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J. -X. Guo[a]; D. G. Gray[a]
[a] Pulp and Paper Research Centre, Department of Chemistry, McGill University, Montreal, Quebec, Canada

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# Induced circular dichroism as a probe of handedness in chiral nematic polymer solutions

by J.-X. GUO and D. G. GRAY*

Pulp and Paper Research Centre, Department of Chemistry, McGill University, 3420 University Street, Montreal, Quebec, H3A 2AT, Canada

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Achiral dyes in isotropic (acetyl)(ethyl)cellulose (AEC) solutions display no induced CD signals irrespective of acetyl content, polymer concentration or dye content. When dissolved in anisotropic AEC solutions, the dye molecules show strong induced CD bands that disappear when the phases are heated above the anisotropic/isotropic phase transition temperature. The liquid crystal induced circular dichroism (LCICD) spectra for the dyes in a series of well-characterized AEC mesophases, whose handedness depends on solvent and acetyl content, reveal that the sign of the LCICD signal is determined by the supramolecular structural features of the host matrices. Thus, acridine orange (AO) dissolved in a left-handed liquid crystalline AEC solution displays a negative LCICD whereas a positive LCICD was observed when the AO is dissolved in a right-handed AEC mesophase. The sign and intensity of the LCICD signals change with acetyl degree of substitution, solvent and temperature. In all cases, changes in sign of the CD peak correlated with changes in handedness of the chiral nematic structure, and the intensity of the CD peak increased with increasing chiral nematic pitch for a given solvent and polymer concentration. Induced circular dichroism is thus a useful probe of chiral nematic structure in these systems.



## 1. Introduction

Chiral nematic liquid crystals possess high optical activity and selectively reflect circularly polarized light because of their orientationally ordered helicoidal structures. Optically inactive (achiral) chromophore molecules incorporated in these helicoidal structures may also develop an apparent optical activity as a result of the interaction between the guest achiral chromophores and the host chiral matrices [1, 2]. The resulting optical activity is called liquid crystal induced optical activity or liquid crystal induced circular dichroism (LCICD). The first observation of this induced optical activity in a thermotropic chiral nematic phase was reported by Saeva and Wysocki in 1971 [3]. Since then, it has widely been observed for achiral chromophores dissolved in thermotropic [4–13] and lyotropic [14–19] chiral nematic phases. Other types of the liquid crystal induced optical activity are also exhibited by achiral chromophores either chemically or physically bound to chiral mesogens. Examples include the benzyl side-chain attached to polypeptides [15, 20–23] and triphenylmethyl groups attached to cellulosic chains [24–26], or acridine orange (AO) and chromophoric antibiotics complexed with polyglutamic acids [27] and DNA [28, 29], respectively.

The LCICD displayed by chromophores incorporated in a chiral nematic phase must be clearly distinguished from the apparent CD of the mesophase: the former results from the chromophore molecules being oriented in a helicoidal arrangement and absorbing differentially right- and light-handed circularly polarized light, whereas the latter is a result of the selective reflection of one hand of circularly polarized light by the chiral nematic phase at a wavelength $\lambda_0$, where $\lambda_0 = \bar{n}|P|$, $\bar{n}$ is the mean refractive index of the mesophase and $P$ is the pitch. These two effects are distinguishable as follows. (i) The shape of the apparent CD peak intensity against wavelength is Gaussian provided that a perfect planar texture is formed in a thin sample. The shape of the LCICD peak generally follows the shape of the absorption bands of the chromophore (but it may be positive or negative). (ii) The position of the apparent CD reflection band is pitch dependent, while that of the LCICD depends on the absorption energy for electronic transition of the chromophores. In addition, the position of the apparent CD of a given sample is a function of angle between incident beam and the chiral nematic optical axis, whereas the LCICD does not depend on geometric factors. (iii) The ellipticity of the apparent CD is much higher than that of LCICD for similar optical densities.

The LCICD technique has been applied to determine the existence and handedness of chiral nematic liquid crystals [1, 14, 15, 19, 25, 26, 30, 31], even for those meso-

*Author for correspondence.

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phases whose pitches are beyond wavelength accessible by commercial CD spectropolarimeters. The polarization direction of the electronic transition for chromophores oriented in chiral nematic phases [4, 7, 10, 32, 33] has also been characterized on the basis of LCICD spectra. In addition, the effects of chemical and geometrical structures of guest chromophores on their orientation [6, 30, 33, 34] in chiral nematic matrices have been reported. There are a few applications of LCICD to cellulosic liquid crystals. LCICD has been observed for AO dissolved in a chiral nematic phase of cellulose acetate solution in trifluoroacetic acid (TFA) [35] and for congo red in a cellulose film with a chiral nematic structure [36].

Chiral nematic (acetyl)(ethyl)cellulose (AEC) solutions in many organic solvents exhibit a change in handedness from left to right with increasing acetyl content [37, 38]. Thus, induced CD signals displayed by suitable dyes dissolved in these AEC mesophases should be able to discriminate between left- and right-handed mesophases, and the sign of the corresponding LCICD signals may be compared with the known handedness of the chiral nematic phases [37, 38]. In this paper, the chiroptical properties of AEC liquid crystals are investigated by the LCICD technique, with acridine orange (AO) as the achiral dye. The dye proflavine was used for solutions of AEC in aqueous phenol.



## 2. Experimental

Preparation of a series of AEC polymers with an ethyl degree of substitution (DS) of 2·5 and acetyl degree of substitution (DS′) ranging from 0 to 0·5 were described previously [37]. The solvents dichloromethane (DCM), dibromomethane (DBM), *m*-cresol, bromoform (Aldrich) and aqueous phenol (AP) (Anachemia) were used without purification. The acridine orange was purified according to the following procedures [39, 40]. Excess of 0·1 N NaOH was added to an aqueous solution of AO hydrochloride (Aldrich). The free base was recrystallized twice from an ethanol–water mixture, washed with water and dried under vacuum. The dried AO was dissolved in chloroform and chromatographed on an alumina column. The main band was collected and concentrated. The precipitates were filtered, dried in air and then dried under vacuum at 70°C. The proflavine was purchased from Sigma Chemical and used without further purification.

Dilute AEC/dye solutions were prepared by adding the polymer to solutions of the dye in solvent, at the desired concentration of polymer and dye. The solutions were transferred to a 1 mm path length quartz spectrophotometric cell for ORD, CD and UV-visible absorption measurements.

The liquid crystalline samples containing dyes were prepared by adding the desired weight of AEC polymer to dye solutions in glass vials, which were stored in the dark until use. Unless otherwise specified, the AO concentration was $5 \times 10^{-3}$ mol l$^{-1}$. Once the contents of the vials were homogeneous, the mixture was sandwiched between quartz plates with a 10 $\mu$m thick Teflon spacer.

The CD and ORD spectra were recorded with Jasco-500C and Jasco ORD/UV Model-5 spectropolarimeters, respectively. In order to check for linear birefringence and linear dichroism, the samples for CD or ORD measurements were mounted on a rotating stage, and spectra were recorded at various sample orientations. UV-visible measurements were carried out with a Pye Unicam SP8-150 spectrophotometer. Linear dichroism was also measured in the UV-visible spectrophotometer by placing a plane polarizer in front of the sample mounted on a rotating stage. For measurements as a function of temperature, the sample was placed in a hot stage (Mettler FP52) mounted in the spectrometer beam and heated at a rate of 0·2°C min$^{-1}$.

## 3. Results and discussion

### 3.1 *Absorption and CD spectra of AO dissolved in isotropic AEC solutions*

Figure 1 shows the absorption spectrum of a dilute solution of AEC in dichloromethane (DCM) containing AO (dashed line). The absorption bands around 497 nm and 295 nm have been assigned to the $\pi$–$\pi^*$ electronic transition of monomeric AO molecules along their long axis ($^1L_b$) and the band around 470 nm to the $^1L_b$ transition of dimeric AO [41]. The band around 270 nm corresponds to electronic transition of monomeric AO molecules along their short axis ($^1L_a$). (The $^1L_a$ band of AO in aqueous phenol (AP), *m*-cresol and dibromomethane (DBM) is overlapped by strong solvent absorption bands. Hereafter, the absorption and CD spectra of AO

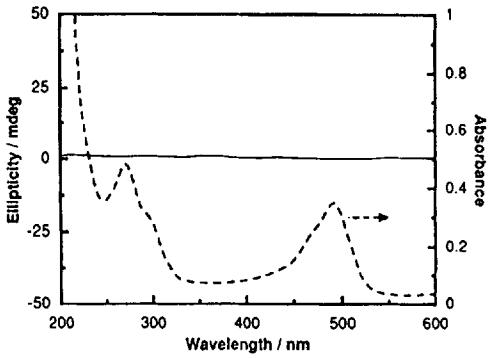


Figure 1. UV-visible absorption (dashed line) and CD (solid line) spectra for an AEC dilute solution (2% wt) in dichloromethane (DCM) containing acridine orange ($1 \times 10^{-4}$ mol l$^{-1}$). The acetyl DS of the sample is 0·26.

in these solvents will be shown only in the visible light region.) The CD spectrum for AO in AEC dilute solution is also shown in figure 1 (solid line). Contrary to observations on AO in poly-γ, L-glutamic acid (PLGA) [42] and sodium carboxymethylcellulose (CMC) dilute solutions [43], no induced CD band is observed for AO in the AEC solutions, indicating that there is no chiral complex formation between AO and AEC in isotropic solution. No induced CD was observed for the AO dissolved in dilute AEC solutions in any solvent.

### 3.2. *Apparent CD spectra of AO dissolved in AEC anisotropic solutions*

When the AO was added to liquid crystalline solutions of AEC, strong induced CD bands appear in the dye absorption region. Figure 2 shows the CD spectrum (solid line) between 300–700 nm for AO dissolved in AEC (acetyl DS = 0·26) lyotropic solution (40 per cent) in AP. As seen in the spectrum, the induced CD band generally follows the shape of AO absorption bands in the absorption spectrum (dashed line) but with a negative sign. Possible effects of linear dichroism and linear birefringence on the apparent CD signals must be considered [44–46]. In order to minimize these effects, the samples were prepared as thin as possible (10 μm) in order to form a planar texture and reduce the potential macroscopic linear birefringence. Secondly, the samples were allowed to equilibrate after sample preparation to minimize any stress-induced birefringence. Thirdly, CD spectra were recorded at 30° intervals as the sample was rotated about the light beam from 0° to 180° and were averaged. This process can remove some of the artifacts resulting from the coupling between instrumental imperfections and the linear dichroism and linear birefringence of the sample [4, 36, 47].

Spectra recorded at different angles were found to be almost identical in sign, shape and intensity. This suggests that their macroscopic linear dichroism was negligible despite the high apparent circular dichroism. An independent measurement of linear dichroism with one sample was also made with a polarized UV–visible spectrophotometer. Again, there was no significant evidence of macroscopic linear dichroism existing in thin and well-equilibrated liquid crystalline samples. The strong induced CD signal is assumed to be due to orientation of the AO molecules by the AEC chiral nematic mesophase to give a helicoidal ordered array, and not to specific chiral interactions of polymer and dye. If this is true, then randomizing the orientation of the host molecules in the helicoidal structure should destroy the induced CD behaviour of the guest AO molecules. This effect can be clearly seen from the change of the LCICD spectra for AO with temperature (see figure 3). Within an increase in temperature, the intensity of LCICD decreases and finally disappears around 81°C. Observation with a polarizing microscope shows that the AEC solution has an anisotropic–isotropic phase transition at this temperature. When the sample is cooled down, the LCICD signal reappears again. A similar temperature dependence of the intensity of LCICD has been observed for pyrene dissolved in thermotropic cholesteryl nonanoate cholesteryl chloride (70 : 30) liquid crystal [48] and for AO dissolved in a poly (γ-benzyl glutamate)/ethylene dichloride lyotropic liquid crystal [15]. The decrease in intensity of LCICD with temperature has been attributed [15] to a reduction in the local orientational order upon heating.

The disappearance of LCICD around 81°C is a clear indication that AO molecules in an isotropic medium are optically inactive irrespective of polymer concentration. In other words, the helicoidal ordering of the host matrix is essential for the observation of ICD.

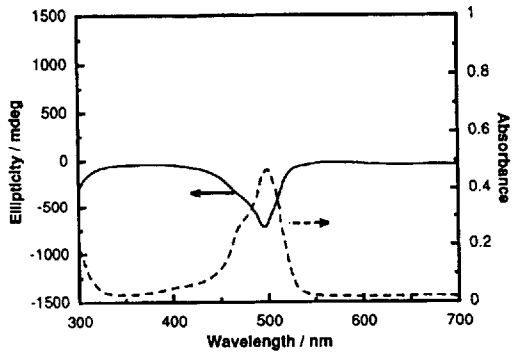


Figure 2. Absorption (dashed line) and CD (solid line) spectra for acridine orange dissolved in an AEC anisotropic solution (40 % wt) in aqueous phenol (AP). The acetyl DS of the sample is 0·26.

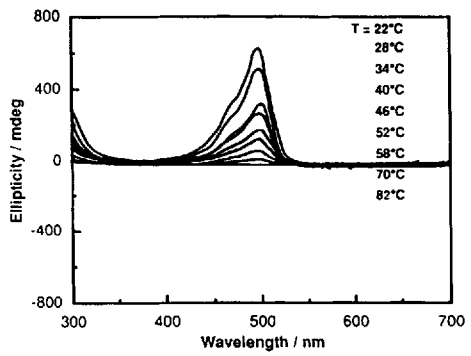


Figure 3. Induced CD spectra as a function of temperature for acridine orange dissolved in anisotropic AEC/AP solution (40 % wt). The acetyl DS of the sample is 0·44.

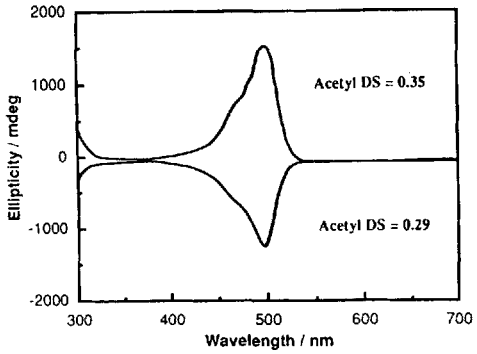


Figure 4. Induced CD spectra for acridine orange dissolved in anisotropic AEC/AP solutions (40 % wt) at room temperature.

### 3.3. *LCICD spectra of AO in left- and right-handed AEC lyotropic solutions*

What happens when AO is dissolved in chiral nematic AEC solutions with opposite handedness? In aqueous phenol, the chiral nematic phase for the lower acetyl content is left-handed, and for the higher acetyl content is right-handed [38]. Figure 4 shows the LCICD spectra of AO in lyotropic solutions of AEC with an acetyl DS of 0·29 and 0·35. The shapes of both LCICD spectra are almost identical, but the sign is reversed. Note that these two AEC polymers share the same chiral cellulosic backbone, differ only slightly in acetyl DS (0·06), and are dissolved in the same achiral solvent. Furthermore, other achiral dyes dissolved in these two matrices give the same result. Figure 5 shows the LCICD spectra of proflavine dissolved in the same polymer solutions as in figure 4. The proflavine dissolved in AEC samples with an acetyl DS of 0·29 and 0·35 also shows negative and positive LCICD bands in the absorption region of the proflavine, respectively. The sign of the LCICD bands thus indicates the handedness of the chiral nematic structure.

If the pitch of the chiral nematic structure falls in the visible range, then it is possible to relate the signal for the LCICD bands to the handedness of the chiral nematic mesophase with a single measurement. Figure 6 shows the apparent CD spectrum in which the large positive band at around 700 nm corresponds to the reflection of circularly polarized light by the left-handed mesophase, and the negative bands below 550 nm generally follow the absorption bands of AO, and are thus attributed to the LCICD of AO in this left-handed mesophase.

### 3.4. *Chiral pitch and LCICD intensity*

The effect of changes in chiral nematic pitch on the intensity of the LCICD signal is also of interest. In the AEC mesophases, the pitch varies with acetyl content over a wide range in a given solvent system, concentration and temperature. They thus provide good samples to study the effect of pitch on LCICD, without changing temperature or introducing any external field which might cause an unwanted macroscopic linear dichroism. Figure 7 shows the LCICD spectra for AO molecules dissolved in a series of AEC/aqueous phenol (AP) mesophases, as a function of acetyl DS. The intensity of LCICD increases with acetyl DS for the samples with an acetyl DS below 0·29, and decreases for the samples with an acetyl DS above 0·35. The intensity of the LCICD is plotted against the magnitude of the pitch in figure 8. The samples have approximately the same thickness and dye content. The change in the sign of LCICD from negative to positive with acetyl DS occurs where there is a reversal of the handedness of the host matrix from left to right, as discussed above. The LCICD intensity thus increases with the increasing magnitude of the pitch, irrespective of handedness. In other words, the more twisted mesophases show the lower LCICD signal. The degree of acetylation at which AEC chiral nematic solutions change handedness depends on the solvent [38]; so the LCICD should also be solvent dependent. Adding AO molecules to AEC mesophases in *m*-cresol gave the

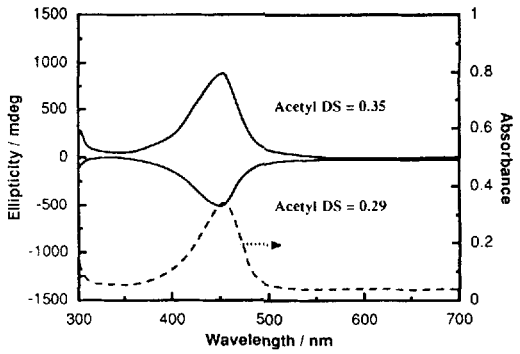


Figure 5. Absorption (dashed line) and induced CD (solid lines) spectra for proflavine dissolved in anisotropic AEC/AP solutions (40 % wt) at room temperature.

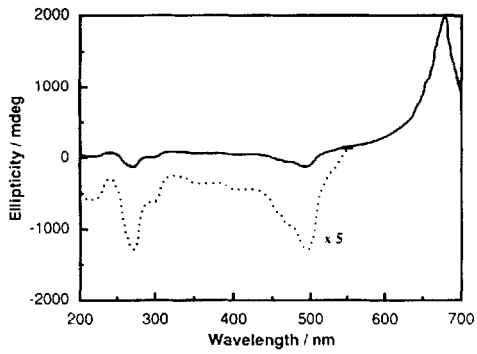


Figure 6. Apparent CD spectrum for acridine orange dissolved in anisotropic AEC/DCM solutions (~45 % wt) at room temperature. The acetyl DS of the sample is 0·16.

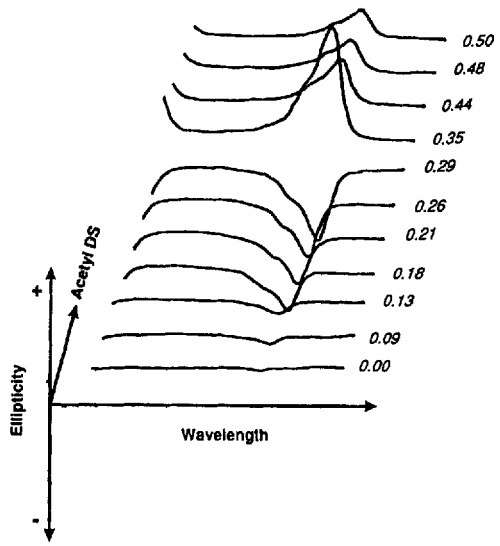


Figure 7. Induced CD spectra as a function of acetyl DS for acridine orange dissolved in anisotropic AEC/AP solutions (40 % wt) at room temperature. All samples have the same thickness (10 $\mu$m).

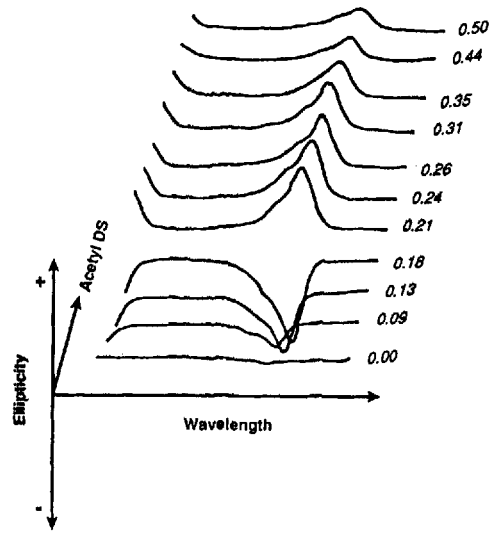


Figure 9. Induced CD spectra as a function of acetyl DS for acridine orange dissolved in anisotropic AEC/*m*-cresol solutions (42 % wt) at room temperature. All samples have the same thickness (10 $\mu$m).



results shown in figure 9. Again the intensity of the LCICD peaks increases as the DS approaches that at which the sign reverses, but this reversal occurs at an acetyl DS greater than 0·18 in this solvent compared with 0·29 in aqueous phenol (see figure 7). These values correspond to the degrees of acetylation at which the mesophase reverses handedness.

The increase in LCICD signal as the pitch increases seems counterintuitive. However, Chandrasekhar and his colleagues developed a theory [49–51] to describe the optical behaviour for dye molecules incorporated in chiral nematic liquid crystals ($|P| \gg \lambda$) that showed that the magnitude of the dichroic power for dye molecules incorporated in a chiral nematic phase is dependent on the pitch. They predicted that a discontinuity in dichroic

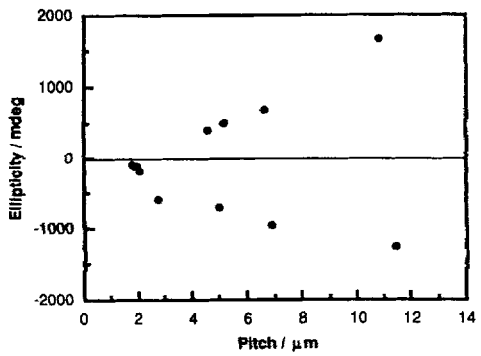


Figure 8. Variation of maximum ellipticity (at $\lambda = 498$ nm) of LCICD with the magnitude of the pitch for the same samples as in figure 7.

power would occur when the chiral nematic pitch was infinite, with dichroic power increasing with decreasing inverse pitch and changing sign at zero inverse pitch. This prediction has been confirmed experimentally by the observation of LCICD as a function of temperature for $\beta$-carotene dissolved in a thermotropic liquid crystal line mixture of cholesteryl chloride and cholesteryl myristate whose handedness changes from left to right with an increase in temperature [50]. Recently, Sisido and Kishi [30] calculated the LCICD of dye molecules incorporated in chiral nematic polypeptide gel films and obtained a semi-quantitative fitting between the calculations and the experimental observations. Qualitatively, the pitch dependence of LCICD intensity observed here also follows Chandrasekhar's theory. (A quantitative comparison requires as yet unknown values for the linear birefringence and linear dichroism of AO in quasi-nematic layers of these mesophases.) Figure 10 is a plot of the experimentally obtained dichroic power of the LCICD peak at $\lambda = 498$ nm against inverse pitch for AO dissolved in a series of AEC/AP liquid crystals. As seen in the plot, the dichroic power increases with decreasing inverse pitch and changes the sign on crossing zero inverse pitch, where a handedness inversion takes place.

### 3.5. *Temperature effects*

An increase in temperature to the clearing temperature of the ordered phase results in a random orientation of the dye molecules and hence the intensity of the LCICD reduces to zero (see figure 3). The pitch of chiral nematic liquid crystals is also temperature dependent. As a result,

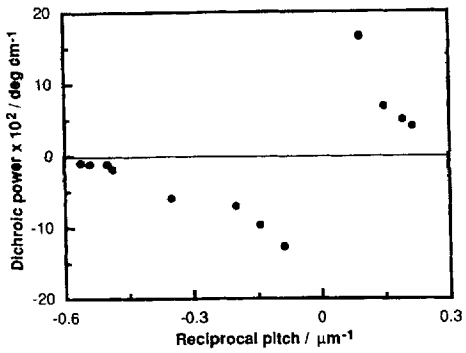


Figure 10. Dichroic power (expressed as $\theta/d$, where $\theta$ is the observed ellipticity and $d$ the sample thickness) at $\lambda = 498$ nm, as a function of reciprocal pitch for the same samples in figure 7.

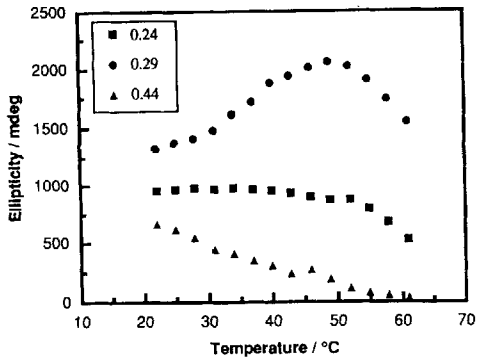


Figure 12. Temperature dependence of LCICD intensity for the same samples as in figure 11.

the variation of the intensity of LCICD upon heating must include contributions from these two effects. The change in intensity of LCICD with temperature is expected to show one of two behaviours. (i) If the temperature dependence of pitch for the host mesophase is negative, the intensity of LCICD for the ordered guest dye molecules will decrease upon heating. (ii) If the temperature dependence of pitch for the host mesophase is positive, the intensity of LCICD for the ordered guest dye molecules will depend on which contribution is dominant in a given temperature range; a decrease for the case where tendency to random orientation predominates over the increase in the pitch upon heating, or an increase for the case that the increase in the pitch predominates over the tendency to disorder.

Figures 11 and 12 show the temperature dependence of pitch and LCICD intensity, respectively, for three AEC/AP lyotropic solutions containing AO. The sample with an acetyl DS of 0·44 shows a slight negative

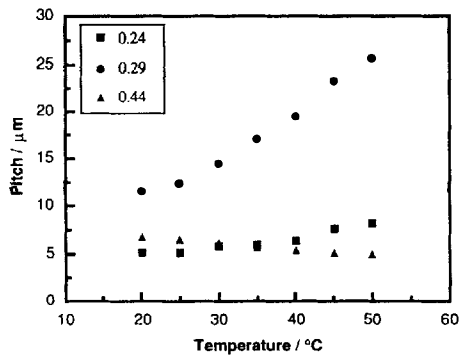


Figure 11. Temperature dependence of the magnitude of the pitch for AEC/AP anisotropic solutions (45 % wt) containing acridine orange. The acetyl DS' of the AEC samples are as indicated.

temperature dependence of pitch and samples with an acetyl DS of 0·24 and 0·29 a positive temperature dependence (see figure 11); the latter sample (acetyl DS = 0·29) displays a greater sensitivity to temperature than the sample with an acetyl DS of 0·24. The temperature dependence of the LCICD is more complex (see figure 12). The sample with an acetyl DS of 0·44 shows a monotonic decrease in intensity with temperature. For the sample with an acetyl DS of 0·24, the intensity of LCICD initially increases very slightly with increasing temperature and then decreases at temperatures over 37°C. A rapid increase in the intensity of LCICD is observed for the sample with an acetyl DS of 0·29 with increasing temperature up to 50°C. Further increasing the temperature results in a decrease in the intensity of the LCICD. The temperature dependence of the LCICD in the latter two cases corresponds to the second case above, where the initial increase is postulated as being due to the increase in pitch, but the subsequent decrease is due to the loss of orientational order of the dye molecules as the temperature is raised, until the order is completely lost when the phases become isotropic.

If the AO molecules take up a chiral nematic orientation in the liquid crystalline phases, then one may also expect that no ICD signal will be observed for AO dissolved in a compensated AEC mesophase because in this type of mesophase the helicoidal order untwists to give nematic-like order. Figure 13 shows the LCICD spectra as a function of temperature for AO dissolved in an AEC/AP liquid crystalline sample with an acetyl DS of 0·31. This sample at room temperature is close to the compensated condition and has an almost infinite pitch as characterized by optical microscope and optical diffraction [38]. As a result, a strong negative LCICD peak (off-scale) is observed for AO dissolved in this sample at room temperature (see figure 13, curve for 28°C), since the intensity of LCICD is proportional to the magnitude of the pitch as discussed above. It has also been shown

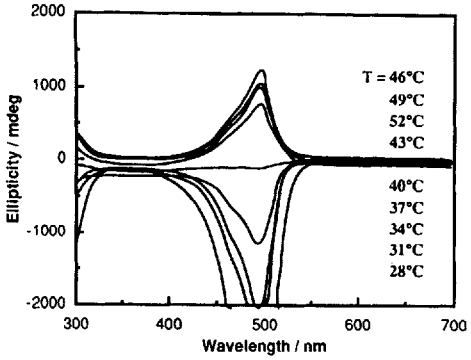


Figure 13. Induced CD spectra as a function of temperature for acridine orange dissolved in an AEC/AP anisotropic solution (40 % wt). The acetyl DS of the sample is 0·31.

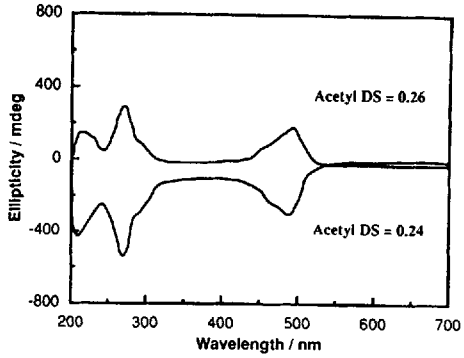


Figure 14. Induced CD spectra for acridine orange dissolved in AEC/dichloromethane anisotropic solutions (~45 % wt) at room temperature.

[38] that AEC/AP liquid crystalline samples with an acetyl DS below 0·32 exhibit a positive temperature dependence of the pitch. This implies that the pitch of the sample with an acetyl DS of 0·31 may become infinite upon heating. The change in pitch is not detectable using a microscope or a diffractometer (because the pitch is too large). As shown in figure 13, the LCICD peak for AO in this mesophase decreases in magnitude with increasing temperature and almost disappears at 40°C, suggesting that at this temperature the mesophase with an acetyl DS of 0·31 and a concentration of 40 per cent (by weight) of AEC in AP loses its twist and forms a nematic structure with an infinite pitch. Further increasing temperature (>40°C) leads to a change in the sign of the LCICD from negative to positive, indicative of the appearance of thermally-induced handedness inversion from left to right. This is the first example of a thermally-induced handedness inversion observed for lyotropic cellulosic liquid crystals, although a thermally-induced handedness inversion has been observed for thermotropic oligomeric cellulose derivatives [52].

### 3.6. *Solvent effects*

Figure 14 shows CD spectra for lyotropic solutions of (acetyl)(ethyl)cellulose containing acridine orange in dichloromethane. The sign of the LCICD obviously changes in dichloromethane solution when the degree of acetylation changes from 0·24 to 0·26. Similar reversals of sign were observed for changes in acetyl DS from 0·18 to 0·21 in *m*-cresol and from 0·26 to 0·29 in dibromomethane. These DS values correspond to the acetyl contents where the chiral nematic mesophases were observed to change handedness in the given solvent, as determined by ORD measurements [38]; left-handed mesophases gave negative LCICD peaks for acridine orange, and right-handed mesophases gave positive peaks. According to Chandrasekhar the negative (positive) LCICD peaks indicate that the electronic transitions of the guest dye that are polarized along its long molecular axis are approximately parallel to the host molecular axis in a left-handed (right-handed) chiral nematic structure. (However, we observed no reversal of sign for the CD peak associated with the electronic transition of AO perpendicular to its long axis; the expected correlation of LCICD peak sign and direction of chromophore transition polarization has been observed in thermotropic [7, 11, 33, 48] but appears to be absent in some lyotropic [15, 16, 18] chiral mesophases.) Obviously the sign of LCICD of guest molecules is determined by the chiral structure of their host matrix, which in turn depends on the solvent. This solvent effect can be further illustrated by an AEC sample with an acetyl DS of 0·24; in *m*-cresol and DCM the dye shows a negative LCICD and in DBM and AP a positive LCICD. This is a clear indication that the LCICD signals originate from the interaction of guest molecules with the supermolecular structure of the host matrix rather than with the individual host molecules.

### 3.7. *Sample thickness effects*

Figure 15 shows LCICD spectra for AO molecules dissolved in the AEC/AP mesophase as a function of sample thickness. The intensity of the LCICD increases with sample thickness up to 45 $\mu$m. However, when the intensity is expressed as ellipticity per unit sample thickness, the dichroic power ($\theta/d$) decreases with increasing in sample thickness, for example, ($\theta/d$) values for 0·10, 0·20, 0·24, and 0·45 $\mu$m thick samples are 235, 227, 205, and 186 deg cm$^{-1}$, respectively. A similar effect has been observed for $\beta$-carotene in liquid crystalline mixtures of cholesteryl chloride and cholesteryl myristate [50]. Presumably, the decrease in the magnitude of the dichroic power with sample thickness is due to a wall effect. In thin chiral nematic liquid crystalline films, the molecules close to the surface of substrates such as quartz or glass have a tendency to orient parallel to the surface and thus

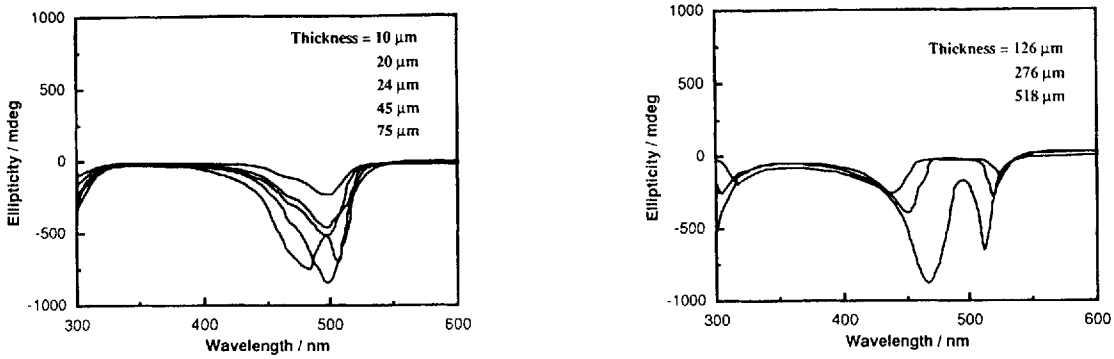


Figure 15. Induced CD spectra as a function of sample thickness for acridine orange dissolved in an anisotropic AEC/AP solution (40 % wt) at room temperature. The acetyl DS of sample is 0·24. Acridine orange content $= 5 \times 10^{-3}$ mol l$^{-1}$.

form a uniform planar texture with optical axes perpendicular to the surface of the substrates [53]. With increasing sample thickness, a focal-conic texture or a polydomain texture is formed, where the chiral nematic axes are tilted to the surface of the glass. This may result in reduced LCICD with thickness. A decrease in intensity of LCICD with applied electric field for pyrene dissolved in cholesteryl esters has also been attributed to a transformation of the texture from planar to focal-conic [10].

The sample with a thickness of 75 μm shows a splitting around 498 nm in the LCICD band. The splitting increases for thicker samples. This is an instrumental artifact due to the excessively high optical densities of thick samples; no splitting is observed when the dye content is reduced.

### 3.8. *Dye content effects*

For dye molecules dissolved in a thermotropic mesophase, Saeva [48] reported that molecular ellipticity did not vary with dye content, but as far as we know, no one has yet investigated the effect of dye concentration in lyotropic systems, where both dye/solvent and polymer/solvent interaction may be significant. It was found that the pitch of an AEC (acetyl DS = 0·35) lyotropic solution in AP was almost independent of dye concentration in the range from $3{\cdot}1 \times 10^{-6}$ to $1{\cdot}5 \times 10^{-2}$ mol l$^{-1}$, for a given polymer concentration and temperature. (It was necessary to check this, because LCICD intensity is very sensitive to pitch, as discussed above.)

The variation of molar ellipticity for AO dissolved in liquid crystalline solutions of AEC in AP is presented as a function of AO concentration in the table. The molar ellipticities of these samples are approximately the same within experimental error, although the difference in dye concentration is four orders of magnitude. This suggests that dye–dye interactions do not play an important role in LCICD.

### 3.9. *ORD evidence for induced optical activity*

The orientation of AO in AEC lyotropic systems, demonstrated by LCICD, should also generate an anomalous Cotton effect in ORD spectra. Figure 16 shows the ORD spectra of AEC lyotropic solutions in AP with and without AO. The plain positive and negative ORD curves (dashed lines) were observed for the AEC/AP mesophases without AO, as described by de Vries' theory [54]. As shown by the solid lines in figure 16, negative and positive Cotton effects superimposed on the ORD curves are observed for AO molecules dissolved in lyotropic solutions of AEC polymers with an acetyl DS of 0·26 and 0·44, respectively. Rotation of the samples about the incident light beam did not change the ORD curves. No Cotton effect was observed for the same polymers in dilute solution. The negative and positive Cotton effects are therefore attributed to the AO molecules oriented by a left- and right-handed helicoidal structure, respectively.

Variation of molar ellipticity [$\theta$] with acridine orange concentration for the LCICD of AO dissolved in AEC/AP anisotropic solutions (40 % wt).

| C | $3{\cdot}10 \times 10^{-6}$ | $6{\cdot}19 \times 10^{-5}$ | $3{\cdot}10 \times 10^{-4}$ | $6{\cdot}19 \times 10^{-4}$ | $'3{\cdot}10 \times 10^{-3}$ | $1{\cdot}54 \times 10^{-2}$ |
|---|---|---|---|---|---|---|
| [$\theta$] | $1{\cdot}29 \times 10^{-5}$ | $1{\cdot}48 \times 10^{-5}$ | $1{\cdot}45 \times 10^{-5}$ | $1{\cdot}26 \times 10^{-5}$ | $1{\cdot}53 \times 10^{-5}$ | $1{\cdot}29 \times 10^{-5}$ |

†[$\theta$] $= \theta/10Cl$ (deg cm$^2$ dmol$^{-1}$), where $\theta$ is the observed ellipticity (deg), $C$ is the concentration (mol l$^{-1}$) and $l$ is the path length (cm).

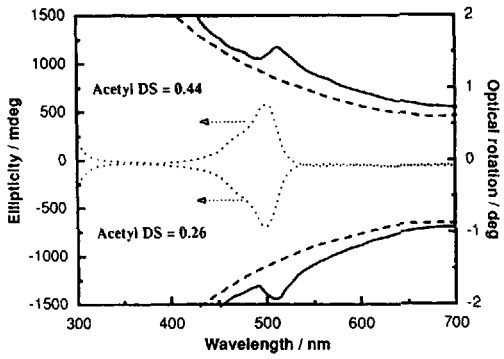


Figure 16. ORD (solid) and CD (dotted lines) spectra for acridine orange dissolved in anisotropic AEC/AP solutions (40 % wt) at room temperature. The dashed lines are ORD curves for the AEC/AP anisotropic solutions without acridine orange.

This is consistent with the results of CD measurements for the same specimens (see figure 16, dotted line). A negative LCICD corresponds to a negative ORD Cotton effect, and a positive LCICD to a positive Cotton effect. These ORD results provide further evidence of a helicoidal arrangement of AO molecules in lyotropic AEC solutions.

## 4. Conclusions

Although there may remain a possibility of artifacts, arising from instrumental imperfections coupling with some residual linear dichroism and linear birefringence [44, 47], it seems from (i) the high ellipticity compared to the intrinsic optical activity of AEC polymer, (ii) the good correlation between the sign of LCICD bands of guest dyes and handedness of their host AEC liquid crystals, and (iii) the good agreement between results obtained by LCICD and other optical methods, that the chiral nematic environment is a dominant source contributing to the induced optical activity in this system.

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