polymer papers

X-ray analysis of the structure of the thermotropic copolyester poly[(phenyl-*p*-phenylene-terephthalate)-co-(1-phenylethyl-*p*-phenylene-terephthalate)]

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X-ray methods have been used to determine the structure of the thermotropic copolyester prepared from terephthaloyl chloride (TPA) and equimolar amounts of phenylhydroquinone (PHQ) and (1-phenylethyl) hydroquinone (PEHQ). The X-ray patterns of annealed melt spun fibres contain a series of sharp Bragg reflections, pointing to a well ordered crystalline structure, despite the random substitution of the phenyl and 1-phenylethyl groups on the polymer backbone. The unit cell is orthorhombic with space group $P2_1$ and dimensions: $a = 12.77$ Å, $b = 10.18$ Å, $c = 12.58$ Å (fibre axis), and $\alpha = \beta = \gamma = 90°$ and contains TPA–PHQ or TPA–PEHQ units of four chains. The random substitution of phenyl and 1-phenylethyl groups was modelled by placing these groups at both the 2- and 3-positions of each hydroquinone and giving each a weight of one quarter. The structure was refined by linked atom least square methods against 13 observed and 26 unobserved reflections, and had a final R value of 0.25. Packing of the side chains is effected by staggering adjacent chains along the b axis by approximately $c/2$, so that the side chains are interleaved. The phenyl–COO and COO–phenyl torsion angles are $-5.3°$ and $65.4°$, respectively, such that the main chain phenyls are mutually inclined at 60.1° (the ester groups are assumed to be planar). The phenyls of the phenyl-hydroquinone units are mutually inclined at 59.7° (ortho) and 60.1° (meta). These torsion angles compare very well with those for poly(phenyl-*p*-phenylene-terephthalate) reported earlier as well as those for model compounds, notably phenylbenzoate. This gives us confidence to use them in analyses of the structure of more complex random sequence copolyesters.

(Keywords: X-ray diffraction; liquid crystalline polymers; aromatic copolyester; thermotropic polymers; structure determination; chain conformation)

INTRODUCTION

In this paper we describe X-ray analysis of the structure of a wholly aromatic polyester prepared from 50% (mole fraction) terephthaloyl chloride (TPA), 25% phenylhydroquinone (PHQ) and 25% (1-phenylethyl)hydroquinone (PEHQ). This polyester[1] is part of a family of aromatic thermotropic polyesters[2] that can be processed as self-reinforcing plastics or high strength fibres[3]. The chemical structures and properties of these thermotropic polyesters have been reviewed by Jin *et al.*[4]. They generally contain aromatic units such as 1,4-phenylene, 4,4-biphenylene, and 2,6-naphthalenes, linked by ester groups. The melting points can be reduced by incorporation of side chain substituents, main chain 'kinks' such as 1,3-phenylene units, or flexible $(CH_2)_n$ spacers[5].

In a previous paper[6] we described the structure of poly(phenyl-*p*-phenylene-terephthalate), which we had determined as a model for the present copolyester. The addition of the third component, (1-phenylethyl)hydroquinone, results in a decrease in the melting point (solid state to nematic transition). This is presumably due to the increased randomness, with the two types of substituents randomly distributed on the backbone hydroquinone units. The X-ray diffraction patterns of annealed-melt spun fibres of this polyester are similar to those of poly(phenyl-*p*-phenylene-terephthalate). There is a high degree of orientation parallel to the fibre axis, and sharp Bragg reflections on well defined layer lines, which indicate the existence of three dimensional order[7], despite the random side chain substitution.

We have refined this structure by linked-atom least square (LALS) methods[8], primarily in order to determine the chain conformation. Our laboratory is now engaged in a study of the structure of thermotropic copolyesters, notably the copolymer prepared from *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid. In our most recent work[9] we have developed three dimensional models for the ordered packing of these random copolymers. This presents us with the need for knowledge of the likely chain conformation.

EXPERIMENTAL

Synthesis

(1-phenylethyl)hydroquinone was synthesized by reacting styrene (41.66 g, 0.40 moles) hydroquinone with (50.00 g, 0.45 moles) of hydroquinone, in the presence of tetraethyleneglycol dimethylether (Tetraglyme, 100 cc) as a diluent and *p*-toluene sulphonic acid (0.6 g) as a Lewis acid. Styrene and hydroquinone (reagent grades) were obtained from Eastman Kodak Co. Styrene was added over approximately 90 min to the hydroquinone, while

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maintaining the temperature at about 140°C and stirring slowly. The reaction was continued at that temperature for approximately 5 h and then cooled overnight. The yield was about 193 g. The crude product was purified by vacuum batch distillation, employing sodium hydrogen sulphite to neutralize the *para*-toluene sulphonic acid catalyst. The fraction of (1-phenylethyl)hydroquinone was collected at about 200°C/25 mmHg and redistilled. The yield was approximately 18 g.

The polymer was synthesized from 50% (mole fraction) terephthaloyl chloride, 25% phenylhydroquinone, and 25% (1-phenylethyl)hydroquinone dissoved in methylene chloride in the presence of pyridine as an acid trap. Phenylhydroquinone and terephthaloyl chloride (reagent grades) were obtained from Eastman Kodak and Sigma Chemical Co., respectively. The reaction was conducted under a moderate nitrogen flow blanket at approximately atmospheric pressure. A solution of (1-phenylethyl) hydroquinone (14.7 g, 0.69 moles), phenylhydroquinone (12.8 g, 0.69 moles), methylene chloride (48.2 g) and pyridine (22 g) was formed in the reactor. A solution of the terephthaloyl chloride (27.92 g, 1.38 moles) in methylene chloride (48.2 g) was added slowly to the diol mixture over about 30 min while stirring vigorously and maintaining the temperature at approximately 0°C. Upon completion of the polymerization the solvent was extracted by distillation. The solid product was washed with water and acetone several times, filtered, and dried in a vacuum oven at approximately 100°C and 500 mm(Hg) overnight. The dried polymer had a melting point of 320°C and inherent viscosity of 0.46 dl/g when dissolved in equal volumes of trifluoroacetic acid and methylene chloride.

X-ray diffraction

Specimens for X-ray analysis were bundles of parallel fibres drawn by hand from the melt. These were examined both in the as-spun state and after they had been annealed at 250°C for 2 h. X-ray fibre diagrams were recorded on Kodak no-screen X-ray film using Ni-filtered Cu-Kα radiation and a Searle toroidal focusing camera. The *d*-spacings were calibrated using calcium fluoride.

The integrated intensities of the observed reflections were determined using an Optronix Photoscan P1000 digital microdensitometer, as has been described elsewhere[10]. The data were recorded as an *x*–*y* scan of optical density. Each reflection was integrated after subtraction of a local background determined as the averages from around its perimeter. Each *hkl* intensity was determined as the average of measurements and converted to $F(hkl)$ by application of Lorentz and polarization corrections (except for the $00l$ reflections). Unobserved reflections produced in the range of the observed data were assigned an intensity equal to half of the threshold for observation of a reflection in this region.

Molecular model building and refinement

Molecular models based on standard bond lengths and bond angles[11–13] were generated using the LALS program package. It was assumed that the phenyl and carboxyl group are planar, and that the phenyl and 1-phenylethyl side chains are distributed randomly between the *ortho* and *meta* positions. The backbone repeat for this polymer consists of a single TPA–HQ unit, for which two models were considered for the positions of the phenyl and 1-phenylethyl substituents:

(1) 2-, 3-, 5- and 6-phenyls and -1-phenylethyls, each weighted by 0.125, allowing for random *o*- and *m*-substitution of both types of substituent on both sides of the chain.

(2) 2- and 3-phenyls and -1-phenylethyls weighted by 0.25, requiring the substituents to be always on the same side of the chain.

The refineable parameters in case 2 are shown in *Figure 1*. All torsion angles are defined as positive for clockwise rotations, and 0° corresponds to the *cis* conformation in each case. The conformation is defined by two backbone torsion angles, Ψ_2 ($=\Psi_1$) and Ψ_3 ($=\Psi_4$) i.e. the phenyl-ester inclinations, and by the side chain torsion angles, ϕ_2 and ϕ_3 for the phenyl, and ϕ'_2, ϕ''_2, ϕ'_3, and ϕ''_3 for the 1-phenylethyl. For model 1, six additional side chain torsion angles, ϕ_5, ϕ_6, ϕ'_5, ϕ''_5, ϕ'_6, and ϕ''_6, are necessary. The unit cell contains four chains, but these form two pairs of two chains related by a 2_1 screw axis along the *b* axis. The axial rotations of the independent chains passing through 0, 0 and 1/2, 0 on the *ab* face are θ_1 and θ_2, and s_1 and s_2 are the shifts for their ester oxygens (O_{a1}) along the *c* axis, respectively.

In the last stages of the refinement we considered the possibility of the small shifts of the chain axis along the *a* and *b* axes from the 0, 0 and 1/2, 0 positions. These shifts are s_3 and s_4 for the *a* axis shifts and s_5 and s_6 for the *b* axis shifts for the 0, 0 and 1/2, 0 chains, respectively. The remaining parameters are K, the scale factor to put the observed structure amplitudes on the same scale as those calculated, and B, an isotropic temperature factor. These parameters were refined, first in groups and then all together, to obtain the best agreement between the observed and calculated structure amplitudes, as des-

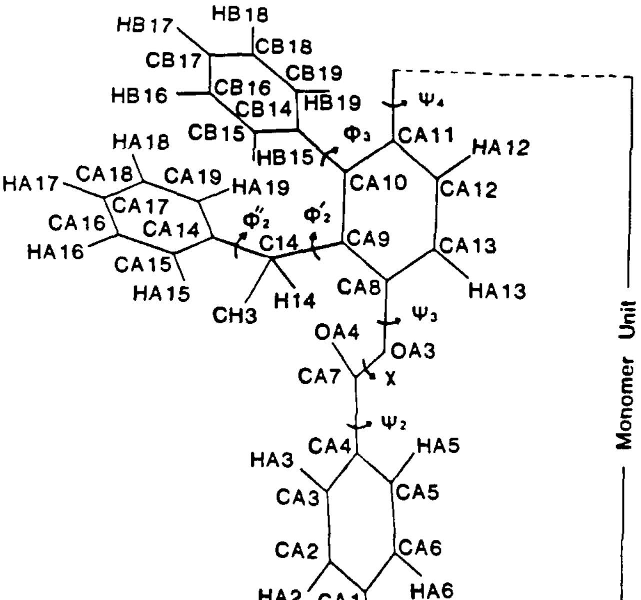

Figure 1 Numbering of the atoms and definition of the refineable torsion angles for the polymer repeat unit (model 2)

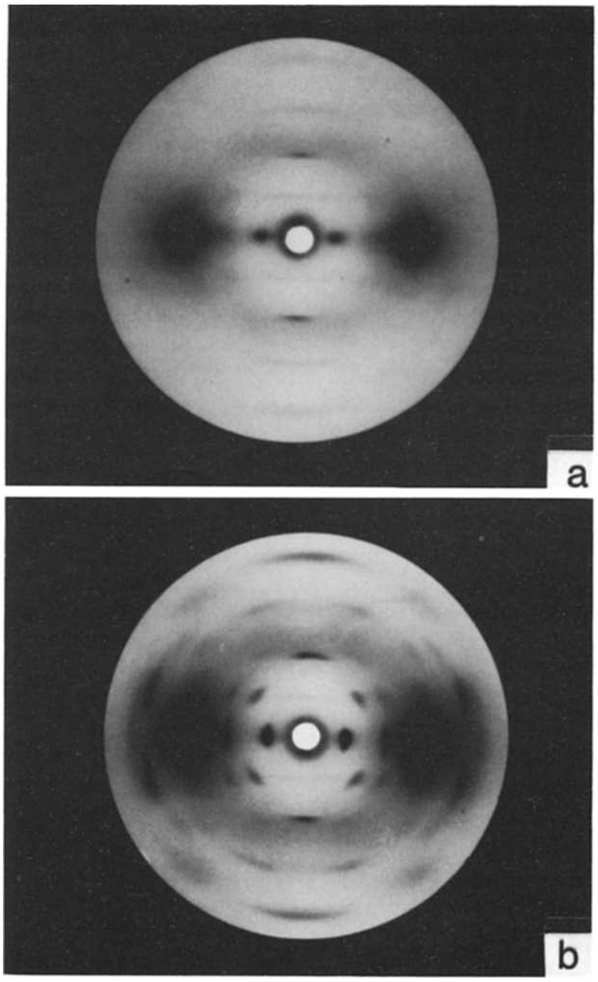

Figure 2 X-ray diffraction patterns for melt-spun fibres of poly[(phenyl-*p*-phenylene-terephthalate)-co-(1-phenylethyl-*p*-phenylene-terephthalate)]. (a) As spun; (b) annealed at 250°C for 2 h

cribed in our previous paper[6], using the LALS procedures of Arnott and Smith[8].

RESULTS AND DISCUSSION

Unit cell determination

The X-ray fibre diffraction patterns of as-spun and annealed samples are shown in *Figure 2*. Annealing leads to the development of sharp Bragg reflections, pointing to an ordered three dimensional structure for the copolymer. This paper analyses the structure of the annealed state.

The unit cell dimensions and other crystal data are shown in *Table 1*. The unit cell was determined by trial and error followed by least square refinement, based on the *d*-spacings of 16 observed reflections with $d > 3$ Å. The unit cell has dimensions: $a = 12.77(0.06)$ Å, $b = 10.18$ (0.03) Å, and *c* (chain axis) = 12.58 (0.07) Å, with orthorhombic geometry ($\alpha = \beta = \gamma = 90°$). These data are very similar to those for poly(phenyl-phenylene-terephthalate), except that the *b* dimension is expanded by 0.1 Å. The agreement between the observed and calculated *d*-spacings is shown in *Table 2*. For most reflections, the match is within 1%. The most obvious discrepancies are 1.3% for the 011 and 1.0% for the 020 reflection. In view of the random substitution of the phenyl and 1-phenylethyl groups, the X-ray data yield only an average unit cell, and the actual packing will vary for the different substituent position on adjacent chains. The distortions inherent in such a structure probably account for the less than perfect agreement between the observed and calculated *d*-spacings. A similar situation occurs for poly(phenyl-*p*-phenylene terephthalate)[6]. The only systematic absences are for the odd order 0*k*0 reflections, pointing to a $P2_1$ space group.

The fibre diagram shows a series of periodic layer lines with spacing $c = 12.58$ Å, which is the same as that for poly(phenyl-*p*-phenylene-terephthalate) and comparable to the repeats of 12.9 Å for poly(*p*-phenylene terephthalamide)[14] and 12.6 Å for poly(oxybenzoate)[15]. Thus we expect that the copolymer has an analogous extended conformation, with *c* corresponding to the length of a single TPA–HQ unit. The unit cell has a volume of 1642 Å^3. If this contains four TPA–PHQ or TPA–PEHQ units, the calculated density is 1.340 g/cm^3, which agrees very well with the observed density of 1.33 g/cm^3 determined by flotation.

Refinement of the structure

Independent chains were positioned with their axes passing through (0, 0) and (1/2, 0) in the *ab* plane. The 2_1 screw axis generates two more chains through (0, 1/2) and

Table 1 Crystal data

a (Å)	12.77 (0.06)
b (Å)	10.18 (0.03)
c (Å)	12.58 (0.07)
Volume (Å^3)	1635.4
Calculated density (g/cm^3)	1.340
Observed density (g/cm^3)	1.33 ± 0.01
Repeat units/unit cell	4
Space group	$P2_1$ (*b* unique)

Table 2 Comparison of observed and calculated *d*-spacings

hkl	*d* (calc) (Å)	*d* (obs) (Å)
100	12.77	12.73
200	6.38	6.39
020	5.08	5.03
300	4.26	4.23
400	3.19	3.18
011	7.91	7.81
201	5.70	5.74
121	4.42	4.39
031	3.28	3.30
002	6.29	6.26
102	5.35	5.37
022	3.95	3.96
302	3.52	3.53
013	3.88	3.89
123	3.13	3.14
104	3.05	3.06

Table 3 Refined torsion angles

	Angle (degrees)
CA3–CA4–CA7–OA4 (ψ_2)	−5.3
CA7–OA3–CA8–CA9 (ψ_3)	65.4
CA8–CA9–CA14–CA15 (ϕ_2)	59.7
CA9–CA10–CB14–CB15 (ϕ_3)	60.1
CA8–CA9–C14–CA14 (ϕ'_2)	80.7
CA9–C14–CA14–CA15 (ϕ''_2)	48.4
CB8–CB9–C14–CB14 (ϕ'_3)	81.9
CB9–C14–CB14–CB15 (ϕ''_3)	46.1

Table 4 Fractional atomic coordinates

Atom	*x*	*y*	*z*
Chain at 0, 0			
OA1	−0.019	0.011	−0.031
CA0	0.050	−0.081	0.005
OA2	0.101	−0.149	−0.053
CA1	0.053	−0.084	0.123
CA2	0.128	−0.160	0.172
CA3	0.134	−0.166	0.281
CA4	0.064	−0.095	0.342
CA5	−0.012	−0.019	0.294
CA6	−0.017	−0.013	0.184
CA7	0.065	−0.096	0.460
OA3	−0.007	−0.009	0.500
OA4	0.119	−0.163	0.515
CA8	−0.016	0.002	0.612
CA9	0.065	0.051	0.672
CA10	0.054	0.061	0.781
CA11	−0.038	0.022	0.830
CA12	−0.119	−0.025	0.769
CA13	−0.109	−0.036	0.660
CA14	0.165	0.092	0.620
phenyl (ortho)			
CA15	0.164	0.190	0.544
CA16	0.256	0.228	0.496
CA17	0.350	0.168	0.523
CA18	0.351	0.070	0.599
CA19	0.258	0.032	0.647
(meta)			
CB14	0.142	0.114	0.847
CB15	0.239	0.050	0.847
CB16	0.320	0.099	0.908
CB17	0.306	0.211	0.969
CB18	0.210	0.274	0.969
CB19	0.128	0.225	0.908
phenylethyl (ortho)			
C14	0.164	0.091	0.621
H14	0.147	0.140	0.551
C1	0.217	0.170	0.686
H1	0.201	0.146	0.764
H2	0.296	0.160	0.672
H3	0.196	0.266	0.673
CA14	0.229	−0.026	0.599
CA15	0.247	−0.118	0.677
CA16	0.308	−0.227	0.656
CA17	0.351	−0.243	0.556
CA18	0.333	−0.151	0.478
CA19	0.272	0.042	0.499
(meta)			
C14	0.142	0.113	0.846
H14	0.198	0.113	0.846
C1	0.106	0.207	0.911
H1	0.029	0.188	0.930
H2	0.150	0.209	0.979
H3	0.111	0.297	0.874
CB14	0.189	0.004	0.908
CB15	0.211	0.021	1.015
CB16	0.256	−0.080	1.072
CB17	0.279	−0.198	1.023
CB18	0.257	−0.215	0.916
OA5	−0.043	0.036	0.942
Chain at 1/2, 0			
OA1	0.480	0.011	0.002
CAO	0.427	−0.097	0.038
OA2	0.389	−0.176	−0.020
CA1	0.426	−0.101	0.156
CA2	0.388	−0.213	0.204
CA3	0.385	−0.221	0.314
CA4	0.420	−0.117	0.375
CA5	0.459	−0.005	0.327
CA6	0.426	0.003	0.217
CA7	0.420	−0.118	0.493
OA3	0.467	−0.009	0.533
OA4	0.383	−0.202	0.548
CA8	0.474	0.006	0.645
CA9	0.532	−0.080	0.705
CA10	0.538	−0.064	0.814
CA11	0.484	0.037	0.863
CA12	0.425	0.123	0.802
CA13	0.420	0.107	0.693
phenyl (ortho)			
CA14	0.591	−0.190	0.653
CA15	0.666	−0.162	0.577
CA16	0.720	−0.264	0.528
CA17	0.699	−0.393	0.556
CA18	0.624	−0.420	0.632
CA19	0.570	−0.319	0.680
(meta)			
CB14	0.602	−0.157	0.880
CB15	0.579	−0.290	0.880
CB16	0.638	−0.375	0.941
CB17	0.720	−0.328	1.001
CB18	0.743	−0.195	1.002
CB19	0.684	−0.110	0.941
phenylethyl (ortho)			
C14	0.590	−0.188	0.654
H14	0.624	−0.155	0.584
C1	0.665	0.232	0.719
H1	0.642	−0.219	0.796
H2	0.678	−0.330	0.705
H3	0.733	−0.180	0.706
CA14	0.518	−0.298	0.632
CA15	0.452	−0.345	0.710
CA16	0.384	−0.448	0.689
CA17	0.384	−0.504	0.589
CA18	0.450	−0.458	0.510
CA19	0.517	−0.355	0.532
(meta)			
C14	0.601	−0.156	0.879
H14	0.646	−0.213	0.830
C1	0.664	−0.087	0.944
H1	0.629	0.001	0.963
H2	0.677	−0.140	1.012
H3	0.734	−0.069	0.906
CB14	0.531	−0.242	0.941
CB15	0.549	−0.265	1.047
CB16	0.484	−0.346	1.105
CB17	0.399	−0.405	1.056
CB18	0.380	−0.383	0.949
CB19	0.446	−0.302	0.891
OA5	0.493	0.047	0.974

* The chains at 0, 1/2 and 1/2, 1/2 are related to those at 0,0 and 1/2, 0, respectively by the 2_1 symmetry operation along the *b* axis: $-X, Y+0.5, 1-Z$ and $1-Z, Y+0.5, 1-Z$

(1/2, 1/2). In the initial refinement we used model 1 for the chain, with phenyls and 1-phenylethyls weighted 0.125 at positions 2-, 3-, 5- and 6- on the hydroquinone. The best *R* values obtained were mid-thirties, and the structure was stereochemically unacceptable because of many side chain–side chain bad contacts.

When we used model 2 for the chain conformation, in which the phenyls and 1-phenylethyls are at the 2- and 3-positions and weighted by 0.25, we obtained considerable improvement. The *R* values fell immediately to below 0.30, and the final refined value was 0.25. When possible shifts of the chain axes along the *a* and *b* axes were

Table 5 Observed and calculated structure factors

hkl	*Fo*	*Fc*	*hkl*	*Fo*	*Fc*
100	330.9	132.3	021	54.9	48.9
200	296.2	331.5	032	54.9	64.9
110	109.8	125.0	102	10.9	26.7
400	257.6	285.7	101	32.9	26.2
011	131.1	104.6	122	65.8	77.9
201	133.3	61.1	113	32.9	34.9
121	169.9	170.2	202	32.9	64.6
301	153.7	164.6	111	32.9	40.6
031	213.8	163.4	112	65.8	62.9
012	66.7	41.6	212	32.9	47.8
022	103.5	84.9	320	65.8	77.3
302	90.5	86.4	211	54.8	50.1
222	164.7	172.6	210	32.9	59.8
013	114.4	117.7	221	32.9	28.9
023	98.8	81.1	303	43.9	29.1
123	156.6	138.8	311	65.8	62.7
213	142.7	151.5	104	17.6	23.1
014	32.9	52.3			

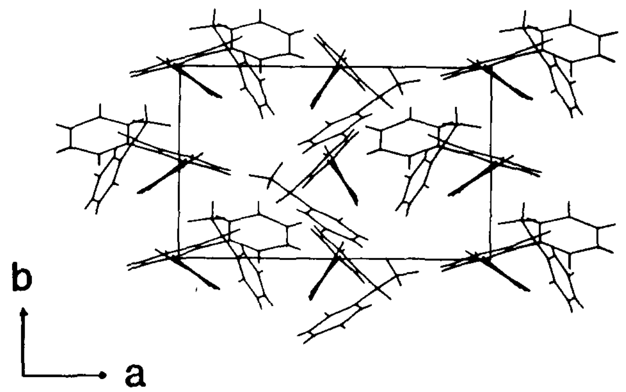

Figure 3 Projection of the refined structure on the *ab* plane

considered, these were found to be negligible. The final *R* value is a little higher than the value of 0.20 for the refined structure of poly(phenyl-*p*-phenylene-terephthalate) and probably reflects the increased disorder due to the fact that 50% of the side chains are ethyl phenyl groups, which have more conformational variability.

The torsion angles and atomic coordinates for the refined structures are given in *Tables 3* and *4*, and the observed and calculated structure amplitudes are compared in *Table 5*. The *ab* projection of the unit cell is shown in *Figure 3*. The packing of the side chains is illustrated in *Figure 4*, which shows two chains, on the 020 and on the 200 plane. The final structure has adjacent chains along the *a* axis with their ester oxygens staggered by 0.033*c* and their phenyl or 1-phenylethyl substituents disposed to opposite sides of the chain. The 2_1 screw axis parallel to *b* has the effect that for the chains in that direction the phenyls or 1-phenylethyls are also disposed to opposite sides. The side chains on chains along the *ab* diagonal point towards one another, but are interleaved because the *HQ* units of chains along the *b* axis are staggered by approximately *c*/2.

The refined structure contains some bad stereochemical contacts between the phenyl substituents of the chains at 0, 0 and 1/2, 1/2. The worst of these is a $C_{16}\cdots C_{16}$ distance of 3.1 Å, approximately 0.5 Å below the limiting acceptable distance, which occurs for 2, 2 and 3, 3 substituent combinations. The additional conformational freedom in the phenylethyl groups allows them to rotate such that there are no phenylethyl–phenylethyl or phenylethyl–phenyl bad contacts, and hence the side chain–side chain bad contacts are limited to 12.5% of the side chain combinations. A similar situation pertained in the refined structure of poly(phenyl-*p*-phenylene-terephthalate), where there were 2, 2 and 3, 3 contacts, in this case involving 50% of the possible side chain combinations. However, it should be noted that we are dealing with an average structure and have assumed that the torsion angles are independent of the neighbouring substituents, whereas the actual torsional angles will vary depending on the local environment. The 1-phenylethyl group is larger than the phenyl group but the conformational freedom allowed by the aliphatic linkage allows for more efficient packing and actually results in an increased crystal density: 1.33 g/cm^3 observed, 1.340 g/cm^3 calculated, *versus* 1.30 g/cm^3 and 1.313 g/cm^3, respectively for poly(phenyl-*p*-phenylene-terephthalate). In the latter polymer the phenyl side chains point approximately along the *a* axis. This orientation is retained for the phenyls in the copolymer, but the 1-phenylethyls are turned so that their phenyls are pointing more along the *b* axis, which accounts for the small increase in this dimension of the unit cell, as compared to poly(phenyl-*p*-phenylene-terephthalate). Given the random substitution of the phenylhydroquinone and (1-phenylethyl)hydroquinone in the main chain as well as the random 2- and 3-substitution of the phenyl and 1-phenylethyl side chains in the backbone hydroquinone, the high degree of crystalline order is perhaps surprising. There must be differences in local packing of these groups depending on the actual substitution, but these distortions do not prevent the refinement of an average structure.

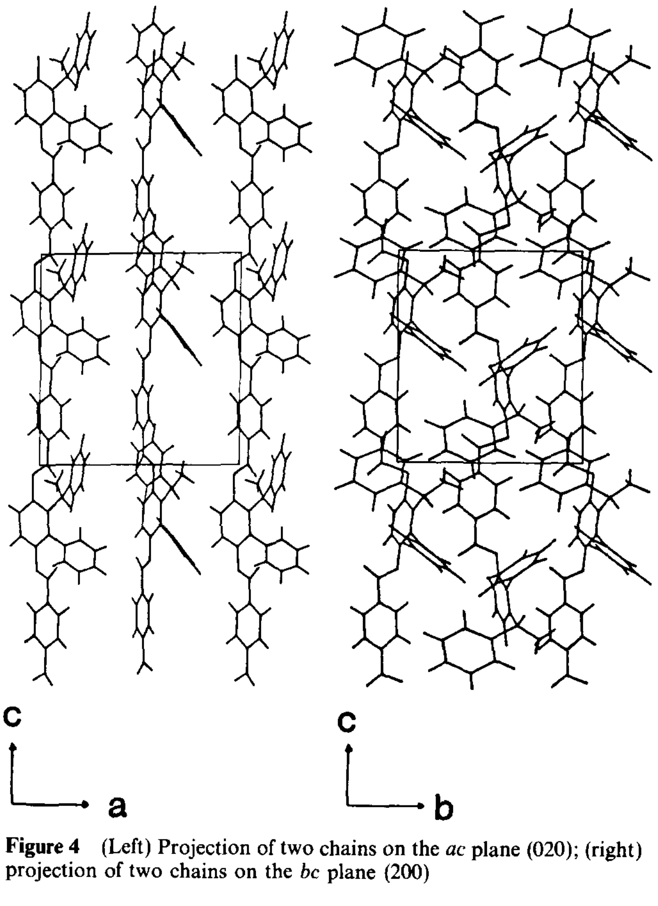

Figure 4 (Left) Projection of two chains on the *ac* plane (020); (right) projection of two chains on the *bc* plane (200)

The backbone chain conformation is defined by the ψ_2 (COO–phenyl) and ψ_3 (phenyl–COO) torsion angles, which are $-5.3°$ and $65.4°$, respectively. These compare well with the observed values of $-7.3°$ and $65.5°$ reported for poly(phenyl-*p*-phenylene-terephthalate), $-9.8°$ and $65.5°$ for phenylbenzoate[16]. Survey of other model compounds shows ranges of $-3°$ to $-10°$ and 60°–70° for the same two angles[17–20]. An *ab initio* quantum chemistry calculation of the minimum energy conformation for an isolated phenylbenzoate molecule resulted in $-3.7°$ and $61.9°$ for the same angles, with $\chi = 0.6°$ (deviation from planarity of the ester group)[21]. Because the structure is symmetrical, it was assumed that the backbone torsion angles were the same on both sides of each monomer, i.e. $\psi_2 = \psi_1$ and $\psi_3 = \psi_4$. Release of those constraints did not lead to any significant improvement for R value.

The mutual inclination of the main chain phenyls is 60.1°, compared to 58.2° in poly(phenyl-*p*-phenylene-terephthalate) and 55.7° in phenylbenzoate and a general observed range of 60–70°, including 68° in poly(*p*-phenylene terephthalate-amide)[14]. In the latter structure, the equivalent torsion angles are 38° and $-30°$, but the linkages are *via* amide rather than ester groups, and it is necessary to form intermolecular hydrogen bonds. The phenyl side chains are inclined at 59.3° (*ortho*) and 59.8° (*meta*) to the main chain phenyl, which compares well with the values of 59.7° (*ortho*) and 60.1° (*meta*) for poly(phenyl-*p*-phenylene-terephthalate), and is very much in agreement with the inclinations of 56.2° and 50.8° for the phenyl rings in 6,7-diphenyl[1,2,4]triazolo[5,1-c]-[1,2,4]triazine (ref. 22). The 1-phenylethyl side chain conformations are defined by ϕ'_2 and ϕ''_2 for *ortho*, ϕ'_3 and ϕ''_3 for *meta*, the phenyl–CCC and CCC–phenyl torsions, which are 80.7° and 48.4° for *ortho*, and 81.9° and 46.1° for *meta*, respectively. These values compared very well with 86.2° and 35.5° in 1,-1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethanol[23]. The differences between the side chain conformation angles at *ortho* and *meta* positions are not significant, and setting $\phi'_2 = \phi'_3$ and $\phi''_2 = \phi''_3$, did not change the R value.

CONCLUSIONS

We have refined this structure in part to provide conformational data for other random copolyesters, for which the chemical sequence is more complex and X-ray data are more diffuse. The similarity of the refined conformation to those for model compounds and poly(phenyl-*p*-phenylene-terephthalate) gives us confidence to transfer them to other structures. Indeed it is shown that the X-ray data are very sensitive to these torsion angles, in spite of the obvious fact that the intensities are largely determined by the mutual inclination of the phenyl groups, and many combinations of ϕ_1 and ϕ_2 are possible that are compatible with a 60° inclination of the backbone phenyls.

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