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LC-polyimide 38. Smectic poly(ester-imide)s of *N*,*N*-bis (4-hydroxy-phenyl)biphenyl-3,3′,4,4′-tetracarboxylic imide having long aliphatic spacers. Part I

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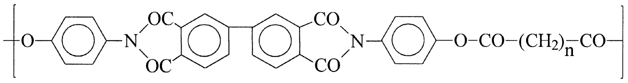
Abstract

A new monomer (**7**) was prepared by alkylation of *N*,*N*,-bis(4-hydroxyphenyl)biphenyl-3,3′,4,4′-tetracarboxylic imide with 11-bromo-undecanol. This imide diol (**7**) did not form a LC-phase, but showed two reversible first-order transitions in the solid state. It was poly-condensed with various aliphatic dicarboxylic acid dichlorides in 1-chloronaphthalene. The phases and phase transitions of the resulting poly(ester-imide)s were characterized by optical microscopy, DSC measurements and X-ray measurements at variable temperature. All poly(ester-imide)s formed a crystalline smectic phase in the solid state. In the case of short spacers enantiotropic smectic-A phase were observed which vanished in the case of long spacers. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: LC-polyimides; Long spacers; Smectic phases

1. Introduction

In the previous publications of this series the syntheses and properties of the poly(ester-imide)s, PEIs, **1**



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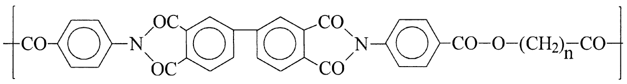

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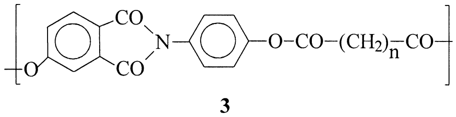
were reported [1,2]. Several members of both series of PEIs showed a monotropic smectic-A phase and a few formed an enantiotropic smectic-A phase. This property differs largely from those of the PEIs **3**



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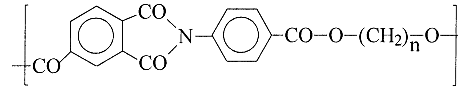

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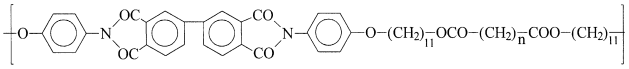
which form either an enantiotropic nematic phase (**3**) [3] or a monotropic smectic phase (**4**) [4–6]. Another interesting observation concerns the influence of the spacer length. In the case of **3** and **4** an increasing length of the spacers (up to 20 CH_2 groups) reduced the temperature range of the LC-phase and finally caused its disappearance. In contrast, a greater temperature range of the smectic LC-phase was found for the PEIs **1** and **2** when the length of their spacer increased. This structure property relationship is quite unusual and prompted us to study the influence of spacers having more than 20 CH_2 groups. Because such long alkane diols or dicarboxylic acids are not commercial and difficult to synthesize, the spacers were composed of three building blocks and the PEIs **5a**–**5d**



5 a-d **a**: n = 4 **b**: n = 8 **c**: n = 12 **d**: n = 20

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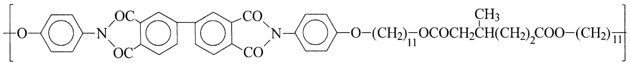
were synthesized. Furthermore, the chiral PEI **5e**



5 e

was prepared and compared to **5a**.

2. Experimental

2.1. Materials

Biphenyl-3,3′,4,4′-tetracarboxylic anhydride (BTCA) was a gift of Dr Becks AG (BASF, Hamburg) and was used as received. The 4-aminophenol was a gift of Bayer AG (Leverkusen). The *N*,*N*′-bis-(4-hydroxyphenyl)biphenyl-3,3′,4,4′-tetracarboxylic imide was prepared from BTCA and 4-aminophenol in refluxing *m*-cresol as described previously [1]. 11-Bromoundecanol, potassium *tert*-butoxide and all dicarboxylic acids were purchased from Aldrich Co. (Milwaukee, WI, USA) and used as received. The acid chlorides of the dicarboxylic acids were prepared in a refluxing mixture of chloroform and freshly distilled thionyl chloride (volume ratio 1:1), and they were purified by distillation.

2.2. *N,N′-bis(4-(11-hydroxyundecyloxy)biphenyl-3,3′,4,4′-tetracarboxylic imide*

N,*N*′-bis(4-hydroxyphenyl-3,3′,4,4′-tetracarboxylic imide (75 mmol) was dissolved in dry dimethylformamide (500 ml) and potassium *tert*-butoxide (160 mmol) was added. After 30 min 11-bromoundecanol (160 mmol) was added, and the reaction mixture was stirred for 24 h at 25°C and for 1 h at 80°C. After cooling the reaction mixture was poured into cold water containing crushed ice. The precipitated product was filtered off, washed with water, dried in vacuo and recrystallized from dioxane.

Yield: 91%, m.p. 220–222°C. Analyses calcd. for $C_{50}H_{60}N_2O_8$ (817.0): C 73.50%, H 7.40%, N 3.43%; found: C 73.13%, H 7.13%, N 3.59%. ^{1}H NMR ($CDCl_3$/TFA, 4/1): δ (ppm) = 1.0–2.0 (m, 36H), 4.2 (t, 4H), 4.4 (t, 4H), 6.9–7.3 (m, 8H), 8.0–8.4 (m, 6H).

2.3. Polycondensations

Procedure A: The monomer (6 mmol) and the dicarboxylic acid dichloride (6 mmol) were weighed into a cylindrical glass reactor equipped with a mechanical stirrer, gas-inlet and gas-outlet tubes and dry 1-chloronaphthalene (60 ml) were added. The reaction vessel was placed into an oil bath, the temperature was rapidly raised to 240°C and maintained for 24 h. The evolved HCl was removed with a slow stream of nitrogen.

Procedure B: The monomer (5 mmol) and a dicarboxylic acid dichloride (5 mmol) were weighed into a cylindrical glass reactor equipped with a mechanical stirrer, gas-inlet and gas-outlet tubes and dry 1-chloronaphthalene (5 ml) were added. The reaction vessel was heated in an oil bath to 200°C and this temperature was maintained for 16 h. The resulting poly(ester-imide) was worked up as described above.

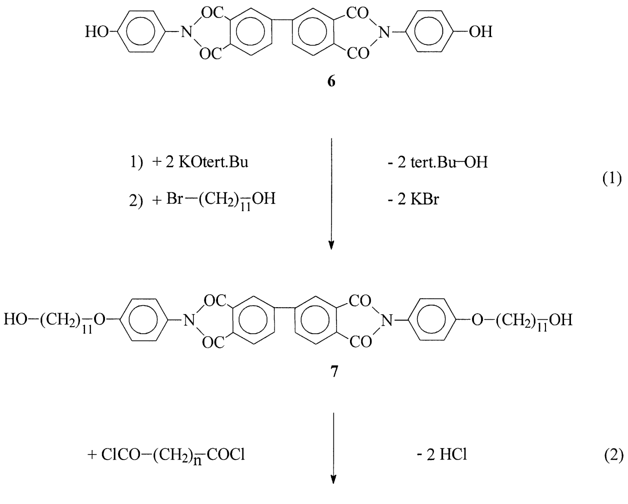
2.4. Measurements

The inherent viscosities were measured with an automated Ubbeholde viscometer thermostated at 25°C. The DSC measurements were performed on a Perkin–Elmer DSC-4 in aluminum pans under nitrogen. Indium was used for the calibration. An Olympus BH-2 microscope equipped with a Linkham hot-stage was used for the optical microscopy. The 400 MHz ^{1}H NMR spectra were recorded with a Bruker AM 400 FT-NMR spectrometer in a $CDCl_3$/TFA mixture (4/1 by volume) containing TMS. The IR spectra were recorded from KBr pellets on a Nicolet FT-IR spectrometer. The X-ray measurements were conducted with synchroton radiation ($\lambda = 1.54$ Å) at HASYLAB (DESY, Hamburg). A position sensitive one-dimensional detector was used along with a heating and cooling rate of 10°C/min.

3. Results and discussion

3.1. Syntheses

The poly(ester-imide)s PEIs, **5a**–**5e** were all prepared by polycondensation of the imide diol **7** with the corresponding dicarboxylic acid dichlorides (Eq. (2)). The monomer **7** was prepared by alkylation of the imide diphenol **6** (described in a previous paper [1]) with 11-bromoundecanol (Eq. (1)).



5 a-d

The thermal properties of this monomer (**7**) were examined by optical microscopy and DSC measurements. The first heating revealed a softening or melting process at 220–222°C followed by total isotropization at 230–232°C. At this temperature a weak endotherm is detectable in the

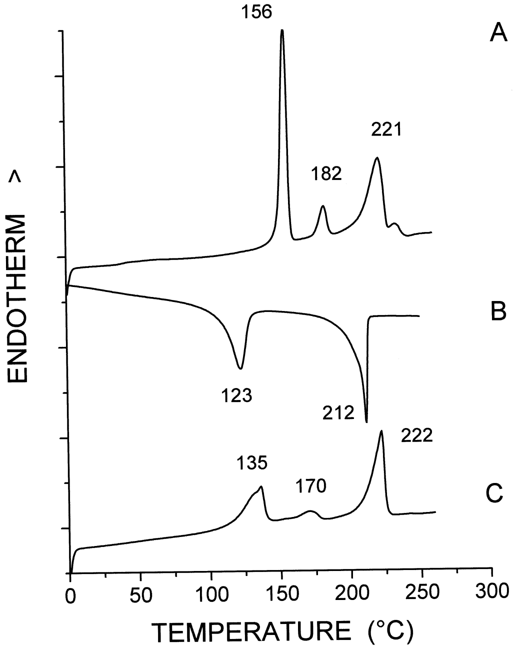


Fig. 1. DSC measurements of the imide diol **7** recorded with a heating and cooling rate of 20°C/min: (A) first heating; (B) first cooling; (C) second heating.

DSC trace (A in Fig. 1), but this endotherm is not reproducible in the second and third heating curves. In contrast, the melting endotherm at 220–222°C was perfectly reproducible (Fig. 1). Due to the narrow temperature range and the lack of reproducibility it is not clear what happens between 222 and 230°C during the first heating. However, two more reproducible endotherms were detectable in the heating curves indicating reversible first order phase transitions in the solid state. A detailed X-ray structure analysis of the individual modifications was not intended in this work.

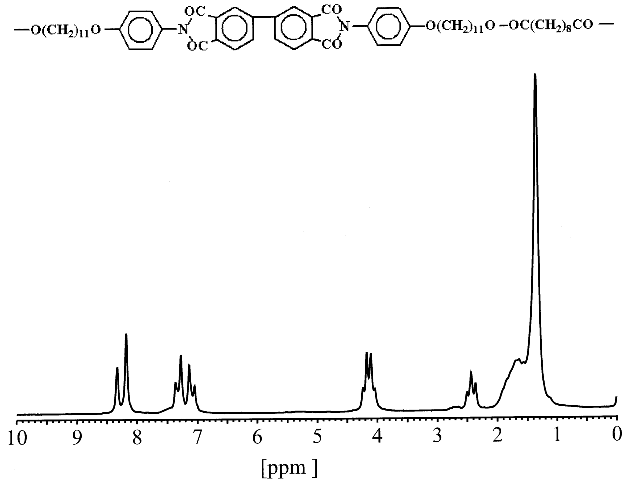


Fig. 2. 400 MHz ^{1}H NMR spectrum of PEI **5b**.

The polycondensation of diol **7** with various aliphatic dicarboxylic acid dichlorides was conducted in 1-chloronaphthalene with elimination of HCl. No HCl acceptor was added to avoid deprotonation of the acid chlorides with the concomitant formation of instable ketene groups. 1-Chloronaphthalene was selected to obtain homogenous reaction mixtures. Nonetheless, only moderate viscosity values were obtained (Table 1). Possibly the reaction temperature was too high and caused side reactions of the acid chlorides despite the absence of a base. The isolated PEIs were characterized by elemental analyses (see Table 1) and by ^{1}H NMR spectra. These analytical results were in good agreement with the expected structures. The ^{1}H NMR spectrum of PEI **5e** is exemplarily displayed in Fig. 2. The protons of the C_6H_3-imide units show up around 8.2 ppm both doublets of the aminophenol units at 7.1 and 7.3 ppm, the O–CH_2 protons at 4.1 ppm, the CH_2CO protons at 2.4 ppm and all other CH_2 protons between 1.0 and 2.0 ppm.

Table 1
Yields and properties of the PEIs **5a**–**5e**

Polymer no.	CH_2 groups	Yield (%)	η_{inh}[a] (dl/g)	Elemental formula (formula weight)	Elemental analyses			
						C	H	N
5a[b]	4	78.0	0.50	$C_{56}H_{66}N_2O_{10}$ (927.1)	Calcd.	72.55	7.18	3.02
					Found	71.57	6.91	3.17
5b[b]	8	85.5	0.60	$C_{60}H_{74}N_2O_{10}$ (983.3)	Calcd.	73.29	7.59	2.85
					Found	72.95	7.32	3.11
5c[c]	12	91.0	0.80	$C_{64}H_{82}N_2O_{10}$ (1039.3)	Calcd.	73.96	7.95	2.70
					Found	72.67	7.81	2.80
5d[c]	20	90.0	0.36	$C_{72}H_{98}N_2O_{10}$ (1151.6)	Calcd.	75.10	8.58	2.43
					Found	73.95	8.33	2.43
5e[b]	–	70.5	0.52	$C_{57}H_{68}N_2O_{10}$ (941.2)	Calcd.	72.44	7.28	2.98
					Found	71.86	7.13	3.31

[a] Measured at 25°C with $c = 2$ g/l in CH_2Cl_2/TFA (volume ratio 4:1).

[b] Prepared via procedure A.

[c] Prepared via procedure B.

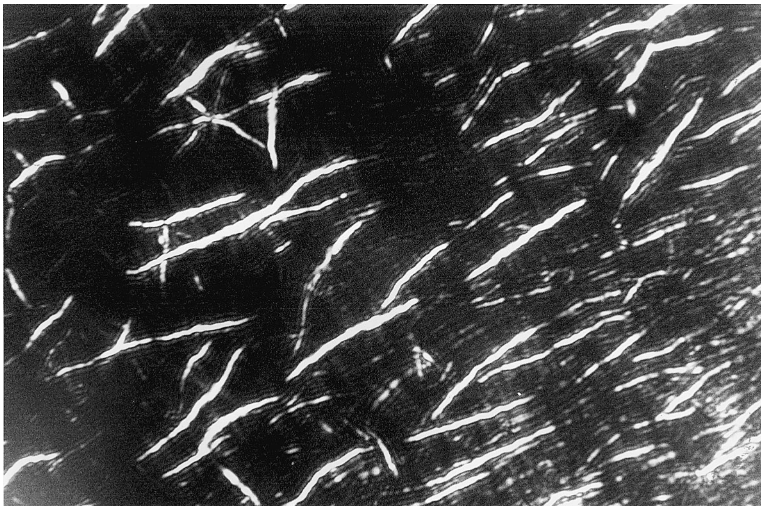


Fig. 3. Bâtonet texture of PEI **5b** observed upon slow cooling from the isotropic melt.

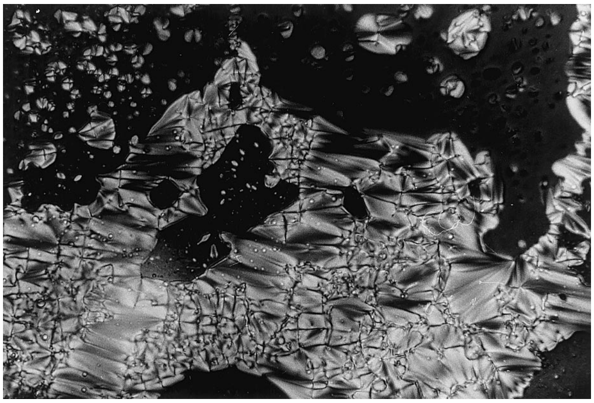


Fig. 4. Fan-shaped texture of PEI **5b** obtained upon further cooling of the bâtonet texture (Fig. 3).

3.2. LC-phases and phase transitions

The thermal properties of the PEIs **5a**–**5e** were characterized by optical microscopy (with crossed polarizers), by DSC measurements (with a heating/cooling rate of 20°C/min) and by middle angle (MAXS) and wide angle (WAXS) X-ray scattering (with variation of the temperature).

By optical microscopy an enantiotropic LC-phase was detected for the PEIs **5a** and **5b** but not for **5c** and **5d**. In the case of **5a** and **5b** a "sandy texture" was found for the LC-phase upon heating. Yet, upon slow cooling a typical "bâtonet texture" was observed (Fig. 3) which slowly changed to a "fan-shaped texture" (Fig. 4). These optical properties are characteristic of a smectic A-phase, and in this connection it is worth noting that smectic A-phases were also found for the related PEIs **1**, **2** and **4**. The results of the optical microscopy and of the DSC measurements clearly indicate that the increasing length of the spacers reduces the isotropization temperature (T_i in Table 2). This tendency is well known from various LC-polyesters containing aliphatic spacers including the PEIs **3** and **4**. However, for the PEIs **1** and **2** it was found that the temperature range of the LC-phase increases with the length of the aliphatic spacer. Yet, the maximum length of the commercial spacers was limited to 22 CH_2 groups. This maximum length is somewhat shorter than the maximum length of the spacers in **5a**–**5d**. When the phase transitions of the PEIs **1**, **2** and **5a**–**5d** are combined in one plot, the scheme of Fig. 5 is the result. This scheme demonstrates that neither short nor very long spacers allow for the existence of an enantiotropic LC-phase. Consequently the temperature range of the

Table 2
Phase transitions and layer distances (*d*-spacings) of PEIs **5a**–**5e**

Polymer no.	T_m[a] (°C)	T_i[a] (°C)	T_{ai}[b] (°C)	T_{cr}[b] (°C)	T_m[c] (°C)	T_i[c] (°C)	Textures
5a	230 (198)	275	265	211 (168)	235–240	280–285	Bâtonet + fan
5b	223 (187/197)	259	250	209 (166)	225–230	265–275	Bâtonet + fan
5c	215	–	213	200	220	–	Bâtonet
5d	209	–	–	192–194	205	–	–
5e	225	255	236	208	235–240	260–265	Bâtonet

[a] DSC measurements: second heating (+20°C/min).
[b] DSC measurements: first cooling (−20°C/min).
[c] Optical microscopy: heating rate 10°C/min.

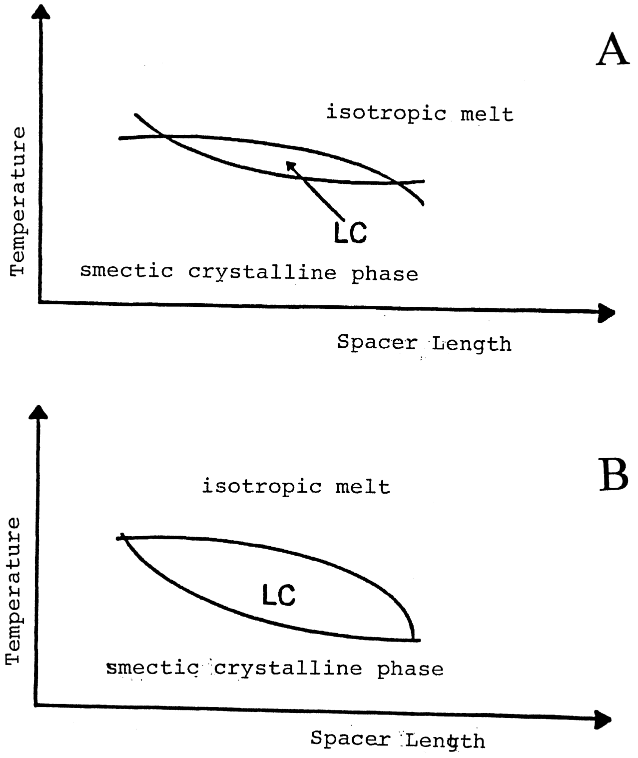


Fig. 5. Schematic illustration of the influence of the spacer length on the stability of the enantiotropic LC-phase (smectic-A) of PEIs **1**–**4** (A) upon heating, (B) upon cooling.

LC-phases passes through a maximum, when plotted against the lengths of the spacers. This "spacer–temperature window" widens upon cooling, because the beginning of the crystallization is kinetically more hindered (i.e. super cooling due to nucleation) than the beginning of the anisotropization. To the best of our knowledge such a scheme has never been formulated before. This interesting LC-phase/spacer relationship requires LC-polymers containing a long mesogen (longer than those of the PEIs **3** and **4**) and spacers with a length up to 40–50 C- or O-atoms. Neat difunctional alkanes of this length are not commercially available and are difficult to synthesize in a pure form in 50–100 g quantities. Therefore, PEIs **1** and **2** in combination with PEIs **5** and **6** represent an unique case of studies of structure-property relationships of segmented LC-polymers.

The DSC measurements of the PEIs **5a** and **5b** showed two endotherms in the heating curves. In agreement with the results of the optical microscopy the first endotherm (T_m in Table 2) indicates the melting process and the second endotherm (T_i in Table 2) the isotropization. The corresponding exotherms, T_{ai} for the anisotropization and T_{cr} for the crystallization, were observable in the cooling traces (Fig. 6). The identification of the exotherm T_{cr} in a crystallization process is not only based on optical microscopy. It is also evident from the observation that this exotherm shows a pronounced supercooling effect, when the measurements are repeated with various cooling rates. By variation of the cooling rate it was also possible to detect the existence of a monotropic LC-phase in the case of **5c** (Fig. 7). This shortlived LC-phase was not detectable by optical

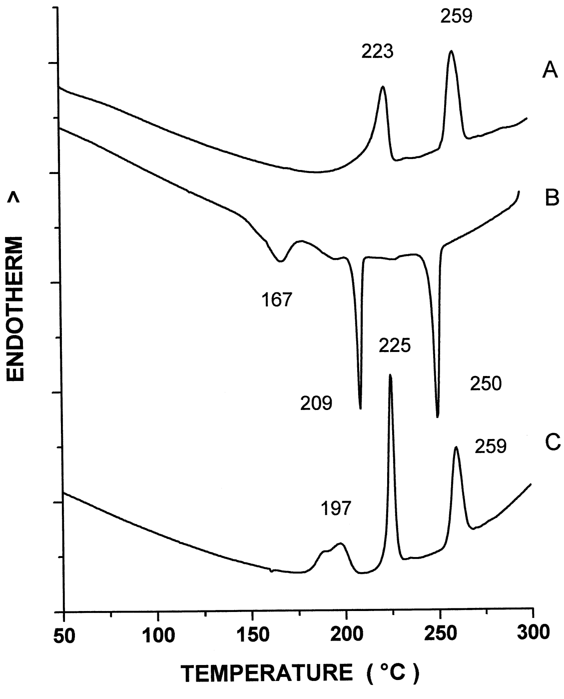


Fig. 6. DSC measurements of PEI **5b**.

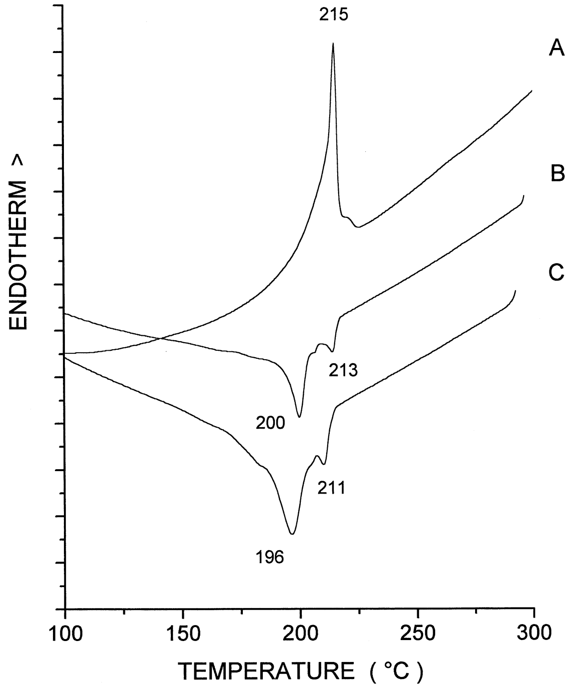


Fig. 7. DSC measurements of the PEI **5c**: (A) second heating (+20°C/min); (B) first cooling (−20°C/min); (C) second cooling (−40°C/min).

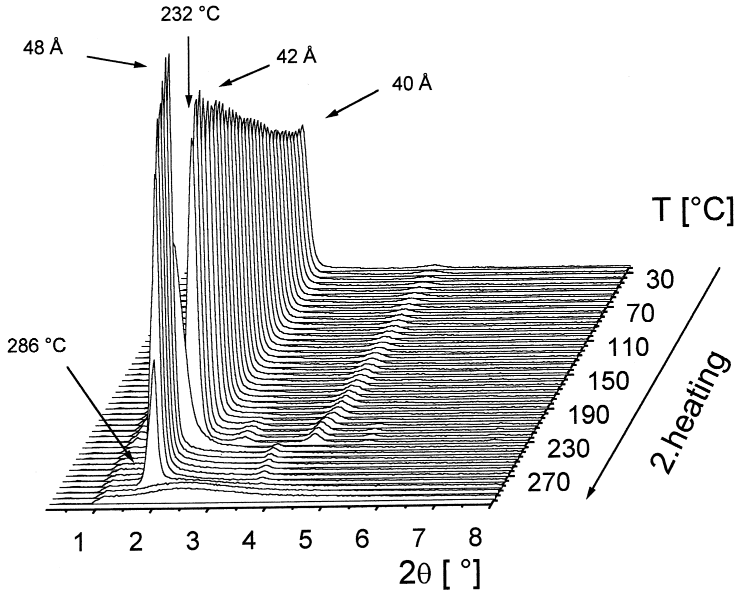


Fig. 8. Synchrotron radiation measurements (middle angle reflections) of PEI **5a** upon heating with 10°C/min.

Table 3
Experimental layer distances and calculated lengths of the repeat units of PEIs **5a**–**5d**

Polymer no.	n	d-Spacing of the solid state (Å)[a]	d-Spacing of the melt (Å)	Lengths of the repeat unit *cisoid*[b]	Length of the repeat unit *transoid*[b]
5a	4	40–42	48.0	47.5	48.5
5b	8	42–44	51.0	51.0	52.5
5c	12	44–46	–	56.0	56.5
5d	20	52–54	–	66.0	65.5
5e	(4)	36–37	46.5	47.5	48.5

[a] Between 25°C and T_m an expansion of the layer distances by 2 Å was observed.

[b] Calculated by molecular modeling programm (ACCU model™) for 1:1 *gt* conformations of the spacers and *cisoid* or *transoid* mesogen.

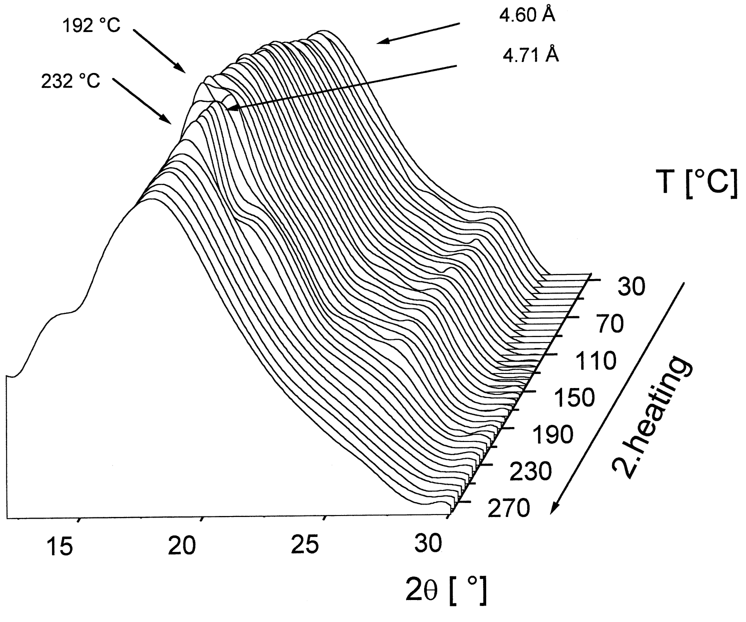


Fig. 9. Synchrotron radiation measurements (wide angle reflections) of PEI **5a** upon heating at 10°C min.

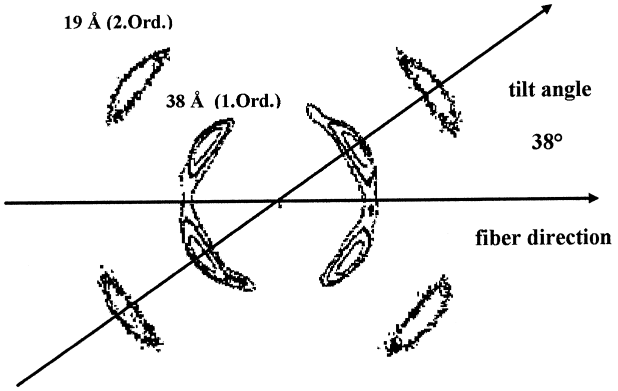


Fig. 10. Fiber pattern of PEI **5b**.

microscopy. However, in the case of **5d** no LC-phase was found regardless which method or cooling rate was applied.

Finally, it should be mentioned that the thermal properties of the chiral PEI **5e** were quite similar to those of **5a**, in agreement with the short spacer introduced by the methyl adipic acid. The optical microscopy revealed a bâtonet texture upon slow cooling from the isotropic melt, and the DSC curves displayed two endotherms in the heating curve and two exotherms in the cooling trace in agreement with an enantiotropic LC-phase.

3.3. X-ray measurements

Synchroton radiation measurements of the middle angle region and of the wide angle region were performed at a heating and cooling rate of 10°C/min. For the second heating of all PEIs, a strong and sharp middle angle reflection (MAR) was observed along with a weak second-order reflection as exemplarily "illustrated" in Fig. 8. These MARs indicate the existence of a layer structure in the solid state and in the LC-melt. The layer distances (*d*-spacing) calculated via the Bragg equation are compiled in Table 3. Furthermore, the lengths of the repeat units were calculated by computer modeling assuming an equimolar population of *gauche* and *trans* conformation of the spacers which is a reasonable approximation of the reality for LC-melt and at least two extreme conformations of the imide group (*cisoid* and *transoid* see Ref. [2]) were also taken into account. The experimental *d*-spacing determined for LC-phase of **5a** and **5b** show a good agreement with the calculated lengths of the repeat unit. This result means that the repeat units adopt a perpendicular array relative to layer plane in perfect agreement with the existence of a smectic A-phase which was assumed on the basis of a bâtonet texture. Furthermore, no sharp wide angle reflections were observed for the LC-phase (Fig. 9). In contrast to the LC-phase, the layers of the solid state possess distances which are considerably shorter than the maximum lengths of the repeat units (Table 3). In principle, the difference between the experimental *d*-spacings and maximum calculated ones may be explained by an intensive coiling of the spacers or by a tilting of the repeat units. A discrimination between both hypotheses should be feasible by X-ray measurements of fiber patterns. Unfortunately, fibers having a high degree of orientation were only obtained in the case of **5b** and **5c** presumably because these PEIs had the highest molecular weights. As demonstrated by Fig. 10 the fiber patterns of **5b** displayed the "8 point pattern" expected for the first- and second-order MARs of a solid smectic phase with tilted repeat units. A tilt angle of 52° relative to the layer (or 38° relative to the fiber axis) was derived from this pattern. Surprisingly, the fiber pattern of **5c** (Fig. 11) did not indicate any tilting of the chains and this result cannot be explained at this time. In this connection it should be mentioned that for all other polyimides having a crystalline smectic solid state with short layer distances a smectic-H with tilted mesogens was proven and not an intensive coiling of the spacers [7].

Finally, the WAXS patterns need short discussion (a detailed study was not intended in this work). The WAXS patterns of all the PEIs studied in this work were almost identical for two reasons. First, the mesogens and their lateral packing were identical in all cases. Second, the neighboring layers of mesogens were too distant to contribute to the X-ray scattering. In other words each mesogen layer behaved like an individual crystallite from the viewpoint of WAX scattering. Characteristic for these WAXS patterns is a broad intensive reflection representing the closest lateral distance of the mesogens (4.60 Å). Weaker, additional reflections indicate that the chain packing is not hexagonal, but orthogonal in analogy to a smectic-E or smectic-H phase. Such a packing of imide mesogens has been observed for numerous PEIs [7].

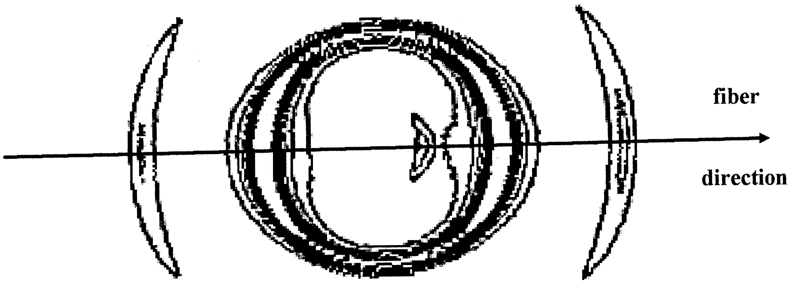


Fig. 11. Fiber pattern of PEI **5c**.

4. Conclusions

A new class of poly(ester-imide)s was prepared from biphenyl-3,3′,4,4′-tetracarboxylic anhydride in combination with unusually long aliphatic spacers. As expected for such a regular sequence polar mesogens and nonpolar spacers crystalline layer structures (most likely of the smectic-H type) were found for the solid state. The existence of an enantiotropic LC-phase was found to depend on the lengths of the spacer in such a way that long spacers reduced the stability of the LC-phase. Taking into account the previously published properties of similar poly(ester-imide)s having even shorter spacers the following conclusion may be drawn. For main chain LC-polyesters containing long mesogens, the temperature range of the enantiotropic LC-phase (most likely smectic-A) passes through maximum when plotted against the lengths of the spacers.

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