**Liquid Crystals**
Publication details, including instructions for authors and subscription information:
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**To cite this Article** Hild, E. , Kocot, A. , Vij, J. K. and Zentel, R.(1994) 'Infrared spectroscopic study of a phenyl benzoate side group—methacrylate main chain polymeric liquid crystal', Liquid Crystals, 16: 5, 783 — 803

**To link to this Article: DOI:** 10.1080/02678299408027850

**URL:** http://dx.doi.org/10.1080/02678299408027850

LIQUID CRYSTALS, 1994, VOL. 16, NO. 5, 783–803

# Infrared spectroscopic study of a phenyl benzoate side group—methacrylate main chain polymeric liquid crystal

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(*Received 15 June 1993; accepted 8 July 1993*)

The temperature dependence of the infrared dichroism of a side chain polymeric liquid crystal was investigated for two homogeneously oriented samples, one aligned with a PVA coating and the other aligned by a magnetic field. From the apparent order parameters, it was found that the rotation of the mesogenic side group was restricted. Not only the rigid part of the side group, but also the alkyl chains were found to be partly ordered. Realignment of the side groups was observed in the case of the magnetically aligned sample at the smectic–nematic transition temperature. Unlike the other absorption bands, the C=O bond vibration band shifted to higher wavenumbers with increasing temperature. This behaviour was explained by the influence of the neighbouring mesogenic groups on the conjugation existing between the $\pi$-electron cloud of the benzene rings and the $\pi$-electrons of the C=O bond.

## 1. Introduction

The properties of liquid crystalline polymers, either linear or cross linked, combine the characteristics of both single-molecule thermotropic liquid crystal materials and those of polymers [1]. They can be oriented by the usual methods applicable to liquid crystals (LCs) through their mesogenic units, but they can also be oriented by drawing, through the interaction of the mesogenic units with the polymer backbone. Like polymers, they exhibit a transition to a glassy state where both the motion of the polymer and the liquid crystalline properties become frozen. The motion of the mesogenic unit in a side chain polymeric liquid crystal (PLC) can be partially decoupled by introducing a flexible spacer—a polymethylene chain—between the polymer backbone and the rigid part of the mesogenic unit, but the interaction of the polymer chain and the mesogenic unit never ceases completely. Moreover, there is a counter effect by the mesogenic unit on the polymer chain—alignment of the former forces some order upon the latter. In the smectic phase, for example, the existence of the smectic layers means that the polymer chain also has to be arranged in layers.

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The phase behaviour and the structure, and the interaction between the polymer chain and the mesogenic unit were thoroughly investigated by Zentel *et al.*, for a series of polyacrylates and polymethacrylates, using X-ray diffraction, DSC and polarizing microscopy [1–5]. It was found that the phase types and transition temperatures, including the glass transition temperature, are influenced both by the mesogenic unit and the polymer backbone, although the introduction of a longer flexible spacer produced liquid crystalline phases which resembled completely those of single-molecule liquid crystalline materials.

When speaking about terms such as alignment or the order parameter, we must be aware of the differences between single-molecule and polymeric liquid crystals arising from the polymeric structure. For the single-molecule materials it is imagined that the

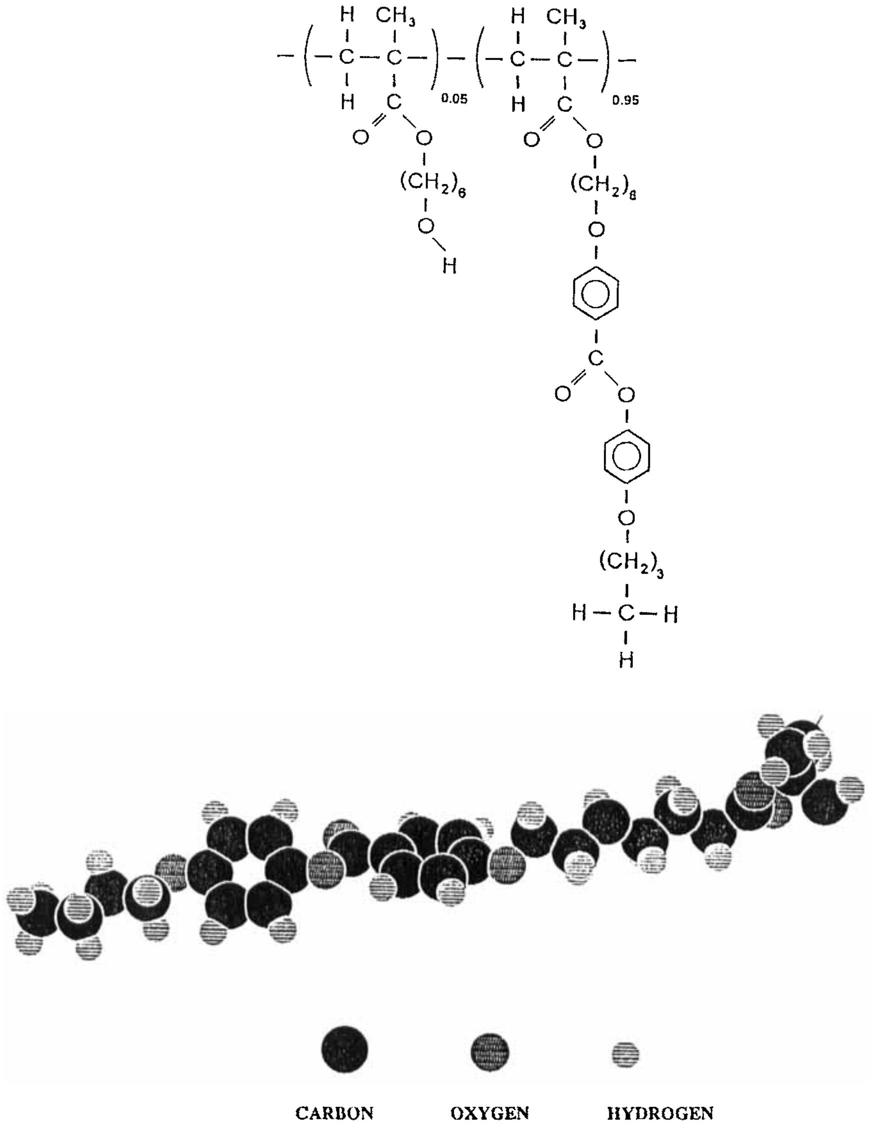


Figure 1. Chemical formula and model of the polymer liquid crystal.

molecules rotate freely around their 'molecular long axes' and these molecular long axes align in the liquid crystalline state. In the case of PLCs, the mesogenic units or parts of them can rotate around a bond between the polymer chain and the spacer, or between the spacer and the core of the mesogenic unit. Unlike a free molecule, the centre of mass during such a rotation does not necessarily remain steady. Moreover, rotation around a short axis can happen only if the polymer chain is distorted. At a smectic–nematic transition, the layer structure is destroyed, and in this process not only the mesogenic units are involved but also the backbone, as was revealed in [6].

In this paper, we report results for one of the cross-linkable polymethacrylate PLCs which was synthesized and investigated by Zentel's group: poly[4-butoxyphenyl 4-(6-methacryloyloxyhexyloxy)benzoate] containing 5 mol % of functional hydroxy groups [2].

Figure 1 shows the chemical formula of the polymer and the molecular model of the repeating unit. The model was obtained with the Desktop Molecular Modeller program [7]. As shown in figure 1, the mesogenic side group is rather rod-shaped, but does not possess any kind of symmetry; and benzene rings are neither coplanar nor are their *para*-axes parallel to each other.

Infrared spectroscopy is a powerful tool for the study of liquid crystals, including the polymeric type. Even early publications on liquid crystals reported considerable intensity changes with increasing temperature, as well as frequency shifts of absorption bands [8]. As liquid crystals are highly anisotropic, the intensity changes are caused mainly and the frequency shifts partly by orientation effects, so using well-aligned samples and polarized light for the measurements is essential. In these conditions, the study of the IR dichroism of those absorption bands which belong to clearly identified groups in the molecule, groups for which the direction of the vibrational transition dipole moment is known, can give reliable information about the structure and alignment of the liquid crystal [9, 10].

## 2. Theoretical

Liquid crystals are anisotropic materials, uniaxial or biaxial. Considering a well-oriented sample of domain, the natural frame of reference is determined by the anisotropy of that piece of material. The orientation of the molecule in the laboratory frame of reference can be described by the three Euler angles, $\vartheta$, $\varphi$ and $\psi$. Denoting the base vectors of the laboratory frame of reference by $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$, and those of the molecular frame of reference by $\mathbf{e}_\xi$, $\mathbf{e}_\eta$, $\mathbf{e}_\zeta$, the following relations connect the base vectors and the Euler angles [11].

$\vartheta$ means the angle between $\mathbf{e}_z$ and $\mathbf{e}_\zeta$,

$$\cos\vartheta = (\mathbf{e}_z \cdot \mathbf{e}_\zeta). \tag{1}$$

$\mathbf{n}$, the normal vector to the plane defined by $\mathbf{e}_z$ and $\mathbf{e}_\zeta$ makes the angle $\varphi$ with $\mathbf{e}_x$

$$\left.\begin{aligned} \mathbf{n} &= [\mathbf{e}_\xi \times \mathbf{e}_z]/\sin\vartheta, \\ (\mathbf{n}\cdot\mathbf{e}_x) &= \cos\varphi, \end{aligned}\right\} \tag{2}$$

$\vartheta$ and $\varphi$ define the $\zeta$ axis in the molecular frame of reference; usually the axis of highest symmetry of the molecule is chosen as the axis $\zeta$. For rod-shaped molecules, this is the molecular long axis.

$\psi$ describes the rotation of the molecule around the axis $\zeta$; this is the angle $\mathbf{e}_\xi$ makes with $\mathbf{n}$

$$(\mathbf{n}\cdot\mathbf{e}_\xi) = \cos\psi. \tag{3}$$

A vector defined with respect to the molecular frame of reference can be transformed into the laboratory frame of reference by the transformation matrix M

$$M=[\mathbf{e}_\xi, \mathbf{e}_\eta, \mathbf{e}_\zeta] = \begin{bmatrix} \cos\varphi\cos\psi-\cos\vartheta\sin\psi & \cos\varphi\sin\psi+\cos\vartheta\sin\varphi\cos\psi & \sin\vartheta\sin\varphi \\ -\sin\varphi\cos\psi-\cos\vartheta\cos\varphi\sin\psi & -\sin\varphi\sin\psi+\cos\vartheta\cos\varphi\cos\psi & \sin\vartheta\cos\varphi \\ \sin\vartheta\sin\psi & -\sin\vartheta\cos\psi & \cos\vartheta \end{bmatrix} \tag{4}$$

The probability of a certain orientation of a molecule is described by the orientational distribution function $f(\vartheta, \varphi, \psi)$. When the molecule is rod-shaped or any orientation around its axis $\zeta$ is equally probable, $f$ does not depend on $\psi$. In the case of a smectic A or nematic phase, the material is uniaxial, that is the distribution function is independent of $\varphi$.

If both conditions hold, the orientational order in the material is described by a single order parameter $S$

$$S=0{\cdot}5\langle 3\cos^2\vartheta-1\rangle, \tag{6}$$

where the bracket means the ensemble average for all molecules in the system. It can happen that the rotation around the molecular long axis is not free. The distribution function then depends on $\psi$, and the axes $\xi$ and $\eta$ have different average inclinations to the $z$ axis. This biaxility of the molecule is characterized by a parameter called dispersion and denoted by $D$ [11]

$$D=\tfrac{3}{2}\langle(\mathbf{e}_{\xi z})^2-(\mathbf{e}_{\eta z})^2\rangle=\tfrac{3}{2}\langle\sin^2\vartheta\cos 2\psi\rangle. \tag{7}$$

*IR dichroism:* The vibrational motions of a molecule can be described as linear combinations of $3N$-6 normal modes, where $N$ is the number of atoms in the molecule. In a normal mode, the vibration is accompanied by a vibrating dipole moment $\Delta\mathbf{p}$

$$\Delta\mathbf{p}=(\partial\mathbf{p}/\partial Q)Q=\mathbf{B}Q \tag{8}$$

where $Q$ is the normal coordinate of vibration and $(\partial\mathbf{p}/\partial Q)$ is called the transition moment belonging to the normal vibration $Q$ and is taken at $Q=0$. When interacting with light, the potential of this interaction is

$$(\Delta\mathbf{p}\,\mathbf{E})=(\mathbf{BE})Q,$$

where $\mathbf{E}$ is the electric field vector in the light beam. The solution of the equation of motion for the normal coordinate $Q$ in a harmonic electric field is a forced oscillation, the amplitude of which is proportional to $(\mathbf{BE})$

$$Q=g(\omega)(\mathbf{BE}), \tag{9}$$

where $g(\omega)$ is a complex function of the angular frequency $\omega$.

Any vibration mode of an individual molecule contributes to the dipole moment of the sample by

$$\Delta\mathbf{p}=\mathbf{B}(\mathbf{BE})g(\omega). \tag{10}$$

This contribution depends on the orientation of the individual molecule with respect to the electric field. Taking all the molecules in a unit volume into account, we get the contribution of the normal vibration to the polarization of the material.

$$\mathbf{P}=Ng(\omega)\langle\mathbf{B}(\mathbf{BE})\rangle, \tag{11}$$

where $N$ is the number of molecules in the unit volume and the bracket $\langle\ \rangle$ means the average for all possible orientations of a molecule

$$\langle \mathbf{B}(\mathbf{BE})\rangle = \int\int\int \mathbf{B}(\mathbf{BE}) f(\vartheta,\psi,\varphi)\sin\vartheta\, d\varphi\, d\psi. \tag{12}$$

As the vector of electric displacement is

$$\mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P} = \varepsilon\mathbf{E}$$

the normal mode with transition moment **B** contributes by

$$N\langle B_k B_l\rangle g(\omega) \tag{13}$$

to the $\varepsilon_{k,l}$ component of $\boldsymbol{\varepsilon}$, the tensor of complex permittivity.

If we choose the $z$ axis of the laboratory frame of reference so that it is parallel to the director of the sample, then the permittivity tensor becomes diagonal and $\varepsilon_{xx} = \varepsilon_{yy} \neq \varepsilon_{zz}$ if the material is uniaxial. Let the sample be oriented either homogeneously or homeotropically, the $z$ axis being parallel to the sample surface in the first case and normal to it in the second case. Let the light beam be incident normally on the sample and the electric field parallel to one of the optical axes. In this case the light beam traverses normally through the sample and behaves as an ordinary ray. Propagation and absorption are determined by the corresponding diagonal element of the permittivity tensor $\boldsymbol{\varepsilon}$, that is by $\varepsilon_{xx}$, if **E** is perpendicular to the director and by $\varepsilon_{zz}$, if **E** is parallel to it. The absorption is governed by the imaginary part of the permittivity, which is, in turn, proportional with $\langle B_x^2\rangle$ and $\langle B_z^2\rangle$, respectively [12].

The dichroic ratio $N$ of an absorption peak is defined as the ratio of the peak intensity measured with the light polarized parallel to the director, to the band intensity when the light is polarized perpendicular to it. The band intensity can be taken as the area of the band in the absorbance spectrum or as the peak intensity.

The normal modes reflect the symmetry of the unit they belong to—either a molecule or a unit cell in a crystal—but these normal modes of vibration are built up from the vibrations of smaller groups of atoms, like those of the benzene ring, the alkyl group or the C=O bond. For those normal modes of the molecule, where the vibrational energy is concentrated in one particular kind of unit, the absorption bands we observe in the sepctra can be assigned to the vibrating bond or group rather than to a vibrational normal mode of the whole molecule. Accordingly, the direction of the transition moment of the vibration is determined by the orientation of this group of atoms.

Assume that the direction of the transition moment is given by the polar angles $\theta$ and $\phi$ in the molecular frame of reference—that is, its components are

$$B_\xi = B\sin\theta\cos\phi, \quad B_\eta = B\sin\theta\sin\phi, \quad B_\zeta = B\cos\theta. \tag{14}$$

In order to calculate how the measurable dichroic ratio is determined by the direction of the transition moment and by the order parameters $S$ and $D$, the vector **B** has to be transformed from the molecular system into the laboratory frame of reference using the transformation matrix M (4), and then the average of the components has to be determined according to (13). Assuming that the distribution function $f$ does not depend on $\varphi$ (that is the material is uniaxial) we get

$$\left.\begin{aligned}\langle B_x^2\rangle = \langle B_y^2\rangle &= 0{\cdot}5B^2\{\sin^2\theta[1-\langle\sin^2(\phi-\psi)\sin^2\vartheta\rangle] + \cos^2\theta\langle\sin^2\vartheta\rangle\}\\ \langle B_z^2\rangle &= B^2\{\sin^2\theta\langle\sin^2\vartheta\sin^2(\psi-\phi)\rangle + \cos^2\theta\langle\cos^2\vartheta\rangle\}.\end{aligned}\right\} \tag{15}$$

Assuming at least $C_{2v}$ symmetry for the distribution function with respect to $\psi$, the averages $\langle B_x^2\rangle$ and $\langle B_z^2\rangle$ will be as follows:

$$\left.\begin{aligned}\langle B_x^2\rangle &= B^2/6\{2(1-S)+\sin^2\theta(3S+D\cos 2\phi)\},\\ \langle B_z^2\rangle &= B^2/3\{2S+1-\sin^2\theta(3S+D\cos 2\phi)\}.\end{aligned}\right\} \tag{16}$$

For homeotropic alignment, the absorbance is proportional to $\langle B_x^2\rangle$ in any direction in the plane of the sample. On warming up the material to the isotropic state, $S$ and $D$ become 0, so $B_x^2(i)=B^2/3$. The dichroic ratio can be defined as

$$N=\langle B_x^2\rangle/\langle B_x^2(i)\rangle = 1-S+\sin^2\theta(1\cdot 5S+0\cdot 5D\cos 2\phi). \tag{17}$$

For homogeneous alignment the dichroic ratio $N$ is

$$N=\langle B_z^2\rangle/\langle B_x^2\rangle \tag{18}$$

and the apparent order parameter, $S_a$ [9]

$$S_a=(N-1)/(N+2)=S-0\cdot 5\sin^2\theta(3S+D\cos 2\phi). \tag{19}$$

For $D=0$ this is equivalent to the well-known relation between $S_a/S$ and the angle $\theta$ of the transition moment with respect to the molecular long axis [13]. From the definition of the Euler angles, it follows that the reference direction from which $\psi$ is measured is fixed by the choice of $\vartheta$ and $\varphi$. The rotation is not free if the $\mathbf{e}_\xi$ axis of the molecule tends to incline at a certain angle to the $z\zeta$ plane. But such an inclination from both sides of the plane is equally probable, which means that $f(\vartheta, \psi)$ is symmetric in $\psi$. If the molecule possesses a plane of symmetry and $\mathbf{e}_\xi$ were chosen normal to that plane, $\psi=0$ means that the plane of symmetry coincides with the $z\zeta$ plane. If the molecule has not got any symmetry, we can imagine that the molecule with its mirror image makes a symmetrical unit and the symmetry of $f(\vartheta, \psi)$ still holds. Assume that two mutually perpendicular vibrations are found in the plane normal to the axis $\zeta$ of the molecule or unit, but that neither of them should lie in the hypothetical mirror plane which determines the axes of the molecular frame of reference. Let the polar angles of both mutually perpendicular transition moments be

$$\theta_1=90^\circ,\quad \phi_1=\phi_0,\quad \theta_2=90^\circ,\quad \phi_2=\phi_0+90^\circ \tag{20}$$

Using (19), the order parameter $S$ and $D\cos 2\phi_o$ are obtained from the apparent order parameters $S_{a_1}$ and $S_{a_2}$ as

$$S=-S_{a_1}-S_{a_2},\quad D\cos 2\phi_o=S_{a_2}-S_{a_1}=D'. \tag{21}$$

For the other vibrations, $S_a/S$ is a linear function of $D'/S$ if the geometry of the molecule is unchanged during the heating cycle

$$S_aS/S=(1-1\cdot 5\sin^2\theta)-\frac{D'}{2S}\sin^2\theta\frac{\cos 2\phi}{\cos 2\phi_o}. \tag{22}$$

From the intercept of this straight line, the angle $\vartheta$, from the the slope $\cos 2\phi/\cos 2\phi_o$, is obtained.

## 3. Experimental

The sample material was produced by radical copolymerization of [4-butoxyphenyl 4-(6-methacryloyloxyhexyloxy)benzoate] and $\omega$-hydroxyhexyl methacrylate. The polymer contained 5 mol% of functional hydroxy groups see figure 1. The molecular mass is 250 000 and the material has glassy, smectic A, nematic and isotropic phases.

(G 318 $S_A$ 375 N 379 I). These temperatures of phase transition (in K) were measured by DSC. The liquid crystalline phases were identified by polarizing optical microscopy and X-ray diffraction [2, 4]. The dielectric behaviour of the similar homopolymer not containing OH groups was investigated in [6].

### 3.1. *Sample preparation and IR spectroscopic measurements*

The material was warmed up above 100°C and spread over a 1·5 mm silicon window. It was then covered with a second window, pressed together and placed into a brass sample holder where the windows were kept firmly together by springs. One sample was prepared with a rubbed PVA coating on the windows. The other was made without an alignment layer. The thicknesses of the samples were estimated from the interference waves in the transparent regions of the spectra. The PVA aligned sample was about 5 $\mu$m thick; the other sample was about 12 $\mu$m thick. The temperature and polarization dependent infrared spectra were recorded with a BIORAD FTS-60A Fourier-transform infrared spectrophotometer, using a SPECAC IR-KRS5 wire-grid polarizer. The temperature of the cell was measured by a 100 $\Omega$ platinum resistance thermometer and controlled by an automatic temperature controller which kept the temperature within a 0·1°C accuracy. Before the measurements, the samples were subjected to the heat-treatment shown in table 1 to give them a defined structure.

This thermal history produced a fairly homeotropic alignment for the sample which was between the bare silicon windows and a homogeneous alignment for the sample in the PVA-coated cell.

After the IR spectra of the homeotropically aligned sample had been measured, the sample was subjected to an alignment treatment in a magnetic field of 7·05 T (**B** was parallel to the surface of the sample) by cooling it down from 422 K in 5 K steps and holding it at each temperature for 20 min. This treatment produced a homogeneous alignment.

The direction of maximum absorbance coincided with the direction of rubbing for the PVA aligned sample, but it made an angle of about 12° with the direction of **B** in the case of the magnetically aligned sample.

The spectra were recorded during a heating cycle with both polarizations—electric field vector either parallel or perpendicular to the alignment direction. A sweep time of 7 min and a hold time of 3 min were used at each temperature step before scanning the spectra with both polarizations of the incident light. The absorbance spectra were recorded from 650 to 4000 $cm^{-1}$, and they were corrected for the absorbance of the Si windows. For the evaluation of the absorption peaks, a band fit program was used which was supplied by the manufacturer.

Table 1. Thermal history of the non-aligned and PVA aligned samples.

| Temperature step/K | | | |
|---|---|---|---|
| From | To | Sweep time/min | Hold time/min |
| 300 | 380 | 30 | 10 |
| 380 | 375 | 30 | 60 |
| 375 | 370 | 60 | 60 |
| 370 | 375 | 60 | 60 |
| 375 | 320 | 300 | 300 |
| 320 | 300 | 600 | 3 days |

### 3.2. *Experimental results*

The characteristic spectral features are summarized in figure 2(*a*)–(*e*) where the spectra of the 12 $\mu$m thick sample, both homeotropically and homogeneously aligned, are shown in the relevant spectral regions; the spectra of the homogeneously aligned sample measured at 330 K both with parallel and perpendicular polarization of the incident light are shown together with the spectra of the homeotropic sample, measured both in the $S_A$ state at 330 K and in the isotropic state at 381 K. Assignment of the main bands [14] is given in table 2.

Figure 2(*a*) shows the overlapping CH stretching vibration bands of the alkyl chains. The peaks which belong to the $CH_2$ and $CH_3$ groups cannot be resolved, but the asymmetric vibration of the $CH_2$ groups looks more or less transverse to the alignment direction, being stronger in $\sigma$ polarization and in the smectic state, and getting weaker in the isotropic state for the homeotropic sample. That would mean greater or lesser alignment of the alkyl chains of the spacer and end tail in the side group of the polymer.

In figure 2(*b*) the band of the C=O stretching vibrations is shown. This band is composed of the C=O vibration of the carboxyl group in the rigid part of the mesogenic unit and that between the main chain and the side group of the polymer, resulting in an unresolved asymmetrical band. These absorption bands exhibit low dichroism.

Figure 2(*c*) shows the most characteristic benzene ring vibration bands. However, the deformation vibrations of the $CH_2$ and $CH_3$ groups also appear in this range. These vibrations are mainly parallel, stronger in $\pi$ than in $\sigma$ polarization when homogeneously aligned, and getting stronger in the isotropic state than they were in the smectic state when the sample was homeotropically aligned. There is some discrepancy in the behaviour of the weak CH deformation bands at 1460, 1420 and at 1395 cm$^{-1}$. Although they show strong dichroism for the magnetically aligned homogeneous sample, almost no intensity change can be detected between the smectic phase and the isotropic liquid for the homeotropic alignment.

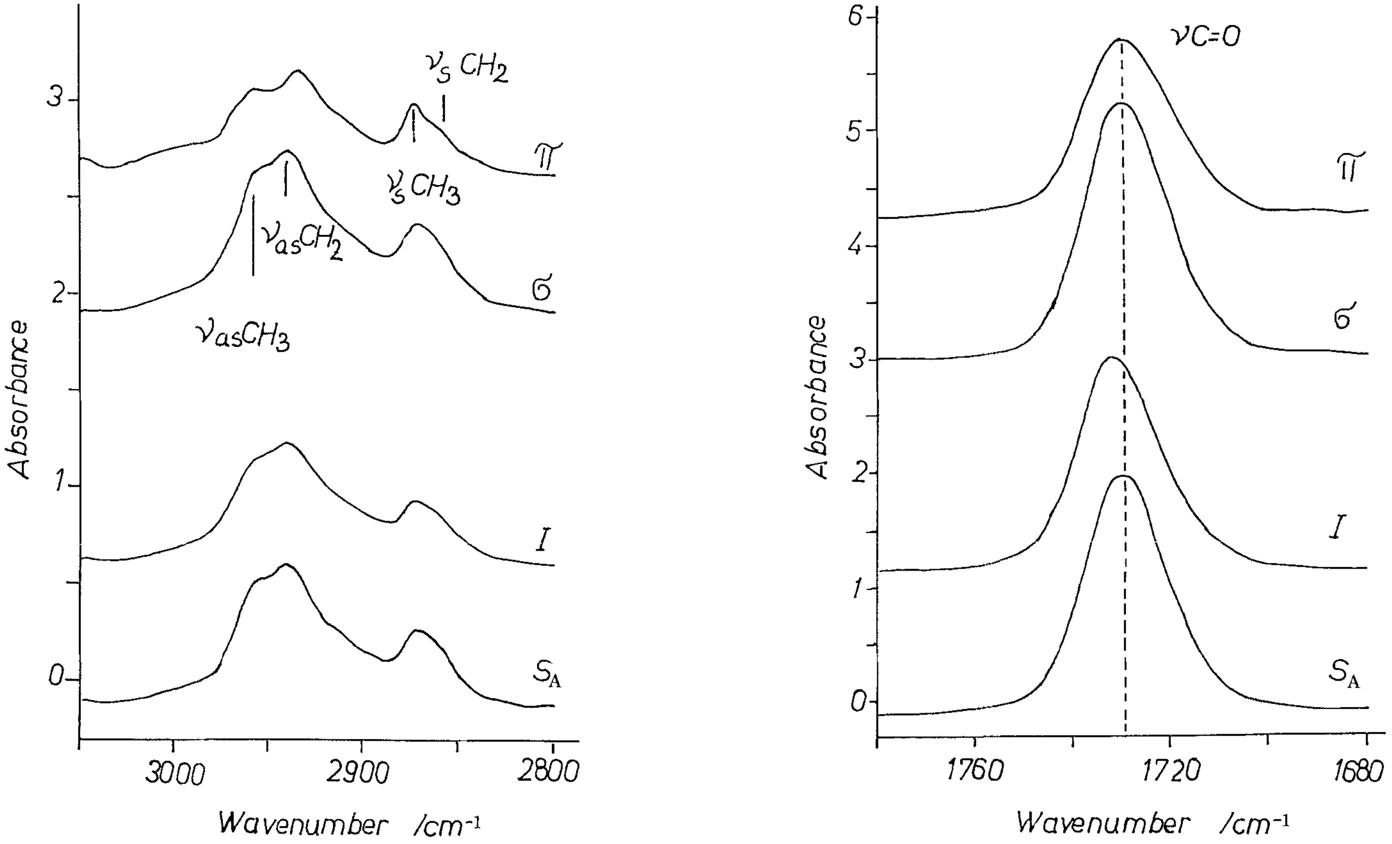
The range shown in figure 2(*d*) is dominated by the strong bands of the C–O vibrations, all of them longitudinal. The weak and sharp band at 1010 cm$^{-1}$ is an in-plane CH vibration of the benzene ring; this is also parallel, while both weak bands at 1110 and 1130 cm$^{-1}$, also in-plane CH vibrations, are transverse. The last range, figure 2(*e*) shows the out-of-plane vibrations of the benzene rings. These are all

Table 2. Investigated absorption peaks.

| Wavenumber†/cm$^{-1}$ | Polarization | Assignation of the vibration | $\vartheta_{PVA}$/° | $\vartheta_H$/° |
|---|---|---|---|---|
| 764 | Transverse | ‡BR, CC out-of-plane (4) | 80 | 90 |
| 847 | Transverse | BR, CH out-of-plane (17 *b*) | 90 | 83 |
| 1103 | Transverse | BR, CH in-plane (18 *b*) | 90 | 90 |
| 1009 | Longitudinal | BR, CH in-plane (18 *a*) | 31 | 27 |
| 1393 | Longitudinal | $CH_3$, symmetric deformation | 27 | 28 |
| 1606 | Longitudinal | BR, CC in-plane | 36 | 23 |
| 1730 | Mixed | C=O bond stretching | 57 | 62 |

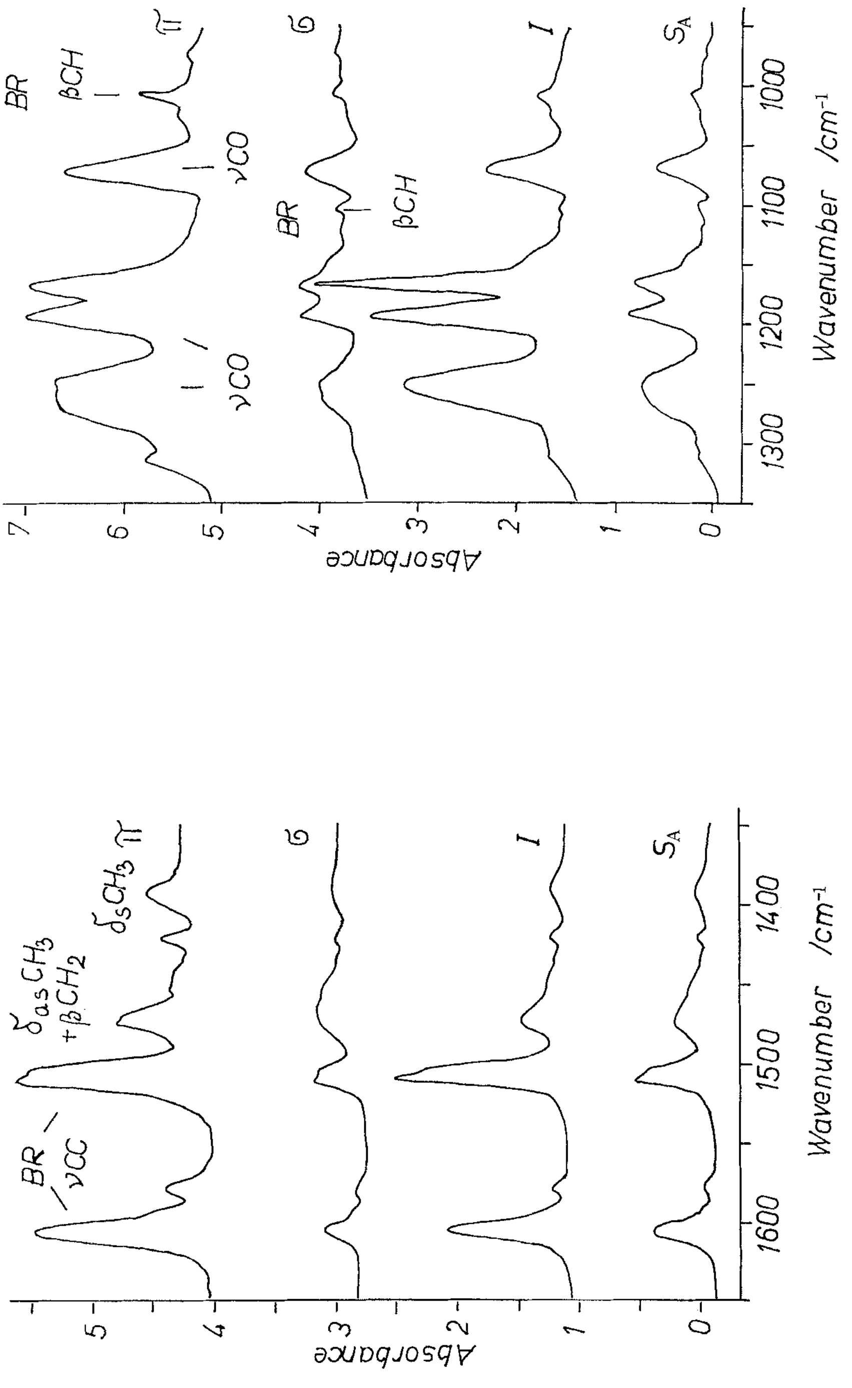
‡ BR stands for benzene ring vibrations; the number if brackets is Varsányi's notation for the vibration [14].

† For the 1606 cm$^{-1}$ band the largest contribution comes from the ring substituted with the carbonyl group. The same is true for the 764 cm$^{-1}$ band. The other ring vibrations at 847 cm$^{-1}$, 1103 cm$^{-1}$ and 1009 cm$^{-1}$ are less sensitive for the substitution.


Absorbance
3
2
1
0
$\nu_s CH_2$
$\nu_s CH_3$
$\nu_{as}CH_2$
$\nu_{as}CH_3$
π
σ
I
$S_A$
3000
2900
2800
Wavenumber /cm⁻¹
Absorbance
6
5
4
3
2
1
0
νC=O
π
σ
I
$S_A$
1760
1720
1680
Wavenumber /cm⁻¹

(*a*) (*b*)

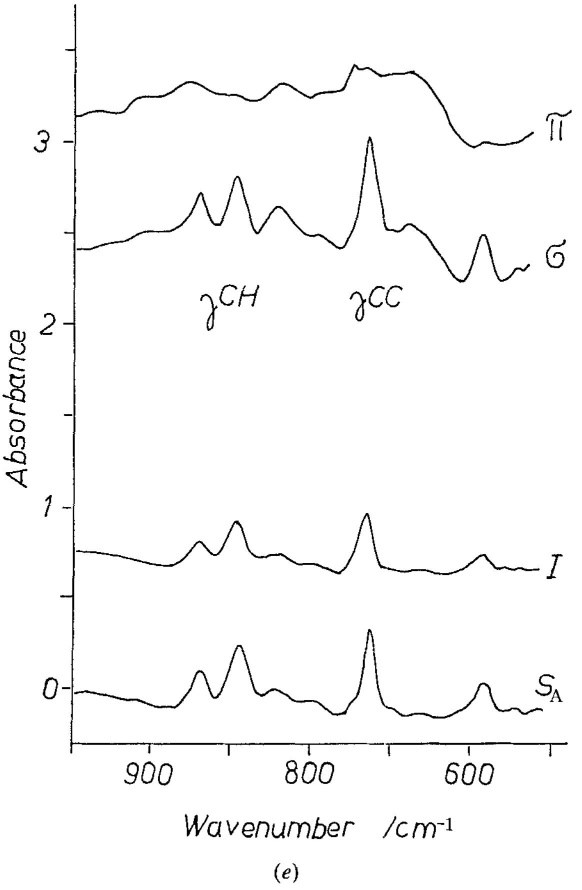
Figure 2.


Absorbance
7
6
5
4
3
2
1
0
BR
βCH
νCO
π
σ
BR
βCH
νCO
I
SA
1300
1200
1100
1000
Wavenumber /cm-1
Absorbance
5
4
3
2
1
0
BR
νCC
δas CH3 + βCH2
δs CH3
π
σ
I
SA
1600
1500
1400
Wavenumber /cm-1

(d)

(c)

Figure 2.



(e)

Figure 2. Infrared dichroism observed in the different spectral ranges. The meanings of the notations are: $S_A$ and I refer to the homeotropically aligned sample, $S_A$: at 330 K (smectic state), I: at 381 K (isotropic state); $\pi$, $\sigma$: magnetically aligned homogeneous sample at 330 K. $\pi$: electric field vector parallel to the director, $\sigma$: perpendicular to it. Further explanation is in the text.

transverse vibrations, weaker in $\pi$ than in $\sigma$ polarization and weaker in the isotropic liquid than in the homogeneously aligned smectic state. Estimating the order parameter from the 847 cm$^{-1}$ band, and assuming that it is perpendicular to the 'molecular long axis', $S \approx 0{\cdot}8$ is obtained for both the homogeneous and the homeotropic alignment.

The dichroic ratio $N = A_\pi / A_\sigma$ and the apparent order parameter

$$S_a = \frac{N-1}{N+2}, \tag{23}$$

were determined for the bands quoted in table 2. $A_\sigma$ and $A_\pi$ represent the peak absorbance of a band in the spectrum, obtained with parallel and perpendicular polarization, respectively. The peak absorbance and the position of the overlapping bands were obtained by using a band-fit program supplied by the manufacturer of the FTS60A spectrophotometer. The program fitted 5 parameters to each of the bands, two for the Gaussian contribution, two for the Lorentzian, and one for the ratio of both. The fitting worked better for the sharp and weak bands then for the strong and broad bands, and it was difficult to find a good fit in the band tails where the intensity was considerably influenced by the interference of multiple reflected light waves.

The peak absorbance was used to calculate the dichroic ratio instead of the integrated intensity; as the width of the bands did not change much with temperature, the peak absorbance was as proportional to the square of the transition dipole moment as the integrated intensity would have been, but it was a better defined characteristic of the band, obtainable with higher reproducibility than the integrated intensity.

The apparent order parameters obtained for the different bands are shown in figures 3 and 4, for both of the homogeneously aligned samples.

The apparent order parameter of the PVA aligned sample in figure 3 exhibits a completely normal behaviour. For all bands, the absolute value of $S_a$ decreases slowly with temperature in the smectic phase, and more steeply at the smectic–nematic–isotropic transitions. The behaviour of the magnetically aligned sample shown in figure 4(*a*) and (*b*) is rather extreme—those bands which were stronger for $\pi$-polarization became weaker, and vice versa when the sample reached the nematic state. The apparent order parameter not only fell to zero at the phase transformation temperature in the absence of the aligning magnetic field, but also changed sign and

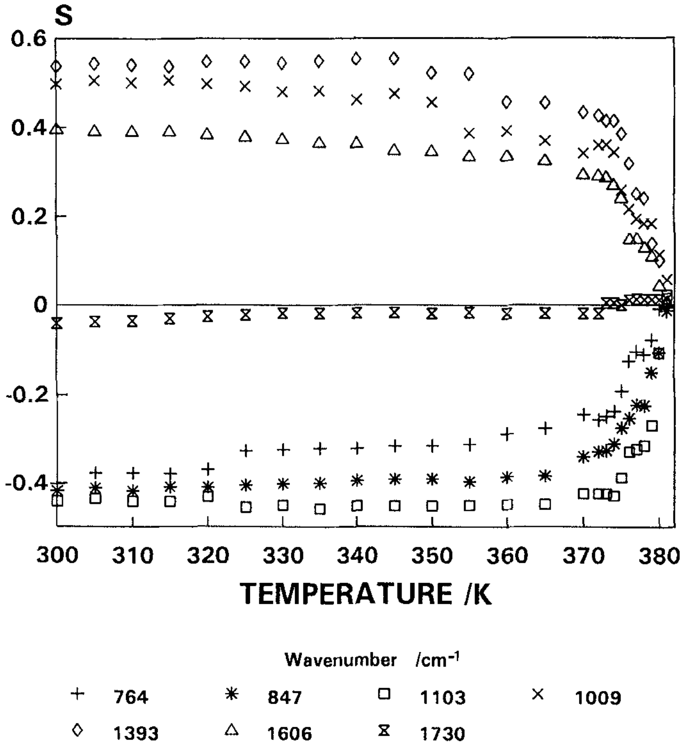
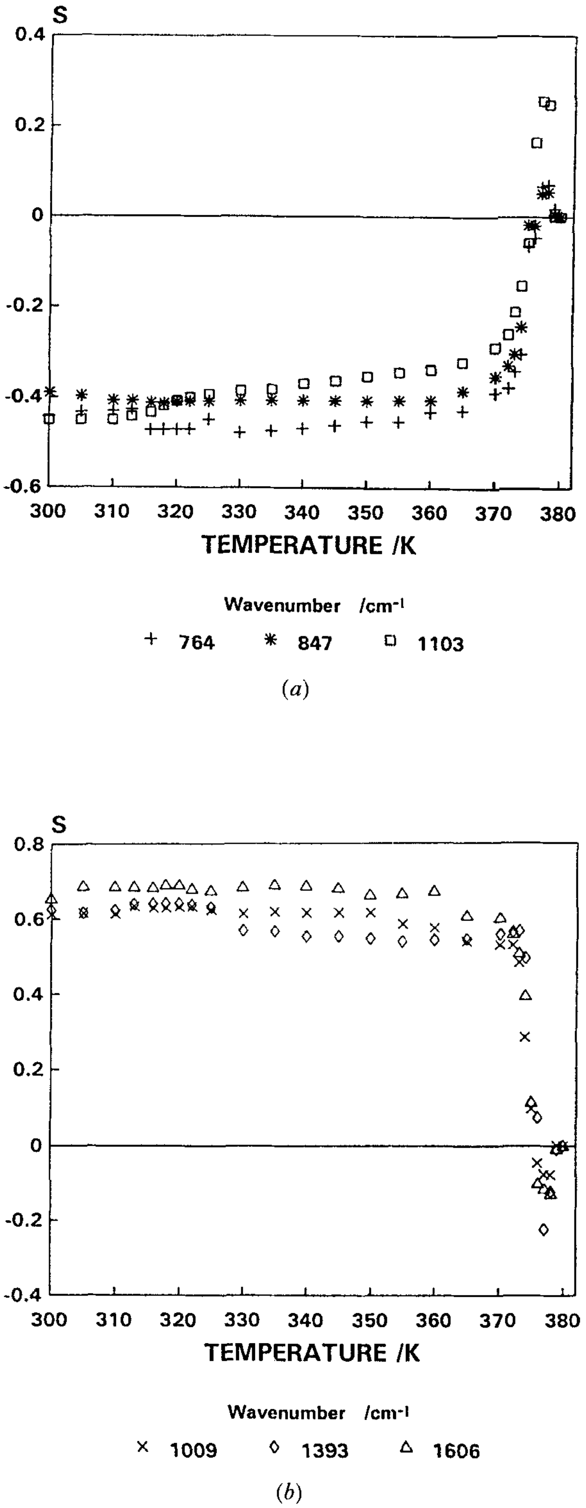


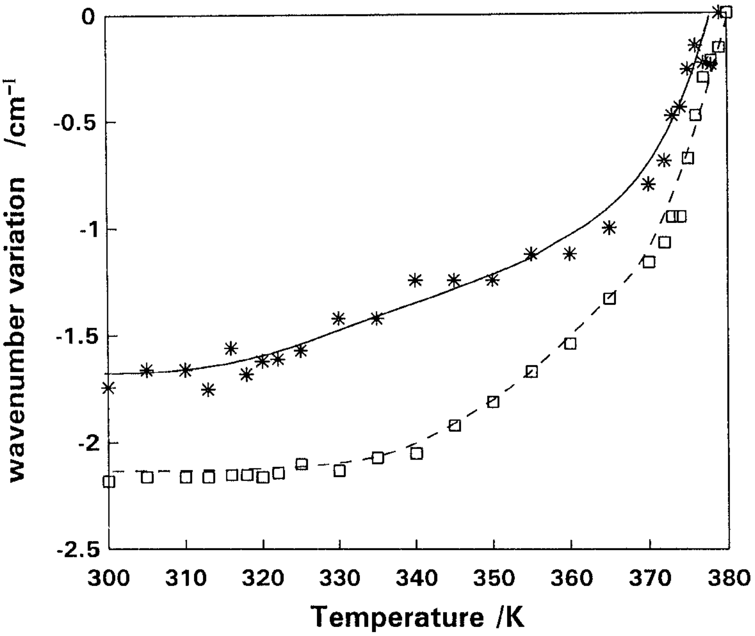
Figure 3. Apparent order parameter obtained for different absorption peaks; PVA aligned sample.



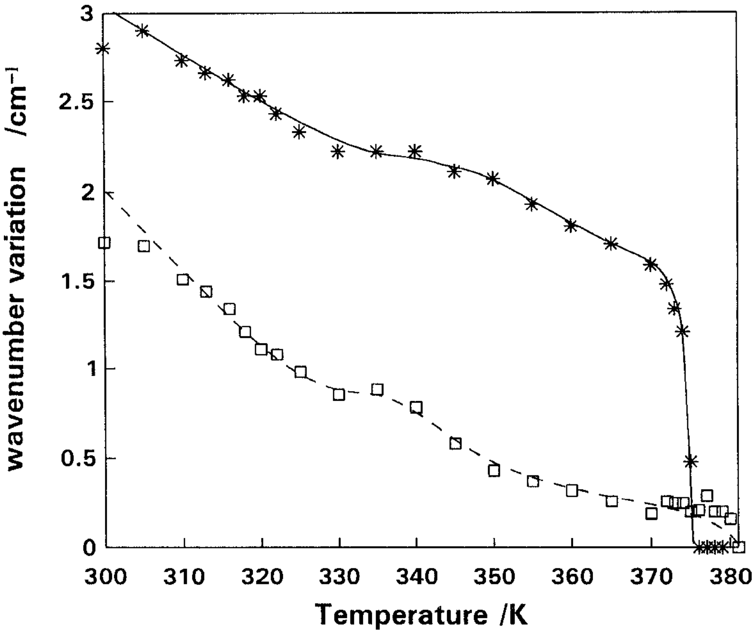
(*a*)

(*b*)

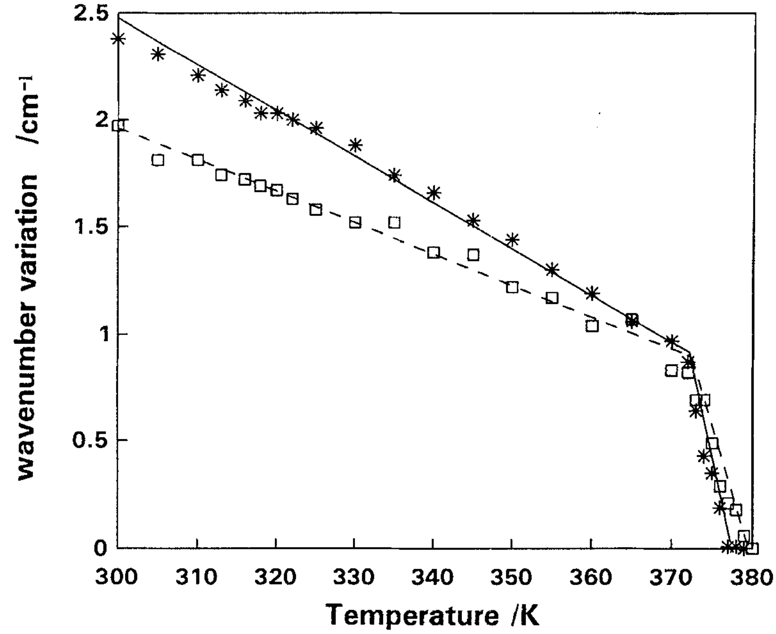
Figure 4. Apparent order parameter for the longitudinal (*a*) and transverse (*b*) vibrations; magnetically aligned sample.


0
-0.5
-1
-1.5
-2
-2.5
wavenumber variation /cm$^{-1}$
300
310
320
330
340
350
360
370
380
Temperature /K

(*a*)


3
2.5
2
1.5
1
0.5
0
wavenumber variation /cm$^{-1}$
300
310
320
330
340
350
360
370
380
Temperature /K

(*b*)



(*c*)

Figure 5. Wavenumber change with temperature with respect to the wavenumber of the band in the isotropic state. (*a*) C=O bond stretching vibration (1730 cm$^{-1}$); (*b*) $CH_3$ symmetric deformation vibration (1393 cm$^{-1}$), and (*c*) benzene ring in-plane CC vibration (1606 cm$^{-1}$): (*), magnetically aligned and (□), PVA aligned.

increased in absolute value in the nematic state. It was as if the material rearranged itself, and not into the expected homeotropic alignment, but into some oblique alignment. For all the bands which were investigated, $S_a$ became about zero at 375 K, and in the nematic phase reached a maximum absolute value at 378 K.

As for the position of the absorption bands, small, but marked wavenumber shifts were detected with increasing temperature for several bands. Figures 5 (*a*), (*b*) and (*c*) show the relative wavenumber changes for the C=O bond stretching vibration (1730 cm$^{-1}$), for the benzene ring deformation vibration (1606 cm$^{-1}$) and for the $CH_3$ symmetric deformation vibration band (1393 cm$^{-1}$), respectively.

The character of the temperature dependence is similar for both the PVA and magnetically aligned samples, although the extents of the wavenumber changes are different. While the wavenumber of an absorption peak usually decreases with temperature as is the case for the 1393 cm$^{-1}$ and 1606 cm$^{-1}$ bands, the C=O vibration frequency increases over the whole range of the liquid crystal phase.

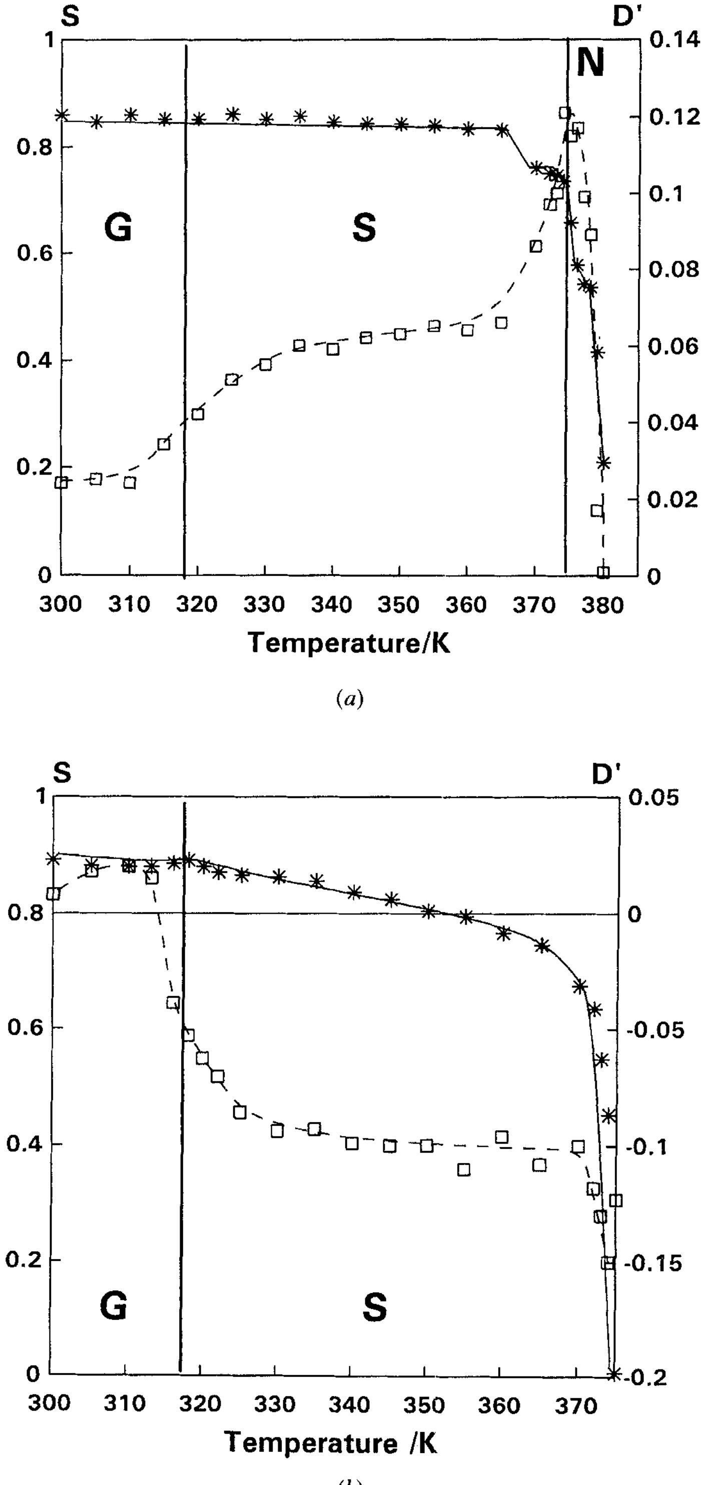
## 4. Discussion

Figure 1 shows the model of a fragment of the polymer. Although the geometry of the side group can be different in the condensed state, from that in the figure the model offers a good impression about the look of the molecule. The side group is really nearly linear in the minimal-energy conformation—with the alkyl chain of the spacer in the all-*trans* form and even the tail quite ordered—but it does not have any kind of symmetry. Moveover, the benzene rings are neither coplanar nor are their *para*-axes parallel to each other. The CO group in this rigid part of the mesogenic unit tends to be coplanar with the benzene ring to which it is attached; therefore considerable conjugation can exist between the C=O bond and the $\pi$-electron cloud of that ring. The flexible spacer allows the rigid part of the mesogenic unit to rotate. In this sense, the structure can be considered symmetrical—rod-like—on average. But from the point of view of its interaction with infrared light, the molecule is unsymmetrical and the transition dipole moment of any normal vibration of the unit can make an arbitrary angle with the assumed 'molecular long axis', which is a direction, associated with the side group, whose angular distribution function has cylindrical symmetry around the director of the sample (that is, around the $z$ axis of the laboratory frame of reference.) We choose this direction as the $\zeta$ axes of the molecular coordinate system.

In order to estimate the order parameters $S$ and $D$ by using equation (21), we have to make some assumptions about the direction of the transition moments. The assumption that any longitudinal vibration is parallel to $\mathbf{e}_\zeta$ yields a smaller value for the order parameter derived rom the apparent order parameters (figures 3 and 4) than the smallest value we get from the transverse vibrations corresponding to the situation that they are at right angles to the axis $\zeta$.

Kiefer and Baur [9] proved the existence of molecular biaxility—non-vanishing dispersion $D$ even in the nematic state of a series of biphenylyl and phenyl benzoate mesogens. They used three mutually perpendicular vibrations, one parallel to the molecular long axis, to get $S$, and two perpendicular vibrations, to estimate $D$. In our case, neither of the longitudinal vibrations proved to be really parallel to the axis $\zeta$. Therefore two mutually perpendicular transverse vibrations were chosen; $\theta = 90^\circ$ was assumed for both of them, and the order parameter and the dispersion were determined with the help of equation (21). One was the transverse $\beta$CH vibration at 1110 cm$^{-1}$ and the other was chosen from the two out-of-plane benzene ring vibrations, selecting the one with the higher absolute value of $S_a$. This was the band at 847 cm$^{-1}$ for the PVA aligned sample and the 764 cm$^{-1}$ band in the case of the magnetically aligned sample. The resulting values of $S$ and $D' = D\cos 2\phi_0$ in terms of temperature are plotted in figures 6 (*a*) and (*b*).

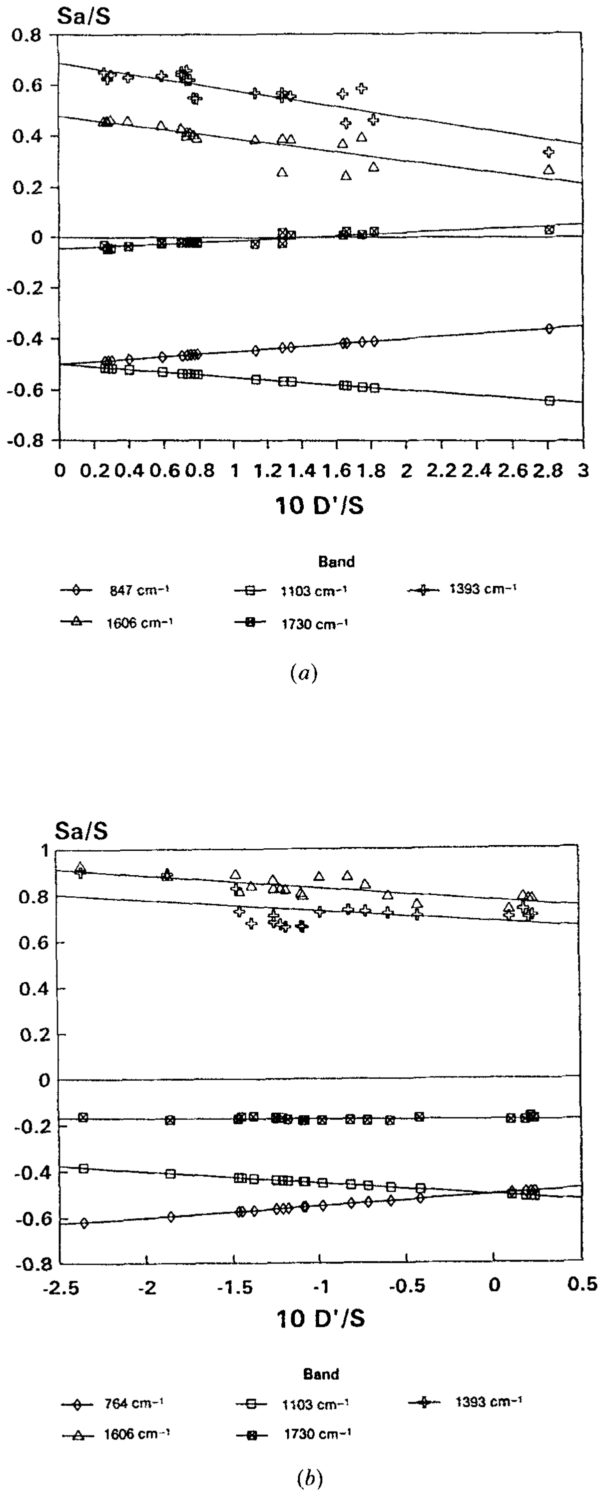
The value obtained for $S \approx 0{\cdot}85$ is quite typical for smectic A materials. The order parameter of the PVA aligned sample decreased very slowly in the smectic state, and this was followed by an abrupt fall in $S$ at the $S_A$–N and N–I transitions. The magnetically aligned sample had a starting value of 0·9 for the order parameter, but then a more gradual reduction followed and $S$ fell to zero at 375 K, when the nematic state was reached. The difference between the two samples can be ascribed to the presence of the alignment layer or its absence. This could keep the thinner sample aligned, while the thicker sample, without the alignment layer, was subjected to thermal disordering; it could, furthermore, be exposed to a different alignment effect from the walls. This influence of the walls and the slight pressure applied during preparation might have been strong enough to produce a new ordering in the nematic state as shown in figures 4 (*a*) and (*b*). The $D'$ values were obtained with a rather low accuracy of about 0·02, but it is clear from figure 6 that they had opposite signs for the two samples. This means not only different dispersion, but even different inclinations of the planes of the benzene rings to the $z\zeta$-plane. On the other hand, both the absolute values and the shapes of the plots are rather similar for both samples.



(*a*)

(*b*)

Figure 6. Order parameters $S$ and $D' = D \cos 2\phi_0$ for both the PVA aligned sample (*a*) and the magnetically aligned sample (*b*): (*) $S$ and (□) $D$.



(*a*)

(*b*)

Figure 7. $S_a/S$ ($S_a$: apparent order parameter) versus $D'/S$ for various absorption bands. (*a*) PVA aligned sample, (*b*) magnetically aligned sample.

The $D'(T)$ curves reflect both the glassy-smectic and smectic–nematic phase transformations very well, and surprisingly enough, the absolute value of $D'$ increases with temperature at both phase transformation; this would mean a temperature-dependent $\phi_0$ rather than an increasing dispersion with temperature. Plotting $S_a/S$ versus $D'/S$ for different bands in the range of temperature 300 K–375 K (figures 7(*a*) and (*b*)), the points scatter around straight lines according to equation (22). From the best fit parameters, the angles $\theta$ were determined and these are presented in table 2. Both vibrations which are parallel to the *para*-axis of the benzene rings, that is at 1009 and 1606 $\mathrm{cm}^{-1}$, make an angle of about 30° with the $\zeta$ axis, and these $\theta$ angles are rather different for the two samples. This means that different methods of alignment have caused the rigid part to incline at different angles to the $\zeta$ axis.

It is very difficult to interpret the slope of the plots, because they result in $\cos 2\phi/\cos 2\phi_0$ values as high as about 10 for some bands. This is compatible only with $\phi_0$ values close to 45° and consequently, with $D$ values approaching unity. This would mean an almost hindered rotation around the $\zeta$ axis and a herring-bone like arrangement of neighbouring mesogenic groups. Such an arrangement is reported as quite common for the side chain liquid crystal polymers [15].

The $CH_3$ groups—one at the tail end of the side group, the other in the main chain—exhibit quite a high apparent order parameter which corresponds to an angle of about 28° made with the $\zeta$ axis. This means that not only the rigid part, but also the end tail and even the polymer chain are ordered. This is the same conclusion reached by Bürkle [10] from his study of the IR dichroism of a side chain liquid crystal polymer acrylate possessing the same phenyl benzoate rigid core and $(CH_2)_6$ spacer as our material, but with a C≡N end group. His measurements also revealed that the *para*-axes of the benzene rings were not parallel with the molecular long axis, which he supposed to coincide with the C≡N bond.

The C=O bond in the rigid part makes an angle of about 60° with the $\zeta$ axis. The sum of this angle and that of the longitudinal $\beta$CH vibration is about 90°, and this is in accordance with the geometry of the molecular model in figure 1.

In the case of the magnetically aligned sample, a sudden realignment took place at the phase transformation from smectic to nematic. The projection of the $\zeta$ axis on the sample plane rotated by about 90°, so that all the apparent order parameters changed sign. It is also very interesting that the dichroism in the nematic state started to increase with temperature, passing through a maximum before falling to zero in the isotropic state. We try to explain this phenomenon in the following way. In the absence of the magnetic field, the surface effects and the slight pressure acted on the side groups which lie parallel to the windows of the sample holder. This effect tended to align the side groups perpendicular to the windows. As they are connected to the polymer backbone, also arranged in layers, their rotation is constrained, and therefore the realignment must happen in some collective way. The side group might turn round the C–O bond of the carboxyl group that connects the side chain to the main chain. In that case the side group moves on a cone and can occupy such a position as to result in the observed dichroism. The conical movement of one side group can involve deformation of the polymer chain and induce the same movement in neighbouring groups. It could therefore happen that the dichroic ratio slightly increases in the warming-up cycle in the nematic phase. Zentel *et al*., observed a relaxation type called $\delta$ relaxation for the homopolymer [6] using dielectric spectroscopy; this was accompanied by a very large dipole moment contribution and seemed to be connected with the smectic–nematic transition. They assigned this type of relaxation to the turning over of the whole side chain around the polymer backbone, because such a relaxation would cause the highest dipole moment contribution. We are convinced that the $\delta$ relaxation in the dielectric behaviour and the turning over effect observed with IR spectroscopy are different manifestations of the same phenomenon of collective rearrangement of the side groups, but that the latter relates to a conical movement of the side groups rather than to a turning over around the main chain.

In the case of the PVA aligned sample, the PVA layer kept the sample in the homogeneous alignment—slight dichroism was observed even above the nematic–isotropic phase transformation. But the abrupt fall in the order parameter above the smectic–nematic transition might be caused not only by the increasing temperature, but also by the realigning surface effects.

Returning to the temperature dependence of the band frequencies (see figures 5 (*a*), (*b*) and (*c*)), it is quite usual that the maximum of an infrared absorption band shifts to a lower wavenumber with increasing temperature or at a phase change accompanied by increasing specific volume. All these can make the structure looser and the potential well for the vibrating atoms broader. The C=O bond was an exception; its wavenumber increased, not only at the phase transition, but also gradullly over the whole smectic range.

The central C=O bond is conjugated with the $\pi$-electron cloud of the next benzene ring and this conjugation is the stronger the more coplanar the C=O bond and the benzene ring. The lone pairs of electrons of the other oxygens also influence the $\pi$-electron cloud, but they have an electron donating effect in contrast to the electron withdrawing effect of the carbonyl group.

As a result, the two benzene rings carry opposite net charges and such a pairing up of neighbouring side groups seems energetically favourable where the oppositely charged rings lie parallel, beside each other (one group tail-up and the other tail-down). The inductive effect between them stabilizes the charge separation, making a $\pi$-electron complex [16] and resulting in a negative charge on the carbonyl oxygen. The neighbouring pairs can be arranged in a herring-bone structure; this lets the negatively charged carbonyl oxygens locate themselves as far from each other as possible. The more polar the C=O bond, the lower is its vibration frequency. Therefore the increase in frequency with rising temperature should mean the loosening of the $\pi$-electron complex. At the smectic–nematic transition, there the smectic layers disappear, the $\pi$-electron complex ceases to exist and with that, the ionic character of the C=O bond is diminished, causing then an increase in the vibration frequency.

In our discussion, the inner field effect was completely ignored. Both Kiefer and Baur [9] and Bürkle [10] suggested that this effect was smaller than our experimental error.

The measurements were carried out in the Department of Microelectronics and Electrical Engineering, Trinity College, Dublin, with funding from the Commission of the European Communities, Grant No. SCI*0291. We wish to acknowledge Professor B. K. P. Scaife and Professor W. G. Scaife (Trinity College, Dublin) for the very useful discussions. We also thank Marco Weber and Arstrid Dahms (Max-Planc Institut für Polymerforschung, Mainz) for the magnetically aligned sample. We express our gratitude to all members of the Department of Microelectronics and Electrical Engineering, TCD, Dublin, for their help and kindness. And forever we keep the memory of our dear colleague Mr George Salmon who died during the period of this work.

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