열방성 액정폴리에스터 Poly (1-phenylethyl-p-phenylene-terephthalate) 의 X-선 결정구조해석

홍 성 권

충남대학교 공과대학 고분자공학과

X-ray Analysis of theThermotropic Liquid Crystalline Copolyester Poly(1-phenylethyl-p-phenylene-terephthalate)

Sung-Kwon Hong

Dept. of Polymer Science & Engineering
Chungnam National University, Taejon 305-764, Korea

요 약

50% terephthaloyl chloride(TPA)와 50%(1-phenylethyl) hydroquinone(PEHQ)으로 부터 합성된 열방성 액정폴리에스터 poly(1-phenylethyl-p-phenylene-terephthalate)의 chain conformation 및 packing 상태를 X-선 회절법을 이용하여 해석하였다.

단위세포상수는 a=12.77 Å, b=10.17 Å(unique axis), c=12.58 Å (fiber axis), β=90.1°, 그리고 공간군은 $P2_1$ 이고 단사정계이며 Z=4 이었다. 미세구조는 주쇄상의 Phenyl-COO그리고COO-Phenyl 평면간의 그리고 주축과 측쇄간의 torsion angle 들을 중심으로 37개의 회절반점에 대해 Linked Atom Least Square(LALS) 방법을 이용하여 해석하였으며, 1-phenylethyl 치환체는 ortho-와 meta- 위치에 각각 확률적으로 0.5의 가중치를 부여함에 의해 구조적으로 모델링 되었다. 주쇄상의 Phenyl-COO 그리고 Phenyl-COO평면간의 torsion angle은 각각 -6.1°와 65.6° 로 주어졌으며 결국 주축상의 Phenyl 평면들은 서로 59.5°로 엇갈려 주축을 형성하고 있음을 알 수 있었다.(단 ester, COO-, 기는 평면으로 가정되었다.)

Abstract

X-ray methods have been used to determine the chain conformation and packing of the thermotropic liquid crystalline copolyester prepared from 50% terephthaloyl chloride(TPA) and 50% (1-phenylethyl) hydroquinone(PEHQ).

The x-ray patterns of annealed melt-spun fibers contain a series of sharp Bragg reflections, pointing to a well ordered crystalline structure, despite the random sense(2- or 3-) of the 1-phenylethyl substiuttion on the TPA-hydroquinone backbone. The crystalline fiber is monoclinic with space group $P2_1$ and the unit cell has dimensions : a=12.77 Å, b=10.17 Å (unique axis), c=12.58 Å (fiber axis), and β=90.1° and contains TPA-PEHQ units of four chains. The random substitution of 1-phenylethyl groups was modelled by placing these groups at both the 2- and 3- positions and giving each a weight of one-half. The structure has been refined by linked atom least square methods(LALS) against 16 observed and 21 unobserved reflections, and had a final R value of 0.20. 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 –6.1° and 65.6°, respectively, such that the main chain phenyls are mutually inclined at 59.5° (the ester groups are assumed to be planar). These torsion angles compare very well with those for the model compounds, notably phenylbenzoate, and can be used in future analyses of the structures of more complex random sequence copolyesters.

INTRODUCTION

In this paper X–ray analysis of the structure of a wholly aromatic polyester prepared from 50% terephthaloyl chloride(TPA) and 50%(1–phenylethyl) hydroquinone(PEHQ) has been described. This polyester[1] is a part of a family of aromatic thermotropic polyesters[2] that can be processed as self–reinforcing plastics or high–strength fibers[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 the side–chain substituents, main–chain 'kinks', such as 1, 3–phenylene units, or flexible$(CH_2)_n$ spacers[5].

The X–ray diffraction patterns of annealed melt–spun fibers of this polyester show a high degree of orientation parallel to the fiber axis. The presence of sharp Bragg reflections on well defined layer lines indicates the existence of three–dimensional order[6], dispite the random 2– and 3– substitution of the backbone hydroquinones. This structure has been refined by linked–atom least square of the thermotropic copolyesters[8–14] recently being studied, notably the copolymers prepared from p–hydroxybenzoic acid(HBA) and 2–hydroxy–6–naphthoic acid, are random copolymers which show the non–periodic layer lines in their fiber diagrams. So their structures have been analyzed based on modelling by random distribution of their components along the main–chain, and thereby the konwledge of the likely chain conformation for these copolyester systems is necessary, for which this paper is presented.

EXPERIMENTAL

Synthesis

(1–phenylethyl) hydroquinone was synthesized by reacting (41.66 g , 0.4 moles) of styrene with (50.00 g , 0.45 moles) of hydroquinone, in the presence of tetraethyleneglycol dimethylether(Tetraglyme, 100cc) 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 a period of approximately 90 min. to the hydroquinone, while maintaining the temperature at about 140℃ and stirring slowly. The reaction was continued at that temperature for approximately 5 h and then reaction mixture was 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℃/25 mmHg and redistilled. The yield was approximately 18 g .

The polymer was synthesized from equimolar quantities of terephthaloyl chloride and (1–phenylethyl) hydroquinone dissolved in methylene chloride in the presence of pyridine as an acid trap. Terephthaloyl chloride was obtained from Sigma Chemical Co. The reaction was conducted under a moderate nitrogen–flow blanket at approximately atmospheric pressure. The terephthaloyl chloride was added slowly to the (1–phenylethyl) hydroquinone solution while stirring vigorously and maintaining the temperature at approximately 0℃. 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℃ and 500mmHg overnight. The dried polymer had a melting point of 320℃ and inherent viscosity of 0.46dl/g when dissolved in equal volum-

es of trifluoroacetic acid and methylene chloride.

X-ray diffraction

Specimens for X – ray analysis were bundles of parallel fibers drawn by hand from the melt. These were examined both in the as-spun state and after they had been annealed at 250℃ for 2h. X – ray fiber diagrams were recorded on Kodak no-screen X-ray film using Ni-filtered CuK$_\alpha$ radiation with a Searle toroidal focussing camera. The d-spacings calibrated using calcium fluoride.

Intensity measurement

The integrated intensities of the observed reflections were determined using an Optronix Photoscan P1000 digital microdensitometer, as has been described elsewhere[16]. The data were recorded as an x – y scan of optical density and each reflection was integrated after subtration of a local background. Each hkl intensity was determined as the average of measurements and converted to F^2(hkl) by application of Lorentz and polarization corrections(except for the 001 reflections). Unobserved reflections produced in the range of 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 model based on standard bond lengths and bond angles[17-19] were generated using the LALS program package. It was assumed that the phenyl and ester groups are planar, and that the 1-phenylethyl side chains are distributed equally between the ortho- and meta- positions. As will be seen below, the axial repeat for this polymer consists of a single TPA-PEHQ unit, for which two models were considered for the positions of the 1-phenylethyl substituents :

(1) 2-, 3-, 5- and 6- phenyls weighted by 0.25, allowing for random o- and m- substition on both sides of the chain ; and

(2) 2- and 3- (1-phenylethyl)s weighted by 0.5, requiring the substituents to be always on the same side of the chain.

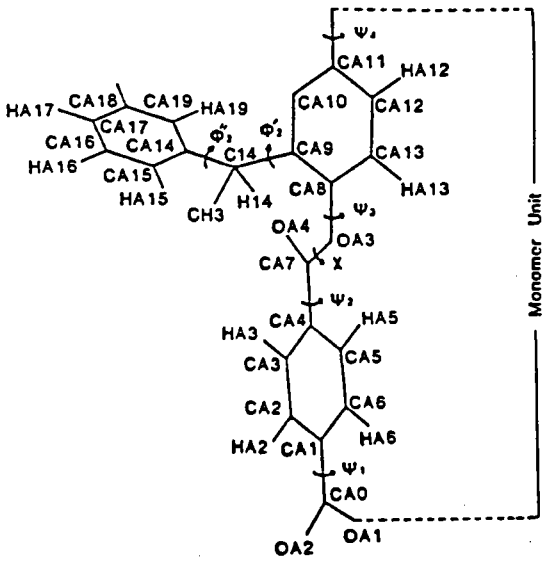

Figure 1 Numbering of the atoms and definition of the refinable torsion angles for the polymer repeat unit(model 2).

The refinable parameters in case 2 are shown in Figure 1. The phenyl groups are assumed to be planar. All torsion angles are defined as positive for anticlockwise rotations, and 0° corresponds to the cis-conformation in each case. The ester groups were assumed to be planar($\chi = 0°$). The conformation is defined by two backbone torsion angles, $\Psi_2(=\Psi_1)$ and $\Psi_3(=\Psi_4)$, i.e. the phenyl-ester inclinations and the side chain torsion angles, ϕ_2, ϕ'_2, ϕ_3 and ϕ'_3 for the 1-phenylethyl. For model 1, additional side chain torsion angles, 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 oxygens (OA1) along the c axis, respectively.

In the last stages of the refinement the possibility of the small shifts of the chain axis along the a and b axes, away from the 0, 0 and 1/2, 0 positions, were considered. These shifts are s_3, s_4 for the 0, 0 chain and s_5, s_6, for the 1/2, 0 chain respectively. The remaining parameters are K, the sxale factor to put the observed structure amplitudes on the same scale as t-

hose calculated, and B, an isotropic temperature factor.

These parameters were varied in the LALS procedure so as to minimize the function :

$$\phi = \sum_i W_i(|\,{}_oF_i\,| - |\,{}_cF_i\,|)^2 + \sum_L A_L G_L + \Sigma\, \epsilon_{ij} \quad (1)$$

where ${}_oF_i$ and ${}_cF_i$ are the observed and calculated structure amplitudes for the i^{th} reflection and W_i is an assigned weight : in the present work, we used w=1 for observed and w=1/2 for unobserved reflections. A_L are Lagrange multipliers assigned to function G_L that define stereochemical constraints applied to the structure. These constraints arise principally from the requirement of helical symmetry. The third summation covers all variable non-bonded interatomic distances d_{ij} less than a specific minimum ${}_od_{ij}$:

$$\epsilon_{ij} = K_{ij}({}_od_{ij} - d_{ij}) \quad d_{ij} < {}_od_{ij}$$
$$\epsilon_{ij} = 0 \qquad d_{ij} \geq {}_od_{ij} \quad (2)$$

The values of K_{ij} were based on the potential energy calculations of Chandrasekaran and Balasubramanian[20], as used by Arnott and Smith[7]. Each ${}_od_{ij}$ was set at 0.2 greater than sum of van der Waals, to ensure that all short contacts were driven to larger values.

RESULTS AND DISCUSSION

Unit-cell determination

The X – ray fiber diffraction patterns of as-spun and annealed samples are shown in Figure 2. Annealing leads to the development of sharp Bragg reflections, indicating the formation of an ordered three dimensional structure for the copolymer. This paper deals with the structure of the annealed state : the as-spun state, which appears to be unoriented powder (nematic or smectic), will be considered later.

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=10.17(0.03) Å and c(chain axis)= 12.58(0.05) Å, with monoclinic geometry ($\alpha = \gamma = 90^o$ and $\beta = 90.1^o$). These data are very simliar to those for poly(phenyl-p-phenylene terephthalate)[15], except that the b dimension is expanded by about 0.1 Å. The observed and calculated d-spacings are shown in Table 2, and for most reflections the agreement is w-

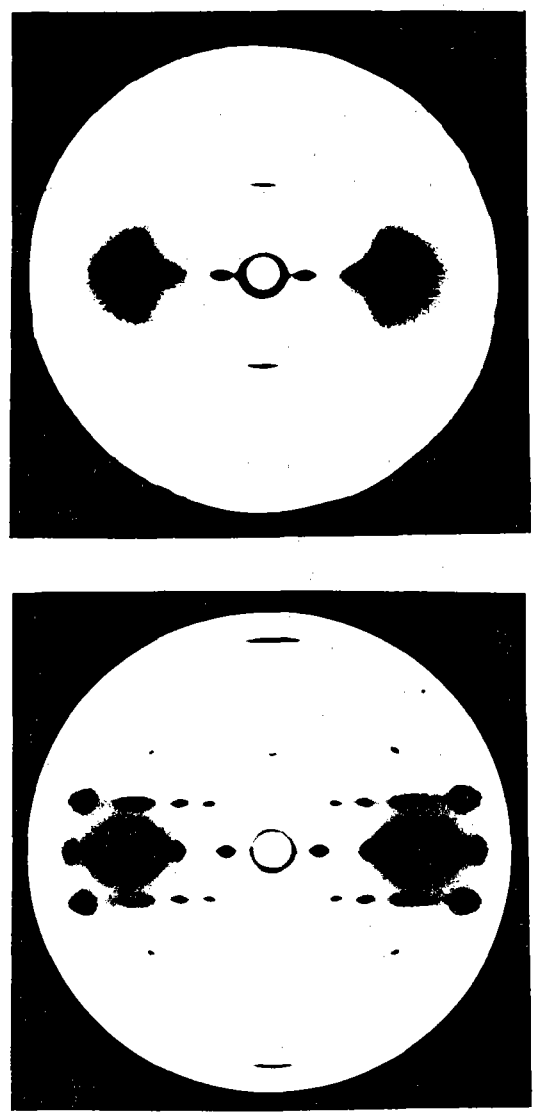

Figure 2 X – ray diffraction patterns for melt-spun fibers of poly(1-phenylethyl-p-phenylene-terephthalate) : (a) as-spun ; (b) annealed at 250℃ for 2 h.

Table 1. Crystal data

a(Å)	12.77(0.06)
b(Å)	10.17(0.03)
c(Å)	12.58(0.05)
β	90.1°
Volume(Å^3)	1633.8
Calculated density(g / cm^3)	1.41
Observed density(g / cm^3)	1.40±0.01
Repeat units/unit cell	4
Space group	$P2_1$(b unique)

Table 2. Comparison of observed and calculated d-spacing

hkl	d(calc)(Å)	d(obs)(Å)
100	12.77	12.74
200	6.38	6.39
020	5.08	5.04
300	4.26	4.23
400	3.19	3.18
011	7.91	7.83
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

ithin 1%. The most obvious discrepancies are for the 011 reflection(1.1%) and for the 020 reflection(0.9%). In view of the random substitution of the 1–phenylethyl groups, the X – ray data yield only an average unit cell, and the actual packing will vary for the different substituent positions on adjacents chains. The distortions inherent in such a structure probably account for the less than perfect agreement between the observed and calculated d–spacings. The only systematic absences are for the odd order 0k0 reflections, pointing to a monoclinic $P2_1$ space group, with the unique axis parallel to b.

The fiber diagram shows a series of periodic layer lines with spacing c=12.58 Å, which is comparable to the repeat of 12.9 Å for poly(p–phenylene terephthalamide)[21] and 12.6 Å for poly(oxybenzoate)[22]. Thus it is expected that the copolymer has an analogous extended conformation, with c corresponsing to the length of a single PEHQ–TPA unit. The unit cell has a volume of 1634 Å^3 : if this contains four PEHQ–TPA units, the calculated density is 1.41 g / cm^3, which agrees very well with the observed density of 1.40 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 (1/2, 1/2). In the initial refinement model 1 was used for the chain with 1–phenylethyls weighted 0.25 at the 2–, 3–, 5– and 6– positions on the hydroquinone. The best R values obtained were mid–thirty percents, and the structure was stereochemically unacceptable because of many bad contacts between side chain. When model 2 was used for the chain conformation, in which the 1–phenylethyls are at the 2– and 3– positions and weighted by 0.5, considerable improvement was obtained. The R value fell immediately to the mid 20 percents, and the final refined value was 0.20. When possible shifts of the chain axes along the a and b axes were considered these were found to be negligible. The torsion angles and atomic coodinates for the refined structure 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 chain is illustrated in Figure 4, which shows projections of two chains on the 200 plane.

The final structure has adjacent chains along the a axis with their ester oxygens staggered by 0.031c and their 1–phenylethyl substituents disposed to opposite sides of the chain. The 2_1 screw axis parallel to b has

Table 3. Refined torsion angles

	Angle(degrees)
CA3–CA4–CA7–OA4(Ψ_2)	–6.1
CA7–OA3–CA8–CA9(Ψ_3)	65.6
CA8–CA9–C14–CA14(ϕ_2)	81.6
CA9–C14–CA14–CA15(ϕ'_2)	45.7
CB8–CB9–C14–CB14(ϕ_3)	82.2
CB9–C14–CB14–CB15(ϕ'_3)	43.1

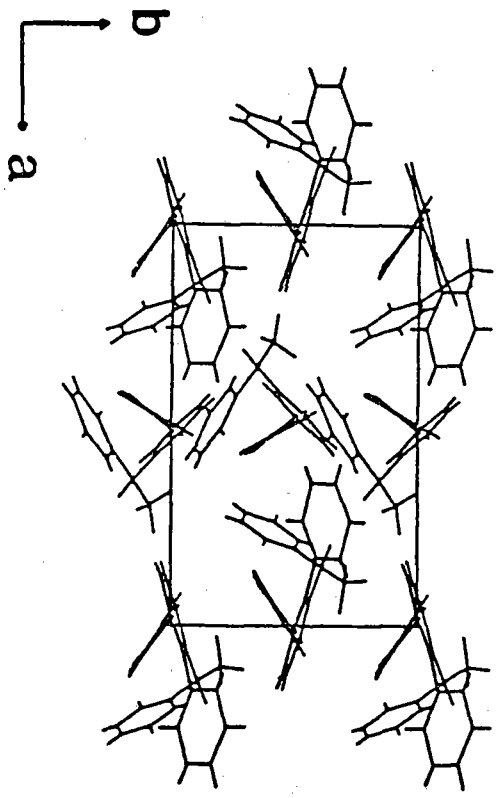

Figure 3 Projection of the refined structure on the ab plane.

a such effect that for the chains in that direction the 1–phenylethyls are also disposed to opposite sides. The side chains on chains along the ab diagonal point towards one anther, but are interleaved since there is an effective stagger of c/2 between chains along the b axis.

The refined structure contains some bad contacts, all of which are between the side groups of adjacent chains at 0, 0 and 1/2, 1/2. Since there are two possible positions for each side chain, each bad contact occurs for only 25% of the possible side chain–side chain combinations and there is space corresponding to the other possible side chain positions which allows for torsional rotation of the 1–phenylethyls so as to eliminate the bad contacts.

The backbone chain conformation is defined by Ψ_2 and Ψ_3, the COO–phenyl and phenyl–COO torsion angles, which are –6.1° and 65.6°, respectively. These compare very well with the observed values of –7.3°

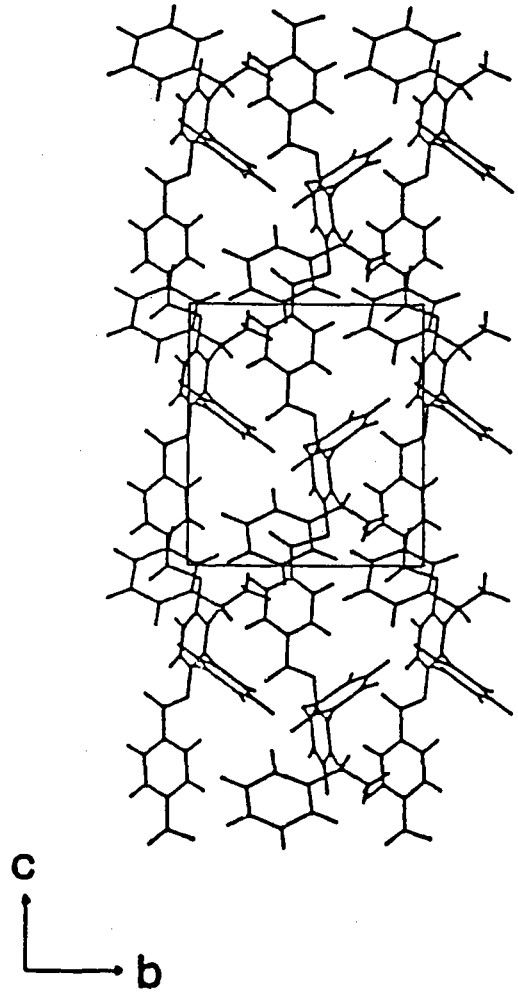

Figure 4 Projection of two chains on bc plane.

and 65.5° for poly(phenyl–p–phenylene–terephthalate)[15], –9.8° and 65.5° reported for phenylbenzoate[16]. Survey of other model compounds shows ranges of –3° to –10° and 60° to 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 χ =0.6°(deviation from planarity of the ester group)[28]. Because the structure is symmetrical, it was assumed that the backbone torsion angles were the same on both sides of each monomer, i.e. $\Psi_2=\Psi_3$ and $\Psi_3=\Psi_4$. Release of those constraints did not lead to any significant improvem-

Table 4. Fractional Atomic Coordinates

Atom	x	y	z	Atom	x	y	z
Chain at 0,0							
OA1	-0.019	0.011	-0.031	H1	0.201	0.146	0.764
CA0	0.050	-0.081	0.005	H2	0.296	0.160	0.672
OA2	0.101	-0.149	-0.053	H3	0.196	0.266	0.673
CA1	0.053	-0.084	0.123	CA14	0.229	-0.026	0.599
CA2	0.128	-0.160	0.172	CA15	0.247	-0.118	0.677
CA3	0.134	-0.166	0.281	CA16	0.308	-0.227	0.656
CA4	0.064	-0.095	0.342	CA17	0.351	-0.243	0.556
CA5	-0.012	-0.019	0.294	CA18	0.333	-0.151	0.478
CA6	-0.017	-0.013	0.184	CA19	0.272	0.042	0.499
CA7	0.065	-0.096	0.460	(meta)			
OA3	-0.007	-0.009	0.500	C14	0.142	0.113	0.846
OA4	0.119	-0.163	0.515	H14	0.198	0.113	0.846
CA8	-0.016	0.002	0.612	C1	0.106	0.207	0.911
CA9	0.065	0.051	0.672	H1	0.029	0.188	0.930
CA10	0.054	0.061	0.781	H2	0.150	0.209	0.979
CA11	-0.038	0.022	0.830	H3	0.111	0.297	0.874
CA12	-0.119	-0.025	0.769	CB14	0.189	0.004	0.908
CA13	-0.109	-0.036	0.660	CB15	0.211	0.021	1.015
1-phenylethyl(ortho)				CB16	0.256	-0.080	1.072
C14	0.164	0.091	0.621	CB17	0.279	-0.198	1.023
H14	0.147	0.140	0.551	CB18	0.257	-0.215	0.916
C1	0.217	0.170	0.686	OA5	-0.043	0.036	0.942

Fractional Atomic Coordinates(continued)

Atom	x	y	z	Atom	x	y	z
Chain at 1/2, 0							
OA1	0.480	0.011	0.002	H1	0.642	-0.219	0.796
CA0	0.427	-0.097	0.038	H2	0.678	-0.330	0.705
OA2	0.389	-0.176	-0.020	H3	0.733	-0.180	0.706
CA1	0.426	-0.101	0.156	CA14	0.518	-0.298	0.632
CA2	0.388	-0.213	0.204	CA15	0.452	-0.345	0.710
CA3	0.385	-0.221	0.314	CA16	0.384	-0.448	0.689
CA4	0.420	-0.117	0.375	CA17	0.384	-0.504	0.589
CA5	0.459	-0.005	0.327	CA18	0.450	-0.458	0.510
CA6	0.426	0.003	0.217	CA19	0.517	-0.355	0.532
CA7	0.420	-0.118	0.493	(meta)			
OA3	0.467	-0.009	0.533	C14	0.601	-0.156	0.879
OA4	0.383	-0.202	0.548	H14	0.646	-0.213	0.830
CA8	0.474	0.006	0.645	C1	0.664	-0.087	0.944
CA9	0.532	-0.080	0.705	H1	0.629	0.001	0.963
CA10	0.538	-0.064	0.814	H2	0.677	-0.140	1.012
CA11	0.484	0.037	0.863	H3	0.734	-0.069	0.906
CA12	0.425	0.123	0.802	CB14	0.531	-0.242	0.941
CA13	0.420	0.107	0.693	CB15	0.549	-0.265	1.047
1-phenylethyl(ortho)				CB16	0.484	-0.346	1.105
C14	0.590	-0.188	0.654	CB17	0.399	-0.405	1.056
H14	0.624	-0.155	0.584	CB18	0.380	-0.383	0.949
C1	0.665	0.232	0.719	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

Table 5. Observed and calculated structure factors

hkl	F_o	F_c	hkl	F_o	F_c
100	315.9	232.3	021	53.2	48.9
200	286.2	331.5	032	55.1	64.9
110	109.8	125.0	102	10.9	26.7
400	257.6	285.7	101	29.8	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	41.1	64.6
301	153.7	164.6	111	33.8	40.6
031	198.8	163.4	112	65.8	62.9
012	66.7	41.6	212	35.2	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	41.2	59.8
013	114.4	117.7	221	31.6	28.9
023	98.7	81.1	303	39.5	29.1
123	156.6	138.8	311	65.8	62.7
213	142.7	151.5	104	17.6	23.1
014	42.8	52.3			

ent for an R value.

The mutual inclination of the main chain phenyls is 59.5°, compared to 55.7° in phenylbenzoate and 58.2° in poly(phenyl–p–phenylene–terephthalate) and a general observed range of 60–70°, including 68° in poly(p–phenyleneterephthalate–amide)[21]. In the latter structure, the equivalent torsion angles are 38° and –30°, but the linkages are via amide rather than ester groups, and the intermolecular hydrogen bonds may be formed. 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 81.6° and 45.7° for ortho and 82.2° and 43.1° for meta, respectively. The differences between the side chain conformation angles at the 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

This structure has been refined 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 confidence to transfer them to other polymeric structure. 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 Ψ_2 and Ψ_3 are possible that are compatible with a mutual inclination of 60° for the backbone phenyls. The high degree of crystalline order is perhaps surprising given the random substitution of the big 1–phenylethyl side chains. There must be differences in local packing of these groups, depending on the actual substitution, but these distortions do not prevent refinement of an average structure.

REFERENCES

1) Payet, C.R. US Patent **4159365**(1979)
2) Jackson, W.J. Brit. Polym. J. **12**(1980), 154
3) Dobb, M.G. and McIntyre, J.E. Adv. Polym. Sci. **60 / 61**(1984), 61
4) Jin, J.I., Antoun, S., Ober, C. and Lenz, R.W. Brit. Polym. J. **12**(1980), 132
5) Kuhfuss, H.F. and Jackson, W.J.J. Polym. Sci., Polym. Chem. Edn.**14**(1976), 2043
6) Stamatoff, J.B. Mol. Cryst. Liq. Cryst. **110**(1984), 75
7) Smith, C. and Arnott, S.Acta Cryst.(A) **34**(1978), 3
8) Blackwell, J. and Gutierrez, G.A. Polymer **23**(1982), 671
9) Blackwell, J., Gutierrez, G.A., Chivers, R.A., Stamatoff, J.B. and Yoon, H. Polymer **24**(1983), 937
10) Blackwell, J., Gutierrez, G.A. and Chivers, R.A. Macromolecules **17**(1984), 1219
11) Blackwell, J., Gutierrez, G.A., Chivers, R.A. and Ruland, W.J. J. Polym. Sci., Polym. Phys. Edn. **22**(1984), 1343
12) Blackwell, J., Biswas, A. and Bonart, R.C. Macromolecules **18**(1985), 2126

13) Blackwell, J., Gutierrez, G.A. and Chivers, R.A. Polymer **26**(1985), 348
14) Blackwell, J., Cheng, H.M. and Biswas, A. Macromolecules **21**(1988), 39
15) Hong, S.K. and Blackwell, J. Polymer **30**(1989), 225
16) Hall, I.H. and Pass.M.G.J. Appl. Crystallogr. **8**(1975), 60
17) Bailey, M. and Brown, C.J. Acta Cryst. **22**(1967), 387
18) Anderson, K.E. Acta Cryst. **22**(1967), 188
19) Hargreaves, A. and Hasan, R.S. Acta Cryst. **15**(1962), 365
20) Chandrasekaran, R. and Balasubramanian, R. Biochim. Biophys. Acta **188**(1969), 1
21) Northolt, M.G. Eur. Polym. J. **10**(1974), 799
22) Blackwell, J., Leiser, G. and Gutierrez, G.A. Macromolecules, **16**(1983), 1418
23) Adams, J.M. and Morsi, S.E. Acta Cryst. **B32**(1976), 1345
24) Brisse, F. and Perez, S. Acta Cryst. **B32**(1976), 2110
25) Desborough, I.J., Hall, I.J. and Neisser, J.Z. Polymer **20**(1979), 545
26) Colapietro, M. and Domenicano, A. Acta Cryst. **B34**(1978), 3277
27) Perez, S. and Brisse, F. Acta Cryst. **B32**(1976), 470
28) Jaffe, R. and Yoon D., private communication. (1988)
29) Schwalbe, C.H. et al. Acta Cryst. **B34**(1978), 3409