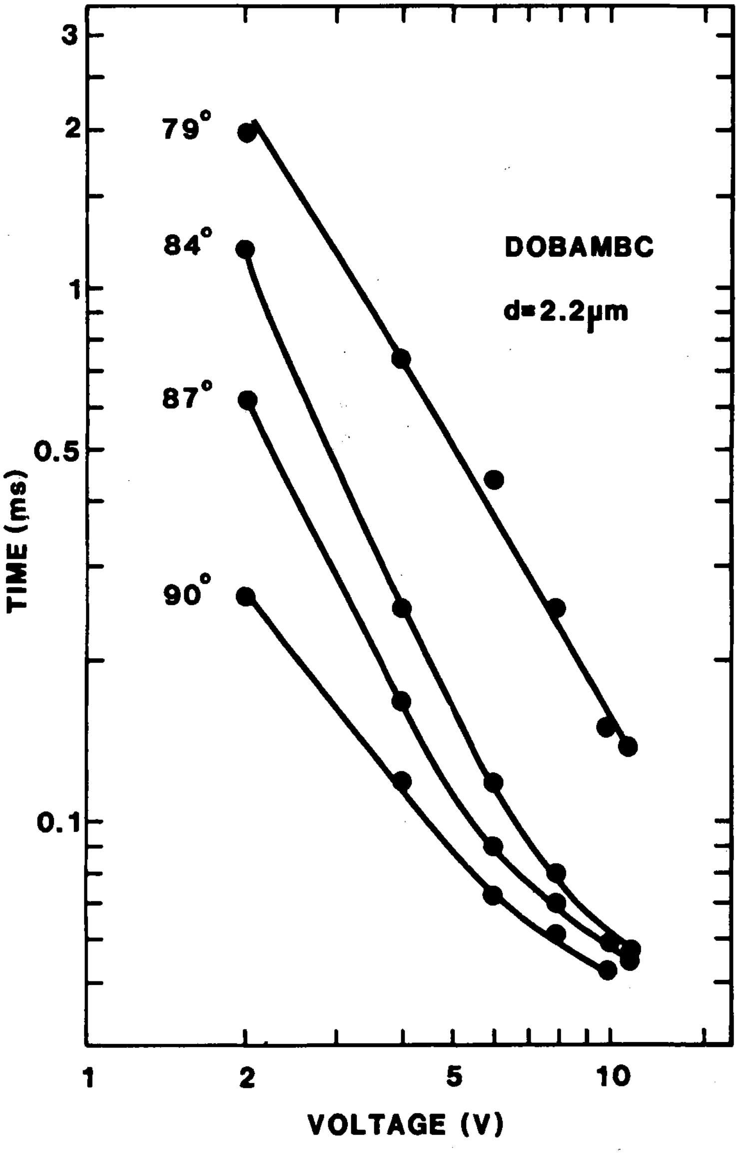


FIGURE 6 (c) *Continued*

zation P we may in this way estimate η from the measurements of τ. The results are given in table III.

The value of HOBACPC at 75°C, $\eta = 2 \times 10^{-2}$ Ns/m^2, may be compared to a typical nematic rotational viscosity γ_1, which is usually

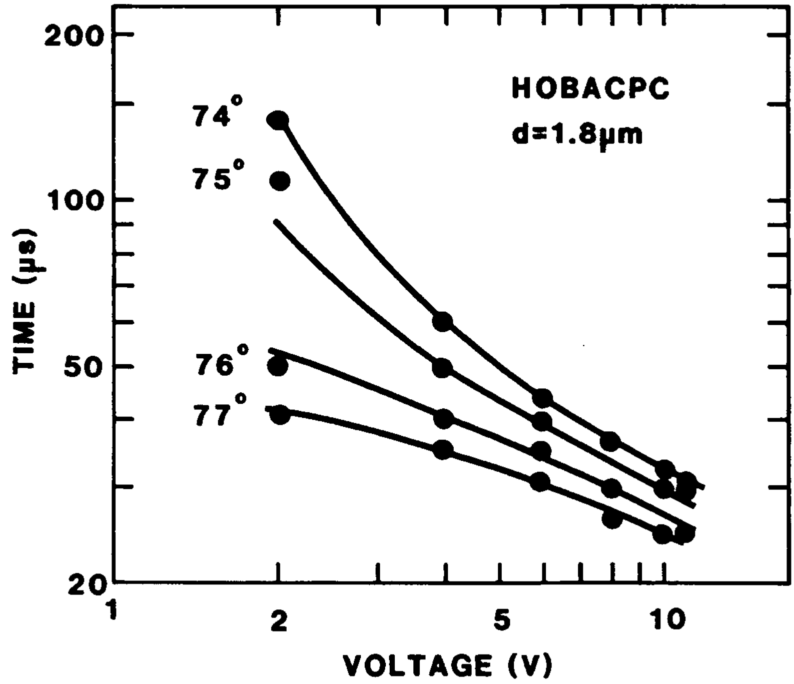


FIGURE 6 (d) *Continued*

of the order of 0.1 Ns/m^2. Since the corresponding viscosity for smectic C liquid crystals may be expected to be scaled[32] by a factor sin θ where θ is the tilt angle (from reference 18, θ in this case is equal to 11 degrees), we would for a nematic-like case get $\gamma_1 \sin\theta = 2 \times 10^{-2}$ Ns/m^2, in line with our result for HOBACPC.

With a step voltage of 11 volts amplitude applied across a 2 μm sample of HOBACPC at 77°C, a response time of 16 μs was measured, in accordance with earlier measurements on shear-aligned cells.[1,8] An oscilloscope trace showing this response is seen in Figure 8(a). The differences in response time between the different materials are displayed in Figure 8(b,c,d), where the wave form of the optical response at 1 kHz is shown for HOBACPC, DOBAMBC and MBRA 8.

If we look at the cells as light modulator elements, we may ask where the frequency cut-off in the optical response occurs. For the different materials there is a frequency band where the modulation amplitude tends to zero. For square-wave excitation of 22 V peak-

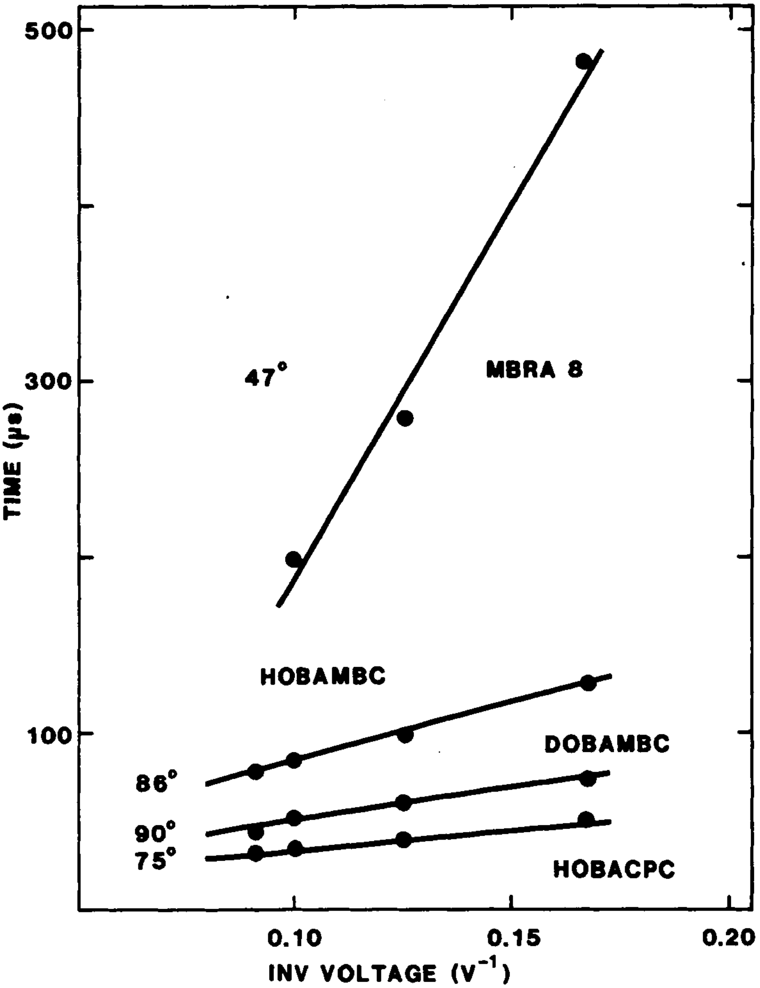


FIGURE 7 Response time τ versus 1/V. From the slopes of the straight lines an estimation of the rotational viscosity can be made (see table III).

to-peak, the modulation amplitude as a function of frequency is given in Figure 9. It is seen that there is good agreement between the frequencies where the modulation amplitudes go to zero and the response times shown in Figure 6.

With a square-wave of 11 volts amplitude and with the simple alignment techniques used, the present cells work as light modulators

TABLE III

Rotational viscosities

Liquid crystal	T (°C)	η/P (Vs/m)	P ($\times 10^{-5}$As/m^2)	η ($\times 10^{-3}$Ns/m^2)
MBRA 8	47°C	2900	1.2[a]	35 ($\theta \sim 12°$)
HOBAMBC	86°C	290	—	—
DOBAMBC	90°C	180	3.7[b]	6.7 ($\theta \sim 15°$)
HOBACPC	75°C	130	16[c]	21 ($\theta \sim 11°$)

[a] Ostrovskii et al.,[30] [b] Blinov et al., [31] [c] Wahl and Jain.[8]

in the kiloherz range. As can be seen from the inserted oscilloscope traces in Figure 9, the modulation amplitude starts to drop at about 10 kHz for HOBACPC at 77°C. A small optical modulation can be seen up to about 70 kHz. For higher speed the voltage has to be increased, which requires samples of high purity in order to avoid large ionic currents and chemical degradation.

For the MBRA 8 sample, a maximum of 20% transmittance was observed ("ON"-state), while 4% was transmitted in the "OFF"-state. (100% = transmittance with parallel polarizers without sample; 0% = transmittance between crossed polarizers without sample.) Corresponding figures for HOBACPC were 13% and 2%, while HOBAMBC and DOBAMBC showed 20% and 2%. These values were measured with a photomultiplier in white light. The transmittance in the ON-state is mainly determined by cell thickness, tilt angle and birefringence of the liquid crystal. The OFF-state transmittance is very sensitive to alignment homogeneity, which is not nearly as good as in the case of a carefully shear-aligned sample.

CONCLUSIONS

It is found that a book-shelf geometry of a reasonable homogeneity for smectic C* liquid crystals may be obtained even with fairly conventional surface treatment. The best alignment effect was found when using a polyimide resin. The texture obtained for the smectic A phase with this method can be compared to the one obtained for the same phase sequence L-A-C in a very strong magnetic field. The obvious practical advantages of a surface-induced alignment method rather than a magnetic field or shear induced method motivates further study of the interaction between aligning layer and liquid crystal

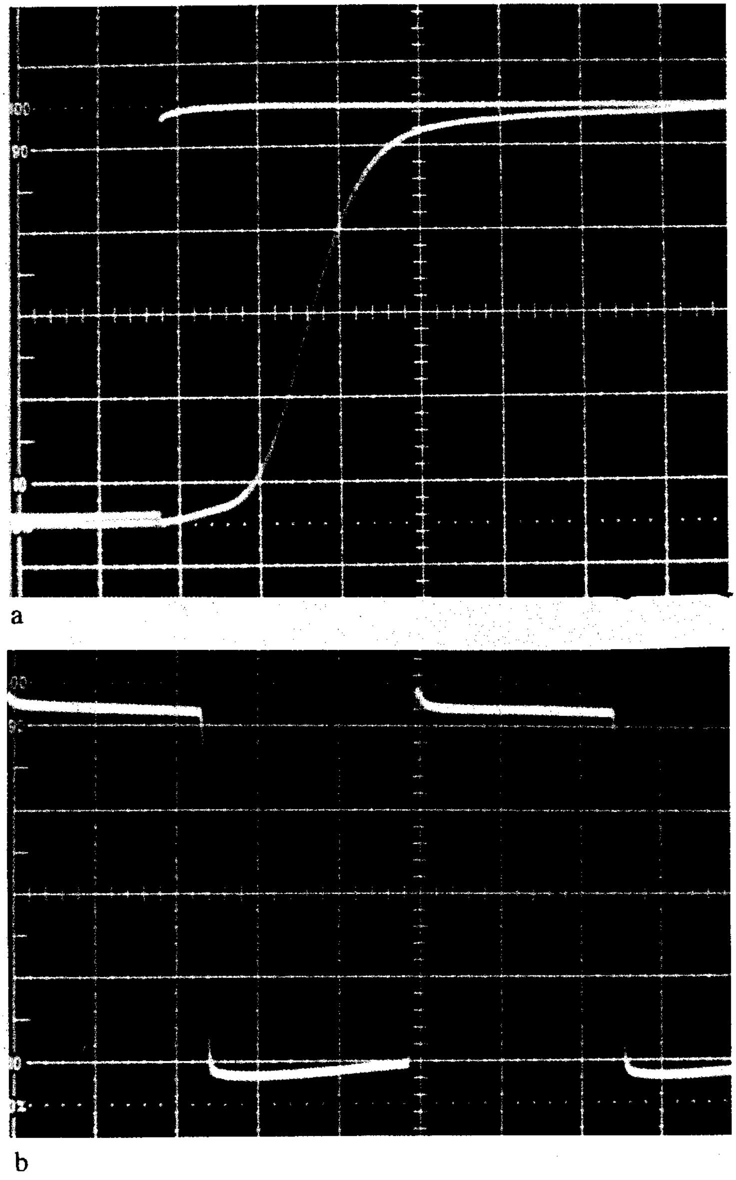
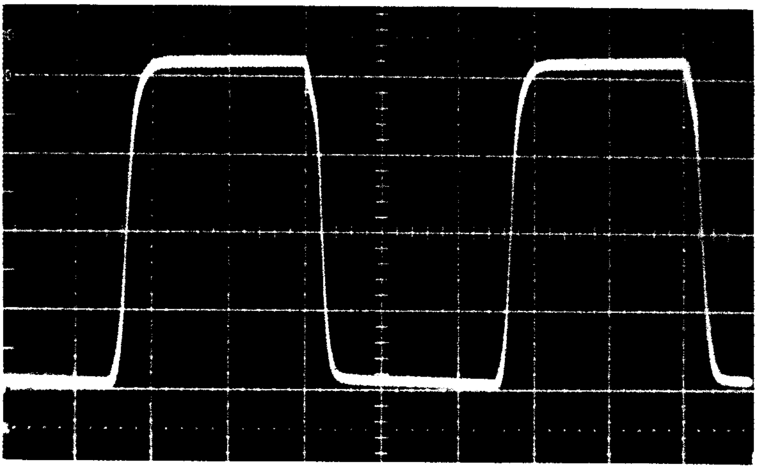


FIGURE 8 (a) Oscilloscope trace of the photodiode output in response to a step voltage for HOBACPC at 77°C. Time scale 10 μs/div. Amplitude of voltage step 11 V. The rise time between 10 and 90% transmission is 16 μs. Figures (b), (c) and (d): Oscilloscope traces for optical response to a 1 kHz square wave excitation of 11 V amplitude; (b) HOBACPC, 77°C; (c) DOBAMBC, 87°C; (d) MBRA 8, 47°C. Time scale 200 μs/div.



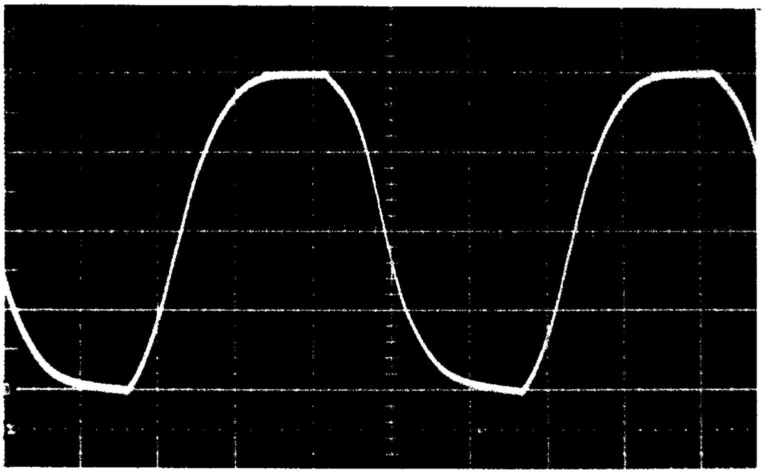


FIGURE 8 *Continued*

molecules. Especially the conditions for obtaining bistable behaviour for inhomogeneous director fields, observed in this work in cells with polyimide coating giving strong anchoring at the boundaries, need closer attention.

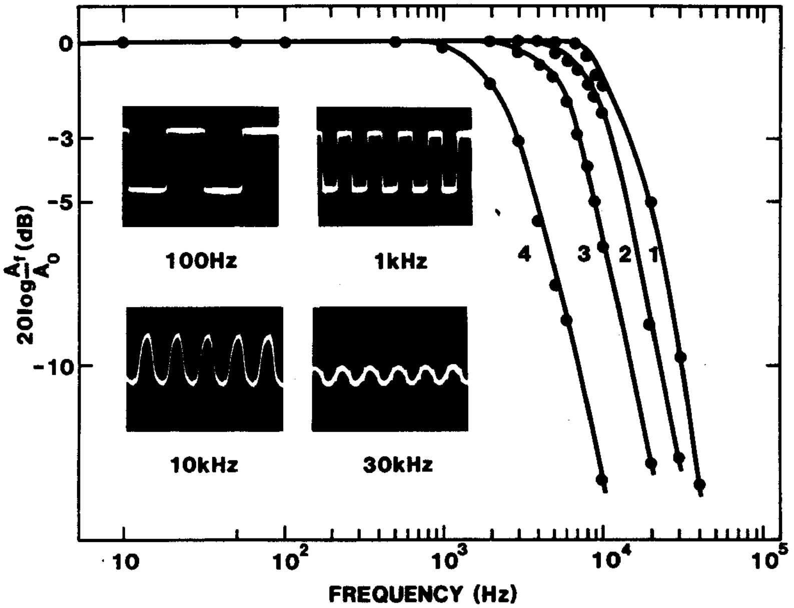


FIGURE 9 Frequency characteristics for the four ferroelectric smectics when applying a square wave of 11 V amplitude: (1) HOBACPC, d = 1.8 μm, T = 75°C; (2) DOBAMBC, d = 2.2 μm, T = 87°C; (3) HOBAMBC, d = 2.3 μm, T = 81°C; (4) MBRA 8, d = 2.3 μm, T = 47°C. A_0 is the amplitude of the optical response at low frequencies. Inserted is shown the response of HOBACPC at 77°C, left to right: 100 Hz, 1 kHz, 10 kHz, 30 kHz.

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