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Structure investigations of regular main chain copolyesters

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Aromatic copolyesters with regular chain structure were investigated in order to correlate their primary chemical structure, some molecular characteristics (inherent viscosity, molecular weight) and crystallographic data as well as melting behaviour. A series of copolyesters were synthesized by polycondensation of complex aromatic dicarboxylic acid chlorides with variable diols. By means of wide angle X-ray diffraction it was found that the kind of diol component strongly influences the phase structure as well as the crystallinity of the polymers. A monoclinic symmetry was supposed for some of the high crystalline samples. Molecular modelling, including *ab initio* calculations and computing of the solid state, was carried out for two representatives of *p*-linked fully aromatic copolyesters. A good agreement of experimental and calculated scattering data was obtained by using the space group $P\bar{1}$. Copyright © 1996 Elsevier Science Ltd.

(Keywords: aromatic copolyesters; solid phase structure; wide angle X-ray scattering)

INTRODUCTION

In the past, a variety of aromatic liquid-crystalline main chain copolyesters with either random or regular chain structure have been reported. Due to their rigid-chain chemical structure, these polymers show excellent mechanical and thermal characteristics which depends on the primary chemical structure, synthesis conditions as well as processing conditions[1–3]. Taking the difficulties to find complete correlations of these parameters and the material properties into account, structure–property relationships are usually clarified stepwise.

For the class of aromatic copolyesters, polymers with defined, regular chain structure were chosen as a model in order to correlate primary chemical structure, some molecular characteristics (inherent viscosity, molecular weight) and crystallographic data as well as melting behaviour.

The properties of a variety of copolyesters with regular chain structure synthesized by polycondensation of complex aromatic dicarboxylic dichlorides with different dihydroxy compounds have been extensively discussed in the past (see e.g. refs 4–9). These investigations published until now were mainly emphasized on determination of the influence of chemical structure on the thermotropic properties and the melting and phase behaviour of the polymers (transition temperatures and kind of lc phase formed)[6,9,10].

In addition, investigations of the solid phase structure of such thermotropic copolyesters were carried out preferably by wide angle X-ray scattering in combination with model calculations. Whereas structure investigations or oriented random copolyesters allow one to describe neighbouring ratios relative to the polymer chain axis[11–13]. Investigation of polymers with alternating chain segment distribution results in information of accurate atomic coordinates[14,15]. Sophisticated structure investigations would actually need analysis of single crystal or oriented samples. These conditions could not be realized for the variety of aromatic copolyesters under investigation because some of them are not meltable due to their chemical structure. Therefore, the investigations were performed using isotropic powders. As already discussed by Windle and Coulter[16], X-ray powder diffraction may contribute to a structure model, assuming a well-researched knowledge of intra- and intermolecular conformational preferences by using molecular mechanic simulation programs.

Due to their similar chain structure it is believed that a general structural principle exists, being valid for most regular aromatic copolyesters. In order to understand the common principles of the solid phase structure of those copolyesters, we synthesized a number of copolyesters with regular chain structure by polycondensation of complex aromatic carboxylic acid chlorides with different dihydroxyl monomers. It was ensured that all samples to be examined were prepared by comparable polycondensation conditions, regardless of whether the structures have been reported in the literature or not. In the work discussed here, only as-polymerized samples were investigated to eliminate the influence of thermal history.

From the WAXS data obtained *d*-spacings were determined. Lattice parameters were calculated and optimized by means of molecular modelling and powder diffraction calculation programs using a monoclinic symmetry as suggested by other authors[16]. The obtained results are substantially necessary for investigations of melt processed samples.

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EXPERIMENTAL

Materials

Dihydroxy compounds and terephthalic acid were obtained from Merck–Schuchardt and used as received. OH-terminated poly(tetramethylene glycol) was kindly provided by BASF AG (Germany), see ref. 17. 1-Chloronaphthalene was obtained from Fluka and dried and stored with molecular sieves before using.

Monomer preparation

The preparation of terephthaloyl dichloride and the complex monomer 4,4′-(terephthaloyldioxy) dibenzoyl dichloride was carried out as described earlier[17]. OH-terminated poly(sulfone) was synthesized as reported elsewhere[24].

Polymer preparation

Regular copolyesters containing (terephthaloyldioxy) dibenzoyl units (polymers **1c–7b**): 4,4′-(terephthaloyldioxy) dibenzoyl dichloride, TOBCl (20 mmol) and the appropriate dihydroxy compound (20 mmol) were placed together with 1-chloronaphthalene (40 ml) in a three-necked flask equipped with N_2 inlet, stirrer and distilling head. The reaction mixture was stirred under continuous nitrogen flow at room temperature for 2 h. Then, the flask was immersed in a preheated woods metal bath and kept at a temperature between 180 and 240°C (depending on the dihydroxy compound, see *Table 2*) for 2 h while stirring and passing a N_2 stream through the reaction mixture. After cooling to ambient temperature, the polymer was precipitated in toluene (200 ml), filtered off, extracted several times with hot acetone, and dried in a vacuum oven at 50°C for 8 h.

Polymers are characterized by their i.r. spectra and the samples soluble in pentafluorophenol/chloroform were additionally characterized by their ^{13}C n.m.r. spectra. Infra-red (KBr): **1c**: 1738 ($\nu C = O_{ester,ar}$), 1603/1507 ($\nu C - C_{ar}$), 1411, 1260, 1181/1158 ($\nu C - O - C$), 1066 ($\delta C - C - O$), 890/874 ($C - H_{ar}$, oop, 1,4-disubst.), 719 ($C - H_{ar}$, oop) cm^{-1}: **2a**: 1739 ($\nu C = O_{ester.ar}$), 1602 ($\nu C - C_{ar}$), 1161/1061 ($\delta C - C - O$ and $\nu C - O - C$), 872 ($C - H_{ar}$, oop), 717 ($C - H_{ar}$, oop) cm^{-1}; **2b**: 1736 ($\nu C = O_{ester.ar}$), 1604/1502 ($\nu C - C_{ar}$), 1179/1158 ($\nu C - O - C$), 1063 ($\delta C - C - O$), 1013, 881 ($\nu C - H_{ar}$, oop), 718 ($C - H_{ar}$, o.o.p.) cm^{-1}; **3a**: 2957/2924 ($\nu_{ass}CH_3$), 2856 ($\nu_s CH_3$), 1738 ($\nu C = O_{ester.ar}$), 1603/1501 ($\nu C - C_{ar}$), 1410, 1260, 1202/1158 ($\nu C - O - C$), 1064, 1014 ($\delta C - C - O$, 872 ($C - H_{ar}$, oop), 754, 718 ($C - H_{ar}$, oop) cm^{-1}; **3b**: 1739 ($\nu C = O_{ester.ar}$), 1603/1500/1481 ($\nu C - C_{ar}$), 1258/1200/1157 ($\nu C - C - O$ and $\nu C - O - C$), 1061 ($\delta C - C - O$), 1012, 888/871/845 ($C - H_{ar}$, oop) cm^{-1}; **4** (all polymers): 1738 ($\nu C = O_{ester.ar}$), 1603 ($\nu C - C_{ar}$.) 1412, 1260/1195/1160 ($\nu C - O - C$), 1053–65, 1011/1013 ($\delta C - C - O$); 873/755, 718 ($C - H_{ar}$, oop) cm^{-1}, additional peaks or shifts: **4a**: 1494 ($\nu C - C_{ar}$, decreased), 1185 ($\nu C_{ar} - O - C_{ar}$); **4b**: 1499/1487 ($\nu C - C_{ar}$, decreased), 1196 ($\nu C - O - C$, decreased), 888 ($C - H_{ar}$, oop, 1,2,4-tri), 871/845 ($C - h_{ar}$, oop, 1,4-di), 631 ($\nu C_{ar} - S - C_{ar}$) [Raman], **4c**: 2968 ($\nu_{as}CH_3$), 2920 ($\nu_s CH_3$), 2850 (νCH_3), 1413 ($\nu_{as}C_{ar} - SO_2 - C_{ar}$) [Raman], 1409, 1205 ($\nu_s - SO_2-$) [Raman]; **4d**: 1588, 1500/1489 ($\nu C - C_{ar}$, decreased), 629 ($\nu C_{ar} - S - C_{ar}$) [Raman]; **4e**: 2913 ($\nu_{as}CH_2$), 2852 ($\nu_s CH_2$) cm^{-1}; **4f**: 1650 cm^{-1}; **5a–i**, **7a,b**: 2963–2932/2918 ($\nu_{as}CH_2$), 2850 ($\nu_s CH_2$), 1739–1731 ($\nu C = O_{ester,ar}$), 1719–1716 ($\nu C = O_{ester,aliph}$), 1604/1500/1470 ($\nu C - C_{ar}$), 1265, 1201–1198, 1162–1160, 1067–1074 ($\nu C - O - C$, $\delta C - C - O$), 1110–1112 (ωCH_2), 887–871, 760/718–716 ($C - H_{ar}$, oop) cm ^{1}; **6**: 2965 ($\nu_{as}CH_2$), 1741 ($\nu C = O_{ester}$), 1585/1504/1487 ($\nu C - C_{ar}$), 1410 (weak, $\nu_{as}C_{ar} - SO_2 - C_{ar}$) [Raman], 1205 (weak, $\nu s{-}SO_2-$) [Raman], 1059 ($\delta C - C - O$), 873/853 ($C - H_{ar}$, oop) see ref. 28, 631 (weak, $\nu C_{ar} - S - C_{ar}$). Assignments with respect to ref. 28.

^{13}C n.m.r. (δ in ppm, selected signals): **2b:** 166.2, 166.0, 165.4 ($C = O$); 155.3, 148.7, 148.5 ($-O - C_{ar}-$); **4b**: 165.45, 165.19 ($C = O$), 155.41, 155.02 ($O - C_{ar}$); **5b**: 167.8, 165.5 ($C = O$); 154.7 ($-O - C_{ar}-$); 63.0 ($-O - CH_2-$); **5h, 5i**: 168.1 ($C = O$); 165.7 ($-\underline{C}OO - CH_2$); 154.5 ($-O - C_{ar}-$); 66.9 ($-O - CH_2-$); **6:** 168.2, 166.4 ($C = O$); 155.5, 152.7, 150.0 ($-O - C_{ar}-$); **7a, b**: 167.8, 165.5 ($C = O$); 154.6 ($-O - C_{ar}-$); 71.0 ($-CH_2 - O - CH_2-$); 66.1 ($-COOCH_2-$) [in $CDCl_3$/pentafluorophenol (1:1 v/v), except **6**, in $CDCl_3$/TFA (1:1, v/v)], assignments according to refs 24, 30.

*Poly(*p-*phenylene terephthalate), (polymer* **1a***)* was synthesized analogously by reaction of terephthaloyl dichloride (20 mmol) with hydroquinone (20 mmol) in 1-chloronaphthalene (40 ml) at 240°C for 2 h, subsequent precipitation in toluene (200 ml), extraction with hot acetone and drying *in vacuo*. Infra-red (KBr): 1731 ($C = O_{ester,ar}$), 1508/1498 ($\nu C - C_{ar}$), 1173 ($\nu C - O - C_{ar}$), 1014, 721 ($\delta(C - H)_{ar}$), cm^{-1}.

*Poly(phenyl-*p-*phenylene terephthalates)* were first prepared by reaction of phenylhydroquinone (20 mmol) and terephthaloyl dichloride (20 mmol) in 1-chloronaphthalene at 200°C for 2 h, followed by precipitation in toluene. The polymers prepared so did not precipitate during polycondensation and were consequently found to be amorphous. Therefore, *polymer* **1b** was synthesized by melt polycondensation as follows: terephthaloyl dichloride (20 mmol) and phenylhydroquinone (20 mmol) were put into a three-necked flask equipped with N_2 inlet, stirrer and distilling head. Before starting the polycondensation, the flask was purged three times. The polycondensation was carried out in two steps. In the first step, the flask was immersed in the preheated bath at 240°C, then the temperature was gradually raised to 300°C during 30 min with continuous flow of dry nitrogen and stirring of the reaction mixture. After 60 min vacuum was applied for another 1 h. After that time, the flask was removed from the metal bath and the resulting product was cooled down to ambient temperature. Infra-red (KBr): 1735 ($\nu C = O_{ester,ar}$), 1573 ($\nu C - C_{ar}$), 1502/1479 (decreased from 1498 by the phenylene substituent)/1445/1407 ($\nu C - C_{ar}$), 1236 1164/1068 ($\nu C - O - C$), 893 ($C - H_{ar}$, oop, 1,2,4-tri), 868/845 ($C - H_{ar}$, oop, 1,4-di), 760/716/697 ($C - H_{ar}$, oop) cm^{-1}. ^{13}C n.m.r. (δ in ppm, selected signals): 166.3, 166.1 ($C = O$), 148.8, 145.6 ($-O - C_{ar}-$) [in $CDCl_3$/pentafluorophenol (1:1 v/v)].

Elemental analyses of the copolyesters are given in *Table 1* and their chemical characterization is shown in *Table 3*.

Polymer characterization

Solution viscosities were determined by a Berger–Deckert viscometer (microcapillary I) at 25°C in a 50/50

Table 1 Elemental analysis of synthesized regular copolyesters

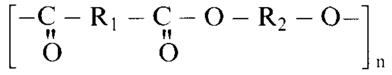
Polymer	Elemental analysis				
		C (%)	H (%)	O (%)	S (%)
1a	calc.	70.00	3.36	26.64	
	found	70.00	3.43	26.65	
1b	calc.	75.94	3.82	20.23	
	found	75.59	3.77	20.65	
1c	calc.	69.99	3.36	26.65	
	found	69.43	3.35	27.22	
2a	calc.	69.99	3.36	26.65	
	found	69.76	3.35	26.89	
2b	calc.	69.99	3.36	26.65	
	found	69.44	3.41	27.15	
3a	calc.	70.43	3.67	25.90	
	found	68.88	3.60	27.52	
3b	calc.	73.37	3.67	23.01	
	found	72.55	3.55	23.90	
4a	calc.	71.31	3.52	25.16	
	found	70.59	3.52	25.89	
4b	calc.	69.38	3.43	21.71	5.44
	found	67.91	3.43	23.30	5.36
4c	calc.	74.23	4.38	21.39	
	found	73.99	4.40	21.61	
4d	calc.	65.80	3.25	25.80	5.16
	found	63.93	3.25	27.83	5.00
4e	calc.	73.67	3.89	22.44	
	found	72.62	3.87	23.51	
4f	calc.	74.05	3.19	22.76	
	found	73.89	3.05	23.06	
4g	calc.	73.38	3.62	23.00	
	found	72.30	3.62	24.08	
5a	calc.	66.67	3.73	29.60	
	found	67.67	3.38	28.95	
5b	calc.	67.26	4.06	28.67	
	found	66.79	4.03	29.18	
5c	calc.	67.82	4.38	27.80	
	found	67.14	4.25	28.61	
5d	calc.	68.35	4.46	26.98	
	found	67.21	4.56	28.23	
5e	calc.	68.85	4.95	26.20	
	found	68.25	4.94	26.81	
5f	calc.	69.31	5.21	25.47	
	found	68.58	5.43	25.99	
5g	calc.	69.76	5.46	24.78	
	found	69.23	5.34	25.43	
5h	calc.	70.18	5.70	24.12	
	found	69.43	5.68	24.89	
5i	calc.	70.57	5.92	23.50	
	found	70.06	5.88	24.06	
6	calc.	73.58	4.79	16.49	5.14
	found	72.00	5.10	17.17	5.73
7a	calc.	67.50	6.24	26.26	
	found	65.67	6.17	28.16	
7b	calc.	67.18	8.11	24.71	
	found	65.56	8.03	26.41	

(v/v) mixture of pentafluorophenol and chloroform with a polymer concentration of 0.5 g dl^{-1}.

Molecular weight distribution curves were determined at ambient temperature by a Knauer GPC using a 1/3 (v/v) mixture of *m*-cresol and chloroform as eluent, Merck Hibar LiChrogel PS Mix 40/Knauer PLgel MIXED B separation columns and r.i. detection. The samples were first dissolved in a 1/1 (v/v) mixture of pentafluorophenol/chloroform and then diluted with the eluent. Molecular weights were calculated with reference to narrow molecular weight polystyrene standards.

^{13}C n.m.r. spectra were recorded on an AMX 300 spectrometer (Bruker) at 75.475 MHz and were referenced on internal $CDCl_3$ ($\delta = 77.00$ ppm *versus* TMS). Infra-red spectra were recorded on a Bruker FT-IR IFS 66 and *FT*-Raman spectra on a Bruker FRA 106 (1064 nm Nd-YAG Laser, 300 mW). Melting ranges were determined on a hot stage polarizing microscope (Cambridge Instruments).

Table 2 Chemical composition of the synthesized regular copolyesters with the general structure



$$\left[-\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}-R_1-\underset{\displaystyle O}{\underset{\|}{C}}-O-R_2-O-\right]_n$$

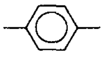
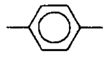
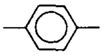
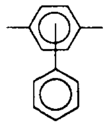
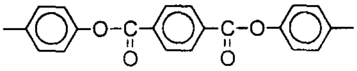
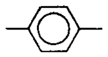
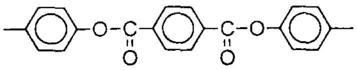
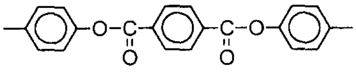
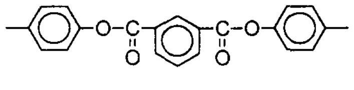
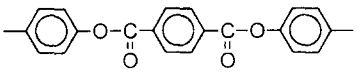
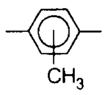
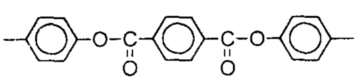
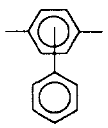
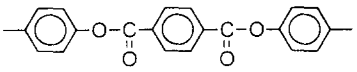
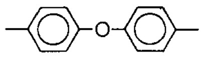
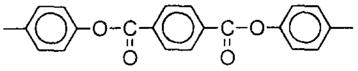
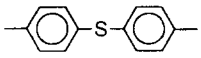
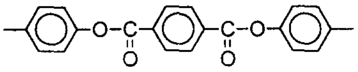
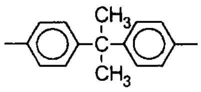
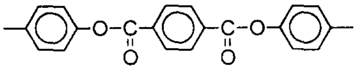
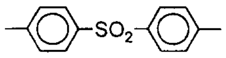
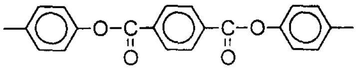
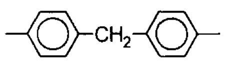
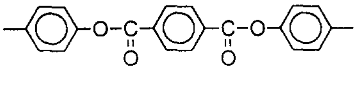
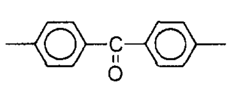
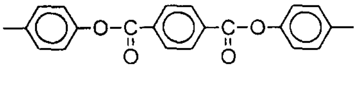
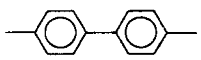
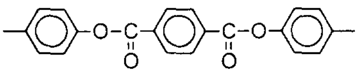
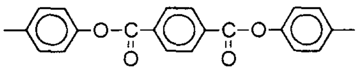
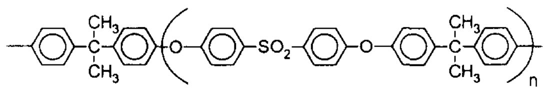
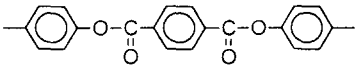
Polymer	R_1	R_2
1a		
1b		
1c		
2a		
2b		
3a		
3b		
4a		
4b		
4c		
4d		
4e		
4f		
4g		
5a-i		$-\!(CH_2)_n\!-$ n = 2; 3 ...; 10
6		 n̄ = 3,3
7a, b		$-(CH_2)_4\!\left(O-(CH_2)_4\right)_{n-1}$ n̄ = 3; 9

Table 3 Chemical characterization of synthesized copolyesters with regular chain structure

Polymer	**Synthesis temperature** (°C)	**Inherent visk.** (dl/g)	$\overline{M}_{n,\,GPC}$ (g/mol)	$\overline{M}_{w,\,GPC}$ (g/mol)	$\overline{M}_w/\overline{M}_n$	$T_{m,\,micr.}$ (°C)
1a	240	not sol.				> T_{dec}
1b	240/300	3.51	64 100	120 000	1.87	325-345 n
1c	240	not sol.				> T_{dec}
2a	240	0.91	18 600	60 600	3.26	332 n 387 i
2b	240	1.11	7 400	27 700	3.70	370-380 lc 390-400 i
3a	240	not sol.				390 lc
3b	240	not sol.				345-355 lc
4a	240	not sol.				278-320 lc
4b	240	not sol.				295-340 lc
4c	240	0.34	11 200	20 600	1.83	350-370 lc
4d	240	1.15	16 700	60 000	3.59	365 lc
4e	240	not sol.				260-310 lc
4f	240	0.81	8 200	33 000	4.02	346-353 lc
4g	240	not sol.				323-365 lc
5a	180/240	not sol.				325 s 365 n 405 i
5b	200	0.13	9 900	20 700	2.10	255 n 367 i
5c	200	not sol.				270 n
5d	200	0.64	18 600	42 300	2.27	215 s 280 n 325 i
5e	240	not sol.				225 n 345 i
5f	240	0.84	24 500	54 000	2.21	185-205 n 300 i
5g	240	1.04	48 800	103 000	2.11	225-240 n 315 i
5h	240	0.97	36 000	95 500	2.63	240 n 282 i
5i	240	1.29	58 900	133 500	2.26	224 s 260 n 282 i
6	240	0.37	8 000	17 300	2.16	235 n 299 i
7a	220	0.65	12 300	39 100	3.21	183 lc 225 i
7b	220	0.50	6 500	15 800	2.42	92 lc 115 i

lc...transition from the solid state into the (non specified) liquid-crystalline melt
n... transition from the solid state into the nematic melt
s... transition from the solid state into the smectic phase
i... transition from the nematic melt into the isotropic melt

Wide angle X-ray diffraction

WAXS investigations were performed using CuK_α radiation with the X-ray diffractometer HZG 4/A-2 (Seifert-FPM Corp., Freiberg i. Sa., Germany) equipped with an energy-dispersive detector EDR 288 (Rön Tec GmbH, Berlin, Germany). The device system allowed reproducible measurements with high accuracy in 2θ of $\pm(0.001\ldots0.002)^\circ$.

Measurements were carried out in a scattering range from 5 to 60° with $\Delta 2\theta = 0.1^\circ$ and $\Delta t = 10\,s$. The powder samples were examined in the 'as-polymerized' state. Transmission and reflection techniques were used to get high precision data.

Modelling

Modelling was carried out by means of IBM RISC System 6000 with operating system AIX 3.2 (IBM Corp. 1993).

Monomer units: the geometry optimization and conformation of monomer units was performed using the software GAMESS[18] for quantum mechanical *ab initio* calculations.

Polymer chain: single polymer chains were calculated using the software AMBER 3.0 (University of California)[19].

Crystal structure: crystal packing and calculation of X-ray diagrams were carried out by using the programs CRYSTAL and XRAY[20].

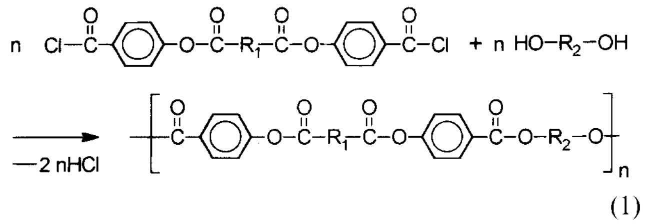
Graphic representation were executed by CERIUS^{2}1.5 (Cambridge Molecular Design)[21] and GNUPLOT 3.5[22].

Structure factors were calculated by means of own program sets[20] and the program APX 63 (Seifert-FPM Corp., Freiberg i. Sa., Germany).

RESULTS AND DISCUSSION

Polymer synthesis and characterization

The copolyesters under discussion were synthesized by polycondensation of dicarboxylic acid chlorides with different dihydroxy compounds according to the general equation shown below [equation (1)].



(1)

Table 2 gives a survey of the chemical structure of polymers included in the investigations discussed here. Starting from the simplest well-known structure of poly(*p*-phenylene terephthalate), sample **1a**, polymers containing a complex mesogenic segment with three phenylene rings, the 4,4′-(terephthaloyldioxy) dibenzoyl unit (TOBA), have been investigated. The mesogenic unit is connected via ester bonds with different dihydroxy compounds (aromatic, aliphatic, oligomeric) to give polyesters with a regular, alternating chain structure (polymers **2–7**).

A high temperature solution polycondensation procedure in 1-chloronaphthalene without HCl acceptor was applied. Bilibin *et al.*[23] showed that even without HCl acceptor side reactions such as alcoholysis of ester bonds of the polymer chain by hydroxyl groups of the comonomer do not take place and polyesters with a complete regular chain structure are formed. Recently, we were also able to demonstrate the regular structure of such copolyesters by ^{13}C n.m.r. sequence analysis[24,30] using diad and triad assignments and the comparison between alternating and random polymers. In complete regular structures diads resulting from oxybenzoyl-oxybenzoyl and terephthaloyl-diol coupling does not occur. Therefore, structures without complete regularity can be distinguished very well. The regular chemical structure of all synthesized copolyesters soluble in pentafluorophenol/chloroform was confirmed by ^{13}C n.m.r. investigation (see Experimental part).

Table 3 summarizes the results of chemical characterization of the polymer samples.

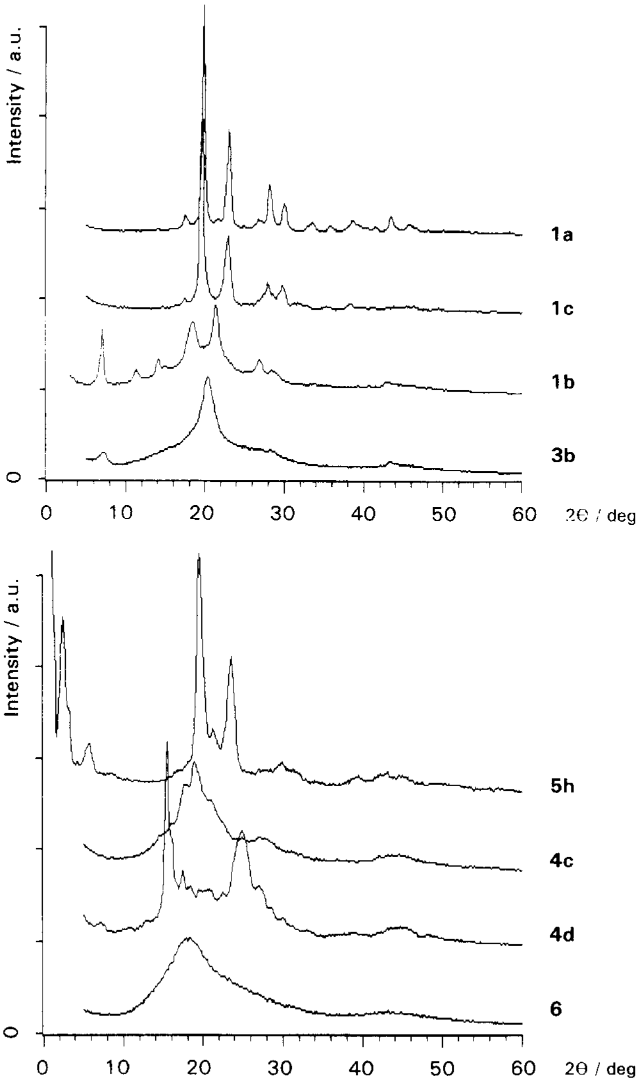


Figure 1 Wide angle X-ray diffractograms of selected copolyesters with regular chain structure (see *Table 2*)

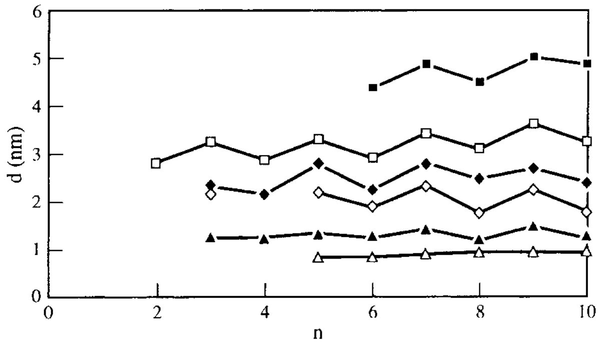


Figure 2 Influence of the number of methylene groups in the flexible spacer on the *d*-spacings of smectic layer reflections in (HBA-TPA-HBA-alkane diol)$_n$. ■, Reflection 1; □, reflection 2; ◆, reflection 3; ◇, reflection 4; ▲, reflection 5; △, reflection 6

A reaction temperature of 240°C was chosen for polycondensation with aromatic dihydroxy compounds and higher aliphatic diols. For lower aliphatic diols and OH-terminated poly(tetramethylene glycol) the temperature was 180 to 220°C due to their lower thermal stability.

Polymers with *p*-linked aromatic monomer units (**1a, 1b, 3a, 3b**) do not dissolve in pentafluorophenol/chloroform. Their structure was confirmed by i.r. spectroscopy (see Experimental part). Polymers containing more flexible diol units, e.g. 4,4′di(hydroxyphenylene) propane

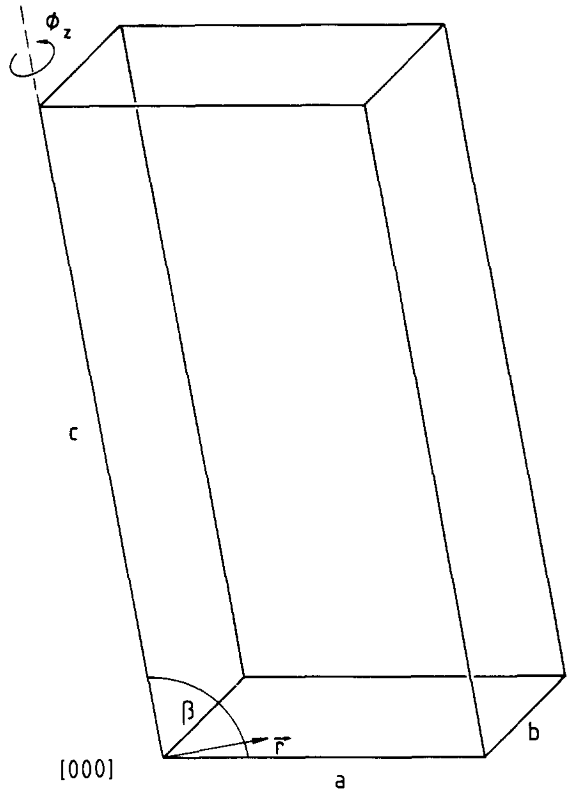


Figure 3 Monoclinic unit of *p*- and *m*-linked regular copolyesters. $a = 0.79–0.81$ nm, $b = 0.54–0.58$ nm, $c = n1.25–n1.30$ nm (n is the number of crystallographic repeating units in the polymer chain) and $\beta = 97–101°$

(**4b**), 4,4′-di(hydroxyphenylene) sulfone (**4d**), or poly(methylene) spacers (polymers **5a–i**), are more soluble in pentafluorophenol/chloroform or other phenolic solvents. Molecular weights were determined by g.p.c. with cresol/chloroform as eluent and were calculated relative to PS standard. *Table 3* illustrates that polymers with molecular weights ($\bar{M}_w$) from 16000 to about 133000 g mol^{-1} were obtained. The tendency found in molecular weights of polymers **5** well agrees with the flexibility of the poly(methylene) spacer incorporated: the higher the number of C atoms in the spacer, the higher is the molecular weight of the resulting polymer. This has to be explained by the specific conditions during the high temperature solution polycondensation: the higher the solubility of the growing polymer chain in the solvent, the higher is the molecular weight of the resulting polymer. Increasing number of methylene groups in the spacer increases the solubility and, consequently, the molecular weight. The relative molecular weights of the segmented block copolymers containing poly(sulfone) units (polymer **6**), respectively, are lower compared to those of polymers **5** which seems to be mainly due to the lower reactivity of the telechelic oligomers with respect to the complex acid chloride (assuming comparable reaction conditions). Additionally, a number of unreacted end groups in the block copolymers was found by n.m.r.

All polymers under investigation except *p*-linked polymers **1a** and **1b** (no melting due to their fully aromatic structure) form a liquid-crystalline phase during melting which exists in a certain temperature range. In the case of the high aromatic polymers an isotropization is not observed until decomposition.

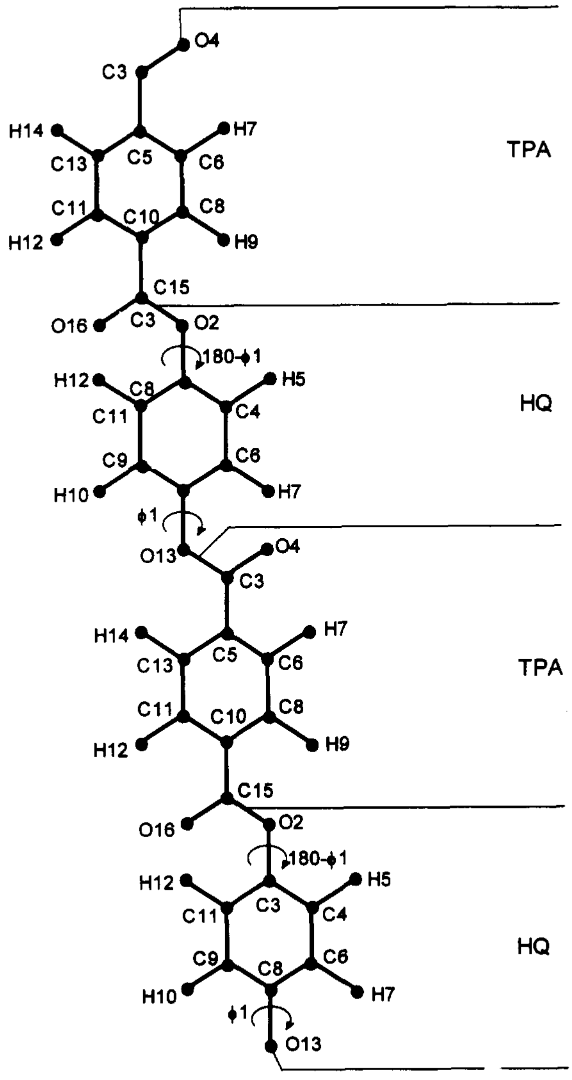


Figure 4 Schematic view on the polymer chain of $(\text{TPA-HQ})_n$

Transition temperatures of polymers **5** with poly(methylene) spacers correlate with those reported in the literature[5,6,8,25–27]. The well-known odd–even effect[5,27] (polymers with even number of C atoms in the spacer have higher transition temperatures $T_{\text{c-lc}}$ and $T_{\text{lc-i}}$ than polymers with odd number) could be detected by polarizing microscopy as well as by d.s.c. Some of them with longer poly(methylene) spacers display smectic phases (*Table 3*), additionally.

The polymers synthesized by high temperature solution polycondensation show a high degree of chain ordering or crystallinity, respectively. Both, slow precipitation of polymer chains with a certain molecular weight during reaction and the regular chain structure of the polymers contribute to the formation of high ordered polymers. Wide angle X-ray diffraction proved a successful method for investigation of the solid phase structure of these polymers.

Wide angle X-ray diffraction results

Wide angle X-ray diffraction investigations were carried out in order to discuss the influence of the chemical structure of the diol unit on the solid chain structure formed during solution polycondensation. For direct comparison of the polymers it seemed very

Table 4 Comparison of experimental and theoretical scattering data of $(TPA\text{-}HQ)_n$

d_{exp} / nm	d_{calc} /nm	hkl		$\lvert F_{calc} \rvert$		$I_{rel,\ calc}$ / %
-	2.509	0 0 1	0 0 -1	5.6	5.6	1.3
-	0.6198	1 0 2	-1 0 -2	27.3	27.3	1.9
0.504	0.5022	0 1 2	0 -1 2	45.4	45.4	3.3
0.448	0.4477	1 1 0	1 -1 0	168.6	168.6	100
		-1 1 0	-1 -1 0	225.3	225.3	
0.411	0.4337	1 1 -2	-1 1 2	47.0	47.0	6.4
		1 -1 -2	-1 -1 2	56.4	56.4	
	0.4105	-1 1 2	1 -1 2	47.7	47.7	2.4
0.3883	0.3881	2 0 0	-2 0 0	227.7	227.7	48.5
0.3178	0.3164	-2 1 2	2 -1 -2	81.5	81.5	11.4
		-2 -1 2	2 1 -2	110.5	110.5	
-	0.3085	2 0 -6	-2 0 6	64.5	64.5	2.4
0.2980	0.2985	-2 -1 -2	2 1 2	78.7	78.7	9.7
		2 -1 2	-2 1 -2	109.5	109.5	
	0.2977	2 1 -4	-2 -1 4	63.4	63.4	2.1
	0.2932	1 1 6	-1 -1 -6	72.7	72.7	4.2
		-1 1 -6	1 -1 6	74.1	74.1	
0.2720	0.2698	2 -1 4	-2 1 -4	71.4	71.4	4.6
0.2681		-2 -1 -4	2 1 4	74.9	74.9	
0.2509	0.2506	1 2 -2	1 -2 2	78.3	78.3	2.2
0.2336	0.2304	-3 -1 0	3 1 0	172.3	172.3	9.1
0.2296						
0.1847	0.1831	3 -2 2	-3 2 -2	87.7	87.7	1.3
-	0.1583	4 2 0	-4 -2 0	113.1	113.1	1.5

important to synthesize all samples with comparable synthesis conditions.

Wide angle X-ray diffractograms of regular copolyesters selected from the structures given in *Table 2* are shown in *Figure 1*.

Taking the kind of X-ray scattering curves together with a formal estimation of crystallinity into account the discussion of following groups is suggested:

(1) high crystalline polymers;
(2) partial crystalline polymers;
(3) frozen nematic structures;
(4) non-crystalline polymers.

The group of high crystalline polymers consists of only *p*-linked phenylene rings connected by ester bonds (polymers **1a** and **1c**). Introduction of kinks by *m*-substituted phenylene rings is expressed in a moderate decrease of crystallinity (polymers **2a** and **2b**). Polymers with rigid bisphenol units with different bridging groups show a compatible decrease of crystallinity (polymers **4** except **4c**). The bridging groups e.g. $-O-$, $-S-$, $-CH_2-$ or $-CO-$ do not in principle give rise to differences in the solid phase structure of the respective polymers. Due to its scattering behaviour, polymer **4c**, with the isopropylidene bridging group, would rather be categorized with the frozen nematic structures. This group is represented by polymers with substituted phenylene rings (side groups such as $-CH_3$ or $-Ph$). Obviously, such polymers are only able to produce a lateral chain order and the crystallinity is suppressed by the bulky side groups. This result corresponds with those discussed in the literature for poly(*p*-phenylene terephthalate)s substituted with arylsulfonyl groups[31–33].

Insertion of aliphatic units leads to an interruption of the rigid aromatic chain (polymers **5a–i**). As in the case of kinked monomers, the crystallinity is reduced as compared to fully aromatic copolyesters. Additionally, larger structures are generated (reflections at intermediate scattering angles). The *d*-spacings of the observed smectic layers show the odd–even effect, as well (compare *Figure 2*). The odd–even effect of melting enthalpies of the transition from the crystalline into the lc state determined by d.s.c. could be established by the WAXS crystallinities. With increasing number of methylene groups in the spacer, a weak reduction of the crystallinity X-ray respective melting enthalpies is found.

An extension of the flexible aliphatic part of the copolyesters with PTMG segments (polymers **7a, 7b**) results in a further decrease of crystallinity (compare ref. 17). Regarding the block copolymers containing non-crystallizable polysulfone segments[35], it should be noted that even with short polysulfone segments ($DP \approx 3.3$, polymer **6**) the length of the mesogenic unit is obviously not sufficient to form ordered structures.

Due to the similarities in the diffraction patterns of the

Table 5 Comparison of experimental and theoretical scattering data of (HBA-TPA-HBA-HQ)$_n$

d_{exp} / nm	d_{calc} /nm	hkl		| F_{calc} |		$I_{rel, calc}$ / %
-	2.538	0 0 1	0 0 -1	11.2	11.2	4.1
0.743	0.7821	1 0 1	1 0 -1	40.3	40.3	5.0
0.708	0.7177	-1 0 2	1 0 -2	40.7	40.7	4.3
	0.7154	1 0 1	-1 0 -1	51.2	51.2	6.8
0.4526	0.4575	-1 -1 1	1 1 -1	91.0	91.0	100
	0.4572	-1 1 0	1 -1 0	188.6	188.6	
		-1 -1 0	1 1 0	225.6	225.6	
	0.4429	1 -1 1	-1 1 -1	44.0	44.0	
-	0.4215	0 1 4	0 -1 -4	36.0	36.0	1.1
0.4130	0.4180	1 1 2	-1 -1 2	37.6	37.6	4.4
		-1 -1 2	-1 1 -2	60.9	60.9	
0.3914	0.3955	-2 0 1	2 0 -1	42.8	42.8	1.4
0.3880	0.3905	-2 0 0	2 0 0	121.1	121.1	25.7
0.3767	0.3771	2 0 1	-2 0 -1	54.2	54.2	2.0
0.3258	0.3259	1 1 -6	-1 -1 6	57.4	57.4	1.7
	0.3251	-1 1 -5	1 -1 5	51.2	51.2	1.3
	0.3238	-2 -1 -1	2 1 -1	72.9	72.9	2.6
	0.3214	-2 1 2	2 -1 -2	53.4	53.4	1.4
0.3184	0.3140	-2 1 3	2 -1 -3	64.4	64.4	5.6
0.3119		2 1 -3	-2 -1 3	89.2	89.2	
0.3046	0.3021	-2 -1 -2	2 1 2	72.8	72.8	8.1
0.3006		-2 1 -2	2 -1 2	116.9	116.9	
0.2384	0.2385	3 1 -1	-3 -1 1	95.0	95.0	2.3
0.2354	0.2364	3 -1 0	-3 1 0	116.2	116.2	3.3
0.2342	0.2296	2 2 -1	-2 -2 1	102.9	102.9	2.5
0.2296	0.2266	-3 1 -2	3 -1 2	72.0	72.0	1.2
0.2274						
0.2210	0.2204	-3 -1 6	3 1 -6	81.4	81.4	1.4

polymers, it was supposed that a monoclinic symmetry discussed in the literature for poly(*p*-phenylene terephthalate)[16] can be used for the formal indication of scattering reflections. Consequently, all examined polymers with *p*- and *m*-linked chains were found to have comparable lattice parameters independent of their individual chain architecture (*Figure 3*).

Despite their similar monoclinic symmetry, the chemical individuality manifests itself in differences in reflection intensities.

In order to support the formal monoclinic indication of the unit cell, calculations were carried out using methods of molecular modelling. The calculations were started with the relative uncomplicated structure of poly(*p*-phenylene terephthalate) and continued with (HBA-TPA-HBA-HQ)$_n$ containing the complex aromatic unit used in all polymers under examination.

Molecular modelling

The calculations required the following steps: determination of geometry of the basic units by means of quantum mechanical *ab initio* methods (basis set 6-31G), generation of the single polymer chain followed by their arrangement in a unit cell taking all symmetry conditions into consideration. Scattering curves were calculated based on the determined atomic coordinates. The model was refined by using the comparison with the experimental scattering curves. This method of structural modelling using powder X-ray diffraction was also applied by Coulter *et al.*[16]. For (TPA-HQ)$_n$ we tried to realize the results reported by Coulter with the calculation programs used in this work. The results are demonstrated in the following.

From *ab initio* calculations of monomeric units (TPA, HQ, HBA) and dimeric units (phenylene-4-benzoate) it was concluded that the phenylene rings can be regarded as being planar. The ester moiety lies approximately in the same plane as the outer phenylene ring of the complex aromatic unit, whereas the following phenylene ring of the diol unit turns out of this plane by the angle Φ_1 due to steric hindrances (*Figures 4* and *5*). Φ_1 was calculated to be 55.5° *in vacuo*. Schürmann *et al.*[36] found

Table 6 Fractional atomic coordinates of TPA-HQ)$_n$

Atom	Residuum	x	y	z
O2	HQ	0.216	0.300	0.032
C3	HQ	0.199	0.339	0.083
C4	HQ	0.097	0.182	0.109
H5	HQ	0.031	0.029	0.087
C6	HQ	0.080	0.222	0.161
H7	HQ	0.000	0.101	0.181
C8	HQ	0.165	0.419	0.189
C9	HQ	0.267	0.575	0.163
H10	HQ	0.333	0.728	0.185
C11	HQ	0.284	0.535	0.111
H12	HQ	0.364	0.657	0.091
O13	HQ	0.148	0.457	0.240
C3	TPA	0.216	0.296	0.277
O4	TPA	0.293	0.121	0.264
C5	TPA	0.198	0.341	0.332
C6	TPA	0.269	0.176	0.371
H7	TPA	0.339	0.014	0.360
C8	TPA	0.252	0.216	0.424
H9	TPA	0.308	0.086	0.454
C10	TPA	0.163	0.421	0.438
C11	TPA	0.092	0.587	0.399
H12	TPA	0.022	0.748	0.410
C13	TPA	0.109	0.547	0.346
H14	TPA	0.053	0.677	0.316
C15	TPA	0.145	0.464	0.494
O16	TPA	0.069	0.641	0.506
O2	HQ	0.217	0.298	0.532
C3	HQ	0.200	0.337	0.583
C4	HQ	0.098	0.180	0.609
H5	HQ	0.032	0.027	0.587
C6	HQ	0.080	0.220	0.661
H7	HQ	0.000	0.098	0.681
C8	HQ	0.165	0.417	0.689
C9	HQ	0.268	0.573	0.663
H10	HQ	0.334	0.726	0.685
C11	HQ	0.285	0.533	0.611
H12	HQ	0.365	0.655	0.591
O13	HQ	0.149	0.455	0.740
C3	TPA	0.217	0.297	0.777
O4	TPA	0.294	0.119	0.765
C5	TPA	0.199	0.339	0.832
C6	TPA	0.270	0.174	0.871
H7	TPA	0.340	0.012	0.860
C8	TPA	0.253	0.214	0.924
H9	TPA	0.309	0.084	0.954
C10	TPA	0.164	0.419	0.938
C11	TPA	0.093	0.585	0.899
H12	TPA	0.023	0.746	0.910
C13	TPA	0.110	0.545	0.847
H14	TPA	0.054	0.675	0.816
C15	TPA	0.146	0.462	0.994
O16	TPA	0.069	0.639	1.006

Table 7 Fractional atomic coordinates of (HBA-TPA-HBA-HQ)$_n$

Atom	Residuum	x	y	z
O2	HQ	0.291	0.282	1.024
C3	HQ	0.285	0.250	0.972
C4	HQ	0.169	0.089	0.945
H5	HQ	0.083	-0.011	0.966
C6	HQ	0.162	0.055	0.890
H7	HQ	0.072	-0.070	0.869
C8	HQ	0.272	0.183	0.863
C9	HQ	0.389	0.344	0.890
H10	HQ	0.474	0.444	0.869
C11	HQ	0.395	0.378	0.944
H12	HQ	0.486	0.503	0.965
O13	HQ	0.266	0.151	0.811
C15	HBA	0.205	0.322	0.777
O16	HBA	0.155	0.506	0.793
C10	HBA	0.198	0.287	0.720
C8	HBA	0.133	0.466	0.684
H9	HBA	0.089	0.631	0.699
C6	HBA	0.127	0.432	0.630
H7	HBA	0.077	0.572	0.603
C5	HBA	0.185	0.219	0.611
C13	HBA	0.249	0.040	0.646
H14	HBA	0.294	-0.125	0.632
C11	HBA	0.255	0.074	0.701
H12	HBA	0.305	-0.066	0.728
O2	HBA	0.178	0.184	0.554
C3	TPA	0.283	0.306	0.528
O4	TPA	0.384	0.446	0.551
C5	TPA	0.276	0.271	0.470
C6	TPA	0.386	0.399	0.443
H7	TPA	0.478	0.525	0.464
C8	TPA	0.380	0.365	0.389
H9	TPA	0.466	0.466	0.367
C10	TPA	0.263	0.204	0.362
C11	TPA	0.153	0.076	0.389
H12	TPA	0.062	-0.051	0.368
C13	TPA	0.160	0.110	0.443
H14	TPA	0.073	0.009	0.465
C15	TPA	0.256	0.168	0.304
O16	TPA	0.156	0.029	0.281
O4	HBA	0.351	0.279	0.281
C5	HBA	0.344	0.243	0.224
C6	HBA	0.280	0.422	0.188
H7	HBA	0.235	0.590	0.203
C8	HBA	0.274	0.389	0.134
H9	HBA	0.223	0.530	0.106
C10	HBA	0.331	0.176	0.115
C11	HBA	0.396	-0.003	0.150
H12	HBA	0.441	-0.170	0.136
C13	HBA	0.402	0.031	0.205
H14	HBA	0.452	-0.110	0.232
C15	HBA	0.324	0.141	0.058

by means of force field calculations (Amber 3.0), considering interactions between neighbouring chains, a Φ_1 of 65° for an aromatic tetramer. Comparable calculations in the literature provided slightly different values (Coulter *et al.*[16]: 67–70°; Blackwell *et al.*[37]: 65.5°).

Using a systematic variation of Φ_1, single polymer chains were calculated. A *trans* conformation of the linked monomer units was assumed for energetical reasons. Structures with defined twisted conformation of the single polymer chains results for both kinds of polymers (compare *Figure 4* and *5*). Consequently, the crystallographic repeating unit is given by four monomer units for both polymers.

The single polymer chains were packed into a finite solid state by variation of the monoclinic parameters a, b, c and β as well as the orientation angle of the chain, Φ_2, and the position vector $\mathbf{r}$, respectively (see *Figure 3*).

The unit cells were constructed taking the center of gravity of the chains on the position $\mathbf{r}$, the maximum moment of inertia in z-direction and the minimal one in x-direction. Consequently, unit cells containing two antiparallel chains were obtained, applying a space group with inversion center. It was tried to calculate a set of optimized parameters by stepwise alteration of the listed variables followed by the comparison of calculated and experimental scattering data. The fit was carried out by minimization of the performance

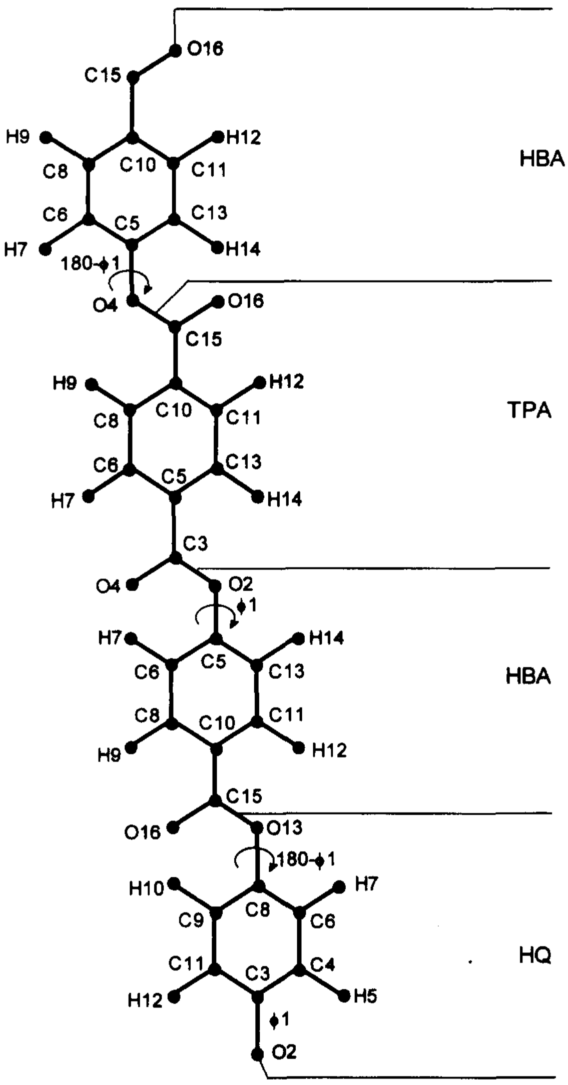


Figure 5 Schematic view on the polymer chain of (HBA-TPA-HBA-HQ)$_n$

coefficient R with

$$R = \frac{\sum(|I_{\mathrm{exp}} - I_{\mathrm{calc}}|)}{\sum(I_{\mathrm{exp}})}$$

Table 4 summarizes experimental and theoretical scattering data for (TPA-HQ)$_n$, and *Table 5* for (HBA-TPA-HBA-HQ)$_n$, respectively. Additionally, the individual lattice parameters are given.

The comparison of experimental and theoretical scattering curves (*Figure 6*: (TPA-HQ)$_n$, *Figure 7*: (HBA-TPA-HBA-HQ)$_n$) shows a good agreement, verified by the respective R values. The result was obtained applying the space group $P\bar{1}$ with $\alpha = \gamma = 90°$.

The rest of the calculation, the theoretical scattering curves, are based on complete sets of aromatic coordinates according to *Tables 6* and *7*. The theoretical peak profiles were computed using Gaussian approximation as the simplest function[38].

The results obtained for (TPA-HQ)$_n$ differ slightly from those reported in literature[16] (see *Table 8*). In this work, a good agreement of experimental and theoretical scattering curves was found by duplication of the crystallographic c-axis caused by the twisted chain conformation and a modified space group.

Owing to the similarities in the WAXS patterns of (TPA-HQ)$_n$ and (HBA-TPA-HBA-HQ)$_n$ the modelling procedure executed for (TPA-HQ)$_n$ including the space group was transferred to the latter. Due to the accordance of experiment and theoretical scattering curve, a similar helical chain conformation can be discussed also for this regular copolyester containing four monomer units.

CONCLUSIONS

The influence of the chemical structure of copolyesters with the general composition (HBA-TPA-HBA-diol)$_n$ on the solid phase structure was examined experimentally by WAXS, as well as theoretically by molecular modelling.

WAXS measurements showed that the solid phase structure of these polymers, as expected, is quite similar due to a common mesogenic unit (HBA-TPA-HBA) included in all polymers. The powder diagrams referred to a monoclinic symmetry. In order to verify that result, the solid phase structure was computed for two polymers, (TPA-HQ)$_n$ and (HBA-TPA-HBA-HQ)$_n$, by means of molecular modelling. Thus, the formal

Table 8 Comparison of lattice parameters experimentally determined and given in literature[16]

	(TPA-HQ)$_n$	(HBA-TPA-HBA-HQ)$_n$	(TPA-HQ)$_n$ Coulter[16]
a (nm)	0.785	0.783	0.834
b (nm)	0.548	0.564	0.550
c (nm)	2.538	2.637	1.265
β (°)	98.62	97.90	98.55
Φ_1 (°)	70	70	67-70
Φ_z (°)	15	19	
$\vec{r}$ [x, y, z]	[1/4, 1/4, 0]	[1/4, 1/4, 0]	
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/a$

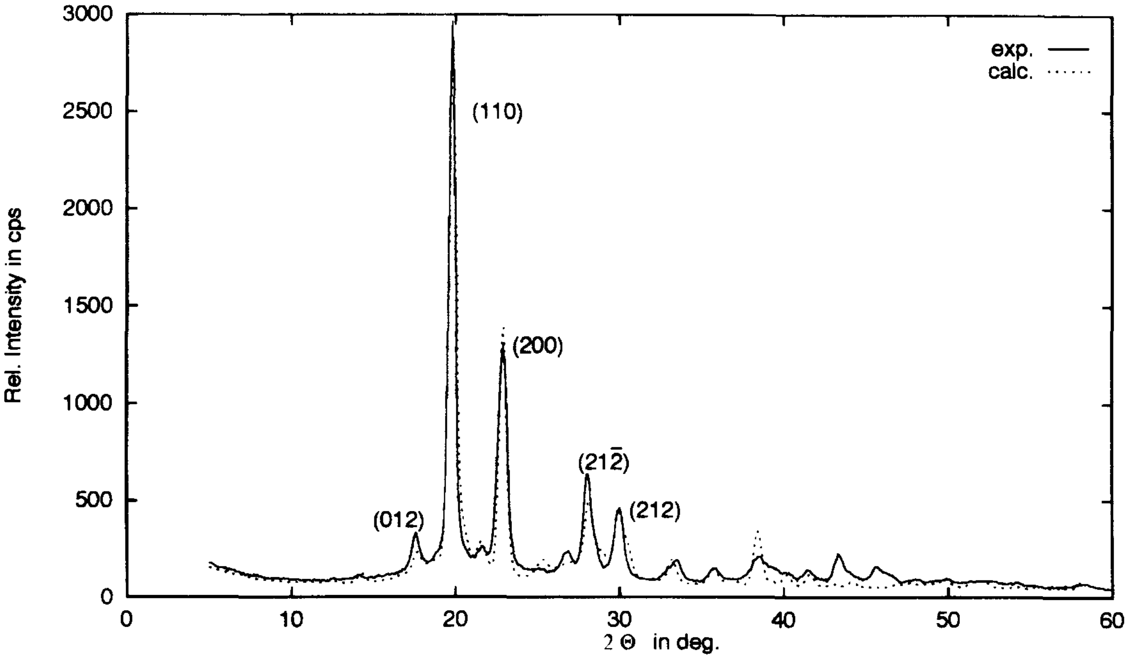


Figure 6 Comparison of experimental and theoretical scattering curves of $(\text{TPA-HQ})_n$, $R = 0.17$

indication of scattering curves was confirmed by the calculated structure.

The obtained results encourage us to continue the combined investigations of WAXS and molecular modelling serving the regular aromatic copolyesters as a model for the partially disturbed structures generated, for instance, by chemical modification of the polymer chain (by introduction of kinked, polar or flexible monomeric units, or changeover to polymers with random chain sequence distribution) or by thermal treatment including melt processing.

Particularly, temperature dependent WAXS investigations of regular aromatic copolyesters with aliphatic spacers in combination with d.s.c. measurements and annealing experiments are in progress in order to describe the structure of re-solidified samples.

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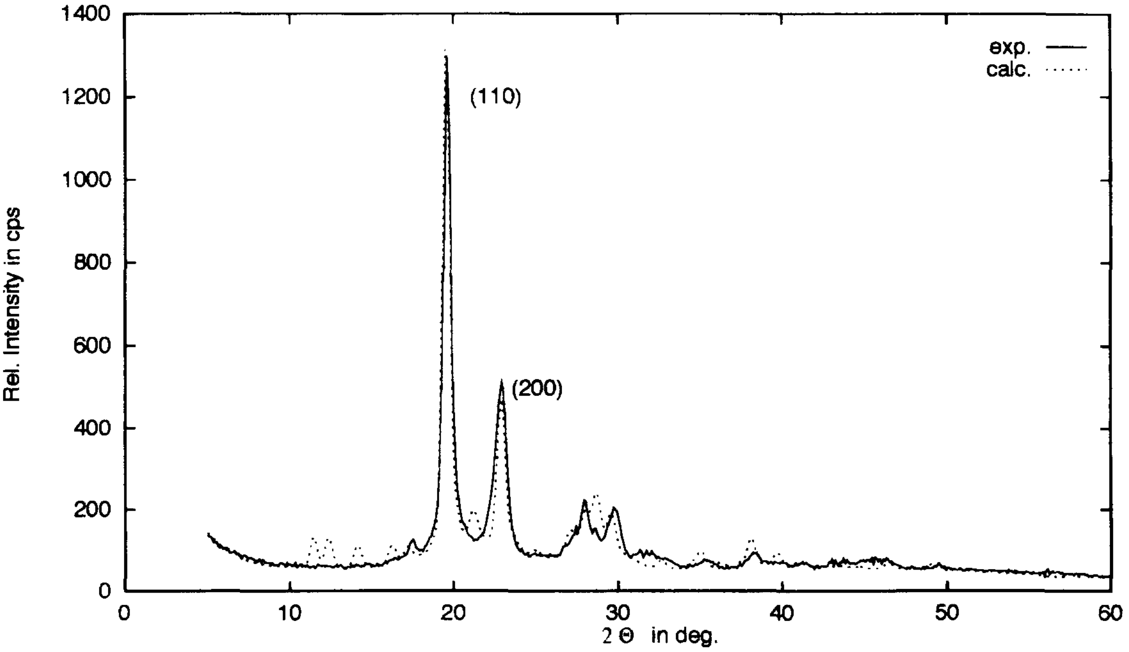

Figure 7 Comparison of experimental and theoretical scattering curves of $(\text{HBA-TPA-HBA-HQ})_n$, $R = 0.16$

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