Thermotropic block copolymers: polyesters with flexible poly(tetramethylene glycol) units in the main chain

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Block copolymers with poly(tetramethylene glycol) (PTMG) spacers of different length and the 4,4'-(terephthaloyldioxy) dibenzoyl unit have been synthesized by high temperature solution polycondensation. The influence of the spacer length on thermal behaviour and solid phase structure of alternating polyesters in comparison with pure PTMG has been determined by d.s.c. and WAXS investigations. Up to spacer molecular weights of 650 g mol^{-1} (degree of polymerization, $\overline{DP} \approx 9$), polymers with thermotropic liquid crystalline phase behaviour are obtained. Above spacer molecular weights of 1000 g mol^{-1} ($\overline{DP} \approx 14$), the coexistence of two crystalline phases resulting in polymers with block-like character is discussed.

(Keywords: aromatic-aliphatic polyesters; thermotropic block copolymers; liquid crystalline; poly(tetramethylene glycol))

INTRODUCTION

In the past 10 years, a variety of thermotropic liquid crystalline polymers (LCPs) with different chemical structures have been synthesized[1–5]. One important group of LCPs are rigid, rod-like materials containing predominantly aromatic units mostly connected by ester links. This group of fully aromatic polyesters has been developed to provide materials with superior mechanical properties (such polymers are distinguished by high strength and high modulus)[5]. Several investigations have been carried out to decrease the comparatively high melting temperature of fully aromatic polymers and to increase their processability, e.g. by incorporation of flexible segments into the polymer main chain[1–3].

Often poly(ethylene glycol)[6–10] and poly(propylene glycol)[11–13] units have been used as flexible spacers. Previously it was shown that polymers in which mesogenic and long flexible elements are linked can have liquid crystalline character. One of the advantages of this special kind of block copolymers is their good solubility as compared to other thermotropic LCPs[14].

Combining liquid crystalline segments and flexible blocks is expected to form new materials with unique properties arising from both components[15]. In order to elucidate the structure–property relationship in LCPs, we synthesized main-chain polyesters with a regular chain structure and poly(tetramethylene glycol) (PTMG) units as the flexible spacers. This alternating chain structure should lead to better chemical characterization[16].

The mesogenic groups used were 4,4'-(terephthaloyldioxy)dibenzoyl units, which are well known from the work of Bilibin *et al.*, who reported segmented liquid crystalline polyesters with this mesogenic unit and poly(ethylene glycol) or poly(propylene glycol) as the flexible spacer[17–19].

Up to now, only a few reports have been published on thermotropic polyesters with PTMG as the flexible unit[20], which shows a high degree of crystallinity in the pure state[21]. The influence of spacer length and concentration on the phase behaviour (solid phase structure and thermal behaviour) have been investigated. The polymers have been synthesized by means of high-temperature solution polycondensation. The synthetic route is shown in *Figure 1*.

EXPERIMENTAL

Materials

PTMG with various molecular weights was supplied by BASF-AG Ludwigshafen (*Table 1*).

Monomer preparation

Terephthaloyl dichloride (1). Terephthalic acid (2 mol) and thionyl chloride (800 ml) were refluxed with dry dimethylformamide (DMF, 4 ml) for 5 h. Excess thionyl chloride was distilled and the crude product filtered off before being recrystallized from dry chloroform (69.9%, m.p. 82°C).

4,4'-(Terephthaloyldioxy) dibenzoic acid (2)[17,18]. *p*-Hydroxybenzoic acid (1.2 mol) was dissolved in 0.5 N NaOH (2.5 l) by stirring for 15 min. Terephthaloyl dichloride (0.5 mol) dissolved in dry tetrachloromethane (1 l) was added dropwise to the first solution by vigorously stirring. Then, 1 N NaOH (1 l) was added to the mixture followed by stirring for 5 h. The resulting

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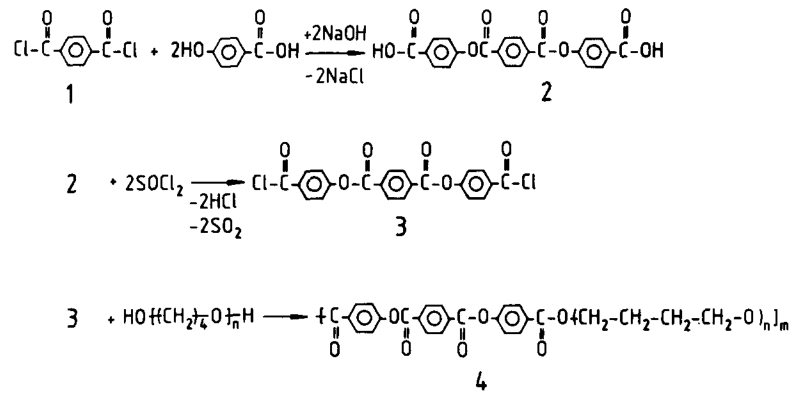

Figure 1 Synthetic route to the block copolymers (**4**)

Table 1 Characterization of the PTMGs used as diol monomers (as given by the producer)

Sample	$\bar{M}_{n,end}$ (g mol^{-1})	$\overline{DP}_{end}$
PTMG 250	248	3
PTMG 650	662	9
PTMG 1000	995	14
PTMG 2000	2026	28
PTMG 2900	2909	40
PTMG 4500	4462	62

Table 2 Elemental analysis of the block copolyesters[a]

Polymer	$\overline{DP}_n$		Elemental analysis C (%)	H (%)
4a	1.00	Calc.	67.83	4.34
		Found	66.91	4.29
4b	3.47	Calc.	67.50	6.24
		Found	67.27	6.20
4c	9.03	Calc.	67.18	8.11
		Found	66.76	8.03
4d	13.89	Calc.	67.05	8.87
		Found	67.04	8.51
4e	27.78	Calc.	66.89	9.81
		Found	67.27	9.13
4f	40.28	Calc.	66.83	10.17
		Found	67.52	8.75
4g	62.50	Calc.	66.77	10.49
		Found	67.17	9.52

[a] Calculations based on **4** in *Figure 1*

product was filtered off, washed successively with 0.5 N HCl, water and acetone, and dried *in vacuo* (74.15%). Found: C, 59.84; H, 3.00. $C_{22}H_{14}O_8$ requires: C, 60.27; H, 3.20.)

I.r.: 3400, 1740, 1610 cm^{-1}.

4,4'-(Terephthaloyldioxy) dibenzoyl dichloride) (*3*)[17,18]. 4,4'-(Terephthaloyldioxy) dibenzoic acid (0.2 mol) was refluxed with thionyl chloride (1.2 l) and dry DMF (4 ml) for 2 h. The crude product was filtered off and recrystallized from dry chloroform (34.15%, m.p. 226°C). (Found: C, 57.52; H, 5.5. $C_{22}H_{12}Cl_2O_6$ requires: C, 59.62; H, 2.71; Cl, 16.02; O, 21.68.)

I.r.: 1790, 1740, 1600, 720 cm^{-1}. ^{13}C n.m.r.: 170.7, 166.1, 156.4, 133.9, 132.1, 131.2 and 122.6 ppm [at 75.475 MHz, in $CDCl_3$/trifluoroacetic acid (1:1 v/v)].

Polymer preparation

4,4'-(Terephthaloyldioxy) dibenzoyl dichloride (20 mmol) and the appropriate PTMG (20 mmol) in α-chloronaphthalene (40 ml) were put into a three-necked flask equipped with a N_2 inlet, stirrer and distilling head. The polycondensation reaction was carried out at 220°C for 2 h in nitrogen atmosphere and by continuous stirring. After cooling to ambient temperature, the polymer was precipitated in methanol (200 ml), filtered off, extracted in a Soxhlet apparatus for 9 h with methanol and dried in a vacuum oven at 50°C for 18 h.

The results of the elemental analysis of the block copolyesters (**4**) are given in *Table 2*.

Polymer characterization

The solution viscosities of the polymers were measured with a Berger–Deckert viscometer (capillary IV) at 25°C in a 50/50 (v/v) mixture of phenol and 1,1,2,2-tetrachloroethane with a polymer concentration of 0.5 g dl^{-1}.

The molecular weight distribution curves of the block copolymers were determined in a 1/3 (v/v) mixture of *m*-cresol and chloroform by a Knauer GPC at ambient temperature with Merck LiChrogel PS 400/PS 4 separation columns and RI detection. The samples were first dissolved in a 1/1 (v/v) mixture of pentafluorophenol/chloroform and then diluted with the eluent. The molecular weights were calculated using narrow distributed polystyrene fractions.

The molecular weight distributions of the PTMG samples were determined by means of a modular built gel permeation chromatograph at ambient temperature on Merck LiChrogel PS1/PS4/PS40 separation columns and RI detection with tetrahydrofuran as eluent. The molecular weight distributions were calculated using a calibration curve based on the results obtained by end group analysis. The results obtained using a calibration by poly(ethylene glycol) gave higher values than expected.

I.r. spectra were recorded on a Bruker FT-IR IFS 66.

Melting ranges were determined on a Boetius hot stage polarizing microscope. The calorimetric investigations were performed with a Perkin-Elmer DSC 7 using a scan rate of 10 K min^{-1}. The uniform thermal history was produced by heating the samples to 30 K above the melting temperature followed by subsequent cooling.

X-ray scattering curves were obtained with a HZG 4A-2 diffractometer (FPM GmbH, Germany), using

Ni-filtered CuKα radiation by a symmetric transmission procedure.

RESULTS AND DISCUSSION

Figure 2 shows the molecular weight distribution curves measured by g.p.c. of the PTMG samples used as diol monomers. *Table 3* gives the chemical characterization of the PTMG samples and the block copolymers. The molecular weights of the copolyesters are in the range of 15000–35000 g mol^{-1}. A correlation between the polydispersities of PTMG and the copolyesters (**4**) was not found.

The thermal behaviour of pure PTMG is influenced by crystallization at ambient temperature. Therefore, a double melting peak is obtained in d.s.c. measurements during the first heating run. The intensity ratio of these peaks depends on the storage time. A similar behaviour is found for block copolymers having PTMG units with molecular weights of >2000 g mol^{-1}. *Figure 3* shows the influence of storage on the transitions of polymer **4g** after 4 and 15 weeks. The d.s.c. curves of the second heating are comparable. For this reason, only the thermal behaviour represented by the second heating run is discussed in the following.

Figure 4 shows the dependence of the melting on the molecular weight of pure PTMG. The peak temperature increases with increasing molecular weight. Coincidentally, the melting ranges become narrower due to a narrower molecular weight distribution in PTMG with a higher degree of polymerization ($\overline{DP}$, see *Figure 2*).

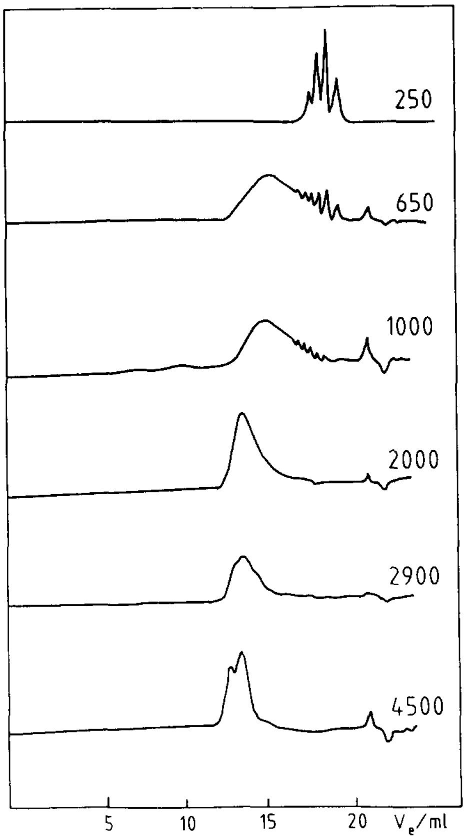

Figure 2 Molecular weight distribution curves of PTMG samples determined by g.p.c.

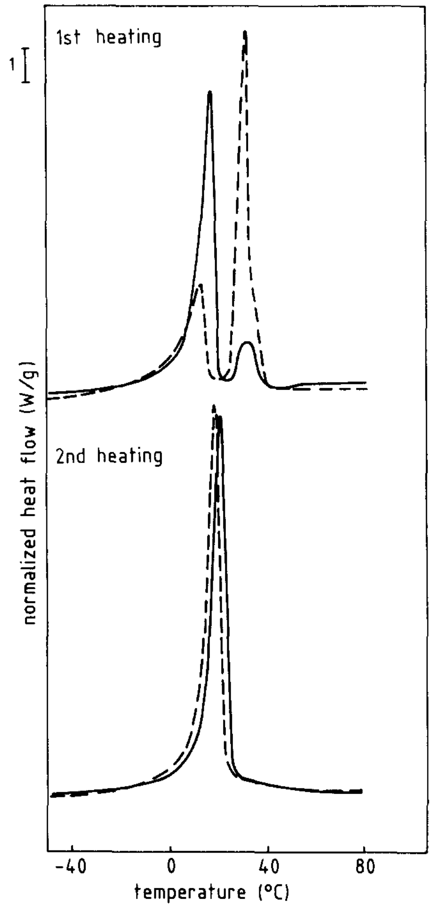

Figure 3 Influence of storage time at ambient temperature on the thermal behaviour of polymer **4g** investigated by d.s.c.: (——) 4 weeks after synthesis; (– – –) 15 weeks after synthesis

Table 3 Chemical characterization of PTMG samples and the copolyesters (**4**) by g.p.c.

	PTMG spacer			Polymer properties			
Sample	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	η_{inh}[a] (dl g^{-1})	$\bar{M}_n$ ($\times 10^4$ g mol^{-1})	$\bar{M}_w$ ($\times 10^4$ g mol^{-1})	$\bar{M}_w/\bar{M}_n$
4a	88	–	–	–[b]	–[b]	–[b]	–[b]
4b	256	278	1.09	0.649	1.23	3.91	3.21
4c	668	1072	1.60	0.501	0.65	1.58	2.42
4d	953	1340	1.40	0.452	1.00	2.53	2.52
4e	2123	2514	1.18	0.563	1.70	3.66	2.16
4f	2275	2615	1.14	0.365	1.14	2.56	2.23
4g	4277	4321	1.01	0.388	1.16	2.58	2.05

[a] Determined by viscosity measurements

[b] Not soluble

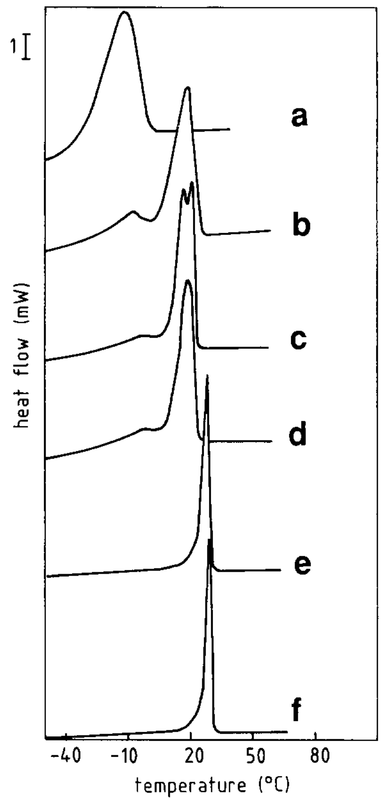

Figure 4 Thermal behaviour of PTMG with different molecular weights investigated by d.s.c.: (a) PTMG 250; (b) PTMG 650; (c) PTMG 1000; (d) PTMG 2000; (e) PTMG 2900; (f) PTMG 4500

PTMG 250 mainly consists of four oligomers characterized by a melting behaviour deviating from those of the higher oligomers. Parts of such oligomers can be detected by g.p.c. up to PTMG molecular weights of 2000 g mol^{-1} (*Figure 2*). The melting of these parts is reflected by the occurrence of a distinct peak situated in the melting range of PTMG 250 (*Figure 4*).

The d.s.c. curves of the block copolymers (**4**) (*Figure 5*) show that their melting behaviour is influenced by the aromatic units and the PTMG (see also *Table 4*).

The thermal behaviour of the block copolymers having PTMG spacers with molecular weights of 2000 g mol^{-1} ($\overline{DP} \approx 28$) and above is dominated by the spacer, whereas those having molecular weights of 1000 g mol^{-1} ($\overline{DP} \approx 14$) are determined by the aromatic units. *Figure 6* shows the melting enthalpies of crystallites representing the aromatic units and the spacer units.

By using polarizing microscopy, a decrease in the melting temperatures with increasing length of the PTMG spacer is observed (*Table 4*). Such behaviour has also been reported for polymers of 4,4′-(terephthaloyldioxy) dibenzoic acid containing poly(ethylene glycol) units[9,18,22,23]. The melting ranges of block copolymers containing PTMG are lower than those of block copolymers with poly(ethylene glycol) spacers of comparable $\overline{DP}$[22].

Polymer **4a** with 1,4-butanediol and polymers **4b** and **c** having PTMG spacers of 250 and 650 g mol^{-1}, respectively, show liquid crystalline behaviour in the melt, similar to results found by Bilibin *et al.*[18] and Galli *et al.*[22] for polymers having ethylene glycol spacers.

The liquid crystalline temperature range of PTMG polymers is lower and smaller than that of poly(ethylene glycol) polymers[9,18,22,23]. According to d.s.c. investigations, in the case of polymer **4b** the transition from the crystalline state to the liquid crystalline one is reversible, whereas polymer **4c** exhibits monotropic nematic phase behaviour (after cooling the polymer from the isotropic melt to the crystalline state, in the next heating run a

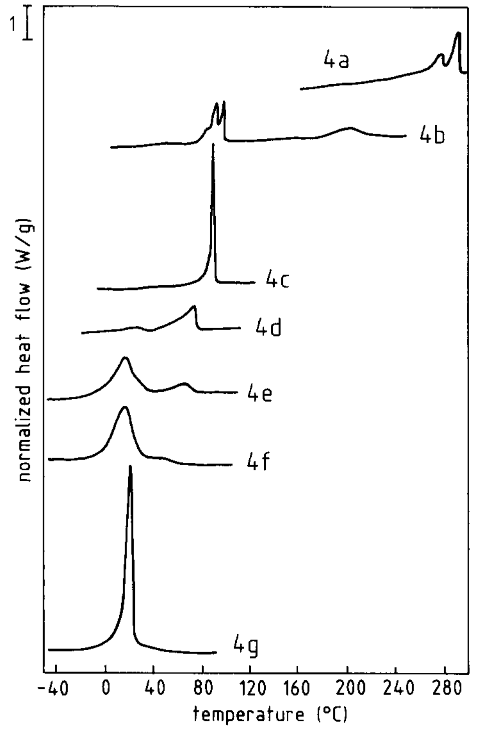

Figure 5 Melting behaviour of block copolymers (**4**) investigated by d.s.c.

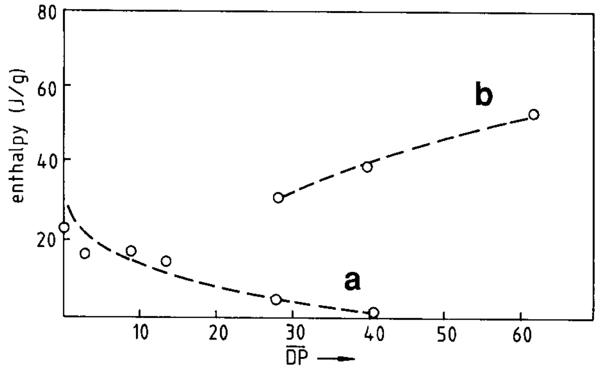

Figure 6 Influence of the $\overline{DP}$ of the PTMG spacer on the melting enthalpy of the block copolymers (**4**): (a) melting of the aromatic units; (b) melting of the PTMG spacer

Table 4 Thermal and phase behaviour of the copolyesters (**4**) determined by means of polarizing microscopy and d.s.c.

	Microscopy[a]			D.s.c. (2nd heating)	
Polymer	$T_{\text{cr-LC}}$ (°C)	$T_{\text{LC-i}}$ (°C)	Phase behaviour[b]	$T_{\text{m,spacer}}$ (°C)	$T_{\text{m,arom.units}}$ (°C)
4a	290	>520	LC	–	276.0/289.0
4b	183	225	LC	–	91.5/97.0
4c	92	115	LC	–	89.5
4d	–	<70	i	289.0	73.0
4e	–	<70	i	17.0	66.0
4f	–	<70	i	17.0	47.5
4g	–	<70	i	21.5	–

[a] Original samples
[b] LC, liquid crystalline; i, isotropic

liquid crystalline phase cannot be observed). Corresponding to results found by Galli *et al.*[22], block copolymers having a spacer with $\overline{DP} \approx 14$ did not exhibit liquid crystalline melts.

In the WAXS investigations of the polymers, comparison with pure PTMGs with different molecular weights was carried out in order to explain the structures obtained. The results of the WAXS measurements are shown in *Figure 7* and *Table 5*.

Low molecular weight PTMG forms at ambient temperature an isotropic melt, whereas partially crystalline states have been found for intermediate molecular weights, and a highly ordered structure for PTMG 4500. The crystalline phase has a monoclinic structure, which has been described by Cesari *et al.*[24], with $a = 0.561$ nm, $b = 0.892$ nm, $c = 1.225$ nm and $\beta = 134°30'$.

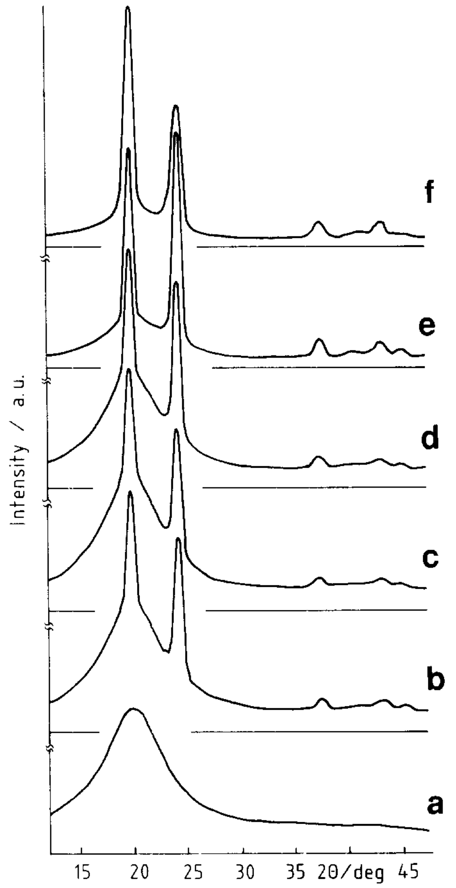

Figure 7 X-ray diffraction patterns of PTMG and the dependence on their molecular weights: (a) 250 g mol^{-1}; (b) 650 g mol^{-1}; (c) 1000 g mol^{-1}; (d) 2000 g mol^{-1}; (e) 2900 g mol^{-1}; (f) 4500 g mol^{-1}

Table 5 Structural data of PTMG 4500

h	k	l	$d_{calc.}$ (nm)[a]	$d_{meas.}$ (nm)	$I_{rel.}$[b]
0	2	0	0.446	0.451	vs
0	2	1	0.400	0.407	w
1	1	0	0.366	0.368	vs
	?		–	0.330	vw
1	3	0	0.239	0.240	m
0	4	0	0.223	0.224	w
−1	1	5	0.221	0.220	w
−2	2	5	0.209	0.210	m
2	0	0	0.200	0.200	w
2	2	0	0.182	0.183	m
−3	1	5	0.185	0.182	m
−1	3	5			

[a] According to ref. 24

[b] w, weak; vw, very weak; m, medium; vs, very strong

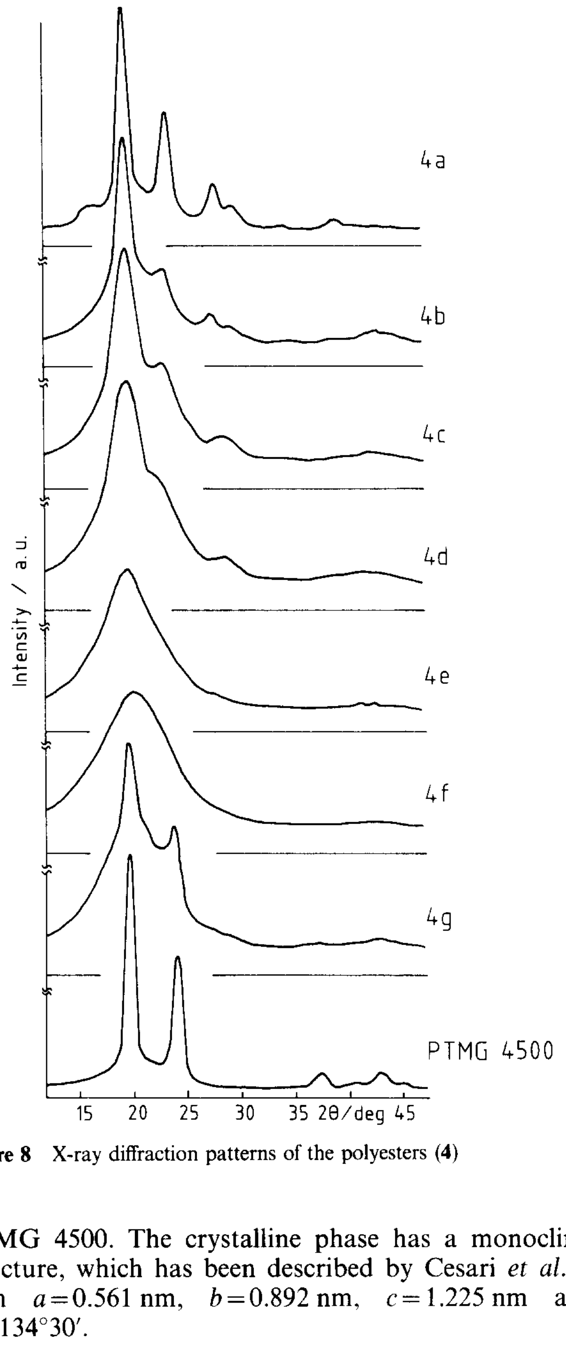

Figure 8 X-ray diffraction patterns of the polyesters (4)

WAXS investigations at ambient temperature reveal two effects superimposed on each other. First, crystalline structures are obtained which are directly influenced by the chemical composition of the sample (spacer length). Second, the diffraction curves are changed by the temperature dependence of the structures obtained.

Figure 8 gives a summary of the WAXS curves of the copolyesters (**4**). Up to spacer molecular weights of 1000 g mol^{-1}, the ordered phase of the polymers is determined by the structure based on poly(oxycarbonyl-1,4-phenyleneoxycarbonyl-1,4-phenylenecarbonyloxy-1,4-phenylenecarbonyloxytetramethylene) (**4a**). With increasing spacer length this structure becomes more and more disturbed, which is evidenced by a reduction in crystallinity and an increase in the half path width of the reflections (the quality of order and the degree of order decrease). For samples **4d**–**f**, the measuring temperature of the WAXS investigations is in the range of the phase transition, i.e. the X-ray diffraction curves of these samples reflect the scattering behaviour of partially molten polymers (polymer **4e** and **f**). Above

Table 6 Structural data of poly(oxycarbonyl-1,4-phenyleneoxycarbonyl-1,4-phenylenecarbonyloxy-1,4-phenylenecarbonyloxytetramethylene)[a]

h	k	l	$d_{\text{calc.}}$ (nm)	$d_{\text{meas.}}$ (nm)	$I_{\text{rel.}}$
0	0	4	?	0.834	vw
0	1	0	0.555	0.554	m
1	1	0	0.459	0.459	vs
0	0	8	?	0.423	w
2	0	0	0.382	0.382	vs
2	1	0	0.322	0.322	s
2 −2	−1 1	0 0	0.308	0.304	m
	?		–	0.288	vw
1	2	0	0.265	0.264	w
2	2	0	0.223	0.231	m
2 −2	−2 2	0 0	0.219	0.220	w
4	0	0	0.191	0.191	vw
	?		–	0.185	vw

[a] Indices of (0 0 1) reflections are uncertain

spacer molecular weights of 2900 g mol^{-1}, the order behaviour of the PTMG sequences determines the structure of the ordered phase.

The structural data of poly(oxycarbonyl-1,4-phenyleneoxycarbonyl-1,4-phenylenecarbonyloxy-1,4-phenylenecarbonyloxytetramethylene) are listed in *Table 6*. The scattering behaviour is typical of a variety of highly aromatic copolyesters[25–27]. These polymers mainly have an orthorhombic or monoclinic crystal structure, and at higher temperatures often have a pseudohexagonal structure.

Calculations of the crystal structure of **4a** refer to a monoclinic structure (*Table 6*) within the bounds of measuring accuracy. The following lattice parameters have been found: $a = 0.764$ nm, $b = 0.555$ nm and $\gamma = 87°23'$. Because of transesterification reactions and irreversible conformation changes occurring in the melt of alternating copolyesters[27,28], it is impossible to produce oriented samples of these polymers having the chain structure and solid phase structure of the as-polymerized samples. Therefore, c, α and β could not be determined using the meridional scattering.

CONCLUSIONS

The polymers synthesized by polycondensation of 4,4′-(terephthaloyldioxy) dibenzoic acid with OH-terminated PTMG show liquid crystalline phase behaviour in the melt up to a PTMG molecular weight of 650 g mol^{-1} and a $\overline{DP} \approx 9$, respectively.

Above a molecular weight of 1000 g mol^{-1}, a biphasic region is observed in which the block-like character of the polymers is increased. In accordance with d.s.c. investigations, the biphasic region is characterized by the coexistence of two distinct crystalline phases. The first one is formed by PTMG units, and the second one by crystallized aromatic units. Both crystalline phases have been distinguished by WAXS as monoclinic structures.

In polyesters with a PTMG spacer of 4500 g mol^{-1} the polymer properties (solid phase structure and thermal properties) are determined by the spacer. The phase separation observed is less significant than in copolyesters of PTMG and longer aromatic units with a random chain structure as described by Wang and Lenz[20]. They reported a phase separation in a 'hard block' phase and a 'soft block' phase. The different results are due to the fact that the polymers regarded in this paper have a shorter mesogenic unit and a less favourable relationship between rigid and soft units. The alternating chain structure of the polymers discussed prevents the formation of a liquid crystalline phase at longer spacer lengths. In order to obtain polymers with longer PTMG spacers which show liquid crystalline behaviour, the length of the aromatic unit has to be increased. Therefore, further investigations have been carried out on copolyesters of 4,4-(terephthaloyldioxy) dibenzoic acid with PTMG and hydroquinone as the aromatic monomer[29].

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