Thermotropic polyesters: structure of poly(*p*-oxybenzoate-*co*-*m*-phenylene terephthalate) fibres

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Wide-angle X-ray diffraction techniques are employed to characterize the structure of 'as-made' and heat-treated fibres produced from nematogenic poly(*m*-phenylene terephthalate), where the molar fraction of the disruptor *m*-phenylenedioxy units is 0.25. As in the case of previously investigated poly(*p*-phenylene isophthalate)s, the 'as-made' fibres consist of a paracrystalline array of chains aligned along the fibre axis. Heat-treated fibre contains a mosaic of thin crystallites, consisting of *m*-phenylene terephthalate sequences, embedded in a paracrystalline matrix. A non-planar chain conformation, arising from the presence of *m*-phenylenedioxy units, is reflected in the shortening of the crystallographic repeat in the chain direction compared with that found for the poly(*p*-phenylene isophthalate) fibres.

(Keywords: aromatic polyesters; thermotropic; nematic; liquid crystalline; crystal structure; poly(*p*-oxybenzoate-*co*-*m*-phenylene terephthalate); fibres; wide-angle X-ray diffraction)

INTRODUCTION

Main-chain thermotropic liquid-crystalline polymers have recently received much attention owing to their growing practical importance. Consequently, various aspects of these materials have been reviewed in detail[1–5].

One of the attractive methods used for obtaining melt-processable nematogenic polyesters is based on partial replacement of rod-like units in rigid polyesters by angular disruptor units containing the *m*-phenylene group[6–16]. Poly(*p*-oxybenzoate-*co*-*m*-phenylene terephthalate)s (POMT) consist of rod-like *p*-oxybenzoyl (OPCO) and terephthaloyl (COPCO) units, and angular *m*-phenylenedioxy (OMO) units (*Figure 1*). Our previous work[16] showed, essentially in agreement with the results obtained by Jin and coworkers[14,15], that these copolyesters are nematogenic provided that the molar fraction of the disruptor units, [OMO], does not exceed 0.30. In contrast, in poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate)s (POPI), consisting of rod-like OPCO and *p*-phenylenedioxy (OPO) units, and angular isophthaloyl (COMCO) units (*Figure 1*), the critical concentration of the disruptor units, [COMCO], is significantly higher[6,8], about 0.40. This has been ascribed[16] to conformational differences between POPI and POMT chains. In the case of POPI chains, an extended quasiplanar conformation is feasible. In contrast, such a conformation is ruled out for POMT chains, where the ester groups and the adjacent *m*-phenylene rings cannot be coplanar owing to steric interactions between the carbonyl oxygen and *m*-phenylene hydrogen atoms[17].

This paper is concerned with the investigation of the structure of 'as-made' and heat-treated fibres produced from POMT ([OMO] = 0.25) copolymer. A range of well established wide-angle X-ray diffraction techniques is used for this purpose. The results are compared with those obtained previously[18–20] for the corresponding POPI ([COMCO] = 0.25) fibres, with the aim of establishing the effect of the differences in chain conformation on the resulting structure.

EXPERIMENTAL

The investigated 'as-made' fibres, produced by melt spinning at drawdown ratios of 5 and 27, were those used previously[16]. The latter fibre was heat treated for 360 min at 250°C under nitrogen.

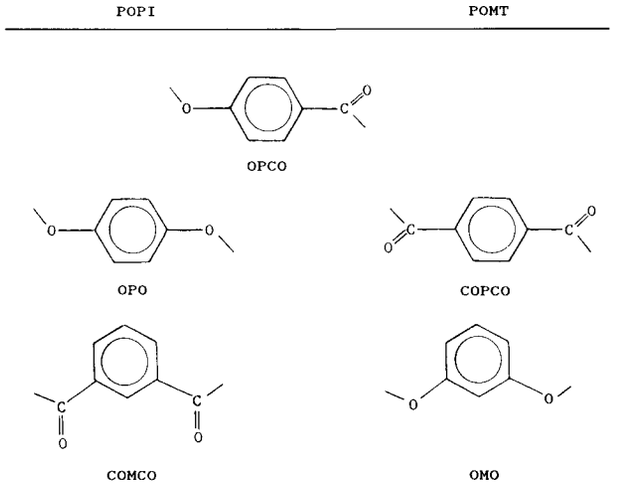

Figure 1 Rod-like *p*-oxybenzoyl (OPCO), *p*-phenylenedioxy (OPO) and terephthaloyl (COPCO) and rigid angular *m*-phenylenedioxy (OMO) and isophthaloyl (COMCO) constituent units

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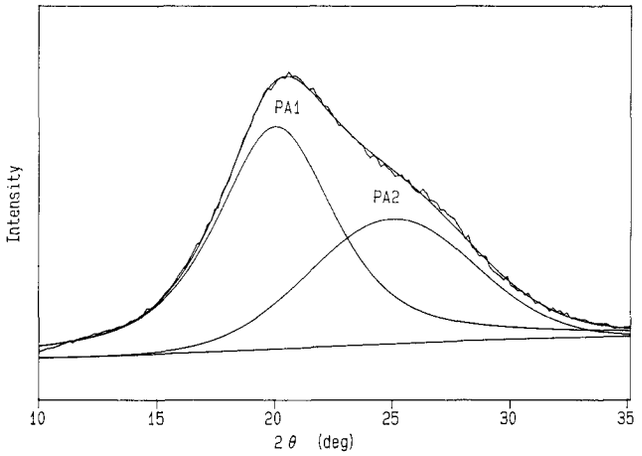

Figure 2 Resolved equatorial X-ray diffraction trace of the 'as-made' fibre ([OMO]=0.25, $\lambda=27$)

Table 1 WAXS features assigned to paracrystalline structure in 'as-made' (AM) and heat-treated (HT) POMT ([OMO]=0.25) and POPI ([COMCO]=0.25) fibres

Material		POMT			POPI	
Drawdown ratio		5	27	27	25	25
Fibre		AM	AM	HT	AM	HT[a]
Equatorial scatter						
PA1	*d*-spacing (nm)	0.451	0.444	0.445	0.444	0.445
	W(deg)[b]	6.40	5.90	4.90	3.33	3.68
	$\langle P_2 \rangle$	0.58	0.81	0.82	0.86	0.86
	$\langle P_4 \rangle$	0.18	0.59	0.62	0.69	0.69
PA2	*d*-spacing (nm)	0.356	0.356	0.352	0.371	0.356
	W(deg)	8.00	8.24	3.92	8.57	6.82
Meridional scatter						
PM1	*d*-spacing (nm)	–[c]	–[c]	–[c]	0.611	0.612
PM2	*d*-spacing (nm)	0.283	0.299	0.300	0.307	0.305
	W(deg)	VW[d]	0.49	0.38	0.75	0.71
PM3a	*d*-spacing (nm)	VW[d]	0.205	0.209	0.205	0.205
	W(deg)	VW[d]	5.77	4.20	2.34	2.11
PM3b	*d*-spacing (nm)	0.203	0.200	0.200	0.204	0.204
	W(deg)	VW[d]	0.79	0.58	1.02	0.84

[a] 30 min at 280°C
[b] Peak width at half-height
[c] Not observed
[d] Too weak for a reliable evaluation of peak width at half-height

Wide-angle X-ray diffraction patterns were taken with a flat-plate camera; contour maps were produced by means of a procedure described earlier[19]. Equatorial and meridional diffraction traces were obtained using an X-ray diffractometer; data evaluation was carried out by established procedures[18]. Orientation parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ were determined from azimuthal intensity profiles of the equatorial scatter[20].

RESULTS AND DISCUSSION

Structure of 'as-made' fibres

Previous qualitative characterization[16] showed that the dominant feature of the WAXS pattern of 'as-made' POMT fibres is a broad equatorial scatter with an average *d*-spacing of around 0.45 nm. The azimuthal spread of this scatter decreases with increasing drawdown ratio λ. The equatorial diffraction trace of the fibre produced at $\lambda=27$ is shown in *Figure* 2; the trace of the fibre produced at a lower drawdown ratio, $\lambda=5$, was similar. As in the case of 'as-made' POPI fibres, the traces are asymmetrical and can be resolved into at least two broad peaks. These peaks are labelled as PA1 and PA2, respectively, in accordance with the notation used for POPI fibres[18]. The *d*-spacings of the resolved peaks are given in *Table 1*, together with those obtained previously[18] for the corresponding POPI fibre.

The orientation parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ were obtained from azimuthal intensity profiles at 2θ corresponding to the *d*-spacing of the peak PA1. It must be emphasized that these parameters are not related directly to chain orientation; they reflect the orientation of rod-like segments terminated at each end by a rigid angular disruptor unit[20]. As expected, the increase in drawdown ratio results in increased segmental orientation (*Table 1*). The orientation parameters of POMT fibre ($\lambda=27$) are slightly lower than those of the corresponding POPI fibre ($\lambda=25$). It is possible that this is caused by an increase in the angles between the rod-like segments and the chain axis in non-planar POMT chains compared with those in quasiplanar POPI chains.

The meridional diffraction trace of tilted (20°) POMT fibres revealed two peaks labelled, as in the POPI fibres[19], PM2 and PM3 (*Figure 3*). The very weak reflection PM1, observed in the case of POPI fibres[19] at a *d*-spacing of 0.611 nm, has not been detected in POMT fibres. The peak PM3 is asymmetrical and can be resolved into two peaks, PM3a and PM3b. *Table 1* shows that the *d*-spacings of the prominent meridional peaks, PM2 and PM3b, of POMT fibres are slightly smaller than those of the corresponding POPI fibres, as is expected for the less extended conformation of POMT chains.

Finally, we note that d.s.c. curves of both POMT and POPI fibres showed very broad endotherms[16,18]. However, the endotherm of POMT fibre ($\lambda=27$) is between 250 and 330°C, whilst that of the corresponding POPI fibre occurs between 300 and 380°C.

The WAXS features of 'as-made' POPI fibres have been ascribed to a paracrystalline array of sinuous chain molecules aligned along the fibre axis[18,19]. The evidence presented above shows that the structure of 'as-made' POMT fibres is similar. The small but significant reduction of meridional *d*-spacings in POMT fibres

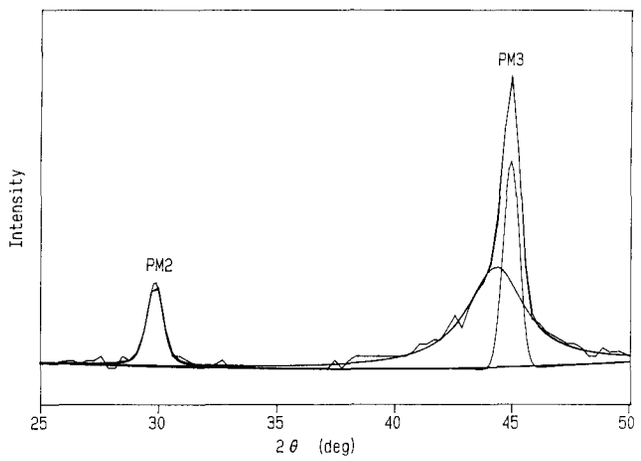

Figure 3 Resolved meridional X-ray diffraction trace of the 'as-made' fibre ([OMO]=0.25, $\lambda=27$)

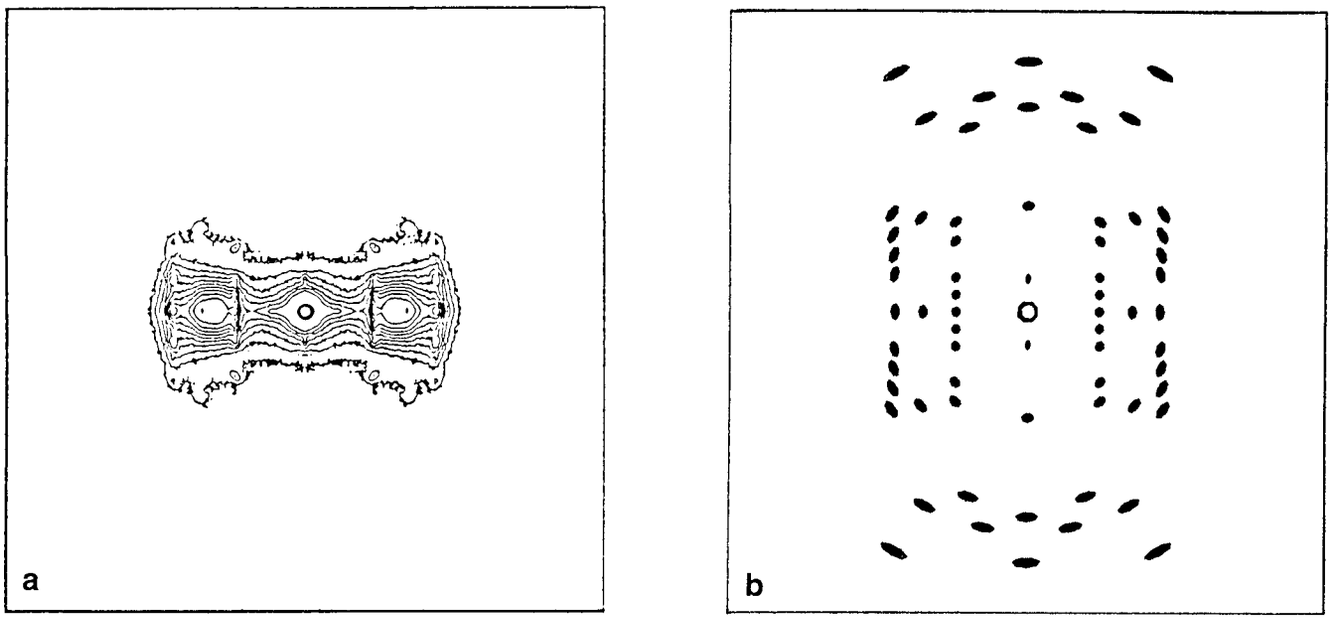

Figure 4 Wide-angle X-ray diffraction pattern of heat-treated (6 h at 250°C) fibre: (a) contour map; (b) schematic diagram showing the positions of sharp reflections observed on the film. Fibre axis is vertical

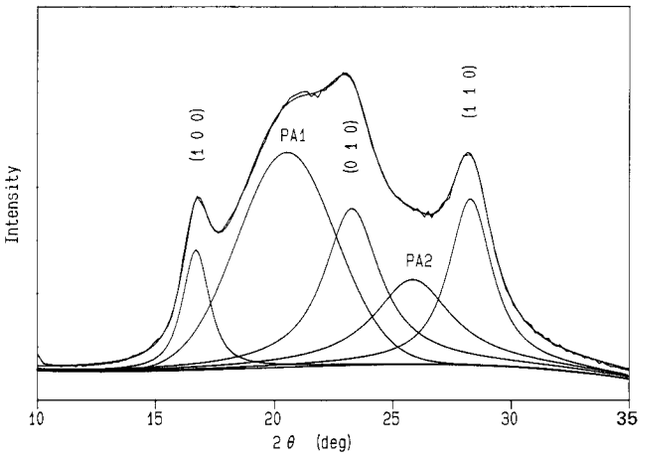

Figure 5 Resolved equatorial X-ray diffraction trace of the fibre ([OMO] = 0.25, $\lambda = 27$) heat treated for 6 h at 250°C

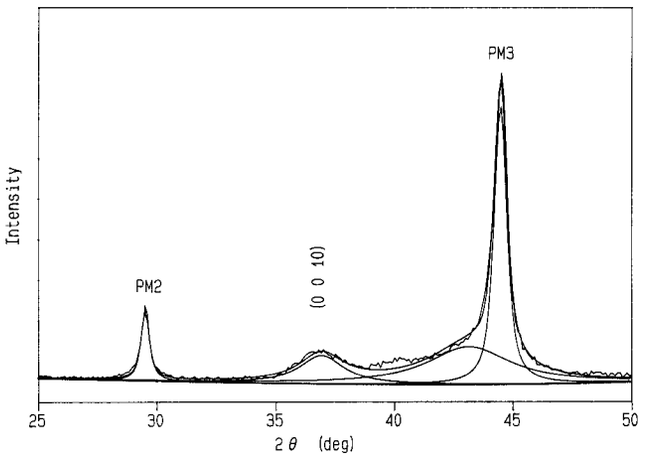

Figure 6 Resolved meridional X-ray diffraction trace of the fibre ([OMO] = 0.25, $\lambda = 27$) heat treated for 6 h at 250°C

compared with the corresponding POPI fibres is consistent with the less extended conformation of POMT chains, as is the small reduction of the segmental orientation parameters.

Structure of heat-treated fibre

In the case of POPI fibres, detailed structural characterization has been carried out[18–21] for fibres heat treated for 30 min at 280°C. Preliminary experiments showed that this temperature is unsuitable for POMT ([OMO] = 0.25, $\lambda = 27$) fibre, as it causes partial melting. This is in accordance with the d.s.c. result. Consequently, the heat-treatment temperature has been reduced to 250°C and the duration of the treatment has been extended to 6 h. This heat treatment resulted in a sharpening of the melting endotherm (range 300–335°C, peak temperature 320°C), but the enthalpy of the transition (approximately 20 J g^{-1}) did not increase significantly. The WAXS pattern of the heat-treated fibre showed a number of sharp reflections (*Figure 4*) arising from a crystalline structure. These reflections are superimposed on the features observed in the 'as-made' fibre, as shown in the resolved equatorial and meridional traces (*Figures 5* and *6*). Data given in *Table 1* show that the features present in the 'as-made' fibre were not affected substantially by the heat treatment.

The sharp reflections in heat-treated POMT fibre are similar to those found previously[18] in heat-treated POPI fibres (*Table 2*). It has been established that the crystallization of POPI fibres arises from regular packing of *p*-phenylene isophthalate (–OPO–COMCO–) sequences[18,21]. This structure, designated previously[18] as type C, differs from that formed after annealing of unoriented POPI materials; this has been confirmed by Blundell *et al.*[9]. Windle and coworkers[22] have also established the presence of crystallites consisting of *p*-phenylene isophthalate sequences in a sheared POPI copolymer by means of transmission electron microscopy.

Owing to the striking similarity between the WAXS patterns of heat-treated POMT and POPI fibres,

Table 2 Structure of heat-treated fibres: *d*-spacings of (a) POPI, calculated for an orthorhombic unit cell with $a=0.558$ nm, $b=0.392$ nm and $c=2.432$ nm; (b) POMT, observed in a fibre ([OMO] = 0.25, $\lambda=27$), heat treated for 360 min at 250°C; (c) POMT, calculated for an orthorhombic unit cell with $a=0.561$ nm, $b=0.396$ nm and $c=2.390$ nm

			d-spacing (nm)		
h	*k*	*l*	POPI[a]	POMT (HT)[b]	POMT
1	0	0	0.558	0.561	0.561
0	1	0	0.392	0.396	0.396
1	1	0	0.321	0.323	0.323
0	0	2	1.216	1.192	1.195
0	0	6	0.405	0.404	0.398
0	0	10	0.239	0.241	0.239
1	0	1	0.544	0.548	0.546
0	1	1	0.387	–[d]	–[d]
1	0	2	0.507	0.506	0.508
1	1	2	0.312	0.312	0.312
1	1	3	0.298	0.302	0.299
1	0	4	0.411	0.413	0.409
1	1	4	0.283	0.289	0.284
1	0	5	0.366	0.366	0.364
0	1	5	0.305	0.308	0.305
1	1	5	0.267	0.269	0.268
1	0	9	0.243	0.241	0.240
0	1	9	0.222	0.222	0.220
1	0	10	0.223	0.225	0.220
1	1	10	0.194	0.195	0.192
1	0	11	0.206	0.207	0.203

[d] Not observed

it is reasonable to assign the crystalline structure in the POMT fibre also to a regular packing of sequences of angular and rod-like units, in this case *m*-phenylene terephthalate (–OMO–COPCO–). As shown previously[16], annealing of unoriented POMT ([OMO] = 0.25) resulted in the appearance of reflections assigned to crystalline form I of poly(*p*-oxybenzoate)[23]. Thus, the crystalline structure resulting from heat treatment of both POPI and POMT is dependent on the orientation of the starting material.

Before we consider the structure of heat-treated POMT fibre in more detail, it is appropriate to amend some of the previous conclusions concerning the type C structure in POPI fibres[18]. Firstly, there is now conclusive evidence[19] that three of the meridional reflections assigned previously to type C structure are in fact the meridional peaks, PM1, PM2 and PM3, arising from the paracrystalline structure. Secondly, using longer exposure times for the X-ray photographs, it was possible to detect additional weak reflections on the ninth, tenth and eleventh layer lines. However, none of the observed reflections justified the previously suggested[18] indexing of the prominent equatorial reflections as 2 0 0, 0 2 0 and 2 2 0. It is therefore concluded that these reflections should be indexed as 1 0 0, 0 1 0 and 1 1 0. The revised dimensions of the orthorhombic unit cell, containing one chain and two *p*-phenylene isophthalate repeat units, are therefore as follows: $a=0.558$ nm, $b=0.392$ nm and $c=2.432$ nm. This is in acceptable agreement with the result obtained by Blundell *et al.*[9], particularly in view of the established effect of annealing temperature and time, as well as copolymer composition, on the observed *d*-spacings[18]. The revised indexing of the observed reflections and their calculated *d*-spacings are given in *Table 2*.

Systematic X-ray investigation of the structure of model compounds by O'Mahoney *et al.*[24] showed that in bis(4-biphenylyl) isophthalate the carbonyl groups are rotated only very slightly out of the plane of the central *m*-phenylene ring (between 1° and 7°); the distance between the centres of *p*-phenylene rings corresponding to the length of the –OPO–COMCO– sequence is 1.212 nm, which is in good agreement with $c/2=1.216$ nm of the proposed unit cell of the POPI type C structure. In bis(4-benzoyloxyphenyl) isophthalate[24], the torsion angles of C_{ar}–C(=O) bonds in the central isophthaloyl unit are larger, between 5° and 24°. However, the distance corresponding to the length of the –OPO–COMCO– sequence is 1.220 nm, which is again close to the $c/2$ value found for POPI. Thus, the studies of model compounds[24] confirmed that the extended quasiplanar conformation proposed[21] for the type C structure in POPI copolymers is realistic.

The similarity of the crystalline structures found in heat-treated POMT and POPI fibres has already been noted. With one exception, all the reflections found in POPI fibres were also found in POMT fibre (*Table 2*). The tentative dimensions of the orthorhombic unit cell proposed for POMT are as follows: $a=0.561$ nm, $b=0.396$ nm and $c=2.390$ nm. Whilst the crystallographic repeat in the chain direction, *c*, is indeed shorter than that of POPI, the difference is significantly smaller than expected. With the bond lengths and bond angles[25,26] employed previously in modelling of POPI chains[19] (set A in *Table 3*), the calculated repeat length of the $(–OMO–COPCO–)_2$ sequence for the fully extended quasiplanar conformation (i.e. $\psi_1=\psi_2=0$, see *Figure 7*) is shorter than the observed *c*-value (*Table 4*). Such a conformation is unrealistic[16] and the required out-of-plane rotations ($\psi_1=58°$, $\psi_2=\mp 58°$, see ref. 17) will result in a further shortening. With the bond lengths and angles employed recently by Blackwell and coworkers[27] (set B in *Table 3*), the calculated repeat length of the quasiplanar conformation increased above the observed *c*-value, but after the required out-of-plane rotations (either $\psi_1=\psi_2=58°$ or $\psi_1=+58°$, $\psi_2=-58°$) the calculated lengths again became too short (*Table 4*). Inspection of the results obtained for crystalline structures of model compounds[24] revealed considerable differences between corresponding bond angles. It is therefore obvious that the calculated repeat length obtained with standard bond lengths and angles can only be used for judging the

Table 3 Bond lengths and angles

	Length (nm)	
Bond[a]	Set A[25,26]	Set B[27]
O–C(=O)	0.137	0.1371
C(=O)–C_{ar}	0.149	0.1487
C_{ar}–O	0.141	0.1413
C_{ar}–C_{ar}	0.139	0.1400
C=O	0.123	0.1194
	Angle (deg)	
Bonds	Set A	Set B
O–C(=O)–C_{ar}	110.9	114.5
C_{ar}–C_{ar}–C(=O)	120.0	120.0
C_{ar}–C_{ar}–C_{ar}	120.0	120.0
C_{ar}–C_{ar}–O	120.0	119.0
C_{ar}–O–C(=O)	118.3	118.3
C_{ar}–C=O	123.0	122.1

[a] C_{ar} denotes aromatic carbon

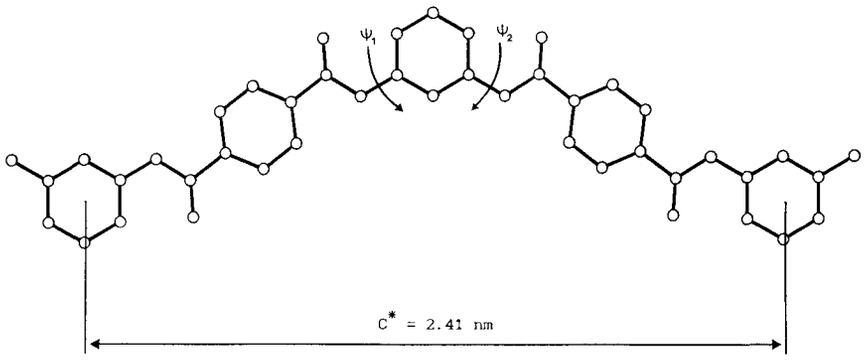

Figure 7 Fully extended planar conformation of poly(*m*-phenylene terephthalate); for bond lengths and bond angles see set B in *Table 3*

Table 4 Effect of bond lengths and angles (sets A and B in *Table 3*) and torsion angles (ψ_1 and ψ_2 in *Figure 7*) on the calculated repeat length of the (–OMO–COPCO–)$_2$ sequence, C^*; the corresponding crystallographic repeat in the chain direction is $c = 2.39$ nm

Set	ψ_1 (deg)	ψ_2 (deg)	C^* (nm)
A	0	0	2.35
B	0	0	2.41
B	58	58	2.32
B	58	−58	2.34

Table 5 Apparent size of the crystallites in the fibre ([OMO] = 0.25, $\lambda = 27$) heat treated for 6 h at 250°C

Reflection			Integral breadth 2θ (deg)	Apparent size (nm)
1	0	0	1.57	5.67
0	1	0	3.48	2.59
1	1	0	2.65	3.44
0	0	10	3.35	2.78

feasibilities of grossly different conformations. Any details, such as the relatively small changes in length resulting from out-of-plane rotations, will be obscured by the variations in bond angles.

Detailed investigation of POPI fibres[18–21] revealed that the crystallites formed during the heat treatment are unusually thin plates embedded in a paracrystalline matrix. Thus, the crystallites in the POPI fibre, heat treated for 30 min at 280°C, contained about 150 laterally packed chains, but their apparent dimension in the chain direction was only about 2 nm, i.e. similar to the *c*-dimension of the unit cell. Such unusual crystallites are feasible only due to a low value of the interfacial free energy in the plane perpendicular to the chain direction, arising from the absence of chain folding and from the similarity of chain cross-sectional areas in the crystallites and in the paracrystalline matrix.

The apparent dimensions of the crystallites in the heat-treated POMT fibres, evaluated from the integral breadths of resolved equatorial and meridional peaks, are given in *Table 5*. These results show that the crystallites, consisting in this case of about 70 laterally packed chains, are again very thin. The smaller lateral dimensions, compared with those found for the corresponding POPI fibre[18], may be due to the difference in heat-treatment temperatures.

CONCLUSIONS

Structural characterization of poly(*p*-oxybenzoate-*co*-*m*-phenylene terephthalate) (POMT) fibres revealed remarkable similarities with the previously investigated poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate) (POPI) fibres. In both cases the 'as-made' fibres consist of a paracrystalline array of chains aligned along the fibre axis. Heat treatment causes crystallization, but the resulting structure is different from that found in heat-treated unoriented materials.

Heat-treated fibres contain crystallites arising from regular packing of sequences where the angular and rod-like units alternate, i.e. *m*-phenylene terephthalate in POMT fibres and *p*-phenylene isophthalate in POPI fibres. The chains emerging from thin plate-like crystallites form paracrystalline matrices similar to those existing in the 'as-made' fibres.

Whilst the chains containing isophthaloyl units are quasiplanar (i.e. ester groups, *m*-phenylene rings and virtual bonds representing *p*-phenylene rings are confined to a plane), those containing *m*-phenylenedioxy units are non-planar. This results in smaller *d*-spacings of the meridional diffraction peaks arising from the paracrystalline structure in both 'as-made' and heat-treated POMT fibres, compared with those found for the POPI fibres. Similarly, the crystalline structure of POMT fibres has a smaller unit-cell dimension in the chain direction. However, this shortening is smaller than predicted using standard bond lengths and bond angles. It appears that the chain packing requirements result in a significant distortion of bond angles, as has been observed in crystals of oligomeric aromatic esters.

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