# Fourier transform Raman spectroscopic study of main-chain thermotropic liquid crystalline polyesters\*

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Abstract—The Fourier transform infrared and Raman spectra of the semi-flexible main-chain thermotropic liquid crystal polyester, poly(heptamethylene terephthaloyl-bis-4-oxybenzoate) are presented, and tentative band assignments given. The polymer is investigated as a function of its thermal history, and Fourier transform Raman spectra are recorded with temperature using a high-temperature cell. The results are discussed along with calorimetric and X-ray scattering data. Spectral evidence is presented which is related to both the sample crystallinity, and the crystal-to-liquid crystal phase transition.

#### INTRODUCTION

LIQUID crystallinity has been known to exist for over a century [2], and is characterised by the existence of both long- and short-range orientational order in the molecules. Polymers can exhibit liquid crystallinity, or mesomorphism, either in solution (lyotropics) or in the condensed state (thermotropics). Polymeric liquid crystals have generated much excitement over recent years not only for their significant technological implications, but for the potential insight they offer to the study of ordered and disordered states in condensed phases [3-5].

Thermotropic liquid crystal polymers (LCPs) consist of two main groups, which are defined by the position of the mesogenic unit. In side-chain (or "comb-like") LCPs the mesogenic units are attached to a polymer backbone, whereas in main-chain LCPs the mesogenic units are linked either directly, or by rigid or flexible spacers in the polymer chain.

There has been much research into the synthesis of thermotropic polyesters [6–8], and a wide variety of systems, each with unique thermal and physical properties, already exists and is finding application [9]. These materials tend to exhibit high crystal-tomesophase transition temperatures which are dependent on the size and structure of the mesogens [10, 11], and are insoluble in most organic solvents. Most main-chain liquid crystalline polyesters with rigid mesogens and flexible methylene spacers in the backbone exhibit a nematic texture, although many reports of smectic materials are appearing [3]. Further, many important structural, textural and thermal differences have been reported to depend on the odd-even effect of the number of methylene units in the flexible spacer [12–14].

The liquid crystal structure can often be frozen-in to the material facilitating the examination of the morphology of the mesophase. However, the poor solubility and elevated transition temperatures can produce difficulties in their study. Among the techniques typically used to characterise thermotropic polymers are X-ray diffraction, differential scanning calorimety and nuclear magnetic resonance (NMR) spectroscopy. Vibrational spectroscopy can provide very useful structural information on polymeric

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materials and has also been shown to be sensitive to important physical parameters such as orientation and crystallinity in many polymeric systems [15]. Infrared (IR) spectra have been recorded from both main-chain [16–21] and side chain [22] LCPs, transitional behaviour has been monitored [20, 21], and IR spectroscopy has been used to determine order parameters [19], but to our knowledge no Raman studies of polymeric liquid crystalline materials have appeared in the literature. However, we recently reported the Fourier transform (FT)-Raman spectra from a thermotropic poly(phosphazene) [23].

In this paper we present the vibrational spectra of a thermotropic liquid crystalline polyester, poly(heptamethylene terephthaloyl-bis-4-oxybenzoate) (PHMTOB), as part of our current investigations into this important and extensively studied [24–27] series of liquid crystal polyesters. Observations from the Raman spectra of PHMTOB as a function of the thermal history of the material are presented.

#### EXPERIMENTAL

### Materials

The polymer PHMTOB was prepared [28] using the method described by BILIBIN *et al.* [26]. Terephthaloyl-bis-4-oxybenzoic acid, TOBA (I), was prepared by condensation of terephthaloyl chloride with 4-hydroxybenzoic acid, and the subsequent dichloride TOBC (II) was prepared by the reaction of TOBA with thionyl chloride. Both these intermediates were separated and characterised during the course of the reaction, and used as models in the subsequent analysis. PHMTOB (III) was prepared by the polycondensation of TOBC and 1,7-heptamethylenediol in a solution of diphenyl, under nitrogen, for 8 h at 200°C. The product, a white powder, was precipitated in toluene, filtered, washed repeatedly in ethanol, and dried under vacuum. The model compound diphenyl terephthalate, DPT (IV), was prepared by a typical esterification reaction between terephthaloyl chloride and phenol in an alkaline environment. Phenyl benzoate (PB) was obtained from Aldrich-Chemie (cat. no. 14,271-9).

Elemental analysis and <sup>1</sup>H-NMR spectra confirmed [28] the chemical structures of compounds I-IV as those shown in Scheme 1.

The inherent viscosity of the polymer PHMTOB was reported to be  $0.67 \text{ dl g}^{-1}$  in *p*chlorophenol at 45°C [28], indicating a significantly higher molecular weight for the polymer when compared with previous studies [25]. The thermotropic behaviour was also studied by DSC [28], and the transitions observed are summarised in Table 1.

A series of samples with different thermal histories was prepared and characterised by X-ray diffraction (WAXS) and differential scanning calorimetry (DSC) for this spectroscopic study. DSC thermograms were recorded using a Mettler TA 3000 with a DSC-30 furnace and TA-72 software. Heating rates of 10°C/min were used, between 30 and 200°C. X-ray diffractograms were obtained using a Phillips PW1050/70 Geiger counter diffractometer. Diffractograms were recorded at a rate of 2°/min, between  $2\theta = 1$  and 30° using copper-filtered CuK $\alpha$  radiation.



#### FT-Raman spectroscopy of thermotropic polyesters

Table 1. Thermal transitions in PHMTOB by DSC

Temperature (°C)	Transition description	
60-70	T,	(glass transition)
115-150	T <sub>c</sub>	(crystallisation)
173	$T_{(1)}$	(crystal-liquid crystal)
296		(isotropisation)
350	Td	(degradation)

The "original sample", O, was that obtained directly from the reaction vessel and purified as described above. Samples Q1-Q4 were heated above the  $T_{(1)}$  transition temperature and held for 30 min before being quenched in liquid nitrogen, and then allowed to equilibrate at room temperature. Further, samples C1-C3 were prepared by evaporation from a solution in trifluoracetic acid. Attempts were made to prepare samples by quenching from the isotropic state. However, the value of  $T_i$  reported in Table 1 is that of the peak maximum in the DSC trace, and, since the endotherm is very broad, complete isotropisation is difficult to achieve without heating the sample to within close proximity of the degradation temperature. Indeed some brown discolouration in the sample is clearly observed on cooling, and attempts to record FT-Raman spectra were foiled by the excessive sample fluorescence subsequently encountered. The samples and their thermal histories are summarised in Table 2. Multiple endothermic peaks were observed, but were not related to crystal polymorphism as previously observed in semi-crystalline polymers [29, 30], since WAXS measurements indicate that the sample exhibits a single crystalline modification [28]. Further, by variation of the heating rate in the DSC experiments, we observed that the polymers exhibited a series of complex melting and recrystallization processes. As such, the crystallinity was difficult to estimate accurately by DSC.

IR spectra were recorded on a Perkin-Elmer Model 1720 FTIR interferometer, fitted with a triglycine sulphide (TGS) detector. Samples were recorded between KBr plates using a liquid paraffin (nujol) mull, collecting 50 scans at a resolution of 2 cm<sup>-1</sup>. Spectra from both the IR and Raman experiments were processed using the CDS-3 software on a Perkin-Elmer 7700 data station.

FT-Raman spectra were recorded on a Perkin-Elmer 1700 Series FTIR interferometer modified for use in the near-infrared (NIR) as a Raman spectrometer, which has been described in detail elsewhere [31, 32]. An InGaAs detector was used at room temperature. The laser excitation at  $v_0 = 1.064 \,\mu\text{m}$  was provided by a Spectron Model 301 Nd<sup>3+</sup> : YAG laser, using a laser power of between 350 and 800 mW. Spectra were recorded at a resolution of 6 cm<sup>-1</sup>, for between 100 and 200 scans. The instrumental conditions are reported on each spectrum. All spectra were corrected for sensitivity variations in the detector, filters, and the optical components of the interferometer [33]. In the heating experiments, the temperature of the sample was varied in a high-temperature cell which is shown diagrammatically in Fig. 1. The sample is mounted in a 3 mm diameter cup in the end of the heating element. The outside diameter of the heating element is deliberately kept small to minimise the area of hot metal viewed by the collection lens of the interferometer, and the

Sample	Thermal history	X-ray crystallinity (%)
0	Original sample as recovered from reaction vessel	23
Q1 Q2 Q3	Samples quenched into liquid nitrogen and allowed to equilibrate at room temperature	7 8 5
Q4	As $Q1-Q3$ , then annealed at 150°C for 2 h	21
C1 C2	Crystallised from a solution in trifluoroacetic acid	29 29
<i>C</i> 3	As C1 and C2 but at a much reduced evaporation rate	34

Table 2. Thermal histories of a series of samples of PHMTOB



Fig. 1. FT-Raman high-temperature cell: L, laser beam; S, sample; C, mounting card; B, baffle; E, heating element; T, thermocouple wire; DT, to digital thermometer; TC, to temperature controller.

bulk of the unit is isolated using baffles. The temperature was monitored using a thermocouple embedded in the sample. At each increment the temperature of the sample was left to stabilise for 15 min. It was noted that some sample heating due to the absorption of the laser radiation was apparent. The beam was consequently defocused, and a spot size at the sample of approximately 1.5 mm was estimated. No degradation or burning of the samples occurred. However, an unfortunate consequence in spectra recorded at high temperatures in NIR FT-Raman spectroscopy between 9400 and 5700 cm<sup>-1</sup> is a broad feature which arises due to the blackbody emission of the sample [34]. It appears at the high-frequency side of the spectrum and obliterates the C-H stretching region, gradually increasing in intensity and further encroaching on the spectrum as the temperature of the sample is increased. Further, due to the magnitude of the feature, its Fourier transformation introduces a significant degree of noise into the resulting spectrum, and thus band intensities and calculated ratios at temperatures higher than 150°C become less reliable. We estimate an upper limit of around 200°C using the current system.

# **RESULTS AND DISCUSSION**

# 1. DSC and X-ray diffraction data from PHMTOB

DSC and WAXS data are presented in Fig. 2, for samples C1, Q1 and O. The sample crystallised from solution (C1) exhibited a crystallinity of around 35% [28] and showed



Fig. 2. DSC and WAXS data from samples of PHMTOB with different thermal histories: (a) O, (b) Q1, and (c) C1.



Fig. 3. Vibrational spectra of PHMTOB: FTIR (upper: 4 cm<sup>-1</sup> resolution, 50 scans) and FT-Raman (lower: 6 cm<sup>-1</sup> resolution, 400 mW laser power, 200 scans). Bands in FTIR spectrum marked with an asterisk contain some contribution form nujol.

no evidence of containing any mesomorphic structure, characterised in the sample Q1 by a low angle reflection at 3.8°, which corresponds to a structural repeat distance of 23.3 Å in the mesophase [28]. Further, the DSC trace shows no crystallisation exotherm, unlike the sample quenched from the mesophase (Q1) which displays a broad crystallisation peak centred at around 125°C, a very low X-ray crystallinity (confirmed by DSC), and the intense low angle reflection. The proportion of liquid crystalline material in the samples is not quantifiable. However, by thermo-optic analysis (TOA) it is possible to deduce relative proportions of mesomorphic material. The chain distribution of the polymer between the different phases in the three samples initially studied can be summarised as follows:

The quenched material, Q1, contains polymer chains frozen in the liquid crystal phase, some amorphous material, and a small amount of crystalline material.

The sample crystallised from solution, C1, contains polymer chains in the crystalline and amorphous phases only, and presents no evidence of the liquid crystalline phase.

The original material, O, contains all three phases-amorphous, crystalline and liquid crystalline material.

Consequently, a comparison of the spectrum of C1 with that of Q1 allows us to relate differences in relative band intensities with the incidence of crystalline and liquid crystalline domains, since amorphous structures are present in both samples.

# 2. The vibrational spectra of PHMTOB

Vibrational spectra recorded from the original sample (O) of PHMTOB are presented between 1800 and 600 cm<sup>-1</sup> in Fig. 3. It can be clearly observed that both the infrared and Raman spectra present many vibrations at corresponding frequencies, and although many modes appear to be strongly coupled, the incidence of a centre of symmetry in the polymer molecules is seriously doubted.

The IR spectrum in Fig. 3 was found to be almost identical to that reported by BENEDETTI *et al.* [20] for poly(decamethylene terephthaloyl-*bis*-4-oxybenzoate) (PDMTOB). We found the FTIR data to be more complex than the FT-Raman data, due to the considerable degree of band superimposition. Characteristic frequencies are

Table 3. Raman and IR frequencies for PHMTOB and tentative assignments

1143 m		$\nu_{C=O}$
1735 m,sh	1733 s	$v_{C=0}$ terephthaloyl [20]
1716 m	1716 s	$v_{C=O}$ oxybenzoate [20]
1710 m,sh		ν <sub>C=O</sub> .
1605 s	1602 m	$v_{C=C}$ ring
1578 w,sh	)	$v_{C=C}$ ring
1551 w		
1488 w	1501 m	
1461 w	1463 s* }	$CH_2$ deformations (bending) [37, 38]
1450 w		
1436 w	)	
1407 vw†	1410 m	Ring mode [38]
1373 w	1377 m*	
1358 w	}	CH. deformations (wagging) [21 37 38]
1340 vw		erry deformations (wagging) [21, 57, 50]
1326 w	J	
1304 m,sh†	1306 m,sh	Ring mode
1285 m, sh		Ring-C=O stretch + O-C stretch + arom. CH in-plane [37]
	1275 s‡	C(O)-O stretch [38]
1269 s		C(O)-O stretch
1230 w		
1206 w†	1205 m‡	Ring mode [36]
1196 w,sh†		Ring mode
1179 w.sh <sup>†</sup>		In-plane ring CH bend [37]
1163 m†	1163 s	Ring mode [36]
1139 vw		0 ( )
1124 w.sh		$\nu$ (C-O) [21, 38]
	1115 m‡	In-plane ring $\nu$ (CH), or $\nu$ (C–O)
1107 w		In-plane ring $v(CH)$ , or $v(C-O)$
1078 m	1078 s‡	Ester C(O)–O stretch or $\nu$ (C–C) in C–C chain
1066 m.sh	•	Ester [20]
1017 w	1016 s	$\nu$ (C-O) asym. [37] or ring mode [38]
1002 vw		$\nu(O-CH_2)$
963 vw	961 w	$\nu$ (C-O) asym.
951 vw		
936 vw		
921 vw		
888 m†	886 m	CH <sub>2</sub> rock [21, 37], ring-breathing $(\nu_2)$
879 vw.sh	875 m	CH <sub>2</sub> rock [21]
858 w		CH <sub>2</sub> rock [21]
836 w†		CH out-of-plane deform. (arom.) [21]
827 w.sh	831 w	CH <sub>2</sub> rock [21]
814 w.sh		2 ( )
785 w†		
763 m	760 m	Ring CH out-of-plane bend
719 m	719 s	Ring CH out-of-plane bend or C-O-C deform, or C=O out-of-plane
		bend + ring CH out-of-plane bend [21]
686 vw	694 m	¢ 1 - L1
670 vw		
663 vw		
645 w.sh	646 w	
629 m†		Ring C-C-C in-plane bend [37]
609 vw		

s = strong; m = medium; w = weak; vw = very weak.

\* Band includes some contribution from nujol.

† Band related to mesogenic unit from study of model compounds.

**‡** Bandhead of broad feature in IR data.

observed in both techniques, and Table 3 presents the bands observed in the vibrational spectra between 1800 and 600 cm<sup>-1</sup>, along with some tentative assignments. An indication is made in the table where bands in the IR spectra are strongly overlapped, and in some cases we are only able to report the bandhead frequency. To assist in the identification of some of the bands due to the mesogenic unit, the spectra of four model

compounds, TOBA, TOBC, DPT and PB, were considered. TOBA and TOBC were isolated during the preparation of the polymer. Bands in the Raman spectra of PHMTOB thought to arise from vibrations within the mesogenic unit are indicated in Table 3.

C-H stretching vibrations appear at  $3077 \text{ cm}^{-1}$  (aromatic) and between 3000 and  $2800 \text{ cm}^{-1}$  (methylenic). The carbonyl stretching vibrations fall between 1750 and 1700 cm<sup>-1</sup>. In the IR spectra two broad and overlapped bands are observed at 1733 and  $1716 \text{ cm}^{-1}$ , which have been assigned to the terephthalate and oxybenzoate groups, respectively [20]. In the Raman spectra the region is better defined, and bands can be identified at 1736 and 1716 cm<sup>-1</sup>, with shoulders at 1748 and 1710 cm<sup>-1</sup>. The strongest feature in the Raman spectrum is the broad band in the aromatic C=C stretching region at  $1605 \text{ cm}^{-1}$ , which is also clearly observed in the IR spectrum. The methylenic deformation modes are strongly observed in the infrared spectrum between 1500 and 1300 cm<sup>-1</sup> (bending and wagging) and between 900 and 800 cm<sup>-1</sup> (rocking), but only appear weakly in the Raman spectrum which is dominated by the stronger vibrations of the aromatic nuclei. The region between 1300 and  $1200 \text{ cm}^{-1}$  is complex in both spectroscopic techniques, with bands arising from a combination of vibrations due to the aromatic nucleus, ring-C(=O) stretches, and (O=)C-O stretching vibrations. The band at  $1163 \text{ cm}^{-1}$ , which is strong in both spectroscopies, is characteristic in polymers which possess para-substituted aromatic moieties in the chain [35], and is in this case thought to be due to a ring-stretching vibration [36] in the terephthaloyl moiety. A medium-intensity band appears at around  $888 \text{ cm}^{-1}$  in the Raman spectrum which is thought to arise from the totally symmetric ring breathing mode,  $v_2$  (Herzberg notation), and in the IR spectrum two characteristic methylene rocking modes [21, 37] are observed at 886 and  $875 \text{ cm}^{-1}$ .

(a) The Raman spectra of poly(n-methylene) polyesters. FT-Raman spectra were recorded from a series of virgin polyesters prepared using the method of BILIBIN *et al.* [26] with n=3, 6, 7 and 10 methylene units. Although very carefully purified, the trimethylene polyester produced an unacceptable level of fluorescence, and no spectral detail was obtained. The decamethylene polyester (PDMTOB) also exhibits a high level of fluorescence, and only basic interpretation is possible. The spectra, recorded at a resolution of 6 cm<sup>-1</sup>, from the polyesters with 6, 7 and 10 methylene units are presented in Fig. 4. All samples show characteristically identical spectra superimposed upon a relatively high level of background. It is unfortunate at this stage in our studies that in the methylene deformation region, where the chemical structure of the individual polymers differs, the signal-to-noise ratio is too poor to enable analysis of the apparent differences in any detail. Slight differences between the samples are also visible in the C=O and C-O stretching regions.

(b) Variations in the Raman spectra of PHMTOB with the thermal history of the material. Samples of PHMTOB with different thermal histories (Table 2) were considered using FTIR and FT-Raman spectroscopy. In the IR data differences between the original sample (O) and that prepared by crystallisation from solution (C1) are very slight. The clearest variation in the IR spectra appeared in the absorbances of the methylene rocking vibrations at 886 and 875 cm<sup>-1</sup>, in which the former appears to be more intense in the crystalline sample. The relative intensity of these bands has been associated previously with the conformational structure in methylene chains [21]. In the Raman data, many spectral variations between samples with different thermal histories are observed. Figure 5 shows the FT-Raman spectra between 1800 and 1000 cm<sup>-1</sup> for three samples of PHMTOB: (a) the original material (O), (b) a sample quenched from the mesophase (Q1), and (c) one crystallised from solution (C1). The following initial differences can be observed between the spectra.

In both O and Q1 the C=O stretching vibration at 1748 cm<sup>-1</sup> is the strongest band, and a shoulder appears at 1736 cm<sup>-1</sup>, which is weaker for the quenched material than the original powder. However, in sample C1 the situation is reversed, and it is the band at



Fig. 4. FT-Raman spectra of polyesters with (a) 6, (b) 7, and (c) 10 methylene units in the flexible spacer (6 cm<sup>-1</sup> resolution, 800 mW laser power, 100 scans).



Fig. 5. FT-Raman spectra of (a) O, (b) Q1, and (c) C1 (6 cm<sup>-1</sup> resolution, 400 mW laser power, 200 scans).

 $1736 \text{ cm}^{-1}$  which is the most intense. No differences are observed in the integrated area of the C=O stretching region relative to that of the C= $C_{arom}$  stretching region. Although the bands between 1350 and 1250 cm<sup>-1</sup> are heavily overlapped, a number of features can be distinguished. The band which appears strongly at 1285 cm<sup>-1</sup> in C1, assigned to either a ring-carbonyl stretching mode or an aromatic in-plane C-H bend [37], diminishes in the samples O and Q1, appearing only as a shoulder. In the region between 1500 and 1300 cm<sup>-1</sup> there seem to be many differences between the samples. Some bands may be related to conformational changes in the methylene chain. For a seven-membered methylene chain, over 150 different conformational structures are possible. However it is unlikely that more than 20 of these conformations will exist because of the severe steric limitations imposed by the bulky mesogenic units when three or more gauche structures are incorporated. The spectrum of Q1 appears to have a guite different vibrational structure in this region to those of both O and C1, although the bands are of low intensity, and it is difficult to distinguish them clearly with the level of noise in the spectra. The methylene wagging vibration at 1375 cm<sup>-1</sup>, previously related to a trans conformation in poly(butylene terephthalate) [37] appears to be much stronger in the quenched material. The band at  $1078 \text{ cm}^{-1}$ , which is assigned to the ester (O=)C-O stretch is considerably more intense for C1 than for Q1 and O. An ester band which appears at  $\approx 1062$  cm<sup>-1</sup> as a shoulder on the strong band at 1078 cm<sup>-1</sup> in Q1, is absent in C1. Further, evidence of a band which appears at 1099 cm<sup>-1</sup> in Q1, and more weakly in O, is absent in the solution-crystallised sample.

A comparison was made between the band peak intensities of a number of bands in the FT-Raman spectra, and the values of the degree of crystallinity by WAXS for the whole series of polyester samples in Table 2. The band intensities were normalised against the aromatic C=C stretch observed at  $1605 \text{ cm}^{-1}$ , which was selected since it was well separated from other spectral bands. However, these modes have been previously associated with physical changes in semi-crystalline polymers, such as the degree of crystallinity and composition [35, 38], and have been demonstrated to be sensitive to phase transitions when the ring forms part of the mesogenic unit in side-chain LCPs [22]. Indeed we observe slight variations in the bandshape during thermal treatment of the samples, and between samples with different thermal histories, suggesting that the modes do manifest some sensitivity to the thermal history of the material. However, by normalising the band intensities on a different band, for example, the low frequency oxybenzoate C=O stretch at  $1716 \text{ cm}^{-1}$ , the same type of behaviour is observed in the calculated ratios for bands which show significant changes when normalised on the C=C stretch. In this respect we should point out that the relative intensity of the 1605 cm<sup>-1</sup> band, when compared with that at  $1716 \,\mathrm{cm}^{-1}$ , is seen to diminish with higher values of crystallinity.

Figure 6 shows a graph of the ratio of the intensity of selected bands against the  $C=C_{arom}$  stretch at 1605 cm<sup>-1</sup> versus the X-ray crystallinity. It can be noticed that for a number of bands the change in relative intensity is quite significant. A series of bands increases in relative intensity. Amongst these the effect is most pronounced in the aromatic C-H stretching vibration, the lower-frequency component of the terephthaloyl C=O stretch at 1736 cm<sup>-1</sup>, the ester mode at 1078 cm<sup>-1</sup>, and the bands at 1163 and 858 cm<sup>-1</sup>. It is interesting to note that two distinct types of behaviour can be observed: a linear change with crystallinity, and a sharper step-like change. For the bands which exhibit a step-like increase, the sample which was quenched and subsequently annealed (Q4) shows an intensity ratio very similar to that of Q1-Q3. Further, some bands, like that at 1269 cm<sup>-1</sup>, appear to be relatively less intense in the samples with higher crystallinity. Bands which demonstrate a relative increase in intensity may be related to the crystallinity of the material, or some degree of chain order or stereoregularity imposed as the crystallinity is increased.

(c) Variations in the Raman spectra of PHMTOB with temperature. The samples O, Q1 and C1 were heated from room temperature to the liquid crystalline state, using the FT-Raman high-temperature cell. In the case of the quenched sample (Q1), no changes



Fig. 6. Normalised intensity ratios for selected bands in the FT-Raman spectra of PHMTOB versus the crystallinity deduced from WAXS.

were obvious between the spectrum recorded at room temperature and that recorded above the  $T_{(1)}$  phase transition, which is complete at 180°C, by DSC and TOA optical microscopy [28]. However, the quality of the spectra was poor, due primarily to absorption and noise generated by the high background feature. Both C1 and O, when heated to above the  $T_{(1)}$  transition exhibited identical spectra, which were in essence the same as that observed for Q1 at room temperature. The largest differences with temperature were observed for the crystallised sample. Figure 7 shows the FT-Raman spectra of the sample C1 obtained at a series of temperatures, and Fig. 8 presents the relative intensities of a series of normalised bands from the FT-Raman spectra versus temperature. The onset of the phase transition appears to be lower than the values from DSC and TOA [28]. This may be explained by local laser-heating of the sample to a temperature slightly higher than that recorded, thus lowering the apparent transition point.

Comparison of the spectrum in Fig. 7f with that of the sample Q1 in Fig. 5b reveals that the two spectra are essentially identical, except that the methylene wagging band at 1375 cm<sup>-1</sup> is much more intense in the spectrum recorded in the mesophase than when the liquid crystalline structure is frozen in. Bands which fall in relative intensity with temperature are clearly observed at 1736, 1285, 1078 and 858 cm<sup>-1</sup>. These all appear to be related to crystalline order in the material, and lose intensity as the crystals rearrange to adopt the liquid crystalline structure. However, bands at 1748 and 1269 cm<sup>-1</sup> show a marked increase in intensity at the onset of  $T_{(1)}$ . Although BENEDETTI *et al.* [20] describe a shift in the terephthaloyl C=O stretch from 1736 to 1748 cm<sup>-1</sup> at the  $T_{(1)}$  transition, we observe two bands which are present in a variety of samples, and vary in relative intensity at  $T_{(1)}$ .

# Molecular structure of the crystalline and liquid crystalline phases

With our WAXS data from crystalline samples of PHMTOB we have estimated the crystal long spacing,  $L_x$ , to be of the order of 100 Å. However, the crystal structure, and hence the molecular arrangement in these small crystallites, is not known. The liquid crystalline phase has a smectic texture [28], and the low angle WAXS reflection corresponds to a molecular repeat distance of 23.3 Å between mesogenic layers.

There is some debate in the literature as to the structure of the mesogenic part of the polymer chain. The aromatic triad has been assumed to be a planar structure, resonancestabilised by the aromatic rings [8, 13, 19, 25, 39]. Nevertheless, it is well documented that in terephthalate moieties the carbonyl and ring planes only approach planarity, with a torsional angle of  $6-9^{\circ}$  [40-43]. However, if we regard the mesogenic unit as being planar, the angle subtended by the methylene chain axis relative to the mesogenic axis is configurationally defined to be around 45°. This angle has been estimated to be as low as 26° when the axis of the mesogen passes through the O-O atoms of the terminal ester linkages [19]. It is important to note that in the case of odd-numbered methylenic chains, the second mesogenic unit will lie at an angle of  $\approx 95^{\circ}$  relative to that of the first, whereas for even-numbered methylene spacers subsequent mesogenic units lie parallel [44].

With the terephthaloyl carbonyl units in the *trans* configuration [8, 42, 43], and the methylene chain in all-*trans* conformation, we calculate the repeat distance, x (i.e. the distance between corresponding oxygen atoms in oxybenzoic ring-methylene chain ester linkages) to be around 28 Å. Conformational changes within the mesogen cause a variation of  $\pm 2$  Å in the value of x. Indeed, with all of the ester linkages rotated by 90° relative to the aromatic ring planes [44, 45], x increases only by about 1.5 Å. Studies on model compounds and aromatic triads have shown that the outer ring planes tend to be rotated to torsional angles of between 50 and 65° out of the plane of the terephthalate ring [41, 46] and it seems likely that the mesogen is non-planar.



Fig. 7. FT-Raman spectrum of C1 versus sample temperature: (a) 66, (b) 116, (6) 132, (d) 160, (e) 182, (f) 204°C. (6 cm<sup>-1</sup> resolution, 350 mW laser power, 100 scans.)



Fig. 8. Normalised intensity ratios for selected bands in the FT-Raman spectra of C1 versus sample temperature.

If we introduce *gauche* conformations into the methylene chain, the repeat distance can be reduced considerably. Depending on the number, sign and position of the *gauche* conformations the calculated spacing can approach 22 Å. However, the relative positioning of consecutive mesogens becomes complicated. Given these values we estimate that around four chemical repeat units would be included in the crystallites, with the bulk of the chains lying in the interfacial and/or amorphous regions.



Fig. 9. Proposed model for the liquid crystalline phase, where L = smectic layer spacing (Å).

Although vibrational spectral changes have been previously related to differences in intermolecular interactions between the crystal and liquid crystal phases [20], our spectroscopic evidence does not rule out conformational variations in the mesogenic units at the phase transition, given that the majority of the changes appear in bands either related to the ester linkages or the aromatic rings. Since relatively small portions of the chains lie in the crystals, one can envisage a reasonable level of distortion in parts of the chain which lie in the amorphous and interfacial regions in order to accommodate the formation of the crystals, and this would explain the evidence from the DSC data of melting and recrystallisation processes.

Although the information available from the vibrations of the methylene spacer is limited, we have an indication that the spacer adopts a particular conformation in the liquid crystalline phase, probably all-trans. It is difficult to achieve a suitable molecular arrangement for the generation of the smectic texture, even with extensive torsions in both the ester linkages and the methylene chains, when the torsional angles inside the mesogenic unit are large. If we assume that the chain is not far removed from the planar arrangement, we can envisage a molecular structure for the mesophase along the lines of that drawn in Fig. 9, where the calculated repeat distance between consecutive mesogenic layers, L, approaches 24 Å, and the orientation axis of the liquid crystal phase lies along the same direction as the methylene chains.

# CONCLUSION

We have recorded the FT-Raman spectra from a series of thermotropic liquid crystal polyesters, and for the polymer PHMTOB we have observed a range of spectral changes which appears to be related to both the thermal history of the material, and the crystalto-crystal phase transition. These spectral changes are apparent in vibrations related with both the mesogenic units, and the flexible methylene spacer. A wide range of studies is now in progress to establish the molecular structure of the crystalline polymer, and the vibrational spectroscopic study of a series of models with similar thermotropic behaviour is underway in order to clarify the origin of the spectral differences observed.

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