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Wide angle X-ray diffraction and force field constrained Rietveld modelling of *m*-linked fully aromatic copolyesters.
2. Poly(*p*-phenylene terephthalate-*co*-*p*-phenylene isophthalate)

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Abstract

Fully aromatic copolyesters with regular chain structure containing kinked monomer units were investigated by powder diffraction experiments combined with structure modelling. The proposed series of copolyester structures including isophthalic acid was continued with (TPA–HQ–IPA–HQ)$_n$ (containing 104 atoms as repeating unit). The monoclinic unit cell has $a = 0.781$ nm, $b = 0.557$ nm, $c = 5.03$ nm and $\beta = 89.2°$ as atom coordinates. The symmetry of the unit cell was determined by means of a force field constrained Rietveld refinement algorithm including nonbonding interactions (Lennard-Jones potentials) and chain continuation enforcement (penalty functions) in the force field. A reliability factor R_{Rietveld} of 9.5% was calculated. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Kinked aromatic copolyesters; Solid phase structure; Powder diffraction

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1. Introduction

The solid state structure and phase behaviour that determine material properties are influenced by primary chemical structures and molecular characteristics. Relations between the structure of aromatic liquid-crystalline main chain copolyesters containing either random or regular chain structure and their anisotropic material properties are of basic interest and have been discussed widely [1–5]. Two views exist pertaining to the symmetry of these crystalline structures. Orthorhombic [1–3] and monoclinic [4] lattices have been assumed, in agreement with the measured diffraction patterns. The assumption of a monoclinic unit cell seems to be correct for all previously investigated structures [4,5]. This is related to almost same values of *a* and *b*-axes, regarding this class of copolyesters, whereas the length of the *c*-axis depends on the length of the chemical as well as the crystallographic repeating unit. The general calculation formula is $|c| \approx i \times 1.25$ nm, with $i = (2, 4, 6, \ldots)$.

The aim of this paper is to continue structural refinement of aromatic main chain copolyesters containing regular chain sequences, that was discussed in the last publication [5]. Here, a new force field constrained Rietveld refinement procedure is applied. Using the (IPA–HQ)$_n$ philosophy of two kinked IPA units, the *c*-axis for poly(*p*-phenylene terephthalate-*co*-*p*-phenylene isophthalate) (TPA–HQ–IPA–HQ)$_n$ had to be expanded up to 5.0 nm in order to realise an extended polymer chain. This concept shall apply to the determination of the structure parameters of the above polymer.

2. Experimental

2.1. Synthesis and characterisation of poly(p-phenylene terephthalate-co-p-phenylene isophthalate)

Poly(*p*-phenylene terephthalate-*co*-*p*-phenylene isophthalate), (TPA–HQ–IPA–HQ)$_n$, was synthesised by polycondensation of terephthaloyl chloride with bis(*p*-hydrochinoyl)-isophthalate in 1-chloronaphthaline at 240°C as described earlier [4].

The following functional groups were identified using I–R spectroscopy (KBr): 1731 ($C{=}O_{\mathrm{ester,ar}}$), 1508/1498 ($\nu C{-}C_{\mathrm{ar}}$), 1173 ($\nu C{-}O{-}C_{\mathrm{ar}}$), 1014, 721 ($\delta(C{-}H)_{\mathrm{ar}}$) cm^{-1}. Additionally, the substance was characterised by elemental analysis: C, 69.43 wt% (calc. 70.00 wt%); H, 3.36 wt%

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(3.36 wt%); O, 27.21 wt% (26.64 wt%). Further chemical analysis could not be carried out due to the insolubility of (TPA–HQ–IPA–HQ)$_n$ in all solvents.

The copolyester was stable up to 360°C as observed on a hot stage polarising microscope. The decomposition maximum found by differential thermal analysis (DTA) was placed at 544°C.

2.2. Wide angle X-ray diffraction

Wide angle X-ray diffraction investigations (WAXS) were performed at room temperature, consistent with the method described in Ref. [5]—powder diffraction using CuK$_\alpha$ radiation, scattering range $2\theta = 3$–$50°$, step width $\Delta 2\theta = 0.05°$ and counting time per step $\Delta t = 125$ s. The device was used was X-ray diffractometer HZG 4/A-2 (Seifert-FPM GmbH, Freiberg i. Sa., Germany) with small beam divergences equipped with an energy-dispersive detector EDR 288 (RÖNTEC GmbH, Berlin, Germany).

2.3. Modelling

Modelling procedures were performed using the method explained in earlier work [5]. Geometry of monomer units was optimised by means of quantum mechanical ab initio calculations. These units were used to build a single polymer chain that was employed as a crystallographic repeating unit. Using space group specific symmetry operators, the unit cell of the crystal was packed and X-ray diagrams were calculated in order to find a good starting point for Rietveld refinement. The refinement was performed by means of the BGMN® [6] software package based on a modified Rietveld algorithm similar to those described in literature [7,8]. The dependence of parameters on device and sample conditions was taken into consideration. This Rietveld algorithm was expanded by including an additional optimisation criterion using force fields between atoms and total energy of the system. Graphics were presented by RASMOL 2.5.1 [9] and GNUPLOT 3.5 [10].

3. X-ray measurements

WAXS measurements were carried out in order to continue the investigations of highly aromatic copolyesters with kinked monomer units [5]. (TPA–HQ–IPA–HQ)$_n$ was investigated for comparison to the copolyesters prepared earlier [4,5], and a direct comparison was possible to *lt*-(IPA–HQ)$_n$ [5]. However, for (TPA–HQ–IPA–HQ)$_n$ there is no hint of high temperature modification (the structure remains stable up to about 360°C).

4. Calculation methods

In a previous publication [5] the procedure was described for constructing these polymers in four single steps. This well-proven concept was applied to the copolyester under discussion. Based on the starting model of (IPA–HQ)$_n$, the monomer unit terephthalic acid (TPA) was introduced. Since only two kinks of IPA were necessary to guarantee an extended chain, the model was designed to contain two TPA–HQ–IPA–HQ repeating units. The unit cell length in c-direction was thus increased to 5.0 nm. The approximation process was carried out by minimisation of the Rietveld performance coefficient Q_{Rietveld} and the reliability factor R_{Rietveld}.

$$R^2_{\text{Rietveld}} = \frac{Q_{\text{Rietveld}}}{\sum_{2\theta} (w_{2\theta} \times I_{\exp}(2\theta))^2} = \frac{\sum_{2\theta} (w_{2\theta} \times (I_{\text{calc}}(2\theta) - I_{\exp}(2\theta)))^2}{\sum_{2\theta} (w_{2\theta} \times I_{\exp}(2\theta))^2} \tag{1}$$

where $w_{2\theta}$ is the weighting factor (constant in this case).

These factors describe the difference between the experimental and calculated intensities $I(2\theta)$ (compare also with formula (1) in Ref. [5]).

In the first step, the initial unit cell parameters were calculated by means of structureless approximation with $R_{\text{Rietveld}} = 2.3\%$ ($a = 0.770$ nm, $b = 0.552$ nm, $c = 4.86$ nm, $\beta = 96.0°$). In the second step, the possible symmetry operators of this monoclinic unit cell were determined. Each possible reflection condition was tested by including only the corresponding reflection triples (*hkl*) which give indications of the following operators; primitive and body centering operators, glide planes and screw axis depending on the unique axis [11]. Results demonstrate that only primitive unit cell symmetries are possible. Any face or body centering was excluded.

The number of repeating units contained in the unit cell was determined by investigating possible values. Assuming the highest symmetry conditions, the choice of two repeating units (=16 monomer units) resulted in space group No. 7. However, four repeating units could not be excluded if additional symmetry conditions (e.g. $P2_1/c$, space group No. 14 [11]) were permitted. Space group No. 14 is a non-isomorphic supergroup of group 7, in other words the 2 groups have similar characteristics, divided only by an additional screw axis in group 14. It is not possible to determine if the corresponding screw axis exists or not.

The influence of the energy (Q_{FF}) and the approximation distance (Q_{Rietveld}) up to the approximation process can be

Table 1
Parameters of penalty functions for bonding interactions (*n* indicates that the named atom lies in the next unit cell in the *z*-direction; f_b, f_v are oscillation constants; $r_{b,\text{eq}}$, $\delta_{v,\text{eq}}$ are equilibrium values)

Atomic identifier	f_b resp. f_v	$r_{b,\text{eq}}$ resp. $\delta_{v,\text{eq}}$
O104–C1$_n$	228 kcal mol^{-1} nm^{-2}	0.132 nm
C97–O104–C1$_n$	70.0 kcal mol^{-1} deg^{-2}	115.1°
O104–C1$_n$–C2$_n$	120.0 kcal mol^{-1} deg^{-2}	111.5°

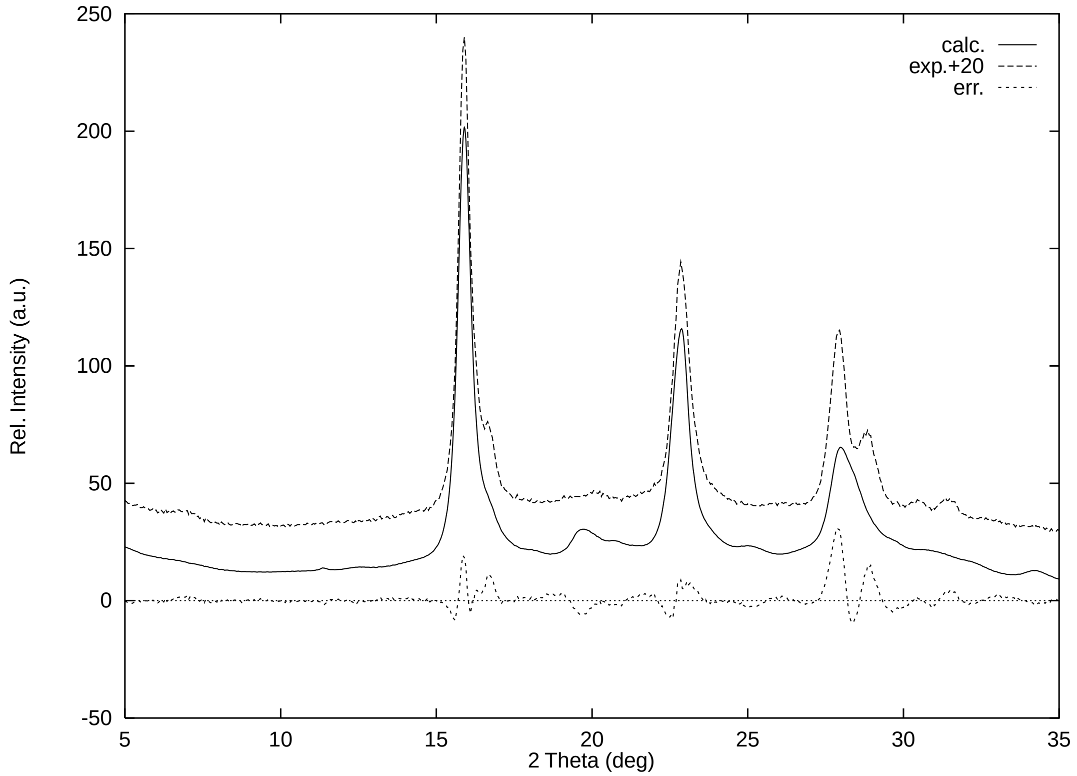

Fig. 1. Calculated WAXS curve of (TPA–HQ–IPA–HQ)$_n$ in comparison with the experimental curve.

controlled by the formula [5]

$$Q^{*}_{\mathrm{Rietveld}} = c_{\mathrm{Theory}} \times Q_{\mathrm{FF}} + Q_{\mathrm{Rietveld}} \tag{2}$$

The choice of $c_{\mathrm{theory}} = 100\ \mathrm{mol\ kcal}^{-1}$ enforces nearly the same weight of both parts. Q_{FF} consists of the bonding and the nonbonding part:

$$Q_{\mathrm{FF}} = Q_{\mathrm{bd}} + Q_{\mathrm{nbd}} \tag{3}$$

Nonbonding terms like Lennard-Jones potential avoid overlapping of atoms, whereas penalty functions (Eq. (4)) enable a correct chain continuation. The parameters of the penalty functions, f_b and f_v, could be reduced to values that are also used to describe force constants by IR spectra and in common empirical force fields [12,13] (Table 1).

$$Q_{\mathrm{bd}} = \sum_b f \times (r_b - r_{b,\mathrm{eq}})^2 + \sum_v f_v \times (\delta_v - \delta_{v,\mathrm{eq}})^2 \tag{4}$$

Table 2
Calculated lattice and orientation parameters of (TPA–HQ–IPA–HQ)$_n$

Monoclinic lattice	a (nm)	0.781 ± 0.001
Space group: *Pc* (No. 7)	b (nm)	0.557 ± 0.001
	c (nm)	5.03 ± 0.01
	β (°)	89.2 ± 0.2
	V (nm^3)	2.19 ± 0.01
	Z	2
	ρ_X (g cm^{-3})	1.45 ± 0.01
Twist angles (°)	ρ_1 (x-axis)	−14.1 ± 0.7
	ρ_2 (y-axis)	−3.6 ± 0.9
	ρ_3 (z-axis)	−5.9 ± 0.6
Shift vector SP (nm)	xx	—[a]
	yy	0.63 ± 0.03
	zz	—[a]

[a] No conditions due to the glide planes.

5. Results and discussion

The combination of (TPA–HQ)$_n$ and (IPA–HQ)$_n$ as alternating copolyesters has never been studied before. Our primary interest was to determine how this combination of chemical units influences the crystalline symmetry behaviour. The copolyesters under discussion are characterised as having a triclinic symmetry [4]; (TPA–HQ)$_n$ space group $P\bar{1}$, No. 2, and a monoclinic symmetry [5], *lt*-(IPA–HQ)$_n$ space group *Pc*, No. 7. Both of these space groups contain two repeating units. Calculation of internal structure began with space group No. 7, because we found it to be similar to *lt*-(IPA–HQ)$_n$. The results are given in Table 2.

Excluding the *c*-axis, the unit cell parameters of (TPA–HQ–IPA–HQ)$_n$ and *lt*-(IPA–HQ)$_n$ [5] are very similar. As expected, the additional TPA–HQ residues increase the repeating unit length. Two kinks in the opposite direction are necessary to obtain an extended polymer chain. Because of the long *c*-axis 87 reflections were found up to $2\theta = 35°$ with $I_{\mathrm{rel,calc}} > 3\%$. Fig. 1 shows the comparison of experimental and calculated powder diagrams. R_{Rietveld} calculations of X-ray structure refinements achieve reliability values of about 10% for powder diffraction experiments in

Table 3
Fractional atom coordinates of (TPA–HQ–IPA–HQ)$_n$

Atom	Residuum	x	y	z
C1	TPA	0.025	−0.273	0.426
C2	TPA	0.070	−0.395	0.400
C3	TPA	0.032	−0.282	0.376
C4	TPA	0.074	−0.395	0.352
C5	TPA	0.155	−0.620	0.352
C6	TPA	0.193	−0.732	0.376
C7	TPA	0.150	−0.620	0.400
H8	TPA	−0.030	−0.107	0.376
H9	TPA	0.045	−0.307	0.333
H10	TPA	0.255	−0.908	0.376
H11	TPA	0.180	−0.708	0.419
C12	TPA	0.198	−0.736	0.325
O13	TPA	−0.045	−0.080	0.428
O14	TPA	0.267	−0.929	0.322
O15	HQ	0.076	−0.696	0.305
C16	HQ	0.080	−0.712	0.278
C17	HQ	−0.010	−0.895	0.265
C18	HQ	−0.006	−0.911	0.237
C19	HQ	0.087	−0.743	0.222
C20	HQ	0.177	−0.560	0.235
C21	HQ	0.173	−0.544	0.263
H22	HQ	−0.083	−1.026	0.277
H23	HQ	−0.076	−1.054	0.227
H24	HQ	0.250	−0.429	0.223
H25	HQ	0.243	−0.401	0.273
O26	HQ	0.087	−0.766	0.194
C27	IPA	0.023	−0.568	0.180
C28	IPA	−0.040	−0.641	0.153
C29	IPA	−0.017	−0.485	0.131
C30	IPA	−0.075	−0.552	0.106
C31	IPA	−0.156	−0.773	0.103
C32	IPA	−0.180	−0.928	0.124
C33	IPA	−0.122	−0.862	0.149
H34	IPA	0.047	−0.313	0.134
H35	IPA	−0.202	−0.825	0.083
H36	IPA	−0.243	−1.101	0.122
H37	IPA	−0.140	−0.983	0.166
C38	IPA	−0.052	−0.388	0.082
O39	IPA	−0.029	−0.388	0.191
O40	IPA	0.016	−0.193	0.082
O41	HQ	−0.034	−0.549	0.061
C42	HQ	−0.041	−0.497	0.034
C43	HQ	0.010	−0.272	0.024
C44	HQ	0.003	−0.220	−0.003
C45	HQ	−0.055	−0.395	−0.021
C46	HQ	−0.105	−0.621	−0.011
C47	HQ	−0.099	−0.672	0.016
H48	HQ	0.043	−0.044	−0.010
H49	HQ	0.055	−0.135	0.038
H50	HQ	−0.150	−0.757	−0.025
H51	HQ	−0.138	−0.848	0.023
O52	HQ	−0.059	−0.336	−0.048
C53	TPA	0.062	−0.453	−0.064
C54	TPA	0.094	−0.382	−0.093
C55	TPA	0.169	−0.545	−0.111
C56	TPA	0.198	−0.479	−0.137
C57	TPA	0.152	−0.250	−0.146
C58	TPA	0.076	−0.086	−0.128
C59	TPA	0.047	−0.153	−0.102
H60	TPA	0.205	−0.724	−0.104
H61	TPA	0.257	−0.606	−0.151
H62	TPA	0.040	0.092	−0.135
H63	TPA	−0.012	−0.025	−0.088
C64	TPA	0.186	−0.184	−0.175
O65	TPA	0.164	−0.597	−0.055
O66	TPA	0.152	0.007	−0.185
O67	HQ	0.094	−0.331	−0.192
C68	HQ	0.088	−0.310	−0.220
C69	HQ	0.169	−0.481	−0.236
C70	HQ	0.163	−0.460	−0.264
C71	HQ	0.075	−0.267	−0.276
C72	HQ	−0.005	−0.096	−0.259
C73	HQ	0.001	−0.117	−0.232
H74	HQ	0.237	−0.631	−0.227
H75	HQ	0.226	−0.594	−0.277
H76	HQ	−0.073	0.054	−0.268
H77	HQ	−0.062	0.016	−0.219
O78	HQ	0.073	−0.254	−0.303
C79	IPA	−0.002	−0.393	−0.323
C80	IPA	−0.042	−0.318	−0.352
C81	IPA	0.004	−0.468	−0.373
C82	IPA	−0.032	−0.399	−0.399
C83	IPA	−0.115	−0.181	−0.404
C84	IPA	−0.161	−0.031	−0.383
C85	IPA	−0.125	−0.100	−0.356
H86	IPA	0.069	−0.638	−0.369
H87	IPA	−0.143	−0.128	−0.424
H88	IPA	−0.226	0.139	−0.386
H89	IPA	−0.161	0.017	−0.340
C90	IPA	0.016	−0.557	−0.423
O91	IPA	−0.087	−0.570	−0.319
O92	HQ	0.088	−0.750	−0.421
O93	HQ	−0.115	−0.651	−0.438
C94	HQ	−0.085	−0.656	−0.466
C95	HQ	−0.131	−0.858	−0.481
C96	HQ	−0.102	−0.863	−0.508
C97	HQ	−0.026	−0.665	−0.521
C98	HQ	0.020	−0.463	−0.506
C99	HQ	−0.009	−0.458	−0.479
H100	HQ	−0.190	−1.012	−0.471
H101	HQ	−0.138	−1.020	−0.520
H102	HQ	0.079	−0.309	−0.516
H103	HQ	0.027	−0.300	−0.467
O104	HQ	0.001	−0.678	−0.549

Bragg–Brentano arrangement. Compared to a R_{Rietveld} value for (TPA–HQ–IPA–HQ)$_n$ at 9.5% reliability obtained here, one can note that this is an excellent result, not confined to polymer studies (cf. the error function in Fig. 1).

The measured diagram contains more features than the calculated one (see shoulder at 16° and double peak at 28°), indicating that the measured diagram contains more crystalline details than the calculated one. One explanation for this behaviour may be a second phase, for example a high temperature modification (by analogy with (IPA–HQ)$_n$ [5]), but the existence of such a phase has not been proven yet. A second explanation may be other conformations of the chain molecule coexisting with the most probable one.

Table 3 summarises the fractional atom coordinates. Fig. 2 allows a perspective view into the unit cell.

The orientation in the (TPA–HQ–IPA–HQ)$_n$ unit cell also

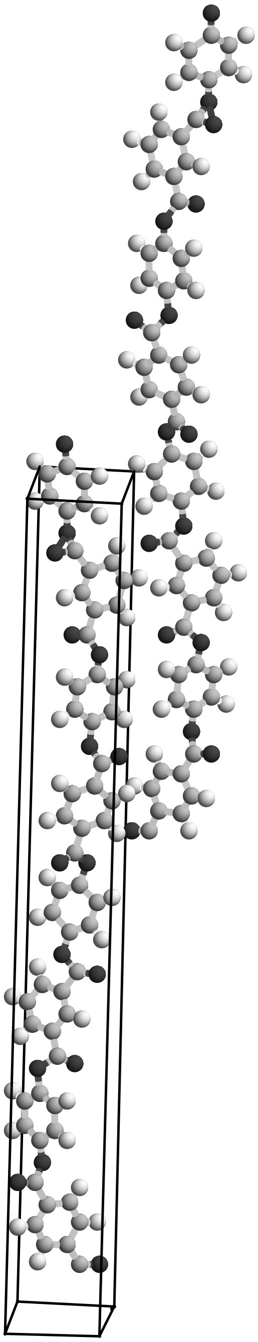

Fig. 2. Perspective view of the (TPA–HQ –IPA–HQ)$_n$ monoclinic cell.

shows similarities to that of *lt*-(IPA–HQ)$_n$. The IPA units are nearly planar. On the contrary, the TPA and HQ units alternate between planar and perpendicular orientations. This symmetry enforces layers of same residue units. Hence, IPA, TPA and HQ do not build mixed layers, and a molecular-level phase separated system is established.

Comparing the current results with the earlier results [5] it can be pointed out that the solid state structure, including the symmetry of (TPA–HQ–IPA–HQ)$_n$ is very similar to (IPA–HQ)$_n$. Knowledge of structure is important for understanding many of the material properties that are directly dependent on the molecular structure and the orientation of the polymer chain. For example, mechanical stability or stress–strain behaviour can be calculated using equations of elasticity theory, the symmetry and the molecular structure.

6. Outlook

In this paper the clarification of structures of *m*-linked aromatic copolyesters containing regular chain sequence was successfully continued. The application of force field constrained Rietveld procedures gave a high probability structure proposal. Although a unit cell with a very long repeating unit (104 atoms) and 33 internal parameters had to be computed, the program ran stable. Therefore, further results of structure investigations for this class of polymer will be published in a future paper.

The new Rietveld method implemented in the software package BGMN® as a combination of the classical Rietveld refinement and force field constraints has proven to be essential for structural investigations in complicated situations involving large unit cells of polymers. The utility for other large crystallised molecules has been previously demonstrated [14].

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