poly(3-n-alkyl-4-oxybenzoate)s

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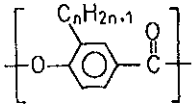
The synthesis of poly(3-*n*-alkyl-4-oxybenzoate)s (PAOB-*n*) with $n = 3$–18 is reported. The sufficient solubility of these comb-like polymers with stiff-chain backbones allows the determination of the Kuhn length (100–200 Å). The unit cells could be determined for PAOB-*n* with $n = 3$ and 5. All PAOB-*n* form thermotropic mesophases. For $n = 3$ a nematic phase is found. For $n = 5$ there is a transition from a smectic-like, layered mesophase to a nematic mesophase. PAOB-*n* with $n \geqslant 6$ solely form layered mesophases. Except for $n = 3$, all PAOB-*n* exhibit a transition to the isotropic state. The transition temperature is lowered monotomically with increasing *n*.

(Keywords: rigid rod polymer; synthesis; phase behaviour)

INTRODUCTION

Rigid rod polymers usually exhibit very low solubility and melting points far above the temperatures of thermal decomposition. In a number of recent publications it has been shown that flexible side chains appended to the rigid backbones lower the melting point and increase the solubility in a systematic fashion[1]. Most of the fully aromatic systems studied so far are composed of rather symmetric repeating units, i.e. the different conformers of these polymers exhibit nearly the same shape. Asymmetric monomers, on the other hand, should cause a further disturbance of crystallization because of the vast number of shapes generated by different conformers. In this work we present a comprehensive study of the poly(3-*n*-alkyl-4-oxybenzoate)s(PAOB-*n*)



as an example of a comb-like polymer composed of asymmetric repeating units. The number of carbon atoms *n* in the side chains is varied between 3 and 18, thus PAOB-12 is poly(3-dodecyl-4-oxybenzoate). The choice of poly(4-oxybenzoate) as the stiff backbone derives from the fact that this polymer has already been the subject of a number of exhaustive studies[2–7]. Hence the influence of the side chains on the structure can be assessed in detail by comparing the results found here with the data obtained on the unsubstituted poly(4-oxybenzoate). Together with a previous investigation[8] of defined oligomers of PAOB-3 the present study aims at a full understanding of the structure and the phase behaviour of these comb-like polyesters.

The synthesis of the monomers, the 3-*n*-alkyl-4-hydroxybenzoic acids (1–*n*), proceeds along the following lines: the monomer bearing the propyl substituent (1–3, $n = 3$) is easily available from the 3-allyl-4-hydroxybenzoic acid[9] through catalytic hydrogenation at atmospheric pressure. The monomers bearing longer *n*-alkyl chains (1–5 to 1–18) are obtained through a Fries rearrangement[10] of the respective O-acylated 4-hydroxybenzoic acids (2-*n*) and subsequent Clemmensen reduction of the ketones 3–*n* (*Scheme 1*). The polycondensation of the monomers 1–*n* is performed by heating the monomer with an excess of acetic anhydride (cf. ref. 3).

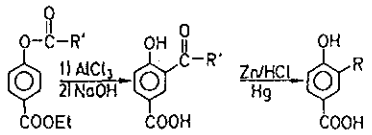
EXPERIMENTAL

Materials

All chemicals were purchased from Merck or Fluka. They were used without further purification unless otherwise stated. All solvents used were of p. a. quality; 1,1,2,2-tetrachloroethane, phenol and *o*-dichlorobenzene employed as solvents for viscosity measurements were distilled prior to use.

Synthesis of monomers

1,3-Propyl-4-hydroxybenzoic acid (*1–3*). The 3-allyl-4-hydroxybenzoic acid was synthesized through Claisen rearrangement of ethyl-4-allyloxybenzoate which was prepared from ethyl-4-hydroxybenzoate[9]. Hydrogenation using palladium on charcoal as catalyst and subsequent saponification in 30% aqueous sodium hydroxide solution led to 3-propyl-4-hydroxybenzoic acid. The monomer



Scheme 1

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Table 1 Melting points and elemental analyses of the 3-*n*-alkyl-4-hydroxybenzoic acids (**1**–*n*)

n	Melting point (°C)	Calc. C (%)	Calc. H (%)	Found C (%)	Found H (%)
3	115–118	66.64	6.73	66.58	6.76
5	126–127	69.20	7.76	69.39	7.75
6	100–101	70.23	8.18	70.11	8.14
10	103–104	73.33	9.43	73.46	9.26
12	98–99	74.45	9.89	74.38	9.77
14	101–102	75.39	10.26	75.53	10.14
16	100–102	76.18	10.58	76.31	10.36
18	100–101	76.86	10.86	76.91	10.77

^{1}H n.m.r. (acetone): $\delta = 0.89$ (t, $CH_2\underline{CH}_3$), 1.2–1.7 (m, $-(\underline{CH}_2)_n-$), 2.69 (t, Ar–$C\underline{H}_2$–), 6.93, 7.72 (d, Ar–$\underline{H}$), 7.82 (s, Ar–$\underline{H}$)

Table 2 Melting points and elemental analyses of the 3-(*n*-alkyl-2-one)-4-hydroxybenzoic acids (**3**–*n*)

n	Melting point (°C)	Elemental analysis: Calc. C (%)	Calc. H (%)	Found C (%)	Found H (%)
6	191–193	66.08	6.84	66.13	6.71
10	185–187	69.82	8.29	70.00	8.13
12	179–180	71.20	8.82	71.32	8.70
14	174–176	72.36	9.27	72.22	9.13
16	173–175	73.35	9.66	73.57	9.53
18	168–170	74.20	9.98	73.07	9.90

^{1}H n.m.r. (trifluoroacetic acid): $\delta = 0.95$ (t, $CH_2\underline{CH}_3$), 1.2–2.2 (m, $-(\underline{CH}_2)_n-$), 3.24 (t, $COC\underline{H}_2CH_2$), 7.18 and 8.34 (d, Ar–$\underline{H}$), 8.81 (s, Ar–$\underline{H}$)

1–3 was purified from H_2O and dried carefully prior to use. The overall yield of the four-step reaction was 45%. The melting point and the elemental analysis of **1**–3 is given in *Table 1*.

Synthesis of monomers 1–5 to 1–18. The ethyl-4-alkanoyloxybenzaotes **2**–5 to **2**–18 were prepared by reacting ethyl-4-hydroxybenzoate with an excess of the respective acid chloride according to the standard procedures given in the literature[11]. The Fries rearrangement of **2**–*n* was achieved in the following way (cf. ref. 10): 0.3 mol of **2**–*n* was dissolved in 500 ml CS_2 and 1.2 mol $AlCl_3$ were added in small portions leading to a slightly exothermic reaction and evolution of HCl. After the last addition the mixture was refluxed for 3 h. Then the solvent was distilled off and the remainder heated to 140–160°C followed by evolution of HCl and strong foaming. After 2 h and cooling to room temperature 800 ml H_2O were added and subsequently 160 g NaOH with caution. The mixture dissolved upon heating to 110–120°C and the resulting ketone **3**–*n* could be isolated by acidification with 400 ml concentrated HCl. Purification was achieved through recrystallization from ethanol, toluene or chloroform (yields 40–45%). *Table 2* shows the melting points and the elemental analyses of **3**–5 to **3**–18.

The Clemmensen reduction was carried out in the usual way following references 10 and 11: 0.1 mol **2**–*n* was refluxed for 24 h in 350 ml of a mixture of H_2O/ethanol/HCl (1:1:2) with zinc amalgam prepared from 200 g zinc powder[11]. During this time 10 ml of concentrated HCl were added several times. The resulting **1**–*n* was isolated from the cold mixture by extraction with diethyl ether. Analysis by ^{1}H nuclear magnetic resonance (n.m.r.) spectroscopy demonstrated that the raw materials still contained a side product having a double bond in the α position of the alkyl side chain. For further purification 20 g of the raw material were dissolved in 300 ml ethanol and hydrogenated after addition of 0.5 g palladium on charcoal (10%) at 50°C for 24–30 h. Then the catalyst was filtered off and the monomers **1**–*n* were recrystallized three times from CH_3OH/H_2O or CH_3OH (yields 50–75%).

Polymerization (cf. ref. 3)

For the polymerization reaction, 1.5–3.0 g of **1**–*n* were added to 1.2 equivalents of acetic anhydride and refluxed under an atmosphere of argon at 180°C for 30 min. Then the condenser was taken off and the acetic acid removed by a slow stream of argon. While raising the temperature to 260°C the evolution of acetic acid started again at ~245°C. By variation of the reaction time from 45 min to 7 h polymers with different molecular weights could be obtained (*Table 3*). Purification of PAOB-3 was carried out by refluxing the polymer with acetone; polyesters with longer side chains were dissolved in hot chloroform and precipitated from methanol. All polymers reported in this investigation gave satisfactory elemental analyses when taking into account the measured molecular weights and the respective end groups.

Determination of molecular weight through end group analysis

According to Kricheldorf and Schwarz[3], 20–30 mg of the polyester PAOB-*n*, ~200 mg 40% NaOD in D_2O and 500 mg CD_3OD were weighed carefully in a n.m.r.

Table 3 Characterization of the PAOB-*n*

Polymer	Reaction time (min) 180°C/260°C	*DP*[a]	M_n[a]	$[\eta]$ (dl g^{-1})
PAOB-3,1	30/45	16	2650	
PAOB-3,2	30/60	22	3600	0.310[b]
PAOB-3,3	30/160	39	6350	0.490[b]
PAOB-3,4	30/240	123	20000	1.620[b]
PAOB-3,5[d]	30/240	74	12100	0.860[b]
PAOB-5,1	30/240	23	4450	
PAOB-5,2	30/360	40	7650	
PAOB-6,1	30/240	16	3350	
PAOB-6,2	30/360	37	7600	
PAOB-10,1	30/240	17	4500	
PAOB-10,2	30/360	41	10750	
PAOB-12,1	30/150	13	3800	
PAOB-12,2	30/300	84	24300	
PAOB-14,1	30/240	20	6400	
PAOB-14,2	60/240	27	8600	
PAOB-16,1	30/60	8	2950	0.096[c]
PAOB-16,2	30/120	16	5650	0.180[c]
PAOB-16,3	30/180	22	7550	0.290[c]
PAOB-16,4	30/240	23	7800	0.350[c]
PAOB-16,5	30/360	30	10400	0.485[c]
PAOB-16,6	30/420	40	13900	
PAOB-18	60/180	35	13100	

[a] Determined by ^{1}H n.m.r. end-group analysis
[b] Measured in phenol/*o*-dichlorobenzene (1:1) at 50°C
[c] Measured in tetrachloroethane/*o*-dichlorobenzene (1:1) at 50°C
[d] Polymerized with addition of 5 mol% 4-methoxyl-3-propylbenzoic acid

tube and heated to 50–60°C. The solution obtained was analysed by 300 MHz or 400 MHz ^{1}H n.m.r. spectroscopy to yield the amount of end groups quantitatively (see below).

Methods

^{1}H n.m.r. spectra were recorded with 80 MHz continuous wave, 300 MHz Fourier transform (*FT*) and 400 MHz *FT* spectrometers (Bruker AW 80, AC 300 and WM 400). Vapour pressure osmometry (v.p.o.) was done at 50°C using toluene as a solvent (Wescan 232 A, Corona). The concentration of the polymer was 2–10 g l^{-1}. For polarizing microscopy a Zeiss Fotomikroskop III equipped with a Leitz hot stage was used. Differential scanning calorimetry (d.s.c.) was done with a Perkin–Elmer DSC-7 calibrated with indium and tin. Thermogravimetric data were obtained by means of a TG 50 of Mettler under an atmosphere of oxygen or nitrogen employing a heating rate of 10 K min^{-1}. The intrinsic viscosity of the polyesters was determined using an Ubbelohde capillary viscosimeter. All data are mean values of at least four measurements corrected[13] according to Hagenbach. High performance liquid chromatography (h.p.l.c.) was carried out on Li Chrosorb RP 18 or Li Chrosorb diol columns (Knauer) using a mixture of diethyl acetate and n-heptane (1:1) with ultraviolet (u.v.) detection at $\lambda = 254$ nm. For gel permeation chromatography (g.p.c.) 10 μm Styragel columns (10^5, 10^3 and 10^2, Polymer Laboratories) with tetrahydrofuran (1 ml min^{-1}) as the mobile phase (u.v. detection at $\lambda = 254$ nm) were used. Wide-angle X-ray analysis (WAXS) was performed using Ni-filtered CuKα radiation in reflection mode on a Siemens D 500 diffractometer equipped with a hot stage. All diffractograms are uncorrected. Electron diffraction was done using a Philips EM 300 calibrated with thallium chloride. The density of polymer films and fibres was determined in a density gradient set up from mixtures of H_2O and $Ca(NO_3)_2$ at room temperature.

RESULTS AND DISCUSSION

All polymers investigated were synthesized by the acetoxy method[3], i.e. by reaction of the unsubstituted hydroxybenzoic acid with acetic anhydride. Since the maximum temperature applied in the course of the polycondensation did not exceed 260°C, no side products as discussed by Economy and co-workers[2] have been observed. The satisfactory degrees of polymerization achieved and the absence of any by-products to be detected in the analysis of the saponificated polyesters are furthermore indicative of the absence of side reactions. Special care has been taken to remove the evolving acetic acid as well as excess acetic anhydride by a slow stream of argon. During the reaction small amounts of a solid material sublimed out of the mixture. Analysis by infra-red (i.r.) and n.m.r. spectroscopy unambiguously demonstrated this substance to be identical with the acetylated monomer. In the case of short side chains ($n = 3$, 5, 6) the melt turned turbid after 40–120 min indicating the formation of a mesophase. For monomers having longer side chains the resulting melt became increasingly viscous during polycondensation but only turned turbid when cooled to temperatures below 200°C. As is obvious from *Table 3* the degree of polymerization (*DP*) can be adjusted by the length of the reaction time. The present data indicate that even higher molecular weights could be obtained if desired. However, raising the *DP* beyond the values given here resulted in difficulties when determining the molecular weight by end-group analysis (see below).

In contrast to the unsubstituted poly(4-oxybenzoate)[3] the PAOB-3 already exhibits sufficient solubility in mixtures like *o*-dichlorobenzene with tetrachloroethane or phenol. Polyesters bearing longer side chains may be dissolved in toluene or chloroform. Therefore purification can be achieved through dissolution in these solvents and reprecipitation into methanol. This finding is in accordance with observations on a number of other rigid rod polymers being similarly substituted by flexible side chains[1]. It indicates that the side chains act as a 'bound solvent'. However, investigations of solutions of PAOB-16 in solvents like toluene lead to the conclusion that these polyesters still have a strong tendency for association in solution. This fact may be also inferred from the formation of gels by these solutions at room temperature. Mixtures of strong polar solvents like *o*-dichlorobenzene and tetrachloroethane prevent the formation of such gels if the concentration is not too high. Up to now attempts to determine the molecular weight and the radius of gyration by light scattering have failed because of either strong association or small refractive index increment. Thus the *DP* of the polymers had to be determined by ^{1}H n.m.r. end-group analysis according to Kricheldorf and Schwarz[3]. For this the magnitude of the triplet of the CH_2 group neighbouring the aromatic core of the monomer is compared to the signal of the acetic acid anion after saponification with $NaOD/D_2O$. When evaluating the magnitude of the latter signal, a small triplet resulting from partial H–D exchange on the acetic acid has to be taken into account. By this method the number average *DP* could be obtained within 10% error for smaller molecular weights; higher *DP*s are determined with less accuracy. For PAOB-16 the *DP* thus measured compares favourably with data derived from v.p.o. The *DP*s given by the latter method are in general higher by 10–15% which certainly can be assigned to association in solution. Therefore only *DP*s derived from end-group analysis are used in this work (cf. *Table 3*).

It has been observed that substitution of the poly(4-oxybenzoate) backbone may lower the thermal stability of the resulting polymers considerably[14]. Thermogravimetric measurements on the PAOB-*n* conducted in nitrogen (10 K min^{-1} heating rate) showed these polymers to be stable up to ~350°C. A residual weight loss at lower temperatures can be traced back to the onset of further polycondensation. Nevertheless the oxidative degradation of the side chains represents a severe constraint for the stability at elevated temperatures in the presence of oxygen. All thermogravimetric data obtained so far indicate the upper limit for long-term stability in air to be at temperatures between 160°C and 220°C. Polyesters having longer side chains are more susceptible to degradation. Hence, measurements at elevated temperatures have to be conducted in an inert atmosphere or *in vacuo*.

Another point of great interest is the stiffness of the main chain. Since the unsubstituted polyester is not soluble in any known solvent there are no experimental data on its persistence length. Calculations by Erman *et al.*[15] using the rotational isomeric state model lead to the prediction of a rather rigid chain with a persistence

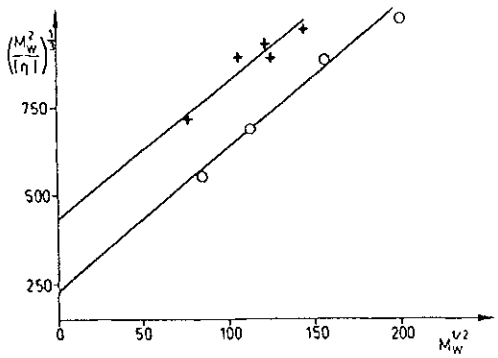

Figure 1 Bohdanecky plot of the intrinsic viscosities of PAOB-3 (○) and PAOB-16 (+)

length of the order of 700 Å. However, these authors remark that such a high value has to be regarded as an upper limit since torsional fluctuation about the ester bonds should lower it appreciably[16]. Molecular dynamics calculations performed by Jung and Schürmann[17] lead to a much smaller value of the persistence length (~60 Å) for this reason. Experimental data on similar polyamides are of limited use for settling this question since the values for the persistence length of these systems given by various methods are not conclusive[1,18]. By virtue of their improved solubility in aprotic solvents the PAOB-*n* are much better candidates for an experimental test of the above conflicting predictions. In the absence of reliable measurements of the radius of gyration by light scattering data, the intrinsic viscosity $[\eta]$ may serve as a first estimate of the chain stiffness. Thus $[\eta]$ has been measured for PAOB-3 in phenol/*o*-dichlorobenzene and for PAOB-16 in tetrachloroethane/*o*-dichlorobenzene at 50°C (cf. *Table 3*). The dependence on temperature as well as the dependence on concentration is well-behaved for these systems whereas solutions of PAOB-16 in toluene and in chloroform did not lead to reproducible results (see above). The resulting Mark–Houwink relations are ($[\eta]$ in dl g^{-1}):

PAOB-3 $[\eta] = 6.95 \times 10^{-2} M_n^{1.06}$
in phenol/*o*-dichlorobenzene at 50°C

PAOB-16 $[\eta] = 2.87 \times 10^{-2} M_n^{1.16}$
in tetrachloroethane/*o*-dichlorobenzene at 50°C

A quantitative interpretation of the data for $[\eta]$ may be given in terms of the worm-like chain model developed by Yamakawa and Fujii[19]. Based on this theory, Bohdanecky[20] has recently given a simple procedure for data evaluation leading to the following relation:

$$(M^2/[\eta])^{1/3} = A_\eta + B_\eta M^{1/2}$$

where A_η is a quantity depending on the hydrodynamic diameter d of the chain and B_η is expressed by

$$B_\eta = B_0 \Phi_{0,\infty}^{-1/3} (\langle r^2 \rangle_0 / M)_\infty^{-1/2}$$

where $\langle r^2 \rangle_0$ is the mean-square end-to-end distance, and the subscript ∞ indicates that the $\langle r^2 \rangle / M$ value obtained from B_η is the random coil value.

The quantity $\Phi_{0,\infty}$ is the viscosity function for infinite chain length ($\Phi_{0,\infty} = 2.86 \times 10^{23}$)[20]. The quantity B_0 varies between 1.10 and 1.00 and may be set to a mean value of 1.05 at the present level of accuracy. *Figure 1* shows a Bohdanecky plot of the present data. The weight average molecular weights have been calculated from the data given in *Table 3* by assuming a most probable distribution.

The Kuhn length is calculated as $l_K = \langle r^2 \rangle / N l_u$ where $N = M/M_u$ with M_u and l_u being the mass per unit length and the length of the monomer unit, respectively. The latter quantity is given by 6.2 Å in good approximation (see below). From these data and the slope of the respective curves in *Figure 1*, l_K is ~90 Å for PAOB-3 and ~190 Å for PAOB-16. The intercept A_η may be used to yield first estimates of the hydrodynamic radius r according to[20]:

$$\frac{d_r^2}{A_0} = (4\Phi_{0,\infty} 1.215 \pi N_A)(\bar{v}/A_\eta) B_\eta^4$$

where $d_r = d/l_K$ is the reduced hydrodynamic radius and d_r^2/A_0 is related to d_r by[20]

$$\ln(d_r^2/A_0) = 0.173 + 2.158 \ln(d_r)$$

If the partial specific volume $\bar{v}$ of the polymer in solution is approximated by unity, we obtain for PAOB-3 a value in the range 7–8 Å, and for PAOB-16 11–13 Å. Similar values have been found recently for substituted cellulose polymers[21] and seem to be quite reasonable. One has to bear in mind that these values have been derived under a number of stringent assumptions[19,20]. On the molecular level the polymer chain is approximated by a cylinder which may be rather questionable when looking at the structure of PAOB-*n* with $n > 6$. Hence, these data should be only regarded as rough estimates and the present investigation of chain stiffness must be certainly supplemented by other methods.

Despite these problems it is clear that our findings data are more in support of the prediction of Jung and Schürmann[17]. Krigbaum and Tanaka[22] recently found l_K values of similar magnitude for poly(phenyl *p*-phenyleneterephthalate) by a variety of methods. Thus the present data indicate that the stiffness of the fully aromatic polyester chain is significantly smaller than anticipated by the calculations neglecting the effect of bond-angle fluctuations. The surprising fact that the stiffness seems to increase with increasing length of the side chains may be explained[23] by the notion that steric interactions between bulky side chains lead to a significant rise in l_K. In the absence of further information on the shape of the PAOB-*n* chain as revealed by small angle X-ray or neutron scattering no firm conclusions can be drawn.

Phase behaviour of PAOB-3

In the following it will become obvious that the phase behaviour of PAOB-3 is significantly different from the phase behaviour of PAOB-*n* bearing longer side chains. In the case of PAOB-3 the main chains control the structure and thermal transitions. For longer side chains the volume fraction of the main chains is decreasing and the most favourable arrangement of the side chains determines the packing of the polymer in the solid state as well as in the mesophase.

Solid state. *Figure 2* shows the WAXS patterns of PAOB-3 recrystallized from the melt (*Figure 2a*) and from dioxane (*Figure 2b*). From this it is evident that two different modifications have been formed through

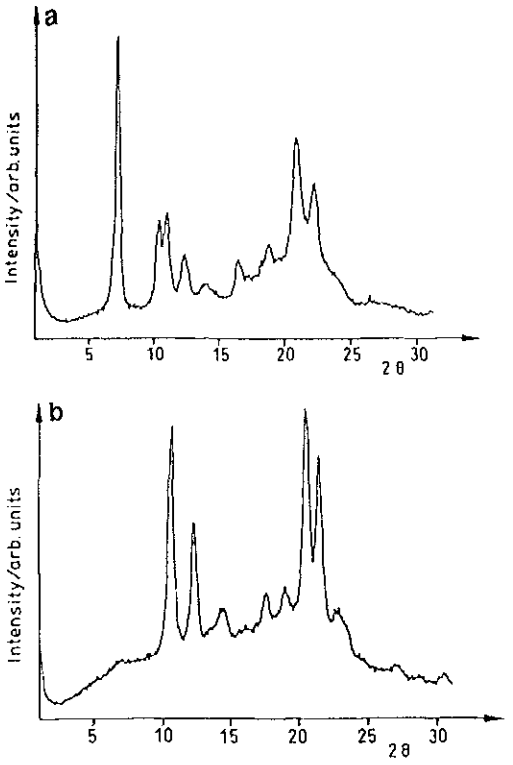

Figure 2 Wide-angle X-ray diffractograms (uncorrected) of PAOB-3 recrystallized from the melt (a) and from dioxane (b)

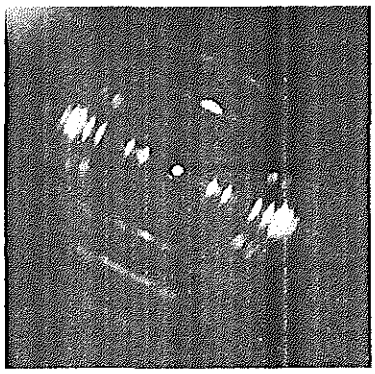

Figure 3 X-ray fibre diagram of PAOB-3 drawn from the melt (modifications Ia and Ib). The Miller indices are given in *Table 4*

the different conditions of crystallization. The WAXS patterns furthermore show both modifications to have a high degree of crystallinity. Melt-crystallized samples (referred to as modification I fibres) with a high degree of orientation may be drawn. The resulting fibre diagram is shown in *Figure 3*.

The distance between the layer lines demonstrates that the identity period along the chain consists of two oxybenzoate monomer units. This is in accordance with the crystal structure of the dimeric model compound[8] in which the planes of subsequent benzene rings are rotated through an angle of 90° with respect to each other. The absence of meridional reflections with odd 1 indices indicates a 2_1 or a 4_2 helical structure of the main chain. An additional feature is the presence of two series of reflections on the different layer lines leading to two hyperbolas per layer. This can be seen most clearly from the splitting of the 002 reflection. Variations of the c-parameter within a range of 12.4–12.9 Å were observed in earlier work on poly(4-hydroxybenzoic acid) and were shown to be a function of the DP[5]. All reflections found in this work may be indexed satisfactorily in terms of two tetragonal modifications, Ia and Ib, which differ only with regard to the c vector of the unit cell. *Table 4* gives the Bragg distances and their respective indices.

The presence of two very similar modifications Ia and

Table 4 Calculated and observed X-ray reflections of modifications Ia, Ib and II of PAOB-3

Reflection index ($h\,k\,l$)	Calculated spacing (Å)	Observed spacing (Å)	Position/modification
Tetragonal modifications Ia and Ib, $a=b=16.95$ Å, $c=12.36$ Å (Ia), $c=12.86$ Å (Ib)			
1 1 0	11.99	11.99(vs)	
0 2 0	8.48	8.47(vs)	
		7.16(vw)	
2 2 0	5.99	5.96(vw)	
1 3 0	5.36	5.34(s)	Equator (a, b)
2 3 0	4.70	4.70(s)	
0 4 0	4.24	4.24(vs)	
1 4 0	4.11	4.12(m)	
3 3 0	4.00	3.99(s)	
2 4 0	3.79	3.78(m)	
1 5 0	3.32	3.34(w)	
1 2 1	6.46	6.50(vw)	
1 3 1	4.92	4.86(m)	1st layer line: a
2 3 1	4.39	4.28(m)	
0 3 1	5.17	5.11(m)	
2 3 1	4.42	4.50(m)	
0 4 1	4.02	4.03(vw)	1st layer line: b
2 4 1	3.64	3.68(w)	
1 5 1	3.22	3.19(vw)	
0 0 2	6.18	6.18(s)	
0 1 2	5.81	5.85(w)	2nd layer line: a
1 2 2	4.79	4.69(w)	
1 3 2	4.05	3.95(vw)	
0 0 2	6.43	6.43(s)	
0 3 2	5.12	5.08(vw)	2nd layer line: b
2 2 2	4.38	4.50(vw)	
0 1 3(a)	4.0(a)	4.06(m)	
0 1 3/1 1 3(b)	4.16/4.04(b)		
0 2 3(a)	3.71(a)	3.77(m)	3rd layer line
0 2 3/1 2 3(b)	3.83/3.73(b)		
0 0 4	3.09(a)	3.11(w)	4th layer line
	3.22(b)		

Reflection index ($h\,k\,l$)	Calculated spacing (Å)	Observed spacing (Å)	
		X-ray	Electron diffraction
Orthorhombic modification II $a=14.20$ Å, $b=9.60$ Å, $c=12.48$ Å			
1 1 0	7.95	7.94(s)	7.99(s)
2 0 0	7.10	7.07(m)	7.12(s)
0 0 2	6.24	6.24(w)	
0 2 0	4.80	4.72(w*)	4.83(w)
3 1 0	4.25	4.22(s)	4.25(s)
2 2 0	3.98	3.96(s)	4.00(s)
4 2 0	2.85		2.87(w)

* Shoulder of 3 1 0 reflection

Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak

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