

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Photomechanically induced phase transitions in ferroelectric liquid crystals

H. J. Coles^a; H. G. Walton^a; D. Guillon^b; G. Poetti^c

^a The Liquid Crystal Group, Department of Physics, The University of Manchester, Manchester, England ^b IPCMS, Strasbourg Cedex, France ^c Dipartimento di Science Chimiche dell'Università, Camerino, MC, Italy

To cite this Article Coles, H. J. , Walton, H. G. , Guillon, D. and Poetti, G.(1993) 'Photomechanically induced phase transitions in ferroelectric liquid crystals', *Liquid Crystals*, 15: 4, 551 – 558

To link to this Article: DOI: 10.1080/02678299308036474

URL: <http://dx.doi.org/10.1080/02678299308036474>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

PRELIMINARY COMMUNICATIONS

Photomechanically induced phase transitions in ferroelectric liquid crystals

by H. J. COLES*†, H. G. WALTON†, D. GUILLON‡
and G. POETTI§

† The Liquid Crystal Group, Department of Physics,
The University of Manchester, Manchester M13 9PL, England

‡ IPCMS, 6 Rue Bousingault, 67083, Strasbourg Cedex, France

§ Dipartimento di Science Chimiche dell'Università,
Via S. Agostino, 1, 62032 Camerino (MC), Italy

(Received 24 June 1993; accepted 26 June 1993)

We demonstrate that the addition of small amounts of a novel azo-dye to a ferroelectric liquid crystal and illumination with low intensity ($\sim 0.8 \text{ mW cm}^{-2}$) UV light can result in reversible, isothermal phase transitions and dramatic changes in the properties of the system. In particular we examine light induced transitions between the S_r^* and S_g^* phases and the consequent photomechanical regulation of spontaneous polarization.

Liquid crystals have excited considerable scientific interest over the past decade or so because of their ability to affect the properties of light transmitted through or reflected from them. Optical properties, such as birefringence, dichroism, fluorescence, light scattering or specular reflection, have all been used in information display devices. These optical properties, which depend on the orientation of the liquid crystal material, may be altered by the application of reorientating electric or magnetic fields, thereby providing a simple device. However, very recently there has been a considerable growth of interest in the counter photomechanical process in which light is used to alter the properties of the liquid crystal itself. Since the energies necessary to alter the ordering in liquid crystals, polymer liquid crystal networks and biological membranes, are orders of magnitude lower than those needed to deform normal ionic crystals, these partially ordered systems are ideal candidates for the observation of photomechanical effects and they offer great potential for use in novel optical devices and transducers. In the present work we will demonstrate that very low light levels may be used to induce, in a controlled and reversible fashion, isothermal phase transitions in a chiral liquid crystal system. Coincident with a phase transition, there are changes in the optical, mechanical and electrical properties of the system. In the present work, we concentrate particularly on reversible, isothermally induced changes in the electrical properties of different ferroelectric phases with a view to producing new photonic-transducers and memory devices.

* Author for correspondence.

Photomechanical effects are most reliably achieved by incorporating soluble photoisomerizable guest molecules into an anisotropic host. On illumination, the guest molecule undergoes an isomeric shape change which leads to a local or microscopic molecular reordering. Since the guest and host closely interact, this reordering is *amplified* from the microscopic scale to produce changes in the macroscopic properties of the host. The literature contains several examples of photonically controllable macroscopic properties such as osmotic potential [1], surface wetting of droplets [2], polymer solubility [3] and the electrical conductivity of Langmuir–Blodgett films [4]. Eich and Wendorff [5] showed that sheets of a side chain polymer liquid crystal, containing an azo-side group, underwent a texture change when illuminated by near UV light, chosen to isomerize the azo units. They were able to demonstrate holographic image storage in this fashion, further illustrating the potential of such materials for optical data storage devices. Ichimura *et al.* [6], used layers of azo-dye molecules as optically controllable alignment surfaces for liquid crystals. In the biological sciences, light induced changes in the properties of membranes lie at the heart of understanding vision.

In the field of liquid crystals, the work has concentrated, until recently, primarily on photomechanical effects occurring in the nematic phase. Legge and Mitchell [7] and Ikeda *et al.* [8], have shown that the *trans*- to *cis*-isomerization of small amounts of an azo-dye dissolved in a nematic host is sufficient to disrupt the order to such an extent as to induce a transition to the isotropic phase. It is thought that the bent *cis*-isomer is less easily packed into the nematic matrix and tends therefore to disrupt the ordering of neighbouring liquid crystal molecules. The azo-dyes are a particularly useful family of isomerizing molecules for studying photomechanical processes because of both the reversibility of the isomerization and the large steric difference between the two isomeric states (see figure 1). As will be discussed in a forthcoming article [9], two discrete processes are involved in converting the material isothermally from the nematic to the isotropic phase. Firstly, the orientational order has to be disrupted and then the material has to be driven through the phase transition. This involves quite marked input power densities ($\geq 10 \text{ mW cm}^{-2}$) for changes taking several tens of seconds to be induced. To gain faster responses or to use lower input power densities requires a much lower distortion energy.

Most recently research has begun to be undertaken on photomechanical effects occurring in the smectic phases of some liquid crystals. Smectic phases have a lamellar or layer like structure with varying degrees of order or disorder in each layer. The smectic A (S_A) phase has orientation in each layer with the molecules pointing, on average, in the same direction as the layer normal. In the S_C phase the system has the same lack of positional order, whilst the molecules are, on average, inclined at some tilt

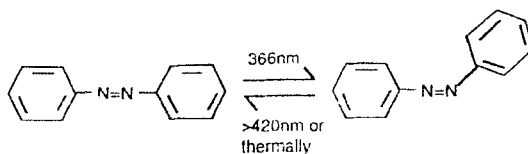


Figure 1. Showing *trans*-*cis* isomerization of azobenzene. The *trans*-isomer is very nearly planar. The *cis*-isomer occupies a plane at 56° to the plane occupied by the rest of the molecule.

angle, θ , to the layer normal. In the S_I phase, the structure is similar to the S_C phase except that the molecules now have a pseudo-hexagonal close packing within each layer plane and are tilted towards the apex of each hexagon (see figure 2). There is long range bond orientational order, but there are no interlayer correlations. There are other higher ordered smectic phases, but herein we are concerned with S_A , S_C and S_I phases. If chiral structures are used, then it is possible to induce twisted structures which lead to interesting display devices due to the altered symmetry. For example, as was originally predicted by Meyer [10] in 1975, any tilted smectic phase composed of chiral molecules such as the chiral S_C^* or S_I^* phase should give rise to finite spontaneous ferroelectric polarization, P_s . Since the twist elastic energy involved is weak, it should be possible to alter the symmetry of the system and therefore P_s by photomechanical reordering of the molecules. Indeed we were able to confirm recently [11] the existence of photomechanically controllable ferroelectricity in a commercially available S_C^* liquid crystal host mixture (SCE13, Merck Ltd. U.K.) incorporating liquid crystalline azo-dyes (see below). We use low power UV illumination ($\sim 0.8 \text{ mW cm}^{-2}$). Ikeda *et al.* [12], were able to repeat the result for a second system. Using a pulsed YAG laser, it was shown that the magnitude of P_s could be reduced by UV-exciting the azo-dopant in the system to the *cis*-state, the assumption being that the *cis*-isomers disrupt the S_C^* ordering, thereby shifting the system towards a less ordered phase. In the present work, we considerably generalize the result to show that full scale transitions between smectic phases are possible. In such situations, there is a change in P_s as well as many other parameters of the system. We show that it is possible to induce a full transition from the S_C^* to the less ordered S_A phase, the non-tilted analogue of the S_C , with a consequent fall of P_s to zero. In addition, instead of beginning with the system in the S_C^* phase and inducing a transition to a non-chiral phase, we show that it is possible to begin with the system in the S_I^* phase and cause a transition to the then comparatively less ordered S_C^* phase. We will show that photomechanical conversion between chiral smectic phases is readily achieved. Thus, as a general phenomenon it is possible to manipulate photonically the spontaneous polarization, or any other chosen parameter of a ferroelectric medium, leading to new device applications.

The liquid crystal material used in the experiments reported here is the commercially available 4-(2'-methylbutyl)phenyl 4'-*n*-octylbiphenyl-4-carboxylate, denoted CE8 (Merck Ltd. U.K.). Its chemical structure is shown below.

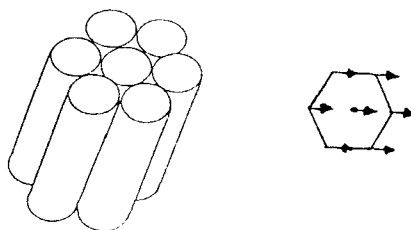
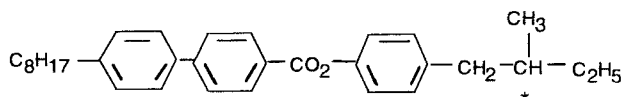
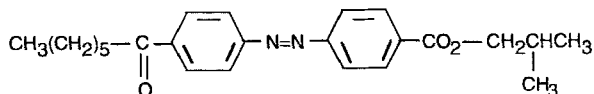


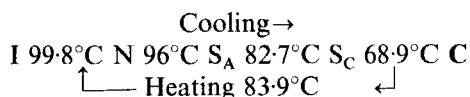
Figure 2. Structure of the S_I phase. Molecules are pseudo-hexagonally close packed within the layers with a tilt toward the apex of the hexagon. There are no inter-layer correlations.

CE8 has a particularly rich sequence of anisotropic phases and these have been characterized in detail by Budai *et al.* [13]. The sequence, as a function of decreasing temperature is given in the top line of the table.

The azo-dye, hereafter denoted N5, used to dope the liquid crystal is shown below:



The dye N5 is an unusual dopant in that it is itself liquid crystalline, exhibiting N, S_A and S_C mesophases, with the following phase sequence:



We used this liquid crystallinity to ensure good miscibility and high solubility in CE8. During the course of the work, concentrations in excess of 10 per cent wt : wt N5 in CE8 were prepared with no obvious signs of N5 crystallizing out of solution. The phases of pure N5 were characterized both by DSC and by polarizing light microscopy. There was no degradation of the liquid crystalline properties of N5 over a 2 year period indicating its long term chemical stability. The dye has a small effect on the phase transition temperatures as shown in the lower line of the table above. There was no evidence of biphasic behaviour within the temperature resolution (0.1°C) of the experiment.

Spectrometry before and after UV-excitation confirmed the presence of a reversible *trans*-/*cis*-isomerization through the induced changes in the absorption spectrum. The *trans*- to *cis*-isomerization had a maximum absorption at 350 nm and the reverse *cis*- to *trans*-change was driven either thermally or via light of 450 nm.

All samples were contained in glass sandwich cells with the inner surfaces coated with a rubbed polyimide alignment layer giving rise to planar sample alignment, and patterned with transparent ITO film which enabled electric fields to be applied across the liquid crystal. The sample thickness was 7.5 μm. To measure the magnitude of P_s, the well-known current pulse technique [14] was used. A short flow of current is measured as the molecules switch between their two ferroelectric states under the influence of an external triangular wave driving voltage. A computer was used to integrate the area of the current pulse to yield the P_s values. To UV illuminate the samples, light from a 100 W Hg-lamp was filtered to select the region 300 to 400 nm with a maximum at 350 nm. The glass cell only strongly absorbed light of wavelength below 270 nm. The power density of such UV light at the cell was always 0.8 mW cm⁻². When not illuminated, the cell was kept in darkness and a microscope hot stage (Linkam THM 600) was used to control the temperature of the sample to ±0.1°C.

System	Phase transition/°C					
	S _G *-S _J *	S _J *-S _I *	S _I *-S _C *	S _C *-S _A *	S _A *-N*	N*-I
Pure CE8	44.8	61.7	67.0	83.5	133.4	138.9
5 per cent wt: wt NS in CE8	42.5	57.1	62.4	79.7	131.0	136.3

Figure 3(a) shows the current pulse response of a sample of CE8 + 5 per cent N5 (wt : wt) held at a reduced temperature, T_{red} , 3°C below the transition from the S_C^* to the S_A phase. A 100 Hz, $22 V_{\text{p-p}}$ triangular wave driving voltage, shown in the upper figure, is applied to the cell. The middle figure shows the polarization current response of the cell in the S_C^* phase. The current pulses in the response indicate the dipolar ferroelectric switching. The lower figure shows the current response after 30 s of applied UV on the sample. It is clear that ferroelectricity has vanished and the switching is characteristic of the S_A phase. Figure 3(b) shows the temporal variation of P_s for a sample at $T_{\text{red}} = 5^\circ\text{C}$. The sample is exposed to UV for 85 s. It is clear that the fall in P_s is fully reversible upon

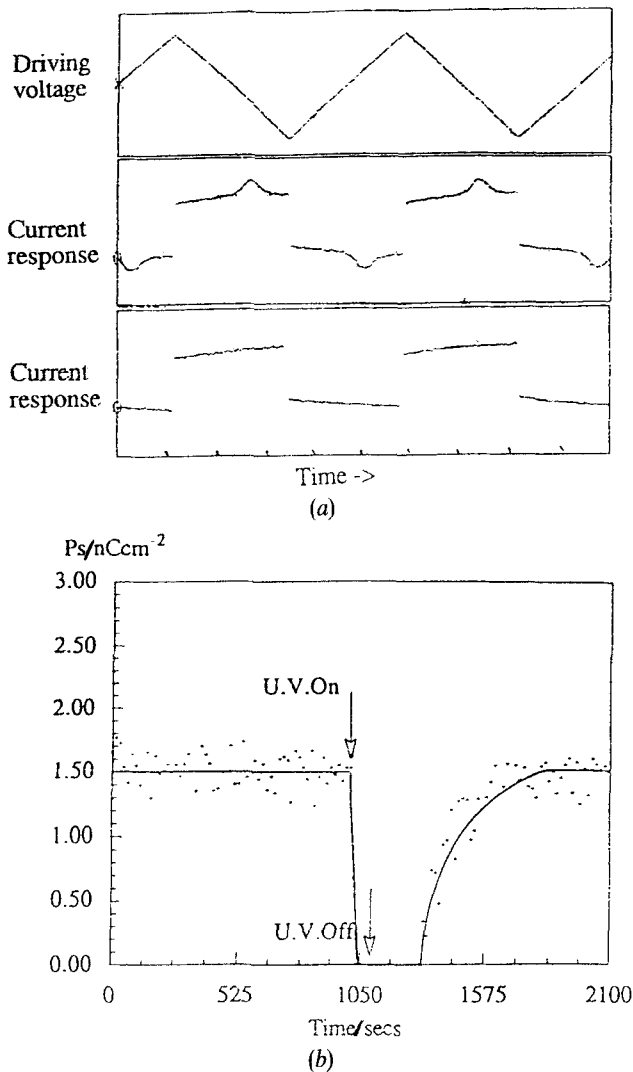


Figure 3. (a) CE8 + 5 per cent N5, $T_{\text{red}} = 3^\circ\text{C}$, showing the driving voltage $22 V_{\text{p-p}}$ (upper frame), the current response in the S_C^* phase (middle) and after UV illumination (lower). The time axis is $2.0 \text{ ms division}^{-1}$. (b) Spontaneous polarization at a reduced temperature of 5°C as a function of time before, during and after UV illumination for CE8 + 5 per cent N5 wt : wt.

removal of the UV and that the sample has undergone no permanent degradation since the P_s returns to its pre-UV illumination value. These effects were exactly reproducible over tens of cycles. We verified that these processes were isothermal and no temperature jumps which could account for such a change in P_s were manifest in the sample. The temperature was constant to within 0.1°C . Thus the change in P_s on UV illumination must be due to an increased population of the N5 *cis*-isomer which disrupts the packing of the CE8 molecules. For $T_{\text{red}} > 5^\circ\text{C}$, the P_s still decreases, but no longer to zero at the same UV power density. As the temperature is decreased still further, the amount by which UV irradiation reduces the P_s is also reduced. Again, as the temperature is lowered and the thermal fluctuations of the CE8 molecules reduce, we would expect the disruption of ordering caused by an N5 *cis*-isomer to be decreased. As a control experiment, the measured P_s of samples of pure CE8 was unaffected by UV illumination under the same conditions. For a 1 per cent wt:wt addition of N5, no changes in P_s could be reliably detected, but 2 per cent samples showed similar results to those of the 5 per cent added N5, the difference being that in order to cause a complete disappearance of P_s the sample needed to be held at a temperature closer to the S_A phase than for the 5 per cent samples. This again fits our proposed mechanism, since fewer azo-molecules are available to photomechanically switch the spontaneous polarization of the CE8 host system. Thus it is clear that in the S_C^* phase, the P_s may be photomechanically switched to a chosen lower value or the material transformed to a S_A phase with a complete disappearance of P_s .

From the above, it is clear that the order of the S_C^* phase is being reduced on application of the UV light. We decided to test this hypothesis further by studying the S_I^* to S_C^* transition. For a CE8 + 7 per cent (wt:wt) mixture held at 0.5°C below the S_I^* to S_C^* transition, we monitored the polarization current pulse as a function of time before and after UV illumination (see figure 4(a)). The UV was applied for 60 s. In the upper frame, the applied triangular wave of $22V_{p-p}$ is again shown. The middle frame shows the weakly deformed current response due to the hexagonal S_I^* structure before UV illumination, whilst the lower frame shows the marked current pulse after UV illumination. The latter switching behaviour is clearly characteristic of the S_C^* phase.

The symmetry of the S_I^* phase is such that it must be ferroelectric and therefore exhibit a spontaneous polarization. The hexagonal packing of molecules in the S_I^* phase results in there being no more than the two simple switched states found for a S_C^* phase (Shao *et al.* [15] reported 8 stable states for a S_I^*). Each time the molecules are switched to a new state, there is a short flow of charge as the P_s vector rotates, and at a high enough resolution, these current pulses can be observed and analysed to determine P_s . At a lower resolution, however, the individual current pulses are not separated and smear out to give an approximately flat current response as the sample is switched. At this resolution, and for CE8, the P_s as determined by the current pulse technique for the S_I^* phase is therefore zero, since the individual current pulses are not separated. We are interested here in the transition from the S_I^* to the S_C^* phase, and hence it is sufficient to record the P_s as zero in the S_I^* phase and finite in the S_C^* phase, and to look for the phase transition. Figure 4(b) shows the time evolution of the measured P_s before, during and after illumination with UV light. Upon illumination, the shape of the current response curve changes to show a single current pulse, as shown in figure 4(a), and the measured P_s rises sharply to a value of 0.6 nC cm^{-2} . On removal of the UV illumination, the P_s returns to its original zero level as the system returns to the S_I^* phase. Thus we conclude that the S_I^* structure has been transformed isothermally to the lower ordered S_C^* phase upon UV illumination.

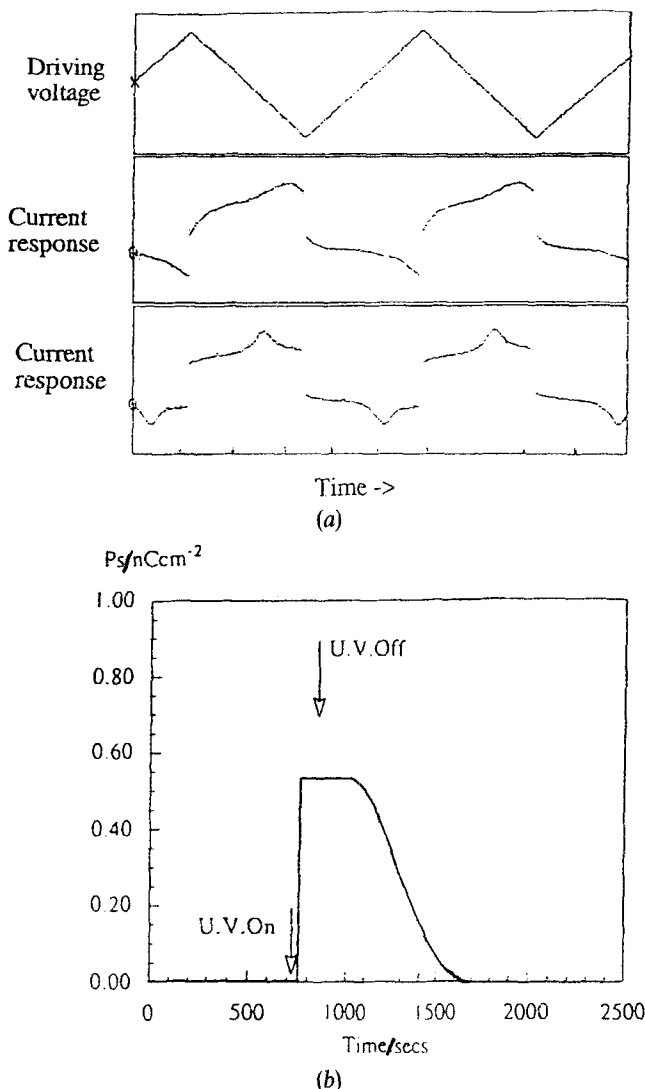


Figure 4. (a) Polarization current for CE8+7 per cent N5 at a reduced temperature of 0.5°C . The upper trace shows the applied voltage, whilst the middle trace shows the current response in the S_1^* phase before UV illumination. The lower trace shows the UV induced polarization. The time axis is $2.0\text{ ms division}^{-1}$. (b) Spontaneous polarization as a function of time for CE8+7 per cent N5 at $T_{\text{red}}=0.5^{\circ}\text{C}$, before, during and after UV illumination.

In conclusion, we have been able to demonstrate the ability to induce phase transitions reversibly and isothermally in a single component ferroelectric liquid crystal doped with a liquid crystalline photoisomerizing azo-dye, using very low light levels (i.e. power densities 0.8 mW cm^{-2}). The results are in agreement with the hypothesis that the bent *cis*-isomer of an azo-dye is less easily packed into the smectic phases than the *trans*-isomer and an increase in *cis*-isomer population produces a corresponding reduction in smectic ordering, even to the extent of inducing a transition to a less ordered phase. By carefully choosing the starting phase and phase sequence, we may alter the spontaneous polarization at will. This effect appears to be cyclable many

times. Since the azo-dyes are stable over a period of years and present at low concentration, it is the stability of the ferroelectric host that is of primary importance for cyclability of any potential device. The use of only low power density UV irradiation is of advantage here. We also point out that a potential device would not need to be continually irradiated to record information. One could envisage a bistable device in which the liquid crystal was initially in one switched state, with an electric field being applied below the level of the threshold field necessary to switch the molecules to their other bistable state. To record a data bit, the system could then be briefly irradiated in order to induce a transition to a less ordered state at which the field being applied was sufficient to switch the liquid crystal. The UV light would then be removed, leaving the system to relax in this second switched state. Such a device would not need to be especially resistant to long term UV light induced degradation.

Although we have focused on photonically induced changes in ferroelectric spontaneous polarization, photomechanical reordering of a liquid crystal will result in changes in any parameter we care to probe and we will report at a later date the concomitant changes in response time, tilt angle, $\Delta\epsilon$ etc., for both high and low P_s systems. These isothermal photomechanically induced changes in the macroscopic properties have applications in photonic transducers and optical data storage devices, as well as implications for smart opto-electronic imaging systems and visualization mechanisms. In this paper we have reported preliminary photoinduced S_i^* to S_c^* and S_c^* to S_A transitions, but one can easily envisage similar transitions involving antiferroelectric, ferroelectric, TGB phases and higher ordered smectics. We are currently exploring these further.

H. G. W. thanks the SERC for financial support.

References

- [1] IRIE, M., and KUNWATCHAKUN, D., 1987, *Macromolecules*, **19**, 2476.
- [2] IRIE, M., and TANAKA, H., 1983, *Macromolecules*, **16**, 210.
- [3] ISHIHARA, K., 1983, *J. polym. Sci. Polym. Chem. Ed.*, **21**, 1551.
- [4] TACHIBANA, H., NAKAMURA, T., MATSUMOTO, M., KOMIZU, H., MANDA, E., NIINO, H., YABE, A., and KAWABATA, Y., 1989, *J. Am. chem. Soc.*, **111**, 3080.
- [5] EICH, M., WENDORFF, J. H., RECK, B., and RINGSORF, H., 1987, *Makromolek. Chem. rap. Commun.*, **8**, 59.
- [6] ICHIMURA, K., SUZUKI, Y., SEKI, T., HOSEKI, A., and AOKI, A., 1988, *Langmuir*, **4**, 1214.
- [7] LEGGE, C. H., and MITCHELL, G. R., 1992, *J. Phys. D*, **25**, 492.
- [8] IKEDA, T., MIYAMOTO, T., KURIHARA, S., and TAZUKE, 1990, *Molec. Crystals liq. Crystals*, **188**, 207.
- [9] COLES, H. J., and TAYLOR, M., *Liq. Crystals* (in preparation).
- [10] MEYER, R. B., LIÉBERT, L., STRZELECKI, L., and KELLER, P., 1975, *J. Phys., Paris*, **36**, L69.
- [11] COLES, H. J., LESTER, G., WALTON, H., GUILLON, D., and POETTI, G., 1992, *Fourteenth International Liquid Crystal Conference, Pisa*. Abstract C-P59, p. 248.
- [12] IKEDA, T., SASAKI, T., and ICHIMURA, K., 1993, *Nature*, **361**, 428.
- [13] BUDAI, J., PINDAK, R., DAVEY, S. C., and GOODBY, J. W., 1984, *J. Phys. Lett., Paris*, **45**, L1053.
- [14] MIYASO, K., ABE, S., TAKEZOE, H., FUKUDA, A., and KUZE, E., 1983, *J. appl. Phys. Japan*, **22**, L661.
- [15] SHAO, R., ZHUANG, Z., and CLARK, N. A., 1991, *Ferroelectrics*, **122**, 213.