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LC-POLYIMIDES. 37. POLY(ESTER-IMIDE)S DERIVED FROM N,N'-*BIS*(4-CARBOXY-PHENYL)BIPHENYL-3,3'-4,4'-TETRA-CARBOXYLIC IMIDE AND VARIOUS α,ω-DIHYDROXYALKANES

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LC-POLYIMIDES. 37. POLY(ESTER-IMIDE)S DERIVED FROM N,N'-*BIS*(4-CARBOXY-PHENYL)BIPHENYL-3,3'-4,4'-TETRA-CARBOXYLIC IMIDE AND VARIOUS α,ω-DIHYDROXYALKANES

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ABSTRACT

A new imide monomer was prepared from ethyl-4-amino-benzoate and biphenyl-3,3'-4,4'-tetracarboxylic anhydride (BTCA). This new momoner was polycondensed with various α,ω-dihydroxyalkanes. The resulting poly(ester-imide)s, PEIs, were characterized by elemental analyses, inherent viscosities DSC-measurements optical microscopy, and X-ray measurements using synchrotron radiation. All PEIs formed a crystalline smectic H-phase in the solid state. Depending on the length of the spacer individual members of this series formed either an enantiotropic smectic-A phase, a monotropic smectic-A phase or no liquid crystalline phase at all. Long spacers and odd numbers of CH_2-groups favored the formation of liquid-crystalline (LC-) phases.

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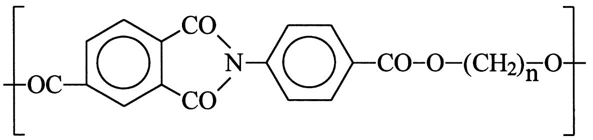
INTRODUCTION

This work is a continuation of previous studies dealing with the PEIs **1** – **3** [1-8]. The PEIs of structure **1** do not form enantiotropic LC-phases, but upon rapid cooling monotropic smectic A phases were detected [2, 9, 10]. The most interesting aspect of these PEIs is the finding that they can adopt three different kinds of layer structures in the solid state depending on the thermal his-



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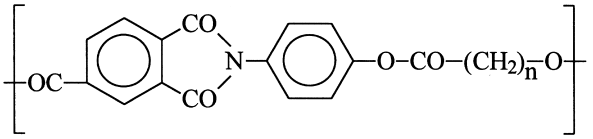

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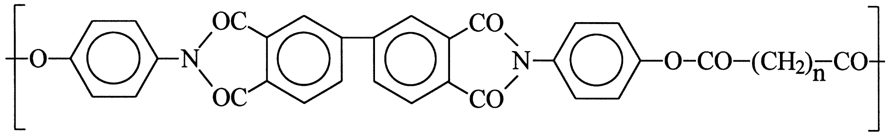

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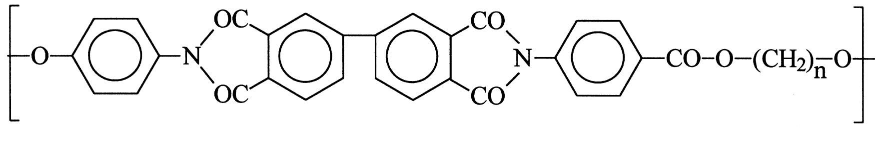


4

a: n = 7
b: n = 8
c: n = 9
d: n = 10
e: n = 12
f: n = 16

tory [2, 3, 11]. The PEI's 2 have similar, exactly isomeric repeating units, but their properties are quite different from those of the PEIs 1, because the PEIs 2 can form an enantiotropic nematic melt [4, 5]. This nematic melt vanishes gradually with increasing length of the spacers [5]. The longer mesogenic moieties of the PEI's 3 have the consequence that several members of this series can adopt an enantiotropic smectic LC-phase but never a nematic phase [6]. In other words, the thermal properties of all three closely related classes of PEIs are quite different. Therefore, it was of interest to study the properties of the PEI's 4**,** and to compare them with those of the PEIs 1 and those of the isomeric PEIs 3.

EXPERIMENTAL

Materials

Biphenyl-3,3'-4,4'-tetracarboxylic anhydride (BTCA) was a gift of Dr. Becks AG (Hamburg, FRG) and was used as received. Ethyl 4-aminobenzoate and all α,ω-dihydroxy alkanes were purchased from Aldrich Co. (Milwaukee, Wisc., USA). The diols were dried over P_4P_{10} *in vacuo* prior to use. The 1-chloronaphthalene was a gift of Bayer AG (Leverkusen, FRG) and was distilled *in vacuo.*

N,N'-Bis(4-ethoxycarbonylphenyl) Biphenyl-3,3'-4,4'-tetracarboxylic Imide

BTCA (0.2 mol) and ethyl 4-aminobenzoate (0.4 mol) were dissolved in dry dimethylfomanide (700 mL) and stirred at 120°C for 4 hours. The reaction mixture was then cooled to 80°C, acetic anhydride (0.5 mol) was added and the stirring was continued at 120°C for an additional 4 hours. After cooling, the reaction mixture was poured into cold water, the precipitated product was isolated by filtration, dried, and recrystallized from chloroform/toluene. Yield 78%, $T_m = 235°C$, determined by DSC at a heating rate of 20°C/min.

Analyses Calcd. for $C_{34}H_{24}N_2O_8$ (588.72): C 69.38, H 4.11, N 4.72, found: C 68.95, H 3.98, N 4.51% ^1H NMR ($CDCl_3$/TMS): $\delta = 1{,}42$ (t, 6 H), 4.42 (q. 4 H), 7.64 (d, 4 H), 8.13-8.26 (m, 11 H) ppm.

Polycondensations

The imide monomer (10 mmol) and an α,ω-dehydroxyalkane 10 mmol) were dissolved in 1-chloronaphthalene (70 ml), and dibutyltin oxide (10 mg) was added. This solution was stirred at 240°C for 24 hours, whereby the eliminated ethanol was removed with a slow stream of nitrogen. The cold viscous reaction mixture was diluted with 1-chloronaphthalene to allow for filtration of the precipitated poly(ester-imide). The product was then dissolved in a mixture of CH_2Cl_2 and trifluroacetic acid (volume ratio 4:1) and precipitated into methanol. The isolated polymer was dried *in vacuo* at 80°C.

Measurements

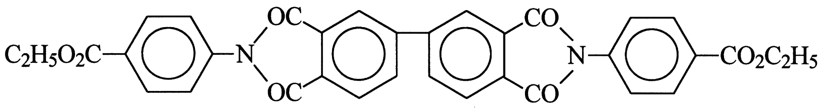
The inherent viscosities were measured in an automated Ubbelohde viscometer thermostated at 20°C. The DSC measurements were conducted with a Perkin Elmer DSC-7 in aluminum pans under nitrogen, using a heating and cooling rate of 20°C/min. The ^{1}H NMR spectra were recorded with a Bruker AC-100 FT NMR spectrometer in 5 mm o.d. sample tubes. A 4:1 (volume ration) mixture of $CDCl_3$ and trifluoroacetic acid containing TMS was used as solvent.

The small angle and wide angle X-ray measurements were performed with synchrotron radiation of $2\Theta = 1.50$ nm at HASYLAB (DESY, Hamburg). A position-sensitive one-dimensioned detector was used and a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Syntheses

All PEIs of this work were prepared by polycondensation of the imide monomer **5** with α,ω-dihydroxyalkanes. The new monomer **5** was prepared in a conventional manner from BTCA and ethyl 4-aminobenzoate by means of acetic anhydride as cyclization agent. Suprisingly, several attempts to obtain soluble PEI's by polycondensation in bulk at temperatures of 230-250°C failed, because the reaction products were partially crosslinked. All polycondensations performed in concentrated solutions of 1-chloronaphthalene or diphenyl ether also yielded partially crosslinked polymers. However, when the concentrations of the monomers in 1-chloronaphthalene were lowered entirely soluble PEI's were obtained. Their yields and inherent viscosities were summerized in Table 1. The structure and purity of all PEI's was checked by elemental analyses (Table 1) and by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra displayed the signals expected for structure **4** and the ratio of aliphatic and aromatic protons also agreed with this structure. An example is presented in Figure 1.



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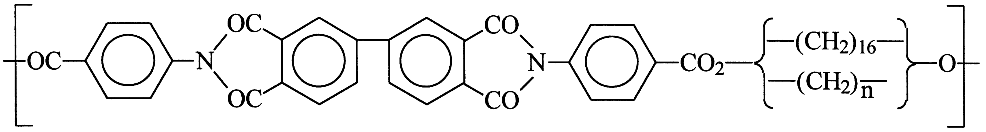
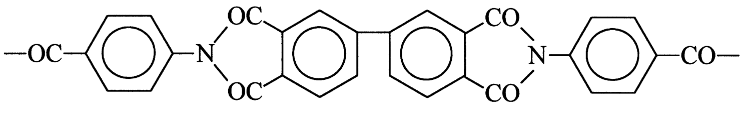
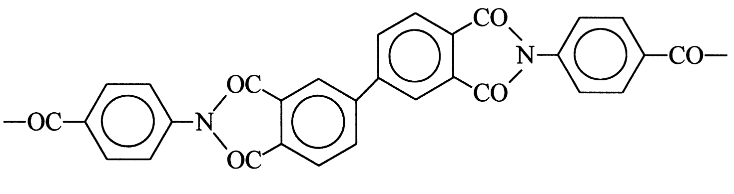


6a: n = 7
6b: n = 8



7a: cisoid



7b: transoid

In addition to the homopolymers **4a-4f**, two copolymers were prepared in an analogous way The imide monomer **5** was polycondensed with an equi-molar mixture of two different diols. The 1,16-hexane diol was either mixed with 1,7-heptandiol or with 1,8-octane diol. The yields and properties of the resulting copoly(ester imide)s **6a** and **6b** were also listed in Table 1.

Properties of the PEIs having Odd Spacers (4a, 4c)

All PEIs of this work were characterized by optical microscopy by DSC measurements and by X-ray scattering using synchrotron radiation with a variation of the temperature. When the PEIs possessing spacers with an odd number of CH_2 groups (odd PEIs, **4a** and **4c**) were examined by these three methods

TABLE 1. Yields, Viscosities, and Elemental Analyses of the Poly(ester-imide)s

Polym. No.	Yield %	$\eta_{inh.}$[a] (dL/g)	Elem. Formula (Form. weight)	Elemental Analyses			
					C	H	N
4a	94.0	0.60	$C_{37}H_{28}N_2O_8$	Calcd	70.69	4.49	4.48
			(628.6)	Found	70.23	4.76	4.29
4b	82.0	0.42	$C_{18}H_{30}N_2O_8$	Calcd	71.02	4.71	4.36
			(642.6)	Found	70.30	4.75	3.82
4c	51.5	0.80	$C_{39}H_{32}N_2O_8$	Calcd	71.33	4.91	4.27
			(656.7)	Found	70.95	5.05	4.08
4d	82.5	0.47	$C_{40}H_{34}N_2O_8$	Calcd	71.63	5.11	4.18
			(670.7)	Found	71.34	5.20	4.01
4e	87.0	0.45	$C_{42}H_{38}N_2O_8$	Calcd	72.19	5.48	4.01
			(698.8)	Found	71.56	5.55	3.83
4f	95.0	0.53	$C_{46}H_{46}N_2O_8$	Calcd	73.19	6.14	3.71
			(765.9)	Found	72.60	6.17	3.39
6a	90.0	0.55	$C_{83}H_{74}N_4O_{16}$	Calcd	72.06	5.39	4.05
			(1383.5)	Found	71.72	5.31	3.88
6b	73.0	0.60	$C_{84}H_{76}N_4O_{16}$	Calcd	72.19	5.48	4.01
			(1397.5)	Found	71.68	5.50	3.70

[a] Measured at 20°C with c=2g/L in CH2Cl2/trifluoroacetic acid (volume ratio 4:1)

quite similar phase transitions, and supermolecular structures were found. Upon cooling the optical microscopy revealed the formation of a viscous LC-phase, which was mobile when slight shear forces were applied. Upon slow cooling the typical Bâtonet texture of a smectic-A phase (Figure 2) was observable for both odd PEIs. However, upon heating a viscous LC-phase showing a sandy texture was only found for **4c**. In other words, **4a** only forms a monotropic smectic-A phase, but **4c** an enantiotropic one.

This interpretation of the optical microscopy was confirmed by DSC and synchrotron radiation measurements (the temperatures of the phase trans-ition were summarized in Table 2). The DSC heating trace of **4a** exhibited one endotherm (T_m in Table 2) and two exotherms were detectable in the cooling trace. The high temperature exotherm showed little supercooling (246 to 240°C) when the cooling rate was varied, whereas a supercooling effect of 17°C was found for the second exotherm representing the crystallization process. In the case of **4c,** the isotropization endotherm (T_i) appeared 11°C above the melting

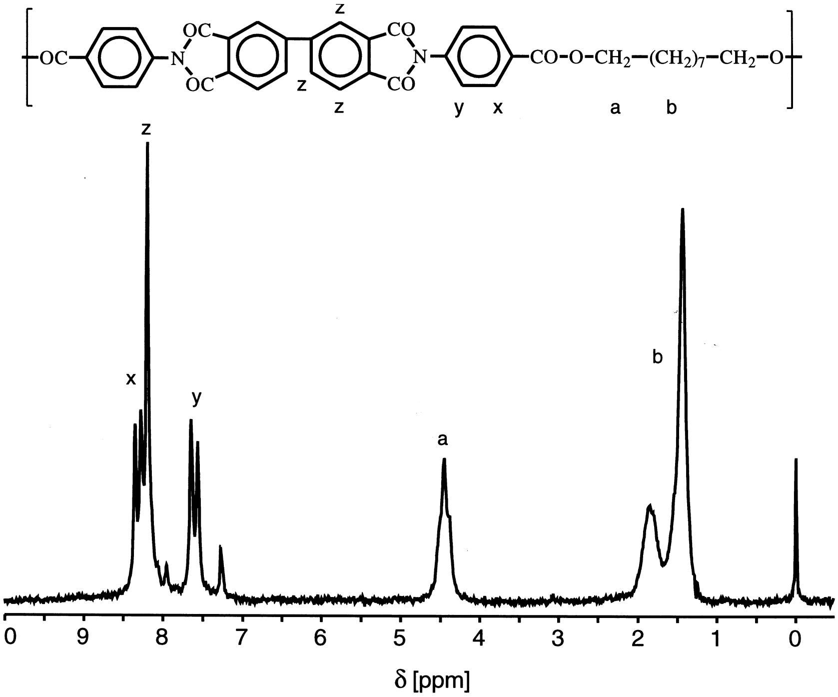


Figure 1. 100 MHz ^{1}H NMR spectrum of the PEI **4c** recorded in $CDCl_3$/trifluoroacetic acid (volume ratio 4:1).

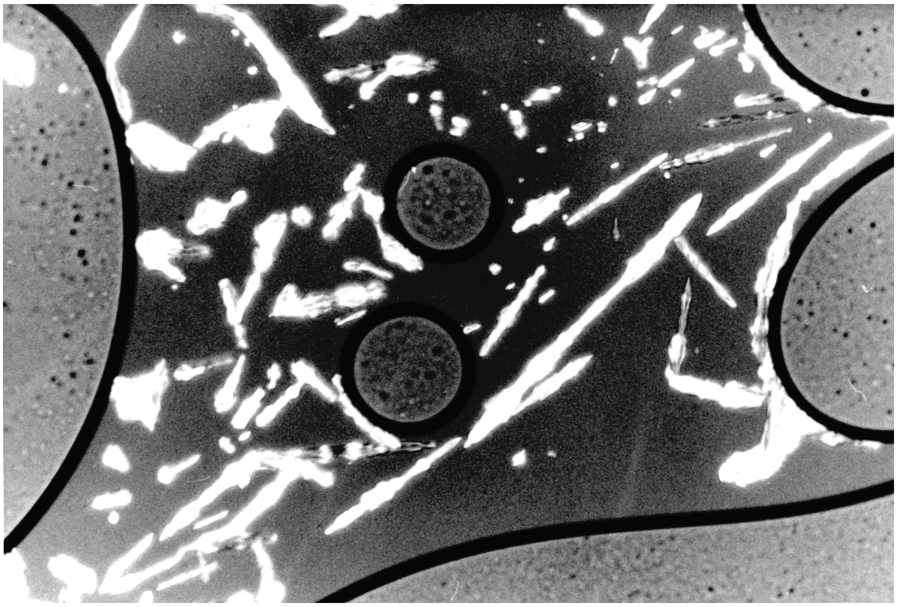


Figure 2. Bâtonet texture of PEI **4c** as observed upon cooling at 265-260°C.

TABLE 2. Phase Transitions of the PEIs as Revealed by DSC Measurements and by Optical Microscopy

Polym. No.	T_m[a] (°C)	T_m[b] (°C)	T_i[a] (°C)	T_{cr}[c] (°C)	T_{cr}[d] (°C)	T_{ai}[c] (°C)	T_{ai}[d] (°C)	T_i[e] (°C)	T_{cr}[f] (°C)	T_{ai}[f] (°C)
4a	260	265	-	174	157	246	240	266	227	265
4b	330	335	-	300	271	-	-	329	302	-
4c	240	244	251	146	131	275	272	274	142	270
4d	300	305	-	280	253	-	-	294	281	-
4e	287	291	-	249	224	274	268	281	251	271
4f	258	264	272	221	177	270	265	267	221	267

a) melting and isotropization temps. from DSC with a heating rate of 10°C/min
b) melting temp. from DSC with a heating rate of 50°C/min
c) crystallization and anisotropization temps. from DSC with a cooling rate of –10°C/min
d) crystallization and anisotropization temps. from DSC with a cooling rate of –50°C/min
e) isotropization temp. from optical microscopy with a heating rate of 10°C/min
f) crystallization and anisotropization temps. from optical microscopy with a cooling rate of –10°C/min

endotherm and again two exotherms, one with a weak (T_{ai}) and one with strong supercooling effect (T_{cr}) were observed in the cooling trace.

Synchrotron radiation measurements were performed with a heating and cooling rate of 10°C/min. The complete X-ray patterns displayed middle angle reflections (MARs, see Figure 3) indicating the existence of layer structures and wide angle reflections (WARs, see Figure 4). The layer distances (d - spacings) calculated from the MARs via the Bragg equation were summarized in Table 3. For comparison the lengths of the repeat units were calculated for four different combinations of conformations (Table 3). As illustrated by the formulas **7a** and **7b** the BICI moiety can in principle exist in a cisoid and a transoid conformation which differ by approximately 2 Å in length. For the aliphatic spacers the assumption of gauche and traces conformations in an equimolar ratio is the most likely approximation to the reality. The data in Table 3 demonstrate a rather good fit of the experimental d-spacings of the LC-phase with the values calculated for the cisoid gt combination. This fit means that the repeat units adopt a nearly perpendicular array relative to the layer plans in agreement with the definition of a smectic-A phase. Furthermore, no sharp reflection was detectable in the wide-angle range.

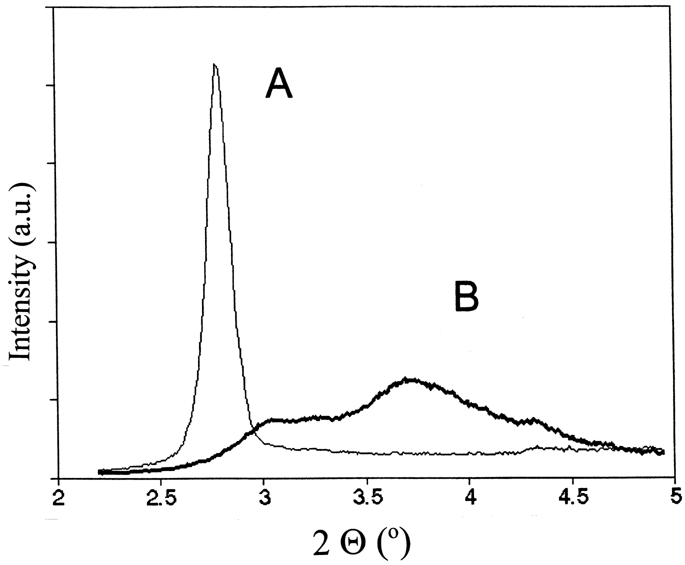


Figure 3. PEI **4c**: middle angle reflections of the smectic-A phase (A) and of the solid state (B).

TABLE 3. Experimental and Theoretical d-spacings (Layer Distances) in Å

Polym. No.	Exp. d-spacings		Theoretical d-spacings Mesogen cisoid		Mesogen transoid	
	Melt	Solid state	tg[a]	tt[b]	tg[a]	tt[b]
A7	28.5-29.2	20.2-20.5	30.7	32.0	32.4	33.8
A8	-	19.0-20.1	31.8	33.3	33.5	35.1
A9	31.0-33.0	24.0-24.6	32.9	34.6	34.6	36.3
A10	-	21.4-22.5	34.0	35.9	35.7	37.6
A12	36.0-36.2	24.4-25.2	36.2	38.4	37.9	40.2
A16	38.3-40.9	30.2-33.9	40.6	43.5	42.3	45.2

[a] calculated for equimolor ratios of gauche and trans conformations

[b] calculated for all-trans conformations of the spacers

When the d-spacings of the solid state of **4a** and **4c** were determined from the MARs significantly shorter layer distances were found. The result proves a tilting of the repeat units relative to the layer planes, and a tilt angle of 50 ± 5°C may be derived from the experimental and theoretical layer distances. Unfortunately, highly oriented samples allowing for the measurement of fiber patterns, and thus a more accurate determination of the tilt angle, could not be obtained. This WAXS patterns of **4a** and **4c** (Figure 6) did not display any sharp reflection indicating a relatively low level of lateral order. Therefore, it was not feasible to assign a smectic F, G, or H structure. However, a frozen smectic-C phase may be excluded, because the freezing-in of a smectic-A or smectic-C

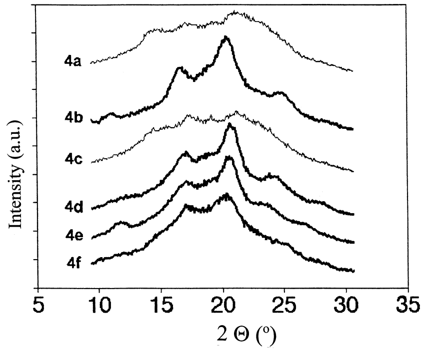


Figure 4. Wide angle X-ray scattering patterns of the PEIs **4a-f**.

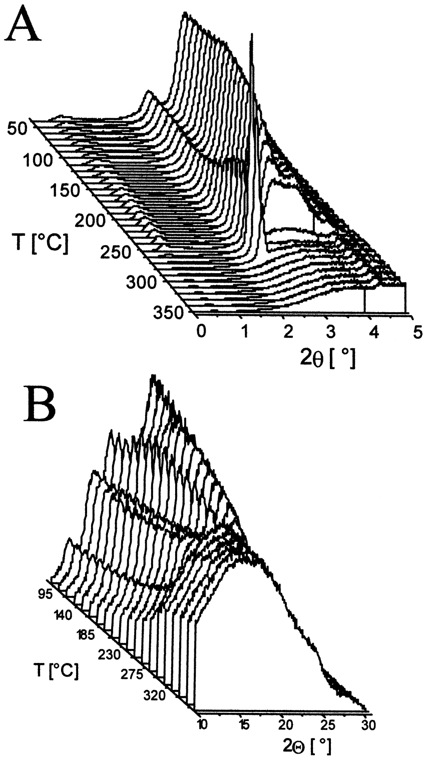


Figure 5. PEI **4e**: middle angle reflection (a) and wide angle reflections (b) recorded with synchrotron radiation upon cooling with a rate of 10°C/min.

phase is a phase transition of 2nd order which (like the formation of a glass from the isotropic melt) does not yield an exotherm in a DSC cooling trace.

Properties of PEIs having Even Spacers (4b, d-f)

When the PEIs having even-numbered spacers were examined by DSC measurements and optical microscopy three different kinds of thermal properties were found:

A) The PEIs **4b** and **4d** (n = 8 and 10) did not show any LC-phase.

B) The PEI **4e** (n = 12) displayed a monotropic smectic-A phase upon cooling.

C) The PEI **4f** (n = 16) exhibited an enantiotropic smectic-A phase.

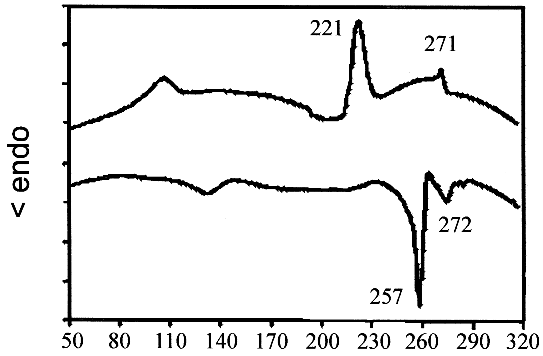


Figure 6. DSC measurements of PEI **4f**: A) 2nd heating, B) 1st cooling.

Typical for the DSC curves of **4b** and **4d** was the appearance of one endotherm in the heating curve and one exotherm (showing a significant supercooling effect) in the cooling curve (Table 2). Furthermore, no LC-phase was detected by optical microscopy.

In the case of PEI **4e**, again no LC-phase was observed upon heating under the polarizing microscopy, but the bâtonet texture of an isotropic smectic-A phase was observed upon cooling. The DSC heating curve exhibited only one endotherm (T_m) whereas, two exotherms were found in the cooling trace. The low temperature exotherm showed the supercooling effect characteristic for a crystallization process. The middle angle and wide angle X-ray measurements conducted with synchrotron radiation at a heating and cooling rate of 10°C/min perfectly agreed with this interpretation of the microscopy and DSC measurements. A sharp MAR (36 Å) was formed over a narrow temperature interval upon cooling representing the layer structure of the smectic-A phase (Figure 5 A). Further cooling yielded the broader MAR (25 Å) of the solid state. The transition from the LC-phase to the crystalline state is also well documented in the series of wide angle reflections by the appearance of several sharp reflections between 3.3 and 6.1 Å (Figure 5 B). These wide angle reflections are typical for all PEIs based on even-numbered spacers (Figure 4) and indicate an orthogonal array of mesogens in the a-b plane (with the c-direction pointing in direction of the chain axes).

When examined by optical microscopy the PEI **4f** displayed a viscous LC-phase with a sandy texture upon heating and the bâtonet texture of a smectic A phase upon cooling. In agreement with the existence of an enantiotropic LC-phase two endotherms were detectable in the DSC heating curve above 200°C and the corresponding two exotherms in the cooling trace (Figure 6). The strong endotherm/exotherm at 257/221°C represents the melting and crystallization process, respectively. The X-ray measurements performed with synchrotron radiation and variation of the temperature confirmed this interpretation. A sharp MAR at 38-41 Å (depending on the temperature) was found for the smectic-A phase and a broader MAR at 30-34 Å for the crystalline smectic phase (Table 3).

Two aspects of these X-ray measurements are particularly noteworthy. First, all PEI's with even-numbered spacers possess the same orthogonal chain packing in the a-b plane. All PEIs (including the odd numbered) possess a tilting angle relative to the layer-plane around 45-50. In other words, **4b** and **4d-f** possess a smectic-H type solid state. Third, the layer distances slightly increase in the solid state and more in the LC-phase when the temperature is raised. This expansion is obviously a normal volume expansion due to intensified vibrational and torsional motions.

The formation of the crystalline smectic-H phase also allowed the detection of typical small angle reflections (SARs). The temperature dependence of both scattering angle and intensity were recorded using synchrotron radiation at a heating or cooling rate of 10°C/min. The scattering properties of PEI **4d** displayed in Figures 7 and 8, are exemplary for all PEIs. A long period of 13.0- 13.5 nm was found in the solid state low temperatures (<200°C) which raises to values around 33-34 nm when the temperature approaches T_m. This change was fully reversible upon cooling. A reversible change was also observed for the intensity of the SAR. The onset of this change (upon heating) or the intensity decrease upon cooling may be interpreted as glass-temperature (T_g). In this way T_gs around 150°C were found for **4b** around 140-145°C for **4c** and **4d** and around 120-130°C for **4c** and **4f**. The accuracy o these measurements is low and the margin of error amounts to ± 10C. However, the T_gs were not detectable in the DSC measurements, a situation which is quite typical for smectic PEIs[1]. In the case of **4a,** the crystallinity was too low for satisfactory SAXS measure-ments.

Thermal Properties of the CoPEIs 6a and 6b

The coPEI **6a** and **6b** were prepared from equimolar mixtures of two different spacers under conditions allowing for rapid transesterification. Therefore, these coPEI's should possess a random sequence of both spacers. This means, in turn, that both the long and the short spacers should be present in all layers provided that these coPEI's are capable of forming a layer structure at all. In other words synthesis and characterization of both coPEI's were undertaken to answer the following questions:

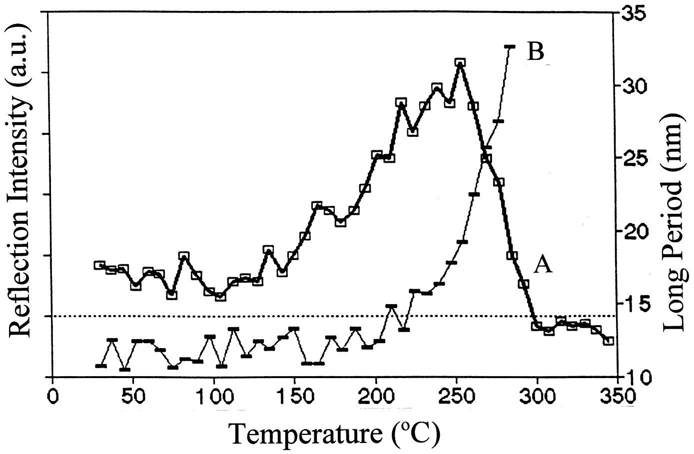


Figure 7. PEI **4d**: reflection intensity and long period derived from SAXS measurements during the heating with a rate of + 10°C/min.

1) Can the coPEIs **6a** and **6b** form a layer structure in the solid state?

2) Can the coPEI form a LC-phase? If yes, do they form a smectic or a nematic phase?

3) Are the properties of **6a** and **6b** quite similar (prevailing influence of the long spacer) or are their properties different (prevailing influence of the short spacer)?

A positive answer on the first question was obtained from X-ray measurements performed with synchrotron radiations under variation of the temperature. A middle angle reflection was found indicating the existence of a layer structure in the solid state of both coPEIs. The change of the MAR and WAR intensities with the temperature (upon cooling) is displayed in Figure 9 for illustration. Furthermore, an exotherm representing the crystallization of a smectic phase was clearly detectable in the cooling curve of both coPEIs. However, other aspects of the thermal properties were quite different reflecting a predominant influence of the short spacer, so that a separate discussion of **6a** and **6b** is required.

In the case of **6a,** the DSC heating curve exhibited one broad endotherm representing the T_m (around 280°C) in the heating trace and two broad exotherms in the cooling curve (T_{ai} around 250°C and T_{cr} around 175°C). The optical

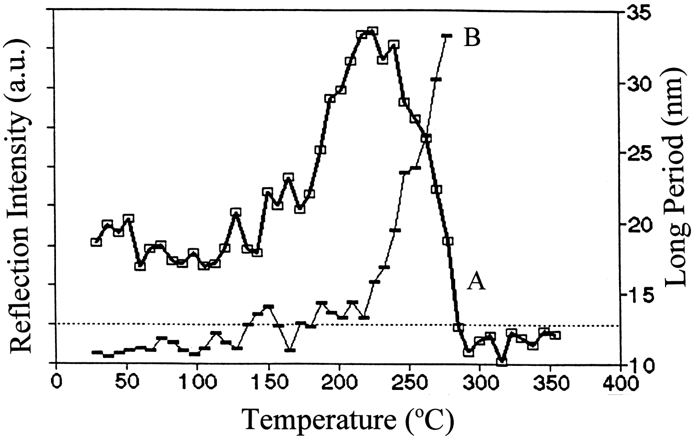


Figure 8. PEI **4d**: reflection intensity and long period derived from SAXS measurements during the 1st cooling with a rate of -10°C/min.

microscopy confirmed the formation of a monotropic LC-phase between 250 and 175°C upon cooling. Therefore, the thermal properties of this coPEI resemble those of the homopolymer **4a** with the difference that the phase transitions of the coPEI were considerably broader. A more interesting difference was found for the layer-distance. The MAR of **6a** gave a d-spacing of 3.45-3.65 nm which is a little shorter than that of **4f** but, significantly longer than that of **4a**.

A close analogy with the homo PEI of the short spacer (**4d**) was also found for the coPEI **6b**. Both optical microscopy and DSC measurements revealed that this coPEI did not form any LC-phase by analogy with the homopolymer **4b**. The DSC heating curve exhibited one melting endotherm at 285-290°C and one crystallization exotherm at 255-260°C (recorded at a cooling rate of -10°C/min). This interpretaion was confirmed by X-ray measurements using synchrotron radiation. As demonstrated in Figure 9, two MARs (1st and 2nd order) and several WARs appear simultaneously in the temperature interval of 255-265°C upon cooling with -10°C/min. A d-spacing of 3.5-3.7 nm was calculated from the MARs which is an intermediate value between those of the homopolymers **4b** and **4f** (Table 3). Therefore, it may be concluded that also both coPEIs adopt a smectic-H phase in the solid state but with a lower degree of crystallinity and a lower degree of perfection when compared to the parent homopolymers. A detailed study of the arrangement of short and long spacers in the layers of these coPEIs was not intended in this work.

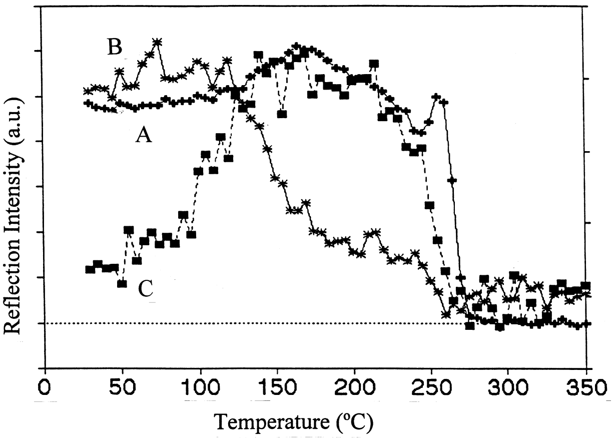


Figure 9. PET **6b**: reflection intensities reorded with synchrotron radiation upon cooling with a rate of –10°C/min; A) 1st layer reflection (MAR), B) 2nd layer reflection, C) with angle (crystal)-reflection.

CONCLUSION

A new series of semirigid poly(ester-imide)s was synthesized based on the long mesogenic N,N'-bis(4-carboxyphenyl)bisphenyl tetracarboxylic imide unit. All these PEIs formed a crystalline smectic layer structure in the solid state (most likely smectic-H), but their thermal properties varied largely with the length of the aliphatic spacer. PEIs melting and crystallizing without formation of any LC-phase were found (**4b, 4d, 6b)**. Other PEIs (**4a, 4e,** and **6a**) formed a monotropic smectic-A phase upon cooling. For PEI **4f** the existence of an enantiotropic smectic-A phase was observed. Particularly, interesting, is the finding that an increasing length of the spacer favored the formation of the LC-phase. Such a thermal behavior was also observed for the PEIs of structure **3** [6], whereas for all other semirigid PEIs reported so far [1] and for most other semirigid LC-polyesters it has been reported that longer spacers reduce the temperature range of the LC-phase. Obviously, the relatively great length of the mesogen and the possibility of rapid change between cisoid and transoid conformation is responsible for this unusual behavior. Further studies which are in progress should shed more light on the structure-property relationships of polyesters derived from the same and similar mesogens.

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