Optical activity studies in the pretransitional isotropic region of strongly chiral propiolate ester liquid crystals

Jaskaran S. Kang[a]; David A. Dunmur[a]; Christopher J. Booth[b]; John W. Goodby[b]; Kenneth J. Toyne[b]; Isa Nishiyama[bc]

[a] Centre for Molecular Materials and Department of Chemistry, The University of Sheffield, Sheffield, United Kingdom [b] School of Chemistry, The University of Hull, Hull, United Kingdom [c] Petroleum Laboratory, Japan Energy Corporation, Saitama, Japan

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by JASKARAN S. KANG* and DAVID A. DUNMUR

Centre for Molecular Materials and Department of Chemistry,
The University of Sheffield, Sheffield S3 7HF, United Kingdom

CHRISTOPHER J. BOOTH, JOHN W. GOODBY, KENNETH J. TOYNE
and ISA NISHIYAMA†

School of Chemistry, The University of Hull, Hull HU6 7RX, United Kingdom

Optical rotation and circular dichroism measurements performed in the pretransitional isotropic region above the chiral smectic phases TGBA*, TGBC*, S_C^*, and S_A^* exhibited by 1-alkylalkyl 4'-(4''-n-alkoxyphenylpropioloyloxy)biphenyl-4-carboxylates are reported. These results revealed a high degree of increasing chiral ordering on cooling in the isotropic phase, particularly in the temperature region where a broad DSC peak appears. However, the behaviour of the pretransitional optical activity was unlike that commonly observed for chiral nematic or blue phase compounds and did not follow a simple Landau–de Gennes temperature dependence. Characteristic features of the pretransitional optical activity may aid in understanding the local structure of chiral smectic phases. Electric fields did not seem to influence the results significantly, but strong electric field-induced optical rotation behaviour was demonstrated for a mixture constituted of the laterally fluorinated propiolate ester component and a nematic with a large positive dielectric anisotropy. These field-induced results could be fitted to expressions from the existing theory of pretransitional optical activity. Circular dichroism studies at low temperatures were performed for two compounds in dilute solution and were found to exhibit very large changes in their extinction coefficient at wavelengths in the ultraviolet region, which may indicate strong chiral interactions even in dilute isotropic solutions of these materials.

1. Introduction

In recent years, considerable effort has been directed towards studying the influence of chirality on liquid crystal phases to improve our understanding of how chiral molecules impart chirality to the mesophase. Consequently, the synthesis of strongly chiral compounds has led to the discovery of several new smectic phases resulting from the competition between helical and layer structures constituted of strongly chiral molecules. One such frustrated phase is the highly dislocated chiral smectic A phase, commonly known as the Twist Grain Boundary smectic A* (TGBA*) phase, in which there is a twisted array of infinite two-dimensional smectic A slabs stacked along an axis parallel to the layer planes resulting in the formation of a macroscopic helical structure. Renn and Lubensky [1] first predicted the TGBA* phase based on the de Gennes model [2] for which a strong analogy was

established between the N–S_A phase transition and the normal–superconducting phase transition in metals. From this analogy, for chiral liquid crystals, the transition between the N* and S_A^* phases would occur either directly or would proceed through an intermediate twisted smectic phase analogous to the Abrikosov phase in type II superconductors induced by an applied magnetic field. However, the TGBA* phase was first discovered between the S_C^* phase and isotropic phase for long alkyloxy chain homologues [3, 4], but the predicted phase sequence (i.e. N*–TGBA*–S_A^*) was reported one year later [5]. Furthermore, it has been shown theoretically [6] that the S_C^* phase can also exhibit transitions to the TGBC* and TGBC** phases, and these phases are known to exist. The structure of the TGBC* phase is analogous to the TGBA* phase except the slabs have a S_C structure. For the TGBC** phase, the structure consists of a twisted stack of helical S_C^* slabs. The TGB phases can be identified by X-ray studies [7, 8], differential scanning calorimetry (DSC) and polarizing microscopy [9].

A sharp increase in many properties (for example,

* Author for correspondence.
† Present address: Petroleum Laboratory, Japan Energy Corporation, 3-17-35, Niizo-minami, Toda-shi, Saitama 335, Japan.

Table. Phase behaviour of 1-alkylalkyl 4'-(4"-*n*-alkoxyphenylpropioloyloxy)biphenyl-4-carboxylates determined by DSC.

$$C_mH_{2m+1}O \cdots \text{(structure)} \cdots C_nH_{2n+1}$$
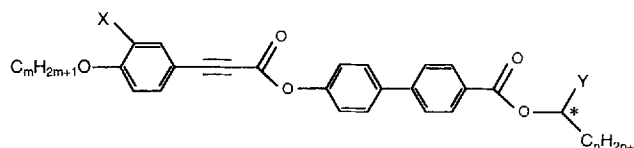
Compound (abs. config.)	*m*	*n*	*X*	*Y*	*T*(liq–liq)/°C	*T*(I–S$^*_C$, S*†‡, or TGBA*†)/°C	*T*(S$^*_C$– TGBA*)/°C	*T*(S$^*_C$–Cr), *T*(S*†–Cr)§/°C
1(R)	14	6	F	CH₃	79·7	74·5		36·7
1(S)	14	6	F	CH₃	79·5	74·3		46·0
2(R)	14	8	H	CH₃	96·5	90·0†	89·0	20·8
3(S)	18	8	H	CH₃	94·7	86·1		28·2
4(S)	18	6	H	C₂H₅	76·5	52·1‡		46·6¶

Data recorded at a cooling rate of − 5°C min⁻¹.

§ Obtained by polarizing optical microscopy on cooling. *T*(liq–liq) corresponds to the onset temperature of the diffuse peak. Phase S† was unidentified.

electric field-induced birefringence) occurs on approaching the isotropic–liquid crystal phase transition by cooling, due to increasing orientational short range ordering as described by the Landau–de Gennes theory [10]. If the liquid crystal phase is chiral nematic, the increased orientational ordering results in increased chiral interactions which enhance chiral fluctuations. This leads to an enhancement of the optical rotation in the pretransitional isotropic region and was first reported by Cheng and Meyer in 1972 [11]. Since then, a great deal of related work on chiral nematics has followed and is reviewed by Collings [12]. It has been established that the degree of chirality of these materials strongly influences the type of pretransitional optical activity behaviour observed. If the phase transition occurs from the isotropic to the smectic liquid crystal phase, then chiral fluctuations involving short range translational order should occur simultaneously with the short range orientational ordering in the pretransitional region. Coupling of the translational and orientational order parameters are likely to have a significant effect on the chiral fluctuations and hence influence the pretransitional optical activity. However, little work has been carried out on the behaviour of the optical activity in the pretransitional isotropic region of chiral smectic liquid crystals [13, 14] and TGB phases [15]. The latter phases are of particular interest since their DSC scans consistently reveal a diffuse peak in the pretransitional isotropic region. In this paper, we have explored the optical rotation and circular dichroism behaviour which characterizes the diffuse peak in the isotropic phase of novel propiolate compounds illustrated in the table. Compounds 1(R) and 1(S) as pure enantiomers do not exhibit TGB phases but both still show a diffuse peak in the pretransitional isotropic region of the S$^*_C$ phase. To understand this new phenomenon, these compounds

and their mixtures were investigated in greater detail. Electric field effect studies on the pretransitional optical activity of compounds 1(R) and 1(S) were performed to understand further the chiral interactions, apparently responsible for the diffuse peak observed in the DSC scans.

2. Experimental

Optical rotation measurements were made using a sensitive polarimeter arrangement as shown in figure 1 and based on the synchronous detection of a modulated optical signal using an EG & G, model 5210 lock-in amplifier. The light from a 5 mW He–Ne (632·8 nm) laser source was modulated by a Hinds International PEM-80 photoelastic modulator. Full details of this technique are described elsewhere [16]. Optical rotation measurements were made with 100 μm thick, planar aligning, electro-optic cells for compounds 1(R), 1(S), and 2; but, 18 μm thick, homeo-
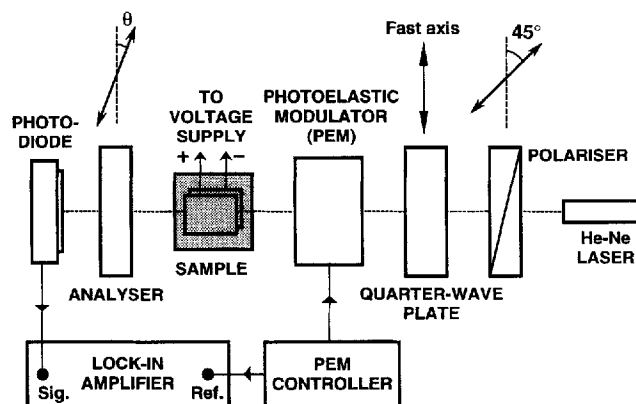

Figure 1. Experimental set-up for measuring the optical rotation and electric field effects on the optical rotation of chiral systems as a function of temperature.

tropic aligning cells were used for compounds **3** and **4**. Electric field effect studies on compound **1**(*S*) and mixtures of compounds **1**(*R*) and **1**(*S*) were carried out using the 100 µm thick planar cells. Electric field-induced optical rotation measurements of one mixture which had a large positive dielectric anisotropy were made using a 20 mm spectrophotometer glass cell. A specially made Teflon plug with vertical parallel plate electrodes of length ~ 16 mm and separated by ~ 2·7 mm was inserted into the glass cell; d.c. voltages as large as 2·5 kV were applied to these electrodes by a Brandenburg high voltage supply. The temperature stability of the cell holder system was ± 0·1°C. Circular dichroism measurements were made using a Jasco J-40CS spectropolarimeter. For this work, 18 µm thick quartz cells were fabricated with homeotropic aligning layers. Each sample cell was maintained at constant temperature (i.e. ± 0·2°C) for ~ 5 min before running a spectrum.

3. Results and discussion

3.1. *Optical rotation and circular dichroism studies of enantiomeric mixtures of compounds 1(R) and 1(S)*

Binary mixtures of compounds **1**(*R*) and **1**(*S*) are known to exhibit various chiral smectic phases [9]. On cooling from the isotropic phase, the S_A^* phase appeared for mixtures with very low optical purity, i.e. ~ 35–65 per cent (w/w) of one enantiomer present. As the optical purity of the mixtures was increased, i.e. ~ 67–75 per cent (w/w) of one enantiomer present, the TGBA* phase appeared on cooling from the isotropic and the TGBC* phase appeared when ~ 75–90 per cent (w/w) of one enantiomer was present. For the pure enantiomers and binary mixtures of relatively high optical purity, i.e. > 65 per cent (w/w) of one enantiomer present, DSC studies have revealed the reproducible occurrence of a diffuse peak in the isotropic phase. If the optical purity was lowered so that only the S_A^* phase appeared below the isotropic phase, then the diffuse peak disappeared, leaving just the sharp peak characteristic of the I–S_A^* phase transition. Hence, it is very unlikely that the diffuse peak was caused by impurities, but instead, we believe it represents the presence of a progressive transition above the S_C^* and TGB phases. Figure 2 shows how the optical activity varies in the isotropic phase just above each of the smectic phases of the pure enantiometer and the binary mixtures. Results for the typical chiral nematic, (*S*)-(+)-4-(2-methylbutylphenyl) 4-*n*-decyl-oxybenzoate (CE6), are included to show that its pretransitional optical rotatory power is very weak in comparison to that of the laterally fluorinated propiolate ester mixtures. For example, close to the phase transition temperature (T_r), the optical rotatory power of CE6 is five to eight times smaller than that of the mixtures. The optical rotatory power above the S_A^* phase starts increasing at
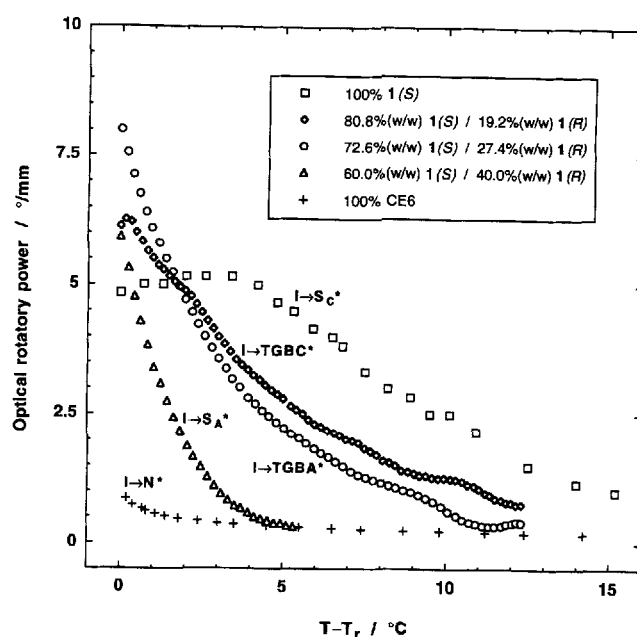

Figure 2. Behaviour of the optical rotatory power in the pretransitional isotropic region of various chiral smectic phases of the pure enantiomer **1**(*S*) and enantiomeric mixtures of compounds **1**(*R*) and **1**(*S*) as a function of normalized temperature. To take account of the differing net chiral content of the mixtures, the optical rotatory power has also been normalised. Results for chiral nematic CE6 are presented for comparison. The sign of the optical rotatory power for CE6 is positive, but negative for the other curves.

$T - T_r = 5$°C and increases sharply thereafter to ~ − 6° mm^{-1} before entering the phase transition. Above the TGBA* phase, the optical rotatory power starts increasing at $T - T_r = 11$°C and there appears to be some modulation in the data between $T - T_r = 7$°C and 12°C. However, the optical rotatory power continues to increase dramatically, but less sharply than that of the I–S_A^* curve, until it reaches a maximum of − 8° mm^{-1}. The I–TGBC* curve remains just above the I–TGBA* curve until they intersect at $T - T_r \sim 2$°C. It seems that the I–TGBC* curve is modulated throughout the pretransitional isotropic region, in contrast to the I–TGBA* curve where the modulation occurs over a smaller temperature range: this modulation suggests step-wise local structural changes in the chiral fluid. Furthermore, the optical rotation above the TGBC* phase saturates within 1°C of the phase transition. The optical rotatory power of the pure enantiomer is largest over the widest temperature range, increasing from $T - T_r = 15$°C and saturating at a maximum of ~ − 5·2° mm^{-1} at $T - T_r \sim 4$°C. The temperature region of this anomalous pretransitional optical activity of the I–S_C^* curve is wider than in blue phases and does not fit the normal Landau–de Gennes temperature dependence which works so well for blue phase compounds. The
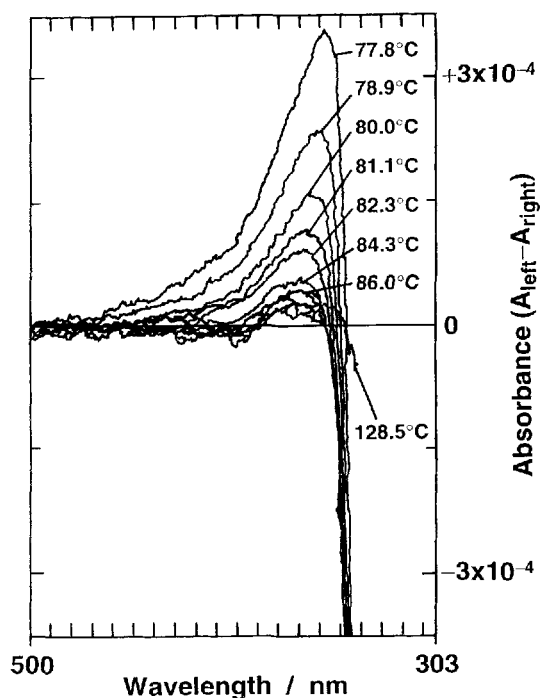
Figure 3. Circular dichroism spectra of compound 1(S) in the pretransitional isotropic region of the S_C^* phase as a function of temperature. The spectrum at 128·5°C corresponds to the 'true' isotropic phase.

curves presented show a progressive change in behaviour from the pure enantiomer to the mixture with an enantiomeric excess of 20 per cent, and these clearly demonstrate the effect of increasing local chiral interactions.

Although optical rotation provides a useful monitor of the bulk chiral interactions, circular dichroism is a powerful technique for probing the local molecular chirality, and such studies have been carried out for chiral dopants in liquid crystals [17]. Circular dichroism spectra of enantiomer 1(S) are presented in figure 3 as a function of temperature. A strong enhancement of the circular dichroism signal occurs just above the I–S_C^* phase transition in the form of a peak increasing in magnitude at $\lambda_{max} \sim 355$–370 nm on cooling from the 'true' isotropic. However, it is important to realize this peak is only the tail of the actual intrinsic circular dichroism peak which is negative and has a much stronger absorption at $\lambda_{max} \sim 340$ nm, and which could not be measured even using cell thicknesses ~ 1–2 μm, because the spectrum always went off scale. The sign of this strong absorption correlates with the negative optical rotation results for compound 1(S). Circular dichroism absorption observed in the wavelength region 300–400 nm occurs over approximately the same temperature range as the DSC anomaly and the circular dichroism can be attributed to the chromophore Z–CO–OR*, where Z is a biphenyl ring.

3.2. Electric field effect studies on the laterally fluorinated propiolate esters

To understand how strongly chiral compounds such as the propiolate esters form TGB phases, it is useful to know how the chiral molecules interact. This can be done by probing the chiral interactions using a technique recently reported for studying the effect of an electric field on the optical rotation in the pretransitional isotropic region of the chiral nematic phase [16]. Figure 4 shows the optical rotation measurements of the pure enantiomer 1(S): the optical rotation with a fixed applied electric field of 3 V μm^{-1} is slightly less than that with no field applied. This experiment was repeated for each of the binary mixtures in figure 2. However, as before, the optical rotation tended to decrease slightly on application of a field without any significant enhancement or appearance of new features. In this case, field-induced effects may be too weak to detect because of poor coupling of the molecules to the electric field. Furthermore, the dielectric anisotropy of these materials is likely to be small and negative, so an external field will tend to align the molecules in a plane perpendicular to the field and light direction. In previous work [16], the chiral component was mixed with a nematic material which has a strong positive dielectric anisotropy such as 4-*n*-pentyl-4'-cyanobiphenyl (CB5). Polarizing optical microscopy studies showed that a mixture of 34 per cent (w/w) 1(R)/66 per cent (w/w) CB5 was completely miscible and suggested that the liquid crystal phase on cooling from the isotropic phase was a smectic, but it was difficult to identify the exact phase type without further analysis. Figure 5 shows the effect of an electric field on the optical rotation in the pretransitional isotropic region. The I–S_2^* phase transition occurred at 44·3°C (where S_2^* is the unidentified chiral smectic phase) and does not change significantly with the increasing applied field. The intrinsic optical rotation and electric field-induced optical
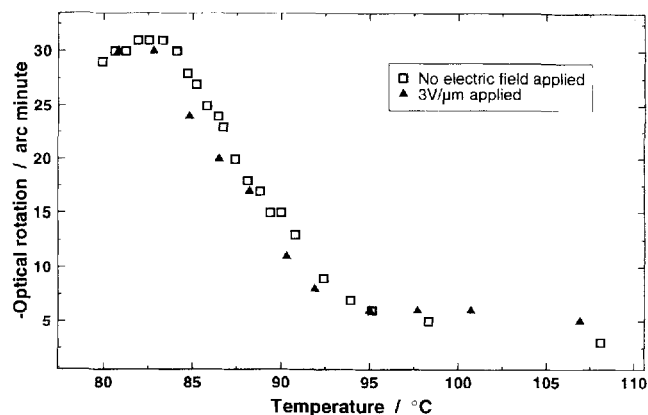

Figure 4. The effect on the pretransitional isotropic optical activity of the pure enantiomer 1(S) on applying a fixed electric field.
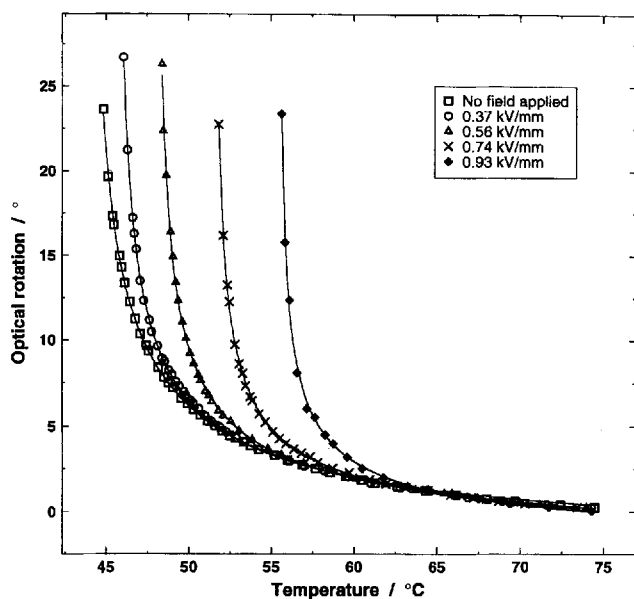
Figure 5. Intrinsic and electric field-induced optical rotation in the pretransitional isotropic region of the mixture containing 34 per cent (w/w) 1(R)/66 per cent (w/w) CB5.

rotation results are more than twice as large as the corresponding results for a mixture of similar composition where the chiral component was CE6 [16], even though the former mixture has an I–S$_2^*$ phase transition which would tend to quench the chiral fluctuations more than if the I–N* phase transition were present. A simplified theoretical expression [16] describing the pretransitional optical activity of typical chiral nematic materials was used to fit the optical rotation results:

$$\phi = \phi_0 + \frac{A}{(T - T_1^*)^{1/2}} \qquad (1)$$

where ϕ_0 is the molecular optical activity, A is a fitting parameter, and T_1^* is the critical divergence temperature. The positively diverging solid lines in figure 5 represent the theoretical curves obtained by fitting the experimental data to expression (1) and show that the agreement between simple theory and experiment is excellent. In figure 6, parameter A obtained from the fitting varies linearly with the applied field and the line has a negative gradient which is approximately five times steeper than that of the corresponding mixture with CE6 as the chiral component [16]. Fitting parameter T_1^* in figure 7 varies as the square of the applied voltage as established for the CE6/CB5 mixture [16]. As expected, parameter ϕ_0 varied negligibly with increasing applied voltage since ϕ_0 is the intrinsic optical activity. The large electric field-induced optical rotation effects observed are indicative of very strong chiral interactions coupled with the optical anisotropy.
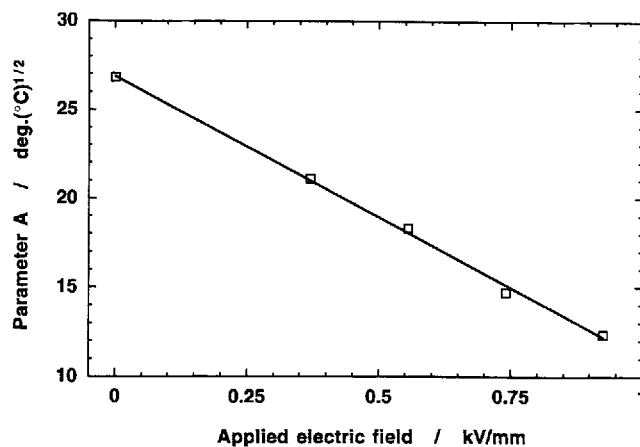

Figure 6. Fitting parameter A as a function of the applied electric field. The solid line is a linear least squares fit of equation $A = -15 \cdot 87E + 26 \cdot 88$.
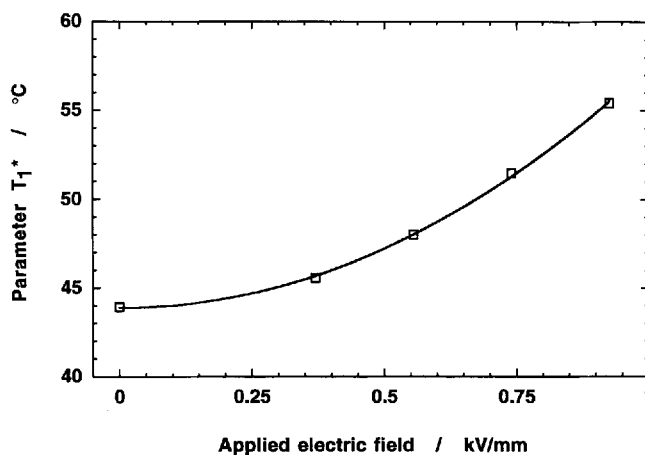

Figure 7. Fitting parameter T_1^* as a function of the applied electric field. The solid line is a quadratic least squares fit of equation $T_1^* = 13 \cdot 83E^2 - 0 \cdot 24E + 43 \cdot 88$.

3.3. Optical rotation and circular dichroism studies on the unfluorinated propiolate esters

Figure 8 shows how the optical rotatory power of compounds 2, 3, and 4 vary on cooling from the isotropic phase to chiral smectic phases. The optical rotatory power in the pretransitional isotropic region of these materials is very large compared to that of CE6. For example, close to the phase transition, the optical rotatory power of the propiolate esters is five to eight times larger than that of CE6. Previous measurements [15] of optical rotation in the pretransitional isotropic region above the TGBA* phase of (R)-1-methylheptyl 4'-[(4''-tetradecyloxyphenyl)propioloxy]biphenyl-4-carboxylate (14P1M7) were similar to the I–TGBA* results in figure 8 for compound 2, but unlike the results for mixtures of compound 1 in figure 2. Hence, it is necessary to be cautious when attempting to identify chiral smectic phases
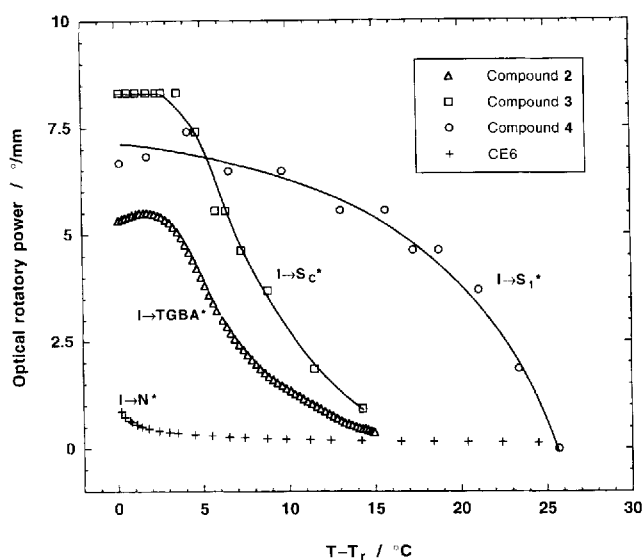
Figure 8. The behaviour of the optical rotatory power in the pretransitional isotropic region of the chiral smectic phases of compounds 2, 3, and 4. Results for chiral nematic CE6 are presented for comparison. The sign of the optical rotatory power of CE6 and of compound 2 is positive, but negative for the other compounds.

based on examination of the pretransitional optical rotatory power curves. Compound 3 has the largest optical rotatory power of $\sim 8°$ mm^{-1} and remains constant at this value within 4°C of the phase transition. On cooling to the S_C^* phase, the optical rotatory power changed sign and was more than an order of magnitude larger compared to that in the isotropic phase, for example, at $T - T_r \sim -0.1°C$, the optical rotatory power $\sim 200°$ mm^{-1}. For compound 4, the shape of the curve is unlike that of the other compounds since the optical rotatory power starts increasing very sharply at first, and then the change in gradient decreases on cooling and eventually levels off within 2°C of the phase transition temperature. For all those compounds the pretransitional optical activity saturates at a temperature above the phase transition temperature, similar to the behaviour observed for the pure fluorinated propiolate esters. This pretransitional optical activity behaviour in the isotropic phase corresponds to the region where the broad peak appears in DSC scans [18].

Circular dichroism spectra for compound 3 are presented in figure 9. As before, the circular dichroism absorption observed in the pretransitional isotropic region in the wavelength range of 300–400 nm can be attributed again to the Z–CO–OR^* chromophore. In figure 9 (a) there is clearly an enhancement in the circular dichroism signal which developed at $\lambda_{max} \sim 355–370$ nm, just above the I–S_C^* phase transition. The peaks shown correspond to the tail of the intrinsic circular dichroism absorption which is negative and has a much larger absorption at ~ 320 nm.

On entering the S_C^* phase, the spectrum changed dramatically, revealing the presence of a pitch band in the visible (i.e. $\lambda_{max} = \sim 540$ nm) associated with selective reflection as shown in figure 9 (b). The circular dichroism enhancement was less pronounced for compound 4 in the tail regions of the intrinsic circular dichroism, but there was an apparent shift in the tail of the strongly absorbing, negative, intrinsic circular dichroism to longer wavelengths on cooling from the isotropic phase. There seems
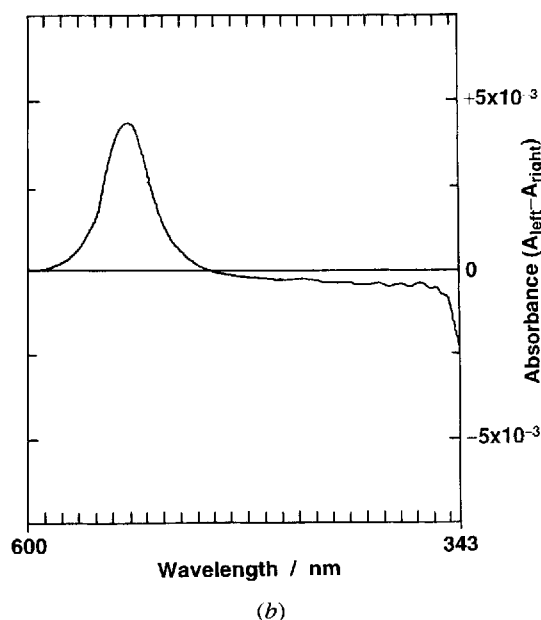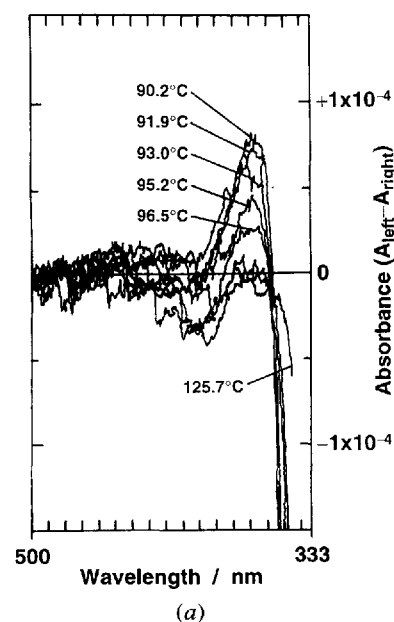

(a)

(b)

Figure 9. Circular dichroism spectra of compound 3 in (a) the pretransitional isotropic region of the S_C^* phase as a function of temperature and (b) the S_C^* phase at 89·3°C.
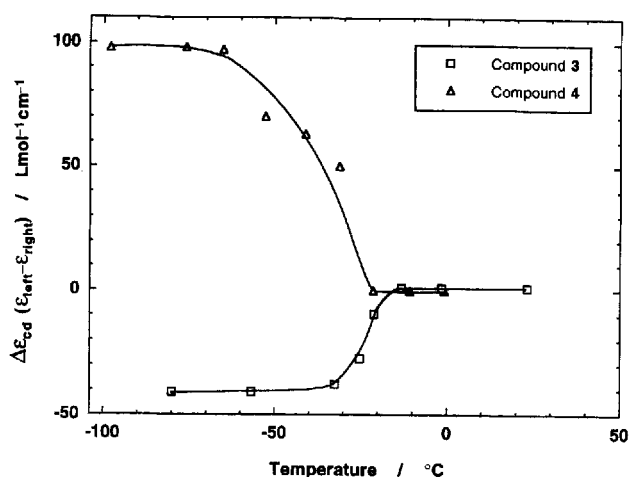
Figure 10. Low temperature circular dichroism plots at $\lambda_{max} \sim 290$ nm for weak solutions of compounds **3** and **4** dissolved in 3-methylpentane.

to be good correlation between the signs of circular dichroism and optical rotation observed.

Preliminary low temperature work on the circular dichroism of compounds **3** and **4** dissolved in 3-methylpentane at a concentration of $\sim 0.1\,\mathrm{g\,l^{-1}}$ was carried out and the results for these solutions are presented in figure 10. The solution containing compound **3** has negative circular dichroism ($\Delta\varepsilon_{cd}$) and shows a very large, step-like change in $\Delta\varepsilon_{cd}$ (i.e. $40\,\mathrm{l\,mol^{-1}\,cm^{-1}}$) in the temperature range $\sim -30°C$ to $-15°C$. In contrast, the solution containing compound **4** has positive $\Delta\varepsilon_{cd}$ and the change in $\Delta\varepsilon_{cd}$ is more than twice as large as the change for the former solution. Since the circular dichroism is outside the wavelength of ordinary absorption, this suggests that something more than conformational freezing is occurring. In fact, the sharp change is indicative of a co-operative process, so may be it is possible that the resemblance of the alkyl chains attached to the chiral centre of the compounds to 3-methylpentane is a factor driving the formation of an ordered macroscopic structure leading to the sudden switch in sign of the circular dichroism. This may explain the larger effect of the solution containing compound **4**, as this material has alkyl chains at the chiral centre that resembles the solvent most closely. However, it is not clear from the present work if the chirality of the materials play a major role in the effect. From an applications point of view, one could envisage using the sharp change in $\Delta\varepsilon_{cd}$ for use in a low temperature warning device.

4. Conclusions

In this paper we have demonstrated the strong anomalous enhancement of the optical activity of chiral propiolate liquid crystals in the pretransitional isotropic region by making measurements of optical rotation and circular

dichroism. There was good correlation between the increasing optical rotatory power on approaching the isotropic–liquid crystal phase transition and the enhancement of the intrinsic circular dichroism, as well as the anomalous heat absorption observed by DSC in the pretransitional isotropic region. The magnitude and wide temperature range of the pretransitional optical activity of these strongly chiral materials is unlike that observed for chiral nematic and blue phase materials. An applied electric field had only a very small effect on the pretransitional optical activity of the pure enantiomer **1**(S) or mixtures of the enantiomers **1**(R) and **1**(S). However, electric field-induced optical rotation of a mixture having a large positive dielectric anisotropy and containing **1**(R) as the chiral component showed a large enhancement in the pretransitional optical activity. Finally, experiments using weak solutions containing compounds **3** and **4** have demonstrated an unusually large change in the circular dichroism at low temperatures which further illustrates the importance of chiral interactions.

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