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Infrared dichroism of liquid crystalline terephthalate and biphenyldicarboxylate polyesters

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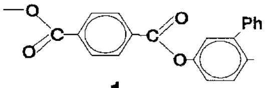
Summary

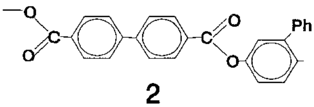
Polarised infrared spectroscopy has been used in the structural elucidation of the liquid crystalline polyesters, poly(2-phenyl-1,4-phenylene terephthalate), poly(2-phenyl-1,4-phenylene-4,4'-biphenyldicarboxylate) and the copolyester containing both terephthalate and biphenyldicarboxylate units. Order parameters have been calculated and the dichroic behaviour of the vibrational modes used to give valuable insight into the polymer chain structure.

Introduction

Polarised infrared spectroscopy is an established technique for studying molecular orientation and has been applied successfully to a variety of polymer systems (1-6). The early pioneering work of Elliott and coworkers (1,3,7) on polypeptides, where polarised infrared spectroscopy proved crucial in the elucidation of α-helical and extended-chain (β) structures, was carried out some 30 years ago. Since then numerous polymer systems have been studied including typical industrial polymers such as polyvinylchloride (8), polypropylene (9), polystyrene (10) and polyethyleneterephthalate (11-14). More recently polarised infrared spectroscopy has been used to probe the orientation in high performance polymers such as polyphenylenevinylene (15,16) and liquid crystalline polyesters (17-19). Whilst the derivation of order parameters from dichroic ratios is now commonplace, this study further encompasses the detailed assignment of vibrational modes in a manner extensively used in the past by Krimm (2). In this way, the observed dichroism can be directly correlated with the polymer structure. Here we adopt this approach to investigate the structures of the liquid crystalline polyesters, poly(2-phenyl-1,4-phenyleneterephthalate) [**1**], poly(2-phenyl-1,4-phenylene-4,4'-biphenyldicarboxylate) [**2**] and the copolyester analogue containing both terephthalate and biphenyldicarboxylate groups [**3**].



1



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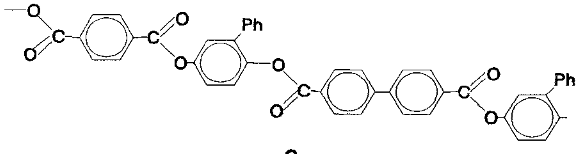

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Principle of Polarised Infrared Spectroscopy

The theory of infrared dichroism for uniaxially deformed polymers has been described in detail elsewhere (6). We adopt the standard equations *viz*

$$R_o = 2\cot^2\alpha \qquad \text{(eq 1)}$$

$$f = \frac{(R-1)(R_o+2)}{(R_o-1)(R+2)} \qquad \text{(eq 2)}$$

where R_o represents the dichroic ratio of a band in the notional fully oriented polymer (all polymer chains exactly parallel to draw direction), α is the transition moment direction (the angle between the direction of dipole moment change for a molecular vibration and the polymer chain axis), f is the order parameter (sometimes designated as P_2) and R is the measured dichroic ratio, defined as $A_\parallel/A_\perp$, of a band in the oriented polymer.

It is interesting to note that a band with a transition moment direction of 54.7° displays no dichroism regardless of the extent of orientation in the polymer. In common with convention bands with α values greater than 54.7° are designated σ and bands with α values less than 54.7° are designated π.

Determination of Order Parameters

From equations 1 and 2 it can be seen that the determination of the order parameter (f) rests on a known transition moment direction for a particular vibration. In the case of **1** and **3**, α was taken respectively as 90 and 88° for the C-H out-of-plane deformation (terephthalate ring) at 721 cm^{-1}. These angles are based on the angle the polymer chain axis of the planar zig-zag structure (C=O groups trans in the terephthalate and biphenyldicarboxylate moieties) makes with a vector perpendicular to the terephthalate ring corresponding to the transition moment of the C-H out-of-plane deformation. This allows a determination of f for **1** and **3** and gives the transition moment direction for the phenylene ring mode at 1574 cm^{-1} as 28° in both cases This suggests that the transition moment direction of this band, common to all 3 polymers, is independent of the comonomer terephthalate/biphenyldicarboxylate ratio. Thus f may be uniformly determined for all 3 polymers on the basis of the calculated transition moment direction for the 1574 cm^{-1} band.

Experimental

Preparation of Liquid Crystalline Polyesters

All the polymers utilised in this study were synthesised by previously reported procedures (20) from the following monomers: 2-phenylhydroquinone (Aldrich), terephthaloyl chloride (Aldrich) used without further purification and 4,4'-biphenyldicarbonyl chloride prepared from 4,4'-biphenyldicarboxylic acid by the method of Sloan and Vaughan (21).

Polarised Infrared Spectroscopy

The measurement of polarised infrared spectra of oriented samples in thin sheet form presents no experimental problems, providing the sample is both uniform and has dimensions greater than the infrared beam size. However, the samples produced for this study were in the form of thin strands of ribbon-like material which were far too small to study by conventional means. All the measurements were therefore carried out on an infrared microscope.

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.

'Frozen' liquid crystalline polymer, drawn from the nematic melt with a spatula, was placed on a potassium bromide window and presented for viewing under the infrared microscope. The sample, which appeared in the form of a ribbon, was manipulated into a "north-south" alignment in the microscope and masked down to an image length as long as convenient, and to an image breadth such that any gaps between the ribbon edges and the aperture blades were eliminated (a typical sample area was 20 x 50 μm). Spectra were then recorded with the polariser set first parallel and then perpendicular to the ribbon axis. Without altering the setting of the aperture, the ribbon was moved aside, and background spectra measured through the potassium bromide support for the corresponding polariser positions. The measurements allow the determination of spectra for radiation polarised parallel and perpendicular to the ribbon axis.

Results and Discussion

Figure 1 shows the polarised infrared spectra of a typical ribbon of **1**. The partial dichroic spectrum, defined as [$A_\perp$ minus $A_\parallel$] versus wavenumber, is also displayed in the Figure. It is immediately evident that many of the bands exhibit very high dichroism. It is also clear that the majority of bands display π dichroism with the exception of the C=O band and most of the features in the C-H out-of-plane deformation region. This is borne out in the partial dichroic spectrum which readily serves as an overall "orientation picture" of the system. Based on the frequencies and dichroism of these bands, assignments can be made (**Table 1**). It is clear that the observed dichroism is in accord with the anticipated transition moment direction for each type of vibration predicted for a planar zig-zag polymer chain structure, *ie* π bands - ring stretching modes, C-C stretch, C-O stretches, C-H in-plane-deformations; σ bands - C=O stretch and C-H out-of-plane deformations.

Table 1

Fingerprint absorptions, dichroism and assignments for **1**, *cf* Figure 1.

υ [cm^{-1}]	Dichroism	General Assignment
1738	σ	C=O stretch
1574	π	A' ring (phenylene)
1504	π	B_{2u} ring (terephthalate)
1481	π	A' ring (phenylene)
1408	π	C-C B_{2u}
1242	π	=C-O stretch
1168	π	O-C stretch
1125	π	A' C-H i.p. def. (phenylene)
1073	π	B_{3u} C-H i.p. def. (terephthalate)
1015	π	B_{2u} C-H i.p. def. (terephthalate)
901	σ	A" C-H o.o.p. def. (phenylene)
873	σ	B_{1u} C-H o.o.p. def. (terephthalate)
763	π	B_2 o.o.p. def. (phenyl)
721	σ	B_{1u} C-H o.o.p. def. (terephthalate)
700		B_2 C-H o.o.p. def. (phenyl)

In the light of the observed dichroism, the results clearly show that the rigid rods align themselves in a common direction parallel to the ribbon axis. This is to be expected for the rigid rod backbone, but what about the phenyl side-groups? Although there are difficulties due to spectral overlap, there is clear evidence that the characteristic monosubstituted aromatic C-H out-of-plane deformation at 763 cm^{-1} displays a small degree of π dichroism. The dichroism in the 700 cm^{-1} band which may also be traced, at least in part, to the phenyl ring is less easily established and is probably overlapped by other bands of opposite dichroism. With the sound assumption of a transition moment

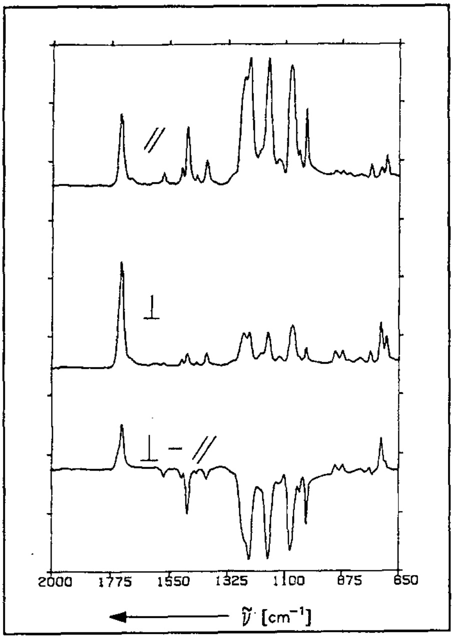

Figure 1. Polarised infrared spectra of **1**

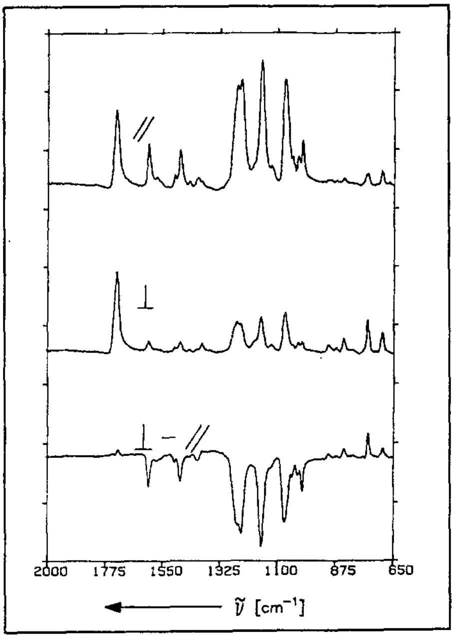

Figure 2. Polarised infrared spectra of **2**

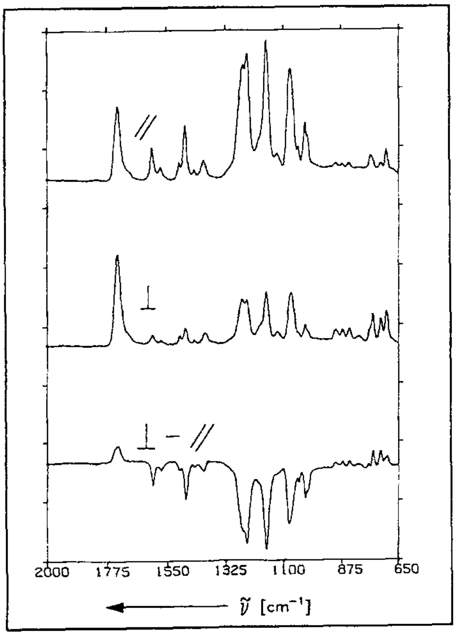

Figure 3. Polarised infrared spectra of **3**

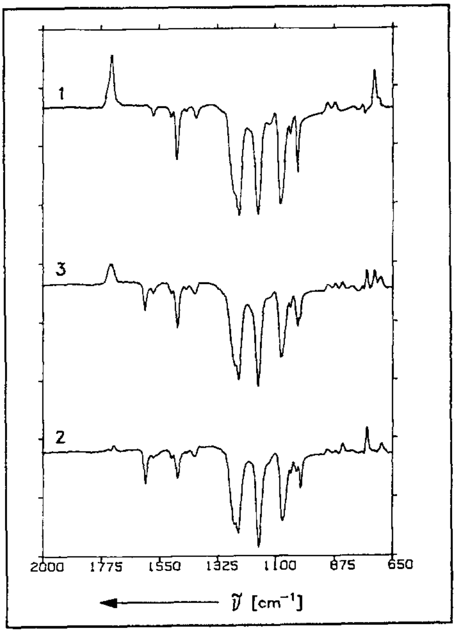

Figure 4. Partial dichroic spectra of **1**, **3** and **2**

direction of 90° with respect to the plane of the side-group phenyl ring, it is noteworthy that a low-level of π dichroism is predicted in the C-H out-of-plane deformations when the phenyl moiety, through the C_1-C_4 direction, makes the anticipated angle of 60° with the polymer chain axis. This calculation is based on a transition moment with two degrees of freedom relative to the polymer chain axis (22) and predicts an overall α value of 52°, *ie* a small degree of π dichroism. These results concur with free rotation of the phenyl side-groups; a finding which has been fully supported by solid-state nmr spectroscopy (23). Using the method described in the Experimental section, the order parameter (f) was determined as 0.83. This gave α for the C=O stretch as 64°.

The polarised infrared spectra of a ribbon of **2** (Figure 2) are broadly speaking similar to **1** (Figure 1). There are, however, some notable differences associated with the biphenyl group. For instance, a prominent ring mode at 1606 cm^{-1} is now evident in the spectrum. This band can be assigned to the out-of-phase combination of the two symmetric ring stretching modes in the biphenyl moiety. There is also a more complex pattern of bands in the C-H in-plane and out-of-plane deformation region, as anticipated from the increased number of C-H groups. Assignments and dichroism of bands are presented in **Table 2.**

Table 2

Fingerprint absorptions, dichroism and assignments for **2**, *cf* Figure 2.

υ [cm^{-1}]	Dichroism	General Assignment
1732	σ	C=O stretch
1606	π	B_2 ring (biphenyl)
1574	π	A' ring (phenylene)
1504	π	B_2 ring (biphenyl)
1481	π	A' ring (phenylene)
1413	π	B_2 C-C stretch
1399	π	B_2 C-C stretch
1244	π	=C-O stretch
1164	π	O-C stretch
1125	π	A' C-H i.p. def.(phenylene)
1071	π	B_3 C-H i.p. def. (biphenyl)
1020	π	B_2 C-H i.p. def. (biphenyl)
1004	π	B_2 C-H i.p. def. (biphenyl)
902	σ	A" C-H o.o.p. def. (phenylene)
872	σ	B_1 C-H o.o.p. def. (biphenyl)
844	σ	B_1 C-H o.o.p. def. (biphenyl)
765 sh		B_2 C-H o.o.p. def. (phenyl)
751	σ	B_1 C-H o.o.p. def. (biphenyl)
696	σ	B_1 C-H o.o.p. def. (biphenyl) + B_2 C-H o.o.p. def. (phenyl)

Analogous to **1**, many of the bands in **2** display very high dichroism. The obvious exception, however, is the C=O stretch which shows only minimal σ dichroism. The very low dichroism in the C=O stretch is clearly illustrated in the partial dichroic spectrum of Figure 2. The order parameter (f) was measured as 0.80 allowing α for the C=O stretch to be calculated as 56°. It is worth noting that the error in this value is negligible even allowing for a large variation in the value of f. In fact, to the nearest degree, α remains at 56° throughout the order parameter range of 0.5 to 1. This lack of sensitivity in α with the order parameter is because of its proximity to 54.7° and further shows that a precise determination of f is not at all critical in this case. It is worth stressing that the α(C=O) stretch values reported here for all 3 polymers are subject to a very small (< 1°) error.

The different values of α obtained for **1** (64°) and **2** (56°) require some discussion. Taking a planar zig-zag structure where the C = O groups are trans in the terephthalate and biphenyldicarboxylate moeities (24), the predicted angle which the C = O group makes with the polymer chain axis in **1** and **2** is 73 and 65°, respectively. This trend fits very well with the observed data and would suggest a 9° displacement of the transition moment from the C = O bond direction. Such a displacement has been well established in the C = O band of polyamides (1,3,6,7) where the deviation is as much as 20°. This surprising effect has been attributed to coupling of the C = O amide stretch with the N-H deformation and the C-N stretch. In contrast, relatively little coupling is to be expected in the ester band which is borne out by the smaller shift observed here. It is worth noting that a displacement of the transition moment from the C = O ester bond has previously been reported for polyethylenesuberate (25). Interestingly the displacement was found to be 9 or 19° and, by analogy with polyamides, it was suggested that 19° was more likely. In the light of the above, however, the 9° displacement seems more appropriate.

Table 3
Fingerprint absorptions, dichroism and assignments for **3**, *cf* Figure 3 .

υ [cm^{-1}]	Dichroism	General Assignment
1736	σ	C = O stretch (terephthalate + biphenyl)
1606	π	B_2 ring (biphenyl)
1574	π	A' ring (phenylene)
1504	π	B_{2u} ring (terephthalate) + B_2 ring (biphenyl)
1481	π	A' ring (phenylene)
1408	π	B_{2u} C-C stretch (terephthalate) + B_2 C-C stretch (biphenyl)
1242	π	= C-O stretch (terephthalate + biphenyl)
1167	π	O-C stretch (terephthalate + biphenyl)
1125	π	A' C-H i.p. def. (phenylene)
1072	π	B_{3u} C-H i.p. def. (terephthalate) + B_3 C-H i.p. def. (biphenyl)
1016	π	B_{2u} C-H i.p. def. (terephthalate) B_2 C-H i.p. def. (biphenyl)
1004	π	B_2 C-H i.p. def. (biphenyl)
898	σ	A" C-H o.o.p. def. (phenylene)
872	σ	B_{1u} C-H o.o.p. def. (terephthalate) + B_1 C-H o.o.p. def. (biphenyl)
845	σ	B_1 C-H o.o.p. def. (biphenyl)
765 sh		B_2 C-H o.o.p. def. (phenyl)
751	σ	B_1 C-H o.o.p. def. (biphenyl)
721	σ	B_{1u} C-H o.o.p. def. (terephthalate)
697	σ	B_1 C-H o.o.p. def. (biphenyl) + B_2 C-H o.o.p. def. (phenyl)

Having assessed the orientation in **1** and **2** in some detail, the logical progression was to investigate the copolyester **3** constructed from the building blocks of both **1** and **2**. With the knowledge of the dichroic behaviour of **1** and **2**, a sound foundation has been laid for the characterisation of **3**. In particular, detailed analysis of the spectra should allow distinction between random and blocky structures. Figure 3 shows the polarised infrared spectra of a ribbon of **3**. The very high dichroism observed in many of the bands can be directly compared with **1** and **2**, *cf* Figures 1 and 2. It is clear from the polarised infrared spectra of Figure 3 , that all bands of **3** behave in the anticipated manner. This is again borne out in the partial dichroic spectrum. Assignments and dichroism of bands are presented in **Table 3**. The order parameter (*f*) for **3** was determined as 0.80 and the α(C = O stretch) value as 59°. For convenience the relevant parameters for **1**, **2** and **3** are assembled in **Table 4**.

Table 4
Order parameters, C = O frequencies, C = O transition moment directions and melting points for samples **1**, **2** and **3**.

Sample	*f*	ν(C = O) [cm^{-1}]	α(C = O) [°]	MP [°C]
1	0.83	1738	64	329
2	0.80	1732	56	~400
3	0.80	1736	59	250

Broadly speaking the polarised infrared spectra of **3** can be rationalised in terms of a super-position of the corresponding spectra of **1** and **2**. For example, an inspection of the C = O stretching region of the spectrum shows that **3** displays a single C = O absorption band occurring at a frequency roughly midway between **1** and **2**. Further, the transition moment direction lies between the values of **1** and **2** (**Table 4**). A more graphic representation of these orientation effects is displayed in the stacked plot of the 3 partial dichroic spectra (Figure 4). This clearly illustrates that the relative dichroism in the C = O bands decreases in the order **1** > **3** > **2**. Such a trend is consistent with the building block composition of the copolyester, but does not serve to distinguish between random and blocky structures. However, a closer analysis of the spectra reveals some interesting findings. For example, the C = O band in the copolyester is broader than can be reconciled in terms of the summation of the C = O bands in the two polyesters. This implies a greater range of C = O environments in **3** than would be expected from simply considering the combined contributions of **1** and **2**. It can also be seen that there are some discernible shifts in certain bands of **3**. For example, the A" phenylene C-H out-of-plane deformation in **3** is shifted some 3-4 cm^{-1} relative to **1** and **2** (**Tables 1-3**).

The above observations provide evidence in favour of randomisation of the building blocks in **3**. This proposal is supported by our expectations based on the chemistry of polyesters (26) and that **3** shows a markedly reduced melting point compared with **1** and **2** (**Table 4**).

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