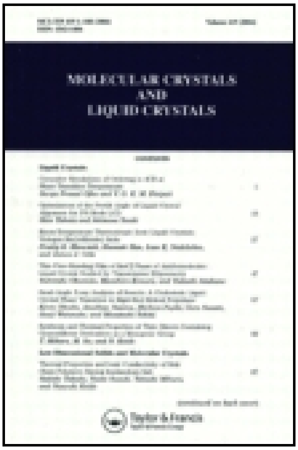

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Unusual Perpendicular Chain Orientation in a Smectic Liquid Crystal Polyester Subjected to Shear or Elongational Flow

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Unusual Perpendicular Chain Orientation in a Smectic Liquid Crystal Polyester Subjected to Shear or Elongational Flow

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In this work, we report on flow-induced orientation in two low molecular weight polyesters, both containing the smectic diol 4,1'-bis (6-hydroxy hexoxy) biphenyl (BHHBP) and either isophthalic acid (IA) or terephthalic acid (TA). The polyester of BHHBP and IA has a mesophase, while the polyester of BHHBP crystallises on cooling from the isotropic melt without any mesophase formation. When the TA polyester was subjected to flow, the chains were aligned parallel to the flow direction. In contrast, when the IA polyester was sheared or subjected to elongational flow in the *mesophase state*, it was found that the chains were surprisingly oriented *perpendicular* to the flow direction or the fibre axis. However, when the IA polyester was sheared or elongated in the *isotropic* molten state, the normal orientation with the chain axis *parallel* to the flow direction was observed. Thus, perpendicular orientation appears to have an association with deformation in the mesophase state. The orientation information was deduced from studying the dichroism of vibrational bands in the polarised infrared spectra.

Keywords: Liquid crystalline polyesters; mesophase; flow orientation; infrared dichroism; perpendicular chain orientation

1. INTRODUCTION

Some of the polysters, polyurethanes and polycarbonates made from the smectic diol BHHBP (1) are reported to have liquid crystalline properties (2). The monomer BHHBP is shown below.

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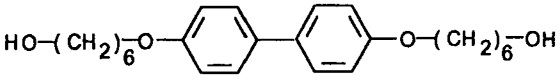
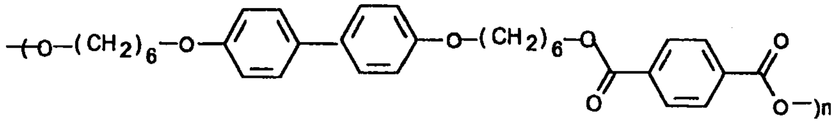
*Author to whom correspondence should be addressed.

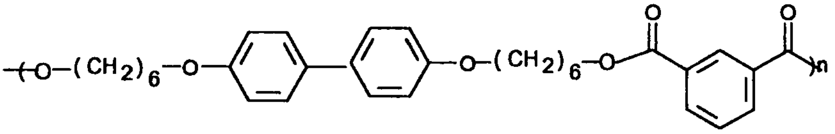


BHHBP SMECTIC MONOMER

We have studied (3) in particular the polyesters made by the condensation of BHHBP with terephthalic acid (TA) and isophthalic acid (IA). These polymers are shown below.



BHHBP-TA POLYESTER



BHHBP-IA POLYESTER

Both polyesters were reported to have a smectic A mesophase by Fischer *et al.* [2] In our investigation, we found definite evidence for a smectic mesophase on cooling the BHHBP-IA polyester from the isotropic melt, but we disagreed [3] with the conclusions of Fischer *et al.* [2] about the BHHBP-TA polyester, in that we thought that crystallisation occurred directly (without mesophase formation) on cooling from the isotropic melt. A further investigation of the BHHBP-IA polyester showed that the mesophase was in fact more complex, being a nematic-smectic biphase [4].

Here we shall present some interesting findings on the orientation behaviour of these two polymers when they were subjected to shear or elongational flow. The orientation information was obtained by examining the infrared dichroism of the oriented polymer. It will be shown that the BHHBP-TA polyester only shows the conventional dichroism resulting from chain orientation parallel to the flow direction (fibre axis), whereas the BHHBP-IA polymer could show either the normal or the reverse dichroism, implying that both parallel and perpendicular orientation could be obtained, depending on the state of the melt before it was deformed.

2. EXPERIMENTAL

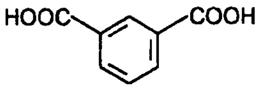
2.1. Monomer Synthesis

The monomer BHHHBP was synthesized according to the procedure described previously [1, 3]. It has been established by Smyth *et al.*, 1 that this diol is a mesogenic compound, forming a highly ordered crystal smectic G or H phase.

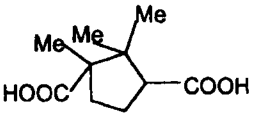
2.2. Polyester Synthesis

In this paper, most of the discussion will be based on the polyesters formed by the condensation of BHHBP with IA or TA. However, we made several other polyesters containing BHHBP, and one of these, namely the polyester of BHHBP and camphoric acid Will also be referred to. The three diacids which were used in the condensation reaction with BHHBP to form the three polyesters discussed in this paper are shown below:

TEREPHTHALIC ACID (TA)



ISOPHTHALIC ACID (IA)



CAMPHORIC ACID

Note that in the actual synthesis, the respective acid chlorides were used instead of the acids, but we shall refer to the polyesters in terms of the parent acid. The details of the polyester synthesis can be found in our previous paper [3]

The number average molecular weights of these polyesters were typically about 4000–6000. This was determined by end group analysis using nuclear magnetic resonance spectroscopy. Hence, these must be considered as low molecular weight polymers.

2.3. Optical Microscopy

Optical microscope textures of undeformed polymer, obtained on cooling the isotropic melt, as well as material that had been sheared in the molten state, were studied with a Zeiss Axioplan Pol Universal polarising microscope and a Linkam THM 600 microscope hot stage and associated TMS temperature controller. Photomicrographs of static textures, sheared melts, and shear-crystallisted polymer were recorded on 35 mm film using an Olympus OM 40 camera.

2.4. Infrared Dichrosim

2.4.1. Preparation of Oriented Samples

The sheared samples were prepared by first melting the polymers on a glass cover slip placed on the heating block of the Linkam hot stage. This hot stage can be opened from the top and it is convenient for the study of liquid crystals as it allows easy access to the silver heating block. The BHHBP-IA polymer was placed on a round coverslip, and a sodium chloride (NaCl) infrared window (13 mm diameter, 2 mm thick) was placed on top of the polymer. This assembly was placed in the Linkam, with the thin cover slip in contact with the heating block. The sample was heated rapidly to 140°C (for isotropisation) and held for 5 minutes after which it was cooled to 110°C at 10°C min^{-1}. From the optical microscopy, it had been previously established that at 110°C, batonnets of the smectic phase appear and grow rapidly at this cooling rate [3,4]. On reaching 110°C, the growth of the mesophase could also be detected by the fact that the transparent melt turned turbid; when this occurred, the NaCl disk was sheared across the glass cover slip and removed immediately from the hot stage to cool, and the shear direction was marked on the disk with an ink pen for future reference. Examination of the hot cover-slip that was left on the heating block under the polarising microscope showed a highly oriented, birefringent melt, this was photographed less than a minute or so after shearing. Similar examination of the cooled NaCl disk under the polarising microscope showed that an oriented, crystallised polymer film was left; this sample was used for obtaining the polarised infrared spectra.

UA similar procedure was used for the BHHBP-TA polyester. With this material, the melt was first formed between the cover slip and the NaCl window at 180°C, then the sample was cooled to 130°C at which temperature spherulites were known to be formed [3]. At 130°C, an attempt was made to shear the NaCl disk as previously. However, this operation was not very successful as the material was not sufficiently mobile at this temperature due to polymer crystallisation. Instead, the melt had to be cooled from 180°C and then sheared at 150°C; this means that the melt was deformed in the isotropic state and quenched. Again, the sheared melt le on the glass cover-slip, as well as the solidified polymer on the NaCl disk were viewed between crossed polars.

In addition to samples prepared by shearing the melt, oriented fibres were produced from both polymers by firstly forming an isotropic melt pool on a coverslip using the hot stage to heat the polymer, secondly cooling the melt (to 110°C for the BHHBP-IA polyester and to 150°C for the BHHBP-TA polyester), and finally dipping a heated spatula into the melt pool and drawing a fibre. The fibre cooled rapidly in air.

2.4.2. Infrared Dichroism Measurements

Infrared microspectroscopy was carried out on a Spectra-Tech IR PLAN microscope, equipped with 15X Cassegrain reflecting objective, wire-grid polariser and MCT detector, coupled to a Nicolet 740 FTIR spectrometer. In all cases, 257 co-added scans at 8 cm^{-1} resolution were collected with one degree of zero filling and Happ-Genzel apodisation.

As described earlier, the sheared samples were prepared on a NaCl window support. Spectra were then recorded with the polariser set first parallel and then perependicular to the shear direction. The geometry of the NaCl window, the sheared polymer and the polarised infrared radiation is shown in Figure 1a. The shear direction was parallel to the *x* direction (see Fig. 1a

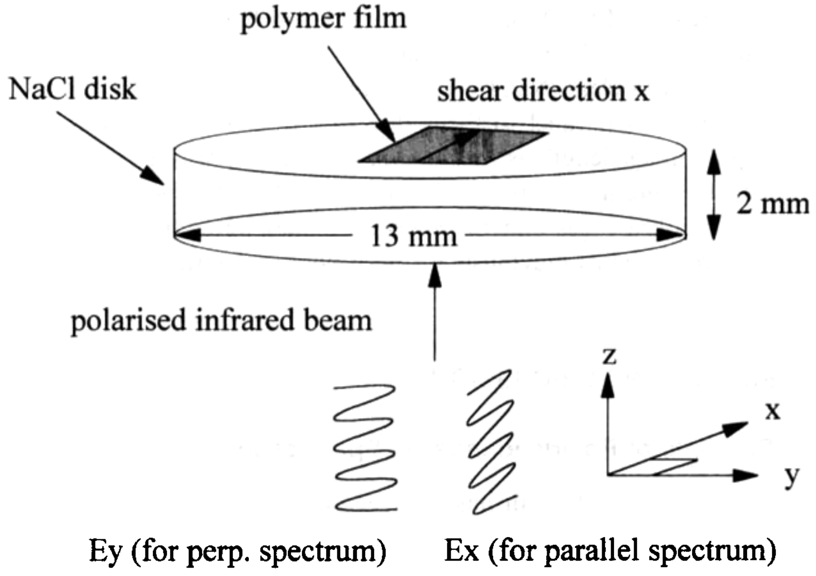


FIGURE 1a The geometry of the NaCl window, the oriented polymer and the polarised infrared radiation. *x* is the shear direction (or fibre axis for fibre specimens). *z* is the propagation direction of the polarised beam. First, the electric field vector **E** is set parallel to the *x* direction in order to record the parallel spectrum; in the subsequent measurement, **E** is set perpendicular to *x* and parallel to *y* to record the perpendicular spectrum.

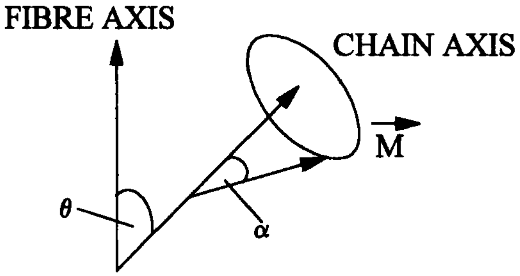


FIGURE 1b The relationship of the transition-moment vector M, the chain and the fibre axes. α is the transition-moment angle for a vibration and θ is the average angle between the chain and fibre axes.

for coordinate system, in practice, the *x* direction was set to be in a north-south configuration). The propagation direction for the infrared beam was *z*. The infrared radiation was polarised in the *xz* plane (electric field vector E_x oscillates in the *x* direction) for obtaining the parallel spectrum, and in the *yz* plane (electric field vector E_y oscillates in the y direction) for the perpendicular spectrum. Without altering the setting of the aperture, background spectra were measured for the corresponding polariser settings through a region of the NaCl support which was free of sample.

The free-standing fibre samples that had been pulled from the melt pool were placed on a clean NaCl window. The fibre was manipulated so that the fibre axis was parallel to the *x* direction (Fig. 1a) and it was masked down, to an image length as long as was convenient, having regard for any residual curvature in the fibre, and to an image breadth such that any gaps between the fibre edges and the aperture blades were eliminated. Spectra were then recorded as previously for both polariser settings.

3. RESULTS AND DISCUSSION

3.1. Principle of Polarised Infrared Spectroscopy

The theory of IR dichroism has been described in detail elsewhere [5, 6]. Briefly, dichroism is the property whereby the Absorbance, A, of electromagnetic radiation is dependent on the direction of polarisation of the radiation with respect to some axis in the sample (such as the fibre axis). Each vibrational mode will have an associated transition moment which has a defined direction with respect to the polymer chain axis. Note that for polymers the transition moment angle of a vibration is often a conformationally-averaged quantity [6]. The polymer chains themselves may have an orientation distribution that will depend on processing factors such as, exposure to shear or elongational flow in the molten state and the subsequent cooling rate, or drawing in the solid-state. The relationship between the transition-moment vector, **M**, the chain axis and the fibre axis is shown in the diagram in Figure 1b. By studying the dichroism of vibrational bands in the polarised infrared spectrum, it is possible to gain valuable information on the orientation of chains in the sample.

The experimental measurement consists of recording firstly the IR spectrum with the electric field vector of the polarised infrared radiation set parallel to the fibre axis (in fibre samples), or the shear direction (in sheared samples), and then re-recording the spectrum at the same location in the sample with the electric field vector now set perpendicular to the fibre axis or shear direction (see Fig. 1a). If the sample is unoriented, then both the parallel and perpendicular spectra would be identical. However, if the sample is oriented, most of the bands will show higher or lower absorbances (i.e. dichroism). The type of dichroism observed for a specific band will depend on the angle, α, between the transition moment vector, **M** *of that particular vibration* and the chain axis, as well as the orientation of the chain axes with respect to the fibre axis (see Fig 1b). For the *normal* case where the chain axes are preferentially aligned *parallel* with the fibre axis ($\theta < 54°44'$), when the angle α is less than $54°44'$, the band will display parallel dichroism (i.e. absorbance in the parallel spectrum is greater than in the perpendicular spectrum) while if α is greater than $54°44'$, the band will display perpendicular dichroism (i.e. absorbance in the perpendicular spectrum is greater than the absorbance in the parallel spectrum). We shall refer to the above case as normal dichroism.

In the *unusual* case where the chain orientation is *perpendicular* to the fibre axis in the *same polymer* system, then α should still be the same for each vibrational mode, but the type of dichroism (i.e. parallel or perpendicular) for each band will be reversed, because the peculiar scenario of $\theta > 54°44'$ has now been realised. We shall refer to this as opposite dichroism.

For comparing the orientation behaviour of the polymers, the parallel and perpendicular spectra will be shown. In addition, the partial dichroic spectrum which is the 1:1 difference spectrum [$A_{\perp}$ (perp.) minus $A_{\parallel}$ (parallel)] versus wavenumber will also be shown. The latter conveys instantly a picture of the orientation in the system, as the perpendicular bands appear as positive absorptions and parallel bands as negative absorptions.

3.2. Approximate Band Assignments in the Polyesters Containing BHHBP

The polyesters of BHHBP were ideal for IR spectroscopy because the absorptions of the $(CH_2)_6$ unit appear in a window in the spectrum in the region of 2900 cm^{-1}. Thus, these bands are diagnostic of the diol fragment of the polyester. Certain other features are characteristic of the isophthalic or terephthalic acid residue in the polymer, although there will be some overlap with the vibrations of the biphenyl portion of the BHHBP diol. The types of vibrations in the polyesters containing BHHBP can be divided into various categories as shown in Table I.

3.3. The Orientation in the BHHBP-TA Polyester

Figure 2 shows the infrared spectra of the polyester of BHHBP and TA, produced from the fibre sample, pulled from the melt at 150°C. Based on the transition moments for the various types of molecular vibrations (Tab. I), it is clear that the chain axis aligns preferentially parallel with the fibre direction. This *normal* dichroism is observed in most polyesters including polyethylene terephthalate and polybutylene terephthalate.

The shear-crystallised BHHBP-TA sample, as we deduced from the polarising microscope, showed birefringence but little preferential orientation. Likewise, the IR spectra displayed very low dichroism in the sheared material (not shown). Note however that the dichrosim displayed was of the normal type. Thus, shearing leads to a low degree of chain orientation parallel to the shear direction.

It was found that when the isotropic melt was sheared at 150°C between two glass plates on the hot stage and observed in-situ under the polarising microscope, the melt became birefringent momentarily, but this disappeared as soon as the shearing was stopped. This contrasts with the behaviour of

TABLE I Approximate frequency bands and their normal dichroism for various vibrations in polyesters contaning BHHBP

Wavenumber/cm^{-1}	*Vibration mode*	*Normal dichroism*
3050–3010	aromatic C—H stretching	parallel
2980–2800	aliphatic C—H stretching	perpendicular
1740–1730	ester C=O stretching	perpendicular
1600–1400	aromatic ring stretching	parallel
1250–1150	C—O stretching	parallel
1140–950	aromatic C—H-in-plane deformations	parallel
920–650	aromatic C—H out-of-plane deformations	perpendicular

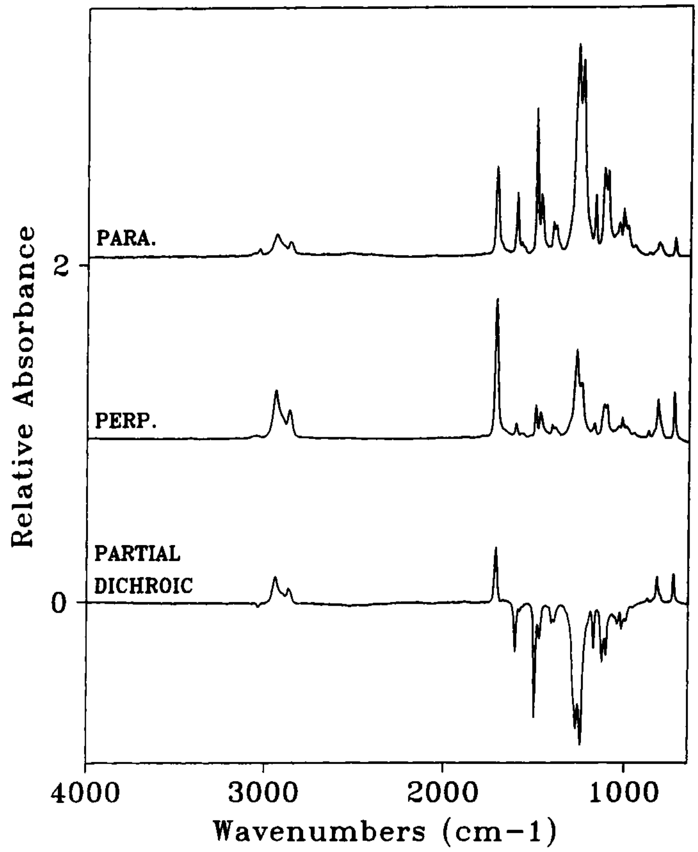


FIGURE 2 Polarised IR spectra of polyester of BHHBP and terephthalic acid (pulled fibre sample).

the BHHBP-IA polyester where the melt remained oriented (this is described in the next section) and tends to support our previous view that the BHHBP-TA polyester has no mesophase (3). On cooling from 150°C to 130°C, the BHHBP-TA melt became turbid. Figure 3 shows the typical optical texture that emerges from the isotropic melt on cooling to 130°C. This spherulitic texture is in our view due to crystallisation, rather than due to formation of a liquid crystal phase (3). This is also consistent with the fact that after the onset of turbidity at 130°C, the glass plates could not be sheared.

As mentioned, the normal dichroism in the fibre of the BHHBP-TA polyester was also found in fibres of polyethylene terephthalate and polybutylene terephthalate, though a direct comparison is not pertinent for

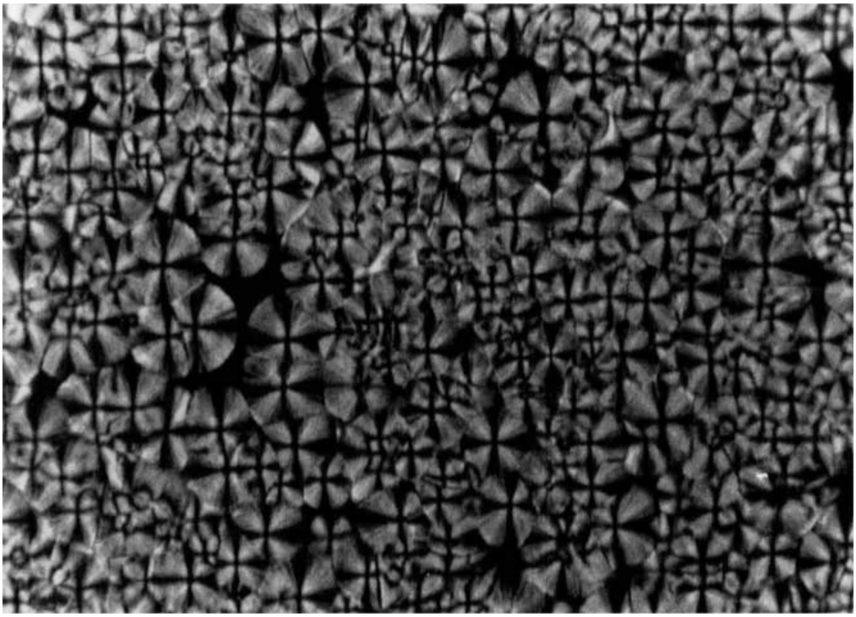


FIGURE 3 The spherulitic crystallisation texture arising when the polyester of BHHBP and terephthalic acid is cooled from the isotropic melt. Crossed polars, 130°C. (See Color Plate I).

what we want to show later, because the bands in the latter two polymers were somewhat different. For making a more direct comparison with the BHHBP-TA polymer, we synthesized a range of non-liquid crystalline polyesters containing the BHHBP diol and various diacids, as the infrared spectra of these materials displayed a similar pattern of bands. We shall thus show another example of the dichroic behaviour of a non-liquid crystalline polyester containing BHHBP. Figure 4 shows the polarised IR spectra obtained from a drawn fibre of a polyester of BHHBP and camphoric acid. We have not disclosed the properties of this polyester previously, but it will suffice here to note that this polymer is non-liquid crystalline and has a low melting point of about 50°C. The fibre was pulled from an isotropic melt at 60°C. It can be seen that essentially the same pattern of bands is present in this polymer, despite the replacement of the terephthalic acid by the camphoric acid which has a five-membered ring, and that these bands show the same type of dichroism as the BHHBP-TA polyester (compare with Fig. 2). In fact, all the non-liquid crystalline polyesters of BHHBP we made produced the normal dichroism in oriented fibres, similar to those in Figures 2 and 4.

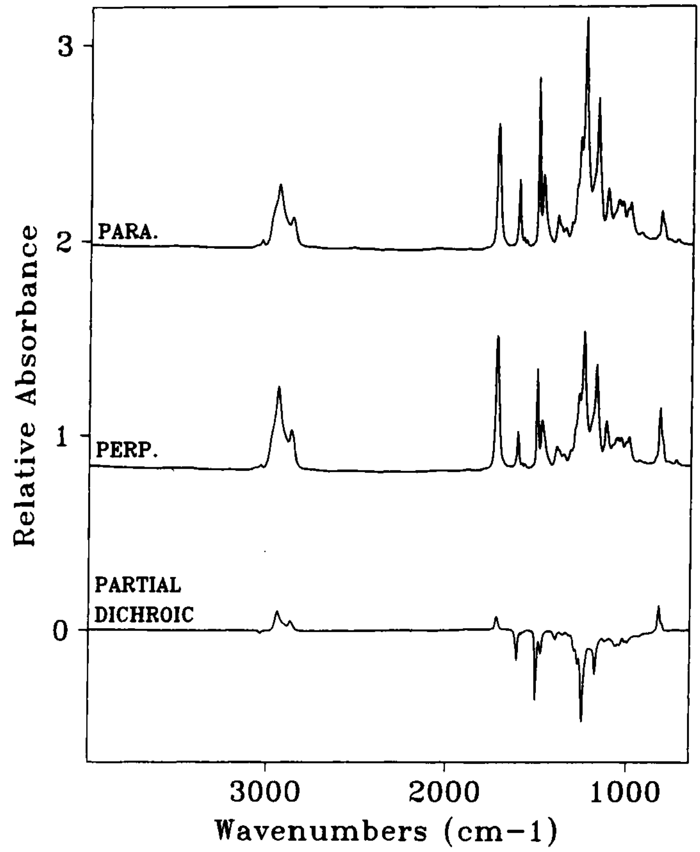


FIGURE 4 Polarised IR spectra of the polyester of BHHBP and camphoric acid (fibre pulled from isotropic melt). This shows similar bands and the same type of dichroism as the BHHBP-TA polyester in Figure 2.

3.3. The Orientation in the BHHBP-IA Polyester

As said before, the BHHBP-IA polyester is different from the TA polyester, in that it does have a smectic mesophase on cooling. The evidence for a smectic phase was presented in previous work where a well-developed focal conic texture was shown [3]. In a subsequent investigation, it was found that the mesophase was in fact a nematic-smectic biphase [4]. However, it was found that this mesophase could be predominantly smectic or nematic depending on how it was cooled, with faster cooling rates favouring the smectic [4]. Here, we have chosen a cooling rate that results in a predominantly smectic phase. Thus, Figure 5 shows rapidly growing small baton-

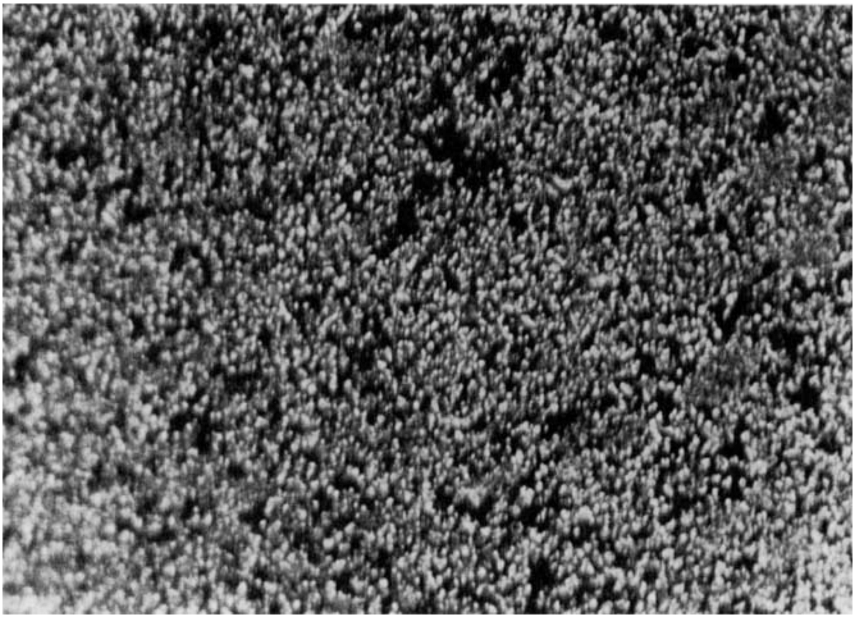


FIGURE 5 Smectic batonnet texture of the polyester of isophthalic acid and BHHBP at 110°C just before shearing. Crossed polars. (See Color Plate II).

nets at 110°C, on cooling from the isotropic state at 10°C/min; the photo was captured just before the battonets coalesced. At this cooling rate, a high density of battonets was nucleated (Fig. 5) and consequently before they could enlarge, they coalesced; the focal conic domains were small and details could only be seen by close inspection. There was no evidence for a nematic texture [4] under the conditions of formation shown in Figure 5. Thus, we shall assume for this work that the mesophase was predominantly smectic and all the flow experiments were conducted in the smectic state. We have also shown that the mesophase of the BHHBP-IA polyester was monotropic, in which case the mesophase would not be thermodynamically stable and it would crystallise after some time if held at 110°C [4]. In order to avoid any complications resulting from monotropic behaviour, we established that at 110°C, crystallisation did not start for at least 20 minutes. This gave ample time to conduct the shearing experiments in the smectic phase at 110°C.

After the texture in Figure 5 was formed, the smectic melt was sheared immediately and a photomicrograph (Fig. 6) was recorded within about 15 seconds. The melt was still fluid after the photo in Figure 6 was recorded

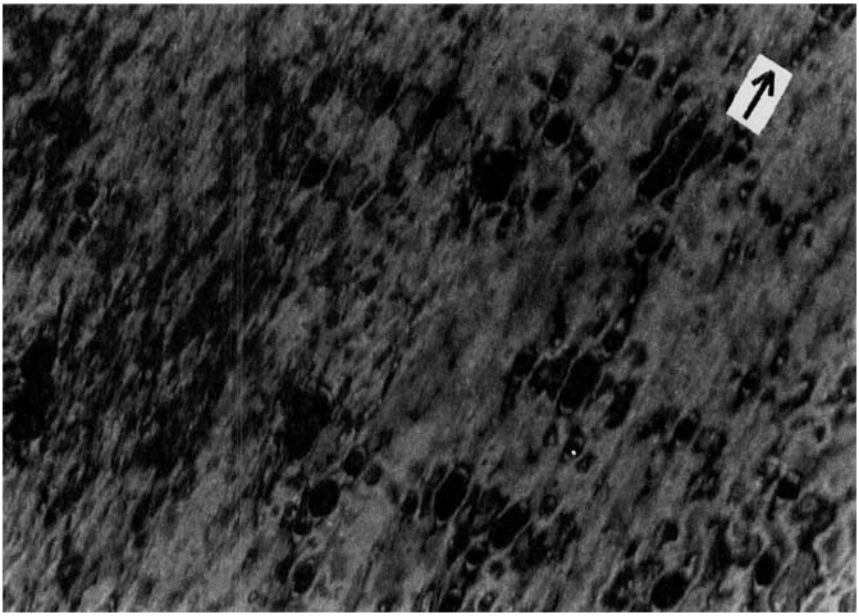


FIGURE 6 Oriented birefringent melt of the polyester of isophthalic acid and BHHBP at 110°C after shearing. Crossed polars, with axes in a north-south, east-west alignment. Shear direction (arrow) at 45° to polar axes . The black oval regions are voids in the melt. (See Color Plate III).

because it could be resheared, hence crystallisation had not occurred. Figure 6 shows that the sheared smectic melt (left on the glass plate on the hot stage) remains *oriented in the molten state* at 110°C, as indicated by the birefringence observed between crossed polars. The oriented melt showed good extinction over most of the sheared region when the shear direction was parallel to the polar axis, implying that an essentially monodomain sample was produced. The fact that the melt remains oriented after shearing at 110°C is consistent with the fact that polymer liquid crystal melts generally have long relaxation times and hence the orientation is not lost rapidly after the cessation of shearing.

Figure 7 shows the crystallised polymer left on the cooled NaCl window after shearing in the smectic state at 110°C, when viewed under the microscope between crossed polars. This indicates that the crystallised material is also highly oriented; again, good extinction was obsered when the shear direction was parallel to a polar axis. The polarised IR spectra of the *crystallised* BHEBP-IA polyester left on the NaCl disk after *shearing in the smectic state* displayed in Figure 8a, show a remarkable effect. The dichroism of all the bands in the spectra are in the opposite direction to commonly

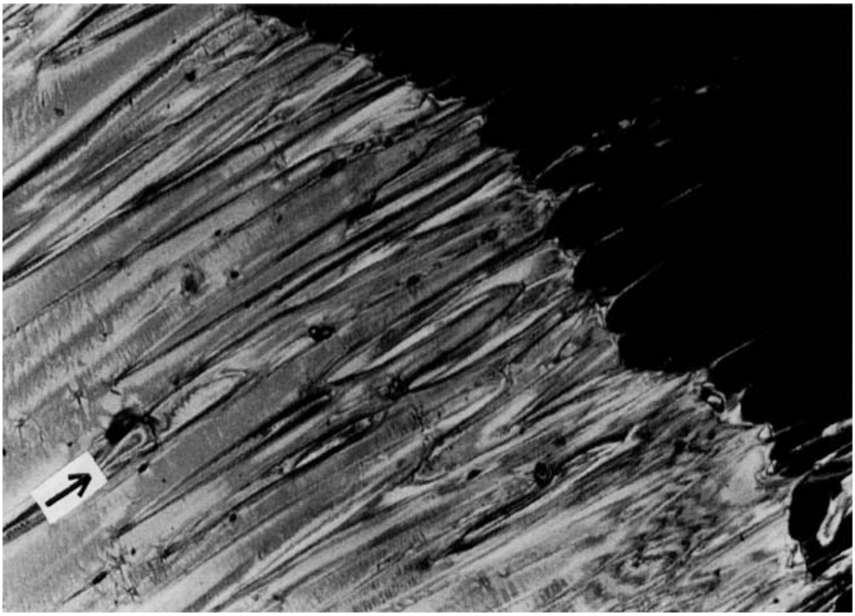
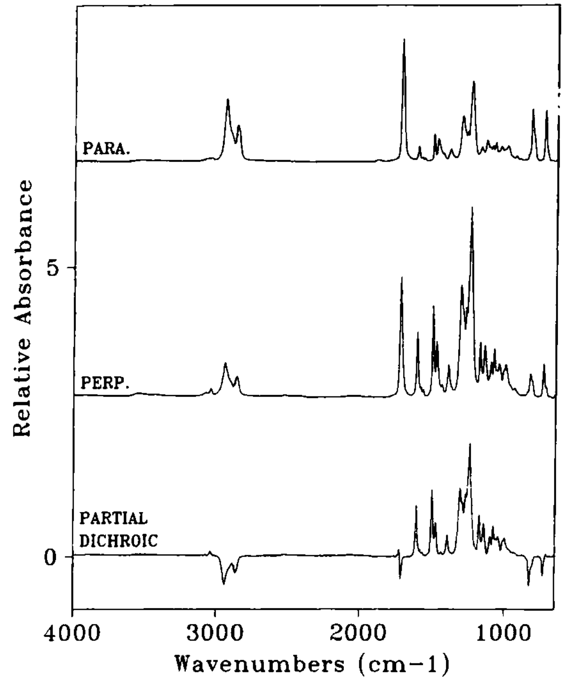


FIGURE 7 Oriented crystallised sample of the polyester of isophthalic acid and BHHBP, left on the NaCl disk after shearing in the smectic melt at 110°C and cooling to room temperature, viewed between crossed polars. Shear direction (arrow) at 45° to polar axes. (See Color Plate IV).

reported polyester fibre systems. This can be easily, gauged by comparing the partial dichroic spectra of the IA polyester with those of the TA and camphoric acid polyesters (Fig. 8a versus Figs. 2 and 4), where it can be seen that the bands in the BHHBP-IA polyester show the reverse dichroism. This surprising result was obtained also with fibre specimens of the BHHBP-IA polyester pulled from the smectic melt at 110°C (see Fig. 8b). It can only be explained by postulating *a preferential alignment of the chains perpendicular to the direction of shear or elongation (i.e. the fibre axis)*. We have not been able to record the polarised IR spectra in the smectic melt state after shearing (i.e. in the birefringent molten state shown in Fig. 6) as we do not have a hot stage suitable for the IR microscope, but we anticipate that this should also show the unusual dichroism observed in the solidified sample that had been sheared in the smectic state.

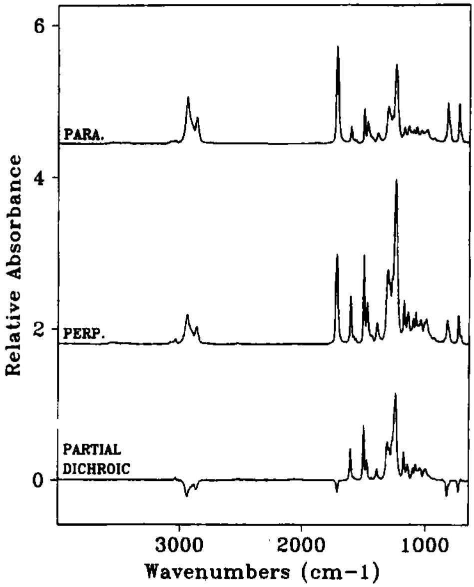
Though there is hardly any work where perpendicular orientation has been deduced from the IR dichroism behaviour, a few papers have established by X-ray that perpendicular chain orientation can occur in some liquid crystal polymers that have been deformed in the *mesophase state*. For instance, Acierno *et al.* [7] have shown perpendicular orientataion occurs in fibres spun from smectic polyesters made by the condensation of aliphatic dicarboxylic acids with the 4,4′ dihydroxy biphenyl. This was establised by studying the X-ray pattern of oriented fibres. Krigbaum and Watanabe [8] reported perpendicular orientation occurs in the smectic polyester formed by the condensation of 1,6-dihydroxyhexane and 4,4′-biphenyldicarboxylic acid. This occurred when a sample was sheared in the smectic melt; again, the orientation information was deduced from the X-ray pattern. They also noted that there was a molecular weight dependence for the orientation behaviour. It was found that the perpendicular orientation was only obtained when relatively low molecular weight polymers were deformed in the smectic state. Perpendicular orientation has also been predicted and observed in some polymer nematic liquid crystals (9–11).

The results of deforming the BHHBP-IA polyester in the *isotropic state* at 145°C need to be mentioned and compared with those arising from the



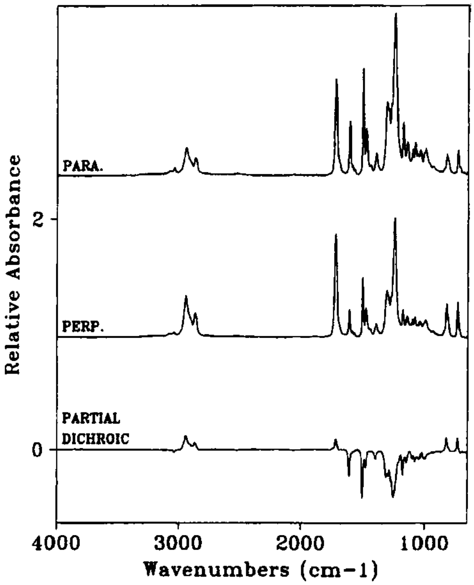
(a)

FIGURE 8 Polarised IR spectra of polyester of isophthalic acid and BHHBP. a) sample sheared in the birefringent smectic phase at 110°C and crystallised. b) fibre sample pulled from the birefringent smectic phase at 110°C. c) Sample sheared in the isotropic state at 140°C and crystallised. d) fibre sample pulled from the isotropic state at 140°C.



(b)

FIGURE 8 (Continued).



(c)

FIGURE 8 (Continued).

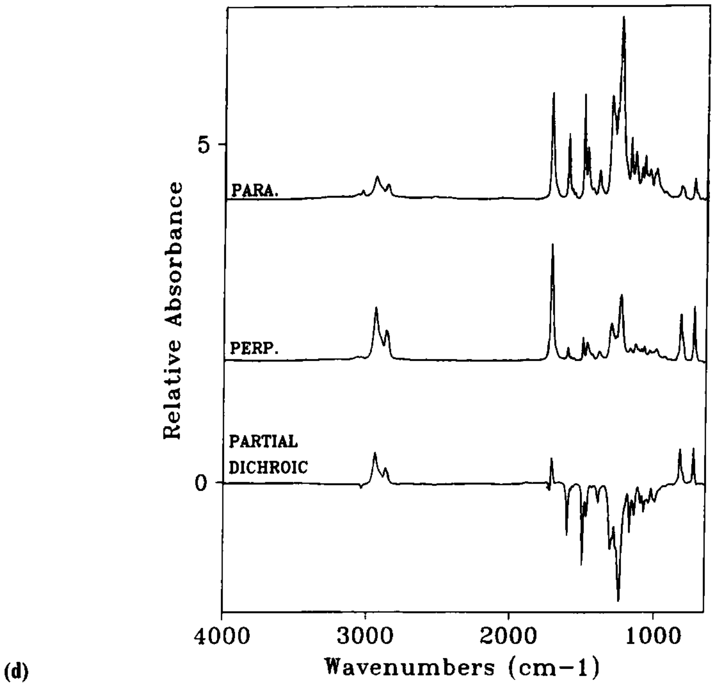


FIGURE 8 (Continued).

samples deformed in the smectic state. Shearing the isotropic melt led to a temporary birefringence that disappeared as soon as the shearing was stopped. Similarly, the shear crystallised sample left on the cooled NaCl disk was largely unoriented, though there were regions with preferential orientation. This could be deduced from the fact that the cooled polymer on the NaCl disk did not show any extinction of the birefringence in most areas of the sample (white arrow, Fig. 9) when it was viewed between crossed polars with the shear direction parallel to a polar axis . However, the oriented regions (black arrow, Fig. 9) in the shear-crystallised sample on the NaCl disk showed good extinction when parallel to a polar axis. The oriented regions presumably arise because of localised high shear rates that were fortuitously achieved in thin areas, and these were selected for the polarised IR measurements.

Figure 8c shows the polarised IR spectra of the oriented regions from the shear-crystallised sample (black arrow, Fig. 9), deformed in the isotropic state. This set of spectra shows the *normal* dichroism, implying the usual chain orientation parallel to the fibre axis. Finally, Figure 8d shows the

FIGURE 9 Shear-crystallised sample of the polyester of isophthalic acid and BHHBP, left on NaCl disk after shearing in the isotropic state at 140°C. The sample was mostly unoriented (white arrow), but there were oriented regions (black arrow) from which the polarised IR measurements in Figure 8c were made. Shear direction is at 45° to polar axes. (See Color Plate V).

polarised IR spectra of a fibre pulled from the isotropic melt at 145°C. Again, this indicates the conventional dichroism resulting from chain orientation parallel to the fibre axis. Krigbaum and Watanabe also reported normal orientation (i.e. chain axis parallel to the fibre axis) when their smectic polyester was deformed in the isotropic state [8]. Hence, our findings on the orientation of the BHHBP-IA polyester after deformation in the smectic and isotropic states has similarities with their observations.

Comparing Figures 8c and 8d (*isotropic-state deformation*) with Figures 8a and 8b (*smectic-state deformation*), it can be seen that the former two cases are mirror images of the latter two when reflected about the baseline, and thus consititute a beautiful and pleasing set of spectra. It is truly surprising that with the BHHBP-IA polyester, one is able to switch from almost perfect orientation perpendicular to the fibre axis to almost perfect orientation parallel to the fibre axis, by deforming in the smectic or the isotropic state.

4. CONCLUSIONS

In this work, we have examined the flow-induced orientation in polyesters containing the mesogenic diol BHHBP and either IA or TA. The orientation information was obtained from the polarised infrared spectra of samples subjected to shear or extensional flow.

The BHHBP-TA polyester, which does not have a mesophase, showed the conventional infrared dichroism and orientation in oriented fibres pulled from the isotropic melt and in shear crystallised samples – that is, the chains were oriented parallel to the fibre axis (flow direction). This is similar to results we have obtained from other non-liquid crystalline polyesters containing BHHBP that we have prepared, as well as from conventional, commercially produced polyesters such as poly (ethylene terephthalate) and poly (butylene terephthalate).

On the other hand, deformation of the BHHBP-IA polyester (which does form a smectic phase) in the mesophase state, led to an oriented melt. Surprisingly, the material that had been *sheared in the smectic state* and then cooled, showed the reverse dichroism indicating chain orientation *perpendicular* to the flow direction. A similar effect was observed in fibres *pulled from the smectic state* of the IA polyester. However, deformation by shear or elongation in the *isotropic* melt state always led to the *normal dichroism* consistent with orientation of the chains parallel to the fibre axis. Thus, it seems that the unusual perpendicular chain orientation is associated with deformation in the polymeric smectic state.

The polyesters containing BHHBP merit further study. The molecular weight and strain rate dependences of the flow-orientation behaviour of these polyesters have not been established and are areas that could be fruitfully probed by future investigators.

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