

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>

Modulating the spontaneous polarization of a ferroelectric liquid crystal via the photoisomerization of a chiral thioindigo dopant: (*R,R*)-6,6'-bis(1-methylheptyloxy) thioindigo

Liviu Dinescu^a; Robert P. Lemieux^a

^a Department of Chemistry, Queen's University, Kingston, Canada

To cite this Article Dinescu, Liviu and Lemieux, Robert P.(1996) 'Modulating the spontaneous polarization of a ferroelectric liquid crystal via the photoisomerization of a chiral thioindigo dopant: (*R,R*)-6,6'-bis(1-methylheptyloxy) thioindigo', *Liquid Crystals*, 20: 6, 741 – 749

To link to this Article: DOI: 10.1080/02678299608033167

URL: <http://dx.doi.org/10.1080/02678299608033167>

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.

Modulating the spontaneous polarization of a ferroelectric liquid crystal via the photoisomerization of a chiral thioindigo dopant: *(R,R)*-6,6'-bis(1-methylheptyloxy)thioindigo

by LIVIU DINESCU and ROBERT P. LEMIEUX*

Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6
Canada

(Received 9 January 1996; accepted 15 January 1996)

Doping the novel chiral photochromic dye *(R,R)*-6,6'-bis(1-methylheptyloxy)thioindigo into the S_C liquid crystal host MX6120 at a concentration of 7.2 mol % gives rise to a ferroelectric S_C^* phase with a reduced polarization (P_0) of $+14.4 \text{ nC cm}^{-2}$. Results of time-resolved experiments demonstrate that the dye undergoes *trans*→*cis* photoisomerization in the S_C phase, although the efficiency of photoisomerization is significantly lower than in the nematic and isotropic liquid phases. A reversible modulation of P_S on the order of 10 per cent is observed for the doped S_C^* phase upon photoisomerization of the dye from a thermally relaxed *trans* form ($+6.2 \text{ nC cm}^{-2}$) to a *cis*-enriched photostationary state ($+5.6 \text{ nC cm}^{-2}$) at $T - T_c = -10^\circ\text{C}$. Control experiments using mixtures of the racemic and optically active dye in a S_C^* host suggest that P_S photomodulation does not arise from a photomechanical effect. Consideration of the Boulder model for the molecular origins of P_S provides a rationale for the observed P_S photomodulation based on changes in the conformational equilibria of the 1-methylheptyloxy side-chains in the S_C binding site going from the *trans* form to the *cis* form of the thioindigo dopant.

1. Introduction

Over the past fifteen years, the search for new chiral materials exhibiting or inducing a S_C^* liquid crystal phase has been motivated by the potential application of such materials in surface-stabilized ferroelectric liquid crystal (SSFLC) displays [1]. These electro-optical switches have high viewing contrasts and switching speeds two to three orders of magnitude faster than those achieved in twisted nematic liquid crystal displays. Furthermore, the unique bistability of the SSFLC display affords the possibility of using this technology in the fabrication of erasable optical memory devices [2, 3]. One of the important challenges remaining in the development of a SSFLC-based optical memory device is the development of a laser addressing mechanism for the liquid crystal display.

In 1980, Clark and Lagerwall [4] showed that the helix of a S_C^* liquid crystal phase spontaneously unwinds when the S_C^* phase is aligned between polyimide-coated glass slides with a S_C^* thickness on the order of $5 \mu\text{m}$. As predicted by Meyer, the dissymmetry of this surface-

stabilized bookshelf orientation gives rise to a finite spontaneous polarization (P_S) oriented perpendicular to the glass slide, i.e. transverse to the molecular long axis [5]. The magnitude of P_S is a function of the chiral component(s) of the S_C^* phase, and depends in part on the degree of steric coupling between the asymmetric centre and the functional group(s) contributing to a dipole moment transverse to the molecular long axis [6, 7]. Switching the SSFLC between bookshelf orientations corresponding to $+P_S$ and $-P_S$ is achieved by applying an electrical field across the glass slides. Unlike conventional electro-optical switches based on the twisted nematic effect, each orientation is maintained by surface interactions upon removal of the electrical field (bistability).

The polarization reversal of a SSFLC is characterized by a sharp switching threshold that is a function of P_S [1]. A SSFLC cell can be envisioned as a capacitor, i.e. upon polarization reversal, a matching charge must be on the capacitor plates to stabilize the surface charges of the FLC. In order to switch from $+P_S$ to $-P_S$, an applied voltage pulse must therefore supply a total charge corresponding to at least $2P_S$ per unit area A . This *pulse* threshold is defined as the lowest value of the product of the applied voltage V and voltage pulse length τ_p that results in polarization reversal $(\tau_p V)_{th}$; for

*Author for correspondence.

†Presented in part at the Fifth International Ferroelectric Liquid Crystal Conference, 5-9 July 1995, University of Cambridge, England.

a SSFLC in a standard RC circuit, the pulse threshold is directly proportional to P_S . Hence, it may be possible to control the switching of a SSFLC display via modulation of P_S by shifting the pulse threshold above and below a set value for $(\tau_p V)$. Ikeda and co-workers recently described a similar approach to the photochemical addressing of a SSFLC display based on the coercive force (or voltage threshold) modulation that results from the reversible *trans*–*cis* photoisomerization of a mesogenic azobenzene dopant in a S_C^* liquid crystal host [8, 9]. The origin of the observed modulation in both the coercive force and spontaneous polarization of the SSFLC is thought to be a mechanical effect associated with the change in shape of the azobenzene dopant from rod-like (*trans*) to bent (*cis*), which affects the stability of the host S_C^* phase. This so-called *photomechanical effect* was also shown by Coles and co-workers to produce significant changes in the magnitude of P_S via isothermal $S_C^* - S_A$ and $S_I^* - S_C^*$ phase transitions in commercial CE8 and SCE13 liquid crystals doped with a mesogenic azobenzene [10, 11].

In terms of a device application, it would be desirable to achieve the photoaddressing of a SSFLC display in the visible range of the spectrum rather than in the near UV region (the *trans*→*cis* photoisomerization of azobenzene dopants is achieved at 355 nm), without concomitant destabilization of the liquid crystal phase. Using the pulse threshold modulation approach (*vide supra*), it may be possible to develop a photoaddressed SSFLC display based on P_S modulation via a photoinduced change in the transverse dipole moment of a chiral dopant that maintains a rod-like shape in both isomeric forms. In an effort to develop chiral photochromic dopants with these specifications, we report the synthesis and characterization of the novel thioindigo dopant **1**, with chiral side-chains derived from optically active 2-octanol.

The photochromism of thioindigo and its derivatives is due to a reversible *trans*–*cis* photoisomerization analogous to that of stilbene (see figure 1) [12]. 6,6'-Dialkoxythioindigo derivatives such as **1** are well suited for device applications: they are characterized by photoisomerization quantum efficiencies on the order of 0.45 in both directions, and by absorption maxima for the *cis*- and *trans*-isomers that coincide almost exactly with two wavelengths available from an ionized argon laser, 458

and 514.5 nm, respectively [13]. As a dopant in a S_C liquid crystal host, it is envisioned that a photoinduced change in transverse dipole moment of the thioindigo core in **1** should result in a corresponding change in P_S that is a function of the rigid steric coupling between the thioindigo core and the asymmetric centre in the 1-methylheptyloxy side-chain. Furthermore, molecular mechanics calculations suggest that a 6,6'-dialkoxythioindigo dopant such as **1** maintains a rod-like shape in either isomeric form, which should therefore minimize photomechanical effects. We report that doping of (*R,R*)-**1** in a S_C liquid crystal host induces a ferroelectric S_C^* phase, and that irradiation of this mixture at two different wavelengths corresponding to the *cis*- and *trans*-isomers of **1** results in a reversible modulation of P_S on the order of 10 per cent.

2. Experimental

2.1. Synthesis

All reagents were obtained from commercial sources and used without further purification. Dimethylformamide (DMF) was distilled from BaO under reduced pressure and stored over molecular sieves. Methylene chloride (CH_2Cl_2) was freshly distilled from P_2O_5 . Methyl 4-hydroxy-2-nitrobenzoate (**2**) was prepared by a literature procedure [14]. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-400 NMR spectrometer in deuteriated chloroform. The chemical shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard. Low-resolution EI mass spectra were recorded on a Fisons VG Quattro triple quadrupole mass spectrometer; peaks are reported as m/z (per cent intensity relative to the base peak). High-resolution mass spectra were recorded on JEOL AX-102 and AX-505 instruments. Optical rotations were measured on a Perkin–Elmer 241 polarimeter at room temperature. Elemental analyses were performed by Guelph Chemical Laboratories Ltd. Differential scanning calorimetry analyses were carried out using a Perkin–Elmer DSC-7 instrument with a cooling rate of 2°C min^{-1} . Melting points were measured on a Mel-Temp II melting point apparatus and are uncorrected.

2.1.1. Methyl (*R*)-(–)-2-nitro-4-(1-methylheptyloxy)benzoate ((*R*)-**3**)

Under a N_2 atmosphere, 0.64 g (3.7 mmol) of diethylazodicarboxylate (DEAD) was added by syringe

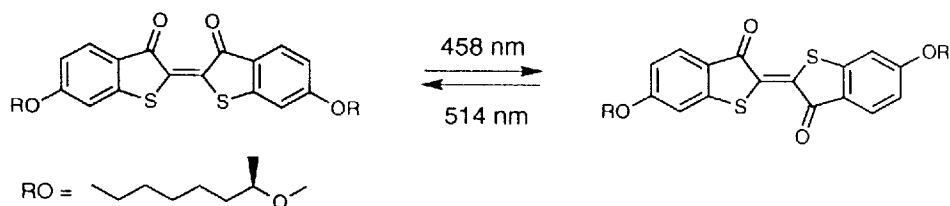


Figure 1. Photoisomerization of the thioindigo dopant (*R,R*)-**1**.

to a solution of **2** (0.48 g, 2.4 mmol), (*S*)-2-octanol (0.42 g, 3.2 mmol) (Aldrich) and triphenylphosphine (0.96 g, 3.7 mmol) in 20 ml of dry CH_2Cl_2 . The mixture was stirred at room temperature for 1 h. The solvent was removed *in vacuo* and the solid residue purified by flash chromatography on silica gel (10 per cent ethyl acetate/toluene) to give 0.59 g of (*R*)-**3** as an oil. Yield 80 per cent. $[\alpha]_{\text{D}} = -9.87^\circ$ (CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 0.87 (t, $J = 6.9$ Hz, 3 H), 1.20–1.42 (m, 8 H), 1.32 (d, $J = 6.1$ Hz, 3 H), 1.52–1.62 (m, 1 H), 1.70–1.79 (m, 1 H), 3.86 (s, 3 H), 4.42 (m, $J = 6.1$ Hz, 1 H), 7.05 (dd, $J = 2.4$ Hz, $J = 8.7$ Hz, 1 H), 7.18 (d, $J = 2.4$ Hz, 1 H), 7.75 (d, $J = 8.6$ Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 19.3, 22.5, 25.2, 29.1, 31.7, 36.0, 52.8, 75.3, 110.5, 117.2, 118.4, 132.0, 150.9, 161.2, 164.9 MS (EI) m/z 309 (M^+ , 8), 278 (8), 197 (26), 181 (82), 166 (100), 151 (18), 120 (13), 112 (34), 107 (21), 92 (23), 83 (32). High-resolution MS; calculated for $\text{C}_{16}\text{H}_{23}\text{NO}_5$: 309.1576. Found: 309.1584.

2.1.2. Methyl (*R*)-(+)-3-hydroxy-6-(1-methylheptyloxy)benzo[*b*]thiophene-2-carboxylate ((*R*)-**4**)

Under a N_2 atmosphere, 0.3 g (2.8 mmol) of methyl thioglycolate and 0.15 g (6.2 mmol) of anhydrous LiOH were added to a solution of (*R*)-**3** (0.55 g, 1.8 mmol) in 20 ml of dry DMF. The mixture was stirred vigorously at room temperature for 24 h. The mixture was diluted with 50 ml of water, neutralized with aqueous HCl and extracted twice with ether. The combined extracts were dried (MgSO_4) and the solvent removed *in vacuo* to give an oily residue. Purification by flash chromatography on silica gel (10 per cent ethyl acetate/toluene) gave 0.36 g of (*R*)-**4** as an oil. Yield 60 per cent. $[\alpha]_{\text{D}} = +12.3^\circ$ (CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 0.87 (t, $J = 6.9$ Hz, 3 H), 1.20–1.42 (m, 8 H), 1.32 (d, $J = 6.1$ Hz, 3 H), 1.52–1.62 (m, 1 H), 1.70–1.79 (m, 1 H), 3.92 (s, 3 H), 4.42 (m, $J = 6.1$ Hz, 1 H), 6.96 (dd, $J = 2.2$ Hz, $J = 8.8$ Hz, 1 H), 7.12 (d, $J = 2.2$ Hz, 1 H), 7.79 (d, $J = 8.8$ Hz, 1 H). MS (EI) m/z 336 (M^+ , 7), 224 (30), 192 (100), 163 (29), 136 (35), 135 (36), 120 (16), 108 (13). High-resolution MS; calculated for $\text{C}_{18}\text{H}_{24}\text{SO}_4$: 336.1395. Found: 336.1385.

2.1.3. (*R,R*)-(+)-6,6'-Bis(1-methylheptyloxy)thioindigo ((*R,R*)-**1**)

A suspension of ester (*R*)-**4** (0.36 g, 1.1 mmol) in a 10 per cent solution of KOH in 1:1 ethanol/water (20 ml) was refluxed for 5 h. After cooling, the mixture was neutralized with aqueous HCl and extracted twice with ether. The combined extracts were dried (MgSO_4) and the solvent removed *in vacuo* to give the crude benzo-thiophenone (*R*)-**5** as an oily residue. Without further purification, (*R*)-**5** was oxidized by treatment with a large excess of potassium ferricyanide in 20 ml of 95 per

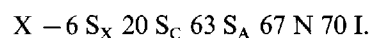
cent ethanol under reflux for 24 h. After cooling, the alcohol was removed *in vacuo* and the residue purified by flash chromatography on silica gel (benzene) to give 70 mg of (*R,R*)-**1** as a red solid. Yield 23 per cent. The dye was further purified by recrystallization from 95 per cent ethanol. m.p. 90–91°C. $[\alpha]_{\text{D}} = +8.90^\circ$ (C_6H_6). ^1H NMR (400 MHz, CDCl_3) δ 0.88 (t, $J = 6.9$ Hz, 6 H), 1.20–1.42 (m, 16 H), 1.34 (d, $J = 6.1$ Hz, 6 H), 1.52–1.62 (m, 2 H), 1.70–1.79 (m, 2 H), 4.49 (m, $J = 6.1$ Hz, 2 H), 6.76 (dd, $J = 2.0$ Hz, $J = 8.6$ Hz, 2 H), 6.92 (d, $J = 2.0$ Hz, 2 H), 7.81 (d, $J = 8.6$ Hz, 2 H). ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 19.6, 22.5, 25.4, 29.1, 31.7, 36.2, 74.9, 109.3, 114.6, 122.2, 128.4, 132.8, 151.6, 165.0, 188.0. MS (EI) m/z 552 (M^+ , 71), 440 (16), 328 (100), 311 (5), 299 (16), 271 (27), 243 (8), 227 (7), 166 (10), 120 (17), 92 (11). Elemental analysis; calculated for $\text{C}_{32}\text{H}_{40}\text{S}_2\text{O}_4$: C, 69.53; H, 7.29; S, 11.60. Found: C, 69.51; H, 7.45; S, 11.72.

2.1.4. (\pm)-6,6'-Bis(1-methylheptyloxy)thioindigo ((\pm)-**1**)

The synthetic sequence described in § 2.1.1–2.1.3 was repeated using (\pm)-2-octanol. m.p. 95–96°C.

2.2. Ferroelectric measurements

The phenyl benzoate liquid crystal mixture MX6120 (Displaytech Inc., Boulder, Colorado) was used as S_C host for the thioindigo dopants; the host phase sequence is



Texture analysis and transition temperatures measurements for the doped liquid crystal mixtures were carried out using a Nikon Labophot-2 polarizing microscope fitted with a Instec HS1-*i* hot stage. Spontaneous polarization values (P_s) for the doped liquid crystal mixtures were measured as a function of temperature by the triangular wave method ($6 \text{ V } \mu\text{m}^{-1}$, 60–80 Hz) using a Displaytech Automated Polarization Testbed II in conjunction with the Instec hot stage. Polyimide-coated ITO glass cells ($4 \mu\text{m} \times 0.25 \text{ cm}^2$) supplied by Displaytech Inc. were used for all the measurements. Good alignment was obtained by slow cooling of the filled cells from the isotropic phase via the chiral nematic and S_A phases. Tilt angles were measured as a function of temperature between crossed polarizers as half the rotation angle between two extinction positions corresponding to opposite polarization orientations.

2.3. Photoisomerization experiments

2.3.1. Photoisomerization of (\pm)-**1** in solution

A 1×10^{-4} M solution of (\pm)-**1** in air-saturated benzene (spectrophotometric grade, BDH) was irradiated in a sealed 1 cm Pyrex cell at room temperature using an Oriol 150 W high-pressure Xe arc lamp. The lamp output

was filtered using colour filters to select light in the ranges $\lambda=420\text{--}460\text{ nm}$ and $\lambda>530\text{ nm}$. The photoisomerization and thermal relaxation of the sample was monitored by UV-visible spectroscopy using a Varian Cary 3 spectrophotometer. A photostationary state was achieved within 15 min of irradiation under these conditions.

2.3.2. Photoisomerization of (*R,R*)-**1** and (\pm)-**1** in a liquid crystal host: P_S modulation

A 7.2 mol % solution of (*R,R*)-**1** in the S_C host MX6120 was introduced in a $4\ \mu\text{m} \times 0.25\ \text{cm}^2$ polyimide-coated ITO glass cell and fitted in the hot stage with the addressed area fully exposed through the stage aperture. Alignment by slow cooling from the isotropic liquid phase gave a sample of good optical quality. The spontaneous polarization of the sample was measured at $T - T_c = -5^\circ\text{C}$ and -10°C while under constant irradiation (Oriel 150 W Xe arc lamp) at wavelengths in the ranges $\lambda=420\text{--}460\text{ nm}$, $\lambda>530\text{ nm}$ and $\lambda>650\text{ nm}$ by integrating the area under the polarization reversal current peak (average of 10 integrations). A photostationary state was achieved within 1 min of irradiation under these conditions. A water filter was used to cut-off the infrared output of the lamp to minimize external heating of the sample. This experiment was repeated at the same concentration for mixtures of (*R,R*)-**1** and (\pm)-**1** in a S_C^* host consisting of a 2 mol % mixture of (*S,S*)-4,4'-bis[(2-chloro-3-methylbutanoyl)oxy]biphenyl (**6**) in MX6120 [15].

2.3.3. Photoisomerization of (*R,R*)-**1** in a liquid crystal host: Time-resolved observations

The procedure described by Barrett *et al.*, was used with some modifications [16]. The aligned sample described in § 2.3.2. was fitted in the hot stage and irradiated with an argon laser beam ($\lambda=514\text{ nm}$) at constant temperature for a period of 15 s. An attenuated reading beam ($\lambda=458\text{ nm}$ or 514 nm) was passed through the sample coincident with the pump beam and into a photodiode detector; the intensity of the reading beam transmitted through the sample was digitally recorded as a function of time to observe the photoisomerization and thermal relaxation of the dopant.

3. Results and discussion

3.1. Synthesis

The thioindigo dopant **1** was synthesized following the route outlined in figure 2. The (*R,R*)-enantiomer of **1** as well as the racemic mixture were prepared. Following a Mitsunobu inversion reaction to introduce the 1-methylheptyloxy side-chain in 80 per cent yield, the key step of this synthesis consists of a nucleophilic displacement by methyl thioglycolate under basic condi-

tions, followed by a Dieckmann condensation to afford the benzothiophene derivative **4** in 60 per cent yield [17, 18]. The latter is converted to the corresponding thioindigo dye in 23 per cent yield via ester hydrolysis and decarboxylation to the benzothiophenone **5**, followed by oxidation with potassium ferricyanide. DSC analysis showed that compound **1** (optically active or racemic form) does not exhibit a liquid crystal phase, although branching of the alkoxy side-chains proved to have a favourable effect on the miscibility of the dye in the liquid crystal host. The straight chain analogue of **1** was previously shown to have poor solubility in phenyl benzoate S_C liquid crystal mixtures ($<2\text{ mol \%}$) [19]; by contrast, compound **1** can be dissolved in the same mixtures at concentrations of up to 10 mol %. Inspection of the doped mixtures in the S_C phase by polarized microscopy did not reveal any phase separation. The effect of **1** on the stability of the host S_C phase appears to be relatively small for a non-mesogenic dopant, as indicated by a relatively small depression of the $S_A\text{--}S_C$ transition temperature (from 63 to 55°C) for a 7.2 mol % mixture in MX6120.

3.2. Ferroelectric properties

Doping of optically active **1** in the S_C host MX6120 gives rise to a ferroelectric liquid crystal phase. Spontaneous polarization (P_S) values were measured in the dark at $T - T_c = -10^\circ\text{C}$ for mixtures of (*R,R*)-**1** in MX6120 at concentrations ranging from 2.5 to 7.2 mol %. A plot of P_S versus dopant concentration shows no evidence of saturation, which is further evidence that dopant **1** is fully compatible with the phenyl benzoate liquid crystal host, and that no phase separation is taking place over that range of concentration (see figure 3). Two other plots show the expected dependence of P_S and tilt angle (θ) on temperature for a 7.2 mol % mixture of (*R,R*)-**1** in MX6120 (see figure 4). The combined P_S and θ measurements give a reduced polarization (P_0) value of $+14.4\ \text{nC cm}^{-2}$ for a 7.2 mol % mixture of (*R,R*)-**1** in MX6120. This can be extrapolated to a P_0 value of $+200\ \text{nC cm}^{-2}$ for (*R,R*)-**1**, which is roughly twice the extrapolated P_0 value of other ferroelectric dopants bearing a single 1-methylheptyloxy side-chain [20]. The sign of the spontaneous polarization is also consistent with that predicted by the Boulder model for the (*R*) absolute configuration of the 1-methylheptyloxy side-chain [21]. The spontaneous polarization values measured in the dark have been assigned to the *trans*-isomer of the thioindigo dye (*vide infra*).

3.3. Photoisomerization experiments

The photochromic properties of **1** were first investigated in solution. A $10^{-4}\ \text{M}$ solution of (\pm)-**1** in air-saturated benzene was irradiated at wavelengths in the

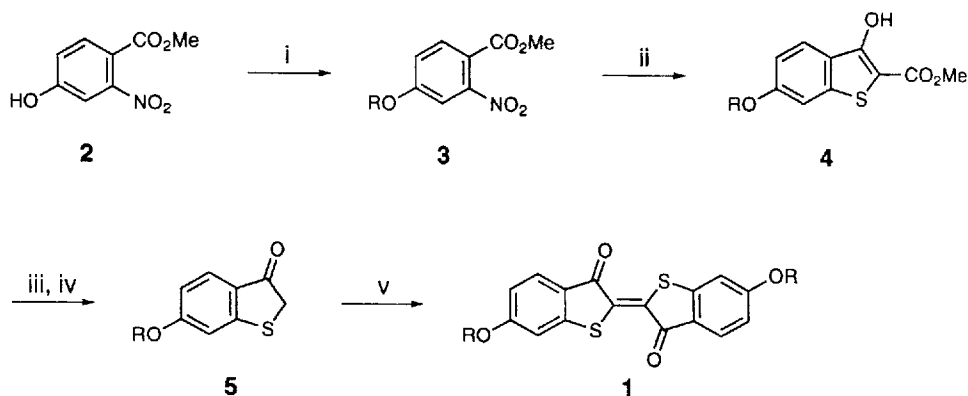


Figure 2. Synthesis of the thioindigo dopant **1**: (i) 2-octanol, DEAD, Ph_3P ; (ii) $\text{HSCH}_2\text{CO}_2\text{CH}_3$, LiOH , DMF; (iii) NaOH , $\text{EtOH}/\text{H}_2\text{O}$; (iv) Δ , $-\text{CO}_2$; (v) $\text{K}_3\text{Fe}(\text{CN})_6$.

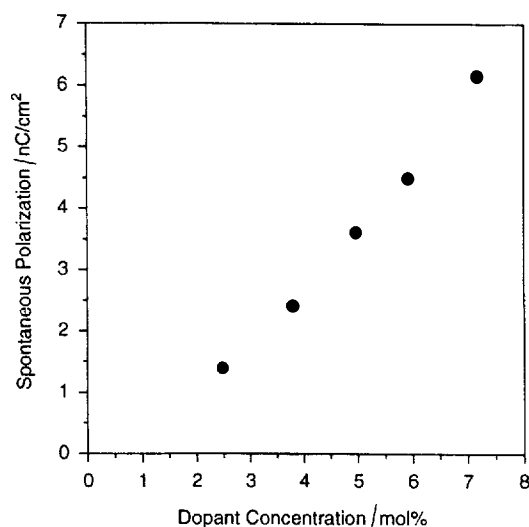


Figure 3. Spontaneous polarization of a mixture of (*R,R*)-**1** in MX6120 measured as a function of dopant concentration at $T - T_c = -10^\circ\text{C}$.

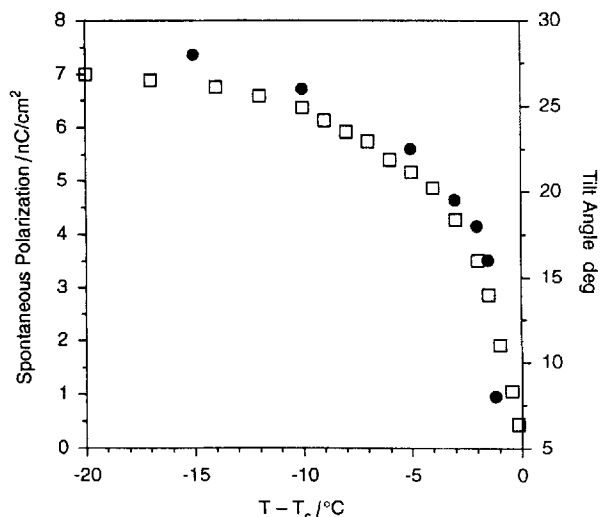


Figure 4. Spontaneous polarization (squares) and tilt angle (circles) of a 7.2 mol % mixture of (*R,R*)-**1** in MX6120 measured as a function of temperature.

ranges $\lambda = 420\text{--}460\text{ nm}$ and $\lambda > 530\text{ nm}$, giving rise to photostationary states that are *trans*-rich ($\lambda_{\text{max}} = 513\text{ nm}$) and *cis*-rich ($\lambda_{\text{max}} = 459\text{ nm}$), respectively (see figure 5). This behaviour is consistent with that previously reported for 6,6'-dimethoxythioindigo [13]. Upon standing in the dark, the *cis*-isomer of **1** thermally isomerizes to the thermodynamically more stable *trans*-isomer, albeit at a very slow rate (see figure 6). This is consistent with results obtained by Ross for the photoisomerization of 6,6'-diisopropoxythioindigo in epoxy resin, which showed that thermal *cis*→*trans* relaxation has no effect on the photostationary state of the dye except at very low light intensity [22].

The photochromic behaviour of dopant **1** in a S_C host was investigated using an aligned sample of the 7.2 mol % MX6120 mixture in a $4\ \mu\text{m} \times 0.25\ \text{cm}^2$ polyimide-coated glass cell. Preliminary experiments using the same approach as for benzene solutions revealed that thermal relaxation of the *cis*-rich photostationary state to the *trans*-isomer is much faster in the S_C phase ($< 10\text{ s}$) than in benzene (c. 24 h). This assessment was confirmed by

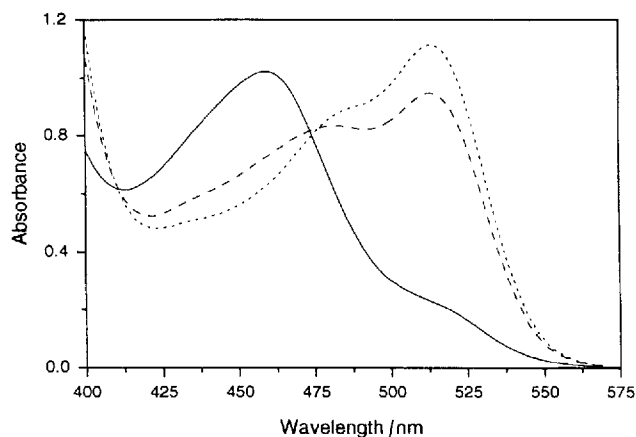


Figure 5. UV-visible absorption spectra of a 10^{-4} M solution of (\pm)-**1** in benzene after irradiation at $\lambda = 420\text{--}460\text{ nm}$ (dashed line), $\lambda > 530\text{ nm}$ (solid line), and after standing in the dark for 24 h (dotted line).

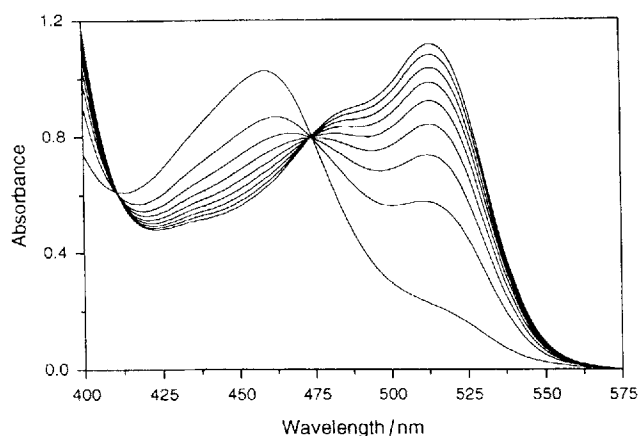


Figure 6. UV-visible absorption spectra of a 10^{-4} M solution of (\pm) -**1** in benzene taken at 3 h intervals while standing in the dark after irradiation at $\lambda > 530$ nm.

time-resolved observation of the *trans*→*cis* photoisomerization and subsequent thermal relaxation of **1** in the S_C phase of MX6120 at $T - T_c = -5^\circ\text{C}$. As shown in figure 7, irradiation of the sample at 514 nm causes a sudden decrease in transmittance at 458 nm, corresponding to an increase in the concentration of the *cis*-isomer via *trans*→*cis* photoisomerization. Upon shutting off the pump beam, thermal relaxation of the sample takes place within 5 s. Raising the temperature of the sample into the nematic and isotropic liquid phases causes the thermal relaxation to slow down considerably, thus suggesting that the more highly organized S_C phase may have the effect of destabilizing the ground state of the *cis*-isomer with respect to the transition state for *cis*→*trans* isomerization. Another time-resolved experiment showed that cooling the sample from the nematic phase to the S_C phase causes a significant decrease in the photostationary state concentration of the *cis*-isomer (see figure 8). This partial suppression of the *trans*→*cis* photoisomerization of **1** by the more highly organized S_C phase is not without precedent: Whitten and co-workers have shown that the *trans*→*cis* photoisomerization of 6,6'-dihexyloxythioindigo is completely suppressed when incorporated in organized media such as monolayer assemblies, Langmuir–Blodgett films and micelles [23]. These results were attributed to an increased energy barrier between *transoid* and perpendicular triplet excited states imposed by the rigid interfacial environment, thus resulting in lower quantum efficiency for the *trans*→*cis* photoisomerization. Whether the partial suppression of *trans*→*cis* photoisomerization observed in this case is due to competing *cis*→*trans* thermal relaxation, or to a decrease in *trans*→*cis* quantum efficiency, or to a combination of both remains unclear.

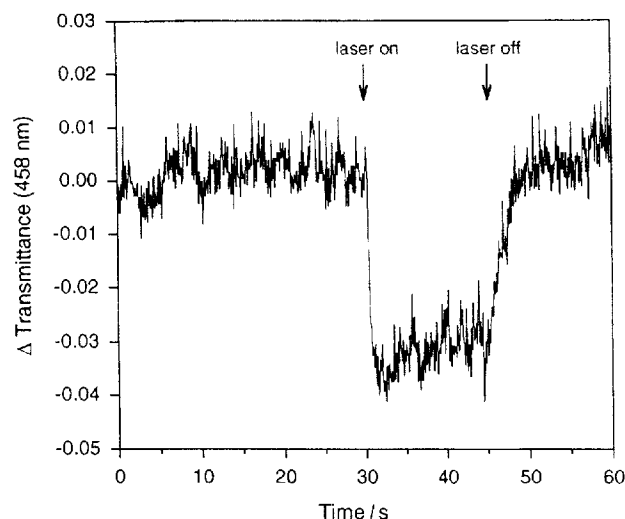


Figure 7. Change in transmittance of a 7.2 mol % mixture of (R,R) -**1** in MX6120 at 458 nm upon irradiation with a 514 nm pump beam for 15 s.

3.4. P_S photomodulation experiments

In order to determine if the photoisomerization of (R,R) -**1** in the S_C phase of MX6120 could lead to a detectable modulation of P_S , we monitored the spontaneous polarization of an aligned sample of the 7.2 mol % MX6120 mixture while under constant irradiation at one of three different wavelengths corresponding to the *cis*-rich and *trans*-rich photostationary states ($\lambda > 530$ nm and $\lambda = 420$ – 460 nm) and to a thermally equilibrated 'dark' state at $\lambda > 650$ nm, where **1** shows no absorption of light. The results summarized in figure 9 and the table show that a reversible change in P_S on the order of 10 per cent is achieved going from the *cis*-rich photostationary state to the thermally equilibrated *trans*-isomer at $T - T_c = -5$ and -10°C . The irradiation cycle was repeated three times at each temperature without any apparent bleaching. The trend in P_S modulation shown in this experiment can be correlated with the photochromic behaviour of **1** in solution, indicating that the spontaneous polarization of the mixture decreases as the *cis*-isomer concentration increases! These results strongly suggest that stereo-polar coupling between the thioindigo core and the 1-methylheptyloxy side-chains is negligible and, consequently, that the photoinduced change in transverse dipole moment of the thioindigo core has no effect on the spontaneous polarization of the mixture. This would indicate that P_S arises from contributions of the 1-methylheptyloxy side-chains exclusively, which is consistent with the fact that the reduced polarization of *trans*- (R,R) -**1** is approximately twice that reported for other FLC dopants bearing a single 1-methylheptyloxy side-chain (*vide supra*).

To test the hypothesis that P_S modulation might be

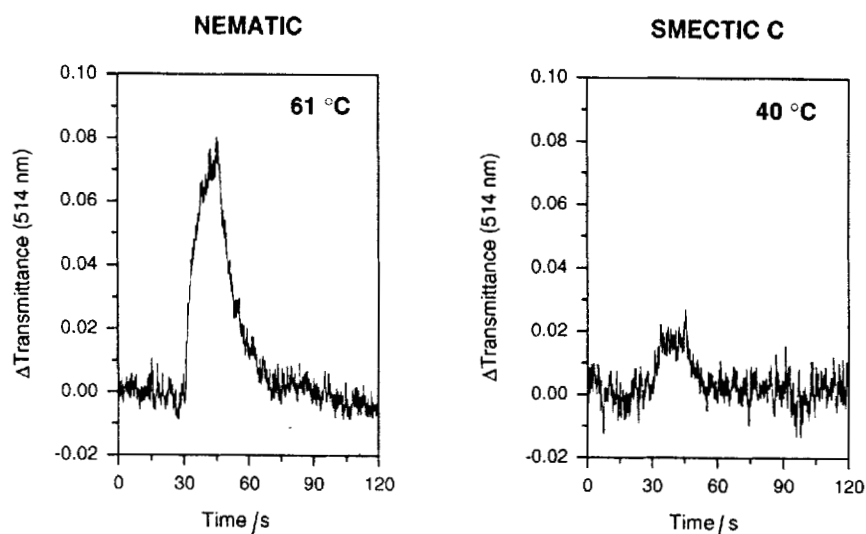


Figure 8. Change in transmittance of a 7.2 mol % mixture of (R,R)-1 in MX6120 at 514 nm upon irradiation with a 514 nm pump beam for 15 s; in the nematic phase (left), and in the smectic C phase at $T - T_c = -15^\circ\text{C}$ (right).

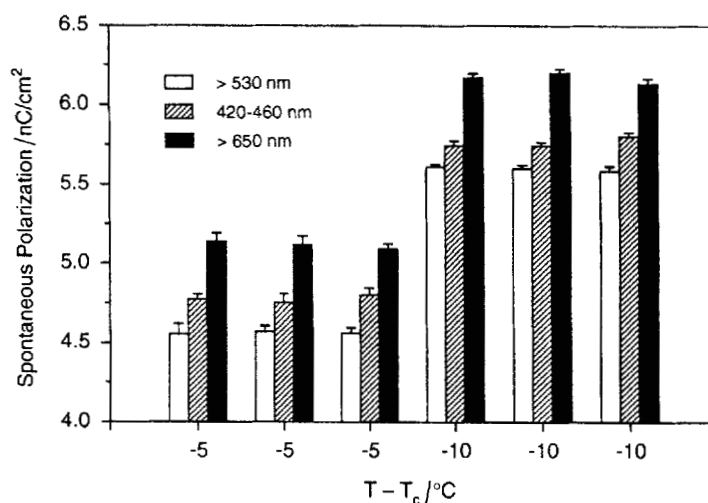


Figure 9. Spontaneous polarization of a 7.2 mol % mixture of (R,R)-1 in MX6120 measured while under constant irradiation at $\lambda > 530$ nm, $\lambda = 420\text{--}460$ nm, and $\lambda > 650$ nm. The values shown correspond to six consecutive irradiation cycles.

Table 1. Spontaneous polarization measured for 7 mol % mixtures of 1 in the S_C host MX6120 and in the S_C^* host MX6120* under constant irradiation at three different wavelengths.^a

λ/nm	$P_s/\text{nC cm}^{-2b,c}$			
	(R,R)-1/MX6120 ^d	(R,R)-1/MX6120	(±)-1/MX6120*	(R,R)-1/MX6120*
420–460	+4.78 ± 0.05	+5.76 ± 0.04	—	—
> 530	+4.56 ± 0.05	+5.60 ± 0.03	-3.16 ± 0.05	+2.06 ± 0.03
> 650	+5.11 ± 0.05	+6.17 ± 0.04	-3.14 ± 0.04	+2.30 ± 0.07

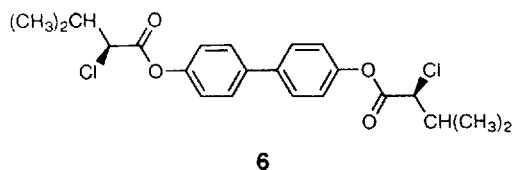
^a The S_C^* host MX6120* consists of a 2 mol % mixture of (S,S)-4,4'-bis[[2-chloro-3-methylbutanoyl]oxy]biphenyl (6) in MX6120.

^b Each P_s value is the average taken from 40 integrations of the polarization reversal current peak over three irradiation cycles. Uncertainties are given as standard deviation. ^c P_s measured at $T - T_c = -10^\circ\text{C}$. ^d P_s measured at $T - T_c = -5^\circ\text{C}$.

caused by a photomechanical effect similar to that postulated by Ikeda and Coles for azobenzene-doped SSFLC systems [8–11], the photomodulation experiment was repeated using a 7.0 mol % mixture of the racemic dopant (±)-1 in a ferroelectric host consisting of a 2 mol % mixture of 6 in MX6120. Results of this

experiment show that P_s remains unchanged going from the *cis*-rich photostationary state ($\lambda > 530$ nm) to the thermally equilibrated *trans*-isomer of (±)-1 ($\lambda > 650$ nm). By contrast, irradiation of a 7.0 mol % mixture of (R,R)-1 in the same ferroelectric host under the same conditions results in a P_s modulation on the

order of 10 per cent (see the table). These results strongly suggest that the P_S modulation observed upon photoisomerization of (*R,R*)-**1** in a S_C or S_C^* host does not arise from a photomechanical effect, nor does it arise from thermal effects due to changes in the output of the light source. Instead, we propose that the observed P_S photo-modulation arises from a change in the conformational equilibria of the 1-methylheptyloxy side-chains in the S_C binding site going from *trans*-**1** to *cis*-**1**.



The Boulder model for the molecular origins of P_S suggests that the contribution of a (*R*)-1-methylheptyloxy side-chain to the spontaneous polarization of a dopant in a S_C host can be rationalized by considering the equilibrium between three conformational states **A**, **B** and **C** (see figure 10) that allow for proper 'docking' of the side-chain in the S_C binding site [21]. In conformations **A** and **C**, the alkoxy dipole is oriented normal to the tilt plane and contributes to P_S in positive (**C**) and negative (**A**) directions, whereas in conformation **B** the alkoxy dipole is oriented in the tilt plane and does not contribute to P_S . Conformation **C** is predicted to be favored over **A** by virtue of relief of the *gauche* interaction between the methyl substituent and the methylene group at C4. This leads to the prediction that a (*R*)-1-methylheptyloxy side-chain should give rise to a positive polarization, which is consistent with results obtained in this and previous studies [21]. Molecular mechanics calculations suggest that the *cis*- and *trans*-isomers of **1** must adopt global conformations that differ in terms of the

orientational state of the alkoxy dipoles in order to properly dock in the S_C binding site. Although our results are consistent with conformation **C** predominating in both *cis* and *trans* forms, *trans*→*cis* isomerization of **1** in the S_C phase could result in a shift in the conformational equilibria of the 1-methylheptyloxy side-chains towards conformations **A** and **B**, which would explain the observed decrease in P_S . At present, it is difficult to predict the structure of any conformational state that would best fit the S_C binding site using standard molecular mechanics approaches. We plan to carry out molecular dynamics calculations to gain further insight into the conformational behaviour of *cis*-**1** and *trans*-**1** in the S_C binding site.

4. Conclusions

The novel thioindigo dopant (*R,R*)-6,6'-bis(1-methylheptyloxy)thioindigo ((*R,R*)-**1**) was synthesized in 11 per cent overall yield starting from methyl 4-hydroxy-2-nitrobenzoate. This compound was doped into the commercial S_C mixture MX6120, giving rise to a ferroelectric liquid crystal phase. A reduced polarization of $+14.4 \text{ nC cm}^{-2}$ was measured for a 7.2 mol % mixture, corresponding to an extrapolated P_0 value of $+200 \text{ nC cm}^{-2}$ for (*R,R*)-**1**. Time-resolved experiments revealed that (*R,R*)-**1** does undergo *trans*→*cis* photoisomerization in the S_C phase, although the efficiency of photoisomerization is significantly lower than in the nematic and isotropic phases. This may be due to a decrease in quantum efficiency of *trans*→*cis* photoisomerization coupled to an increase in the rate of thermal *cis*→*trans* relaxation arising from the higher degree of organization of the S_C phase.

Switching an aligned sample of a 7.2 mol % mixture of (*R,R*)-**1** in MX6120 between a photostationary state

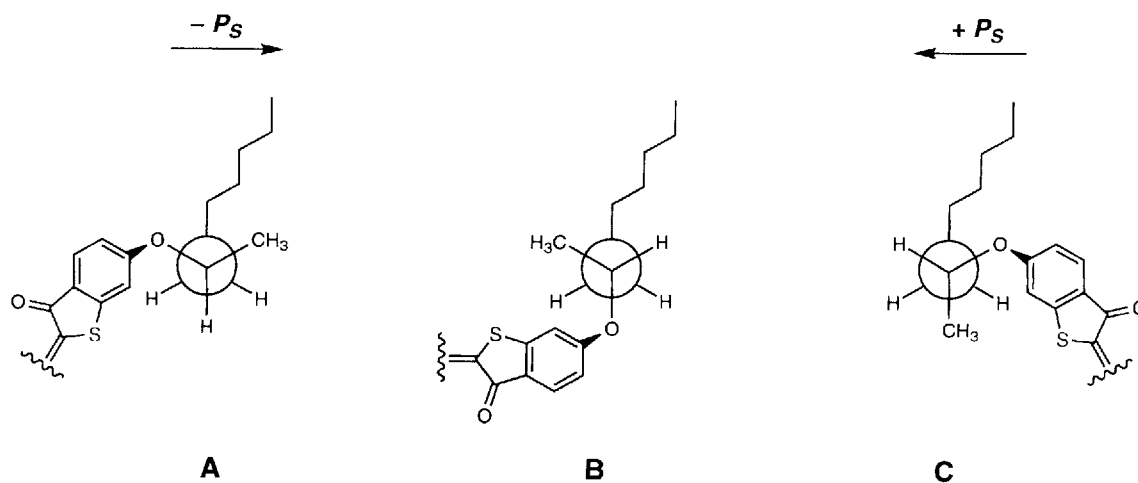


Figure 10. Representations of three conformational states of one of the 1-methylheptyloxy side-chains of (*R,R*)-**1** in the S_C binding site as Newman projections about the C2–C3 bond. The tilt plane is perpendicular to the plane of the page.

favours the *cis*-form and a thermally equilibrated state favouring the *trans*-form of the thioindigo dye results in an increase in P_S on the order of 10 per cent at $T - T_c = -10^\circ\text{C}$. This process was shown to be fully reversible through six irradiation cycles with no evidence of bleaching. Control experiments using mixtures of both racemic and optically active **1** in a S_C^* host suggest that P_S photomodulation does not arise from a photomechanical effect, nor does it arise from thermal effects related to the light source. Consideration of the Boulder model for the molecular origins of P_S provides a rationale for the observed P_S photomodulation based on changes in the conformational equilibria of the 1-methylheptyloxy side-chains in the S_C binding site going from the *trans* form to the *cis* form of the thioindigo dopant.

We are grateful to the Natural Sciences and Engineering Research Council of Canada, and to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work. We thank Mr Chris Barrett and Professor Paul Rochon of the Royal Military College of Canada for their assistance in the time-resolved measurements, and Dr Michael Wand of Displaytech for a generous gift of S_C host mixture.

References

- [1] GOODBY, J. W., BLINC, R., CLARK, N. A., LAGERWALL, S. T., OSIPOV, M. A., PIKIN, S. A., SAKURAI, T., YOSHINO, K., and ZEKI, B., 1991, *Ferroelectric Liquid Crystals: Principles, Properties and Applications* (Philadelphia: Gordon & Breach).
- [2] FERINGA, B. L., JAGER, W. F., and DE LANGE, B., 1993, *Tetrahedron*, **49**, 8267.
- [3] EMMELIUS, M., PAWLOWSKI, G., and VOLLMANN, H. W., 1989, *Angew. Chem., Int. Ed. Engl.*, **28**, 1445.
- [4] CLARK, N. A., and LAGERWALL, S. T., 1980, *Appl. Phys. Lett.*, **36**, 899.
- [5] MEYER, R. B., LIEBERT, L., STRZELECKI, L., and KELLER, P., 1975, *J. Phys. (Paris) Lett.*, **36**, L69.
- [6] LAGERWALL, S. T., OTTERHOLM, B., and SKARP, K., 1987, *Mol. Cryst. liq. Cryst.*, **152**, 503.
- [7] YOSHINO, K., TANIGUSHI, H., and OZAKI, M., 1989, *Ferroelectrics*, **91**, 267.
- [8] IKEDA, T., SASAKI, T., and ICHIMURA, K., 1993, *Nature*, **361**, 428.
- [9] SASAKI, T., IKEDA, T., and ICHIMURA, K., 1994, *J. Am. chem. Soc.*, **116**, 625.
- [10] COLES, H. J., WALTON, H. G., GUILLON, D., and POETTI, G., 1993, *Liq. Cryst.*, **15**, 551.
- [11] WALTON, H. G., COLES, H. J., GUILLON, D., and POETTI, G., 1994, *Liq. Cryst.*, **17**, 333.
- [12] 1971, *Photochromism*, edited by G. H. Brown (New York: Wiley).
- [13] KIRSCH, A. D., and WYMAN, G. M., 1977, *J. phys. Chem.*, **81**, 413.
- [14] STEPHEN, J. M. L., TONKIN, I. M., and WALKER, J., 1947, *J. chem. Soc.*, 1035.
- [15] BOMELBURG, J., HANSEL, C., HEPPKE, G., HOLLIDI, J., LOTZSCH, D., SCHERF, K.-D., WUTHE, K., and ZASCHKE, H., 1990, *Mol. Cryst. liq. Cryst.*, **192**, 335.
- [16] BARRETT, C., NATANSOHN, A., and ROCHON, P., 1994, *Macromolecules*, **27**, 4781.
- [17] MITSUNOBU, O., 1981, *Synthesis*, 1.
- [18] BECK, J. R., 1973, *J. org. Chem.*, **38**, 4086.
- [19] DINESCU, L., MEZO, A., LUYI, L. G., and LEMIEUX, R. P., 1994, *Tetrahedron Lett.*, **35**, 7549.
- [20] WAND, M. D., VOHRA, R., WALBA, D. M., CLARK, N. A., and SHAO, R., 1991, *Mol. Cryst. liq. Cryst.*, **202**, 183.
- [21] WALBA, D. M., 1991, *Advances in the Synthesis and Reactivity of Solids*, Vol. 1, edited by T. E. Mallouk (Greenwich, CT: JAI Press, Ltd), pp. 173–235.
- [22] ROSS, D. L., 1971, *Appl. Opt.*, **10**, 571.
- [23] COLLINS-GOLD, L., MÖBIUS, D., and WHITTEN, D. G., 1986, *Langmuir*, **2**, 191.