

Layer structures: 7. Thermotropic poly(ester-imide)s based on trimellitic anhydride and branched diamino alkane spacers

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Two new dicarboxylic acids were synthesized from trimellitic anhydride and 1,5-diamino-2-methylpentane or from a mixture of isomeric 1,6-diamino-trimethyl hexanes. These dicarboxylic acids were polycondensed either with the bisacetate of 2,6-dihydroxynaphthalene or with the bisacetate of 4,4'-dihydroxybiphenyl. D.s.c. measurements, WAXD powder patterns and optical microscopy revealed that all four poly(ester-imide)s derived from 1,5-diamino-2-methylpentane still form a highly ordered, quasi crystalline smectic layer structure in the solid state, but a nematic phase in the molten state. The poly(ester-imide)s derived from the trimethyl substituted spacers only form a smectic glass in the solid state. This smectic glass is a frozen smectic-A phase in the case of **4a** but may be a mixture of frozen smectic-C and smectic-A phases in the case of **4b** (derived from 4,4'-dihydroxybiphenyl). Upon heating above the glass-transition the layer structures gradually disappear with formation of a nematic phase. Due to this gradual change revealed by synchrotron radiation measurements no endothermic phase transition is detectable in the d.s.c. traces. © 1997 Elsevier Science Ltd.

(Keywords: poly(ester-imide)s; nematic phase; smectic phase)

INTRODUCTION

The poly(ester-imide)s of structures **1a-h** were the first class of thermotropic polyimides described by the main author of this work^{1,2}. The characterization of these poly(ester-imide)s, PEIs, and that of other semi-rigid poly(ether-imide)s³⁻⁵, poly(ether-imide)s⁶ and poly(amide-imide)s^{7,8} revealed that polyimides having a regular sequence of imide moieties and alkane spacers possess an unusual high tendency to form layer structures. The layer structures were usually formed in the solid state and in some cases also in the melt (smectic LC-phases). It was found that the formation of layer structures is mainly a consequence of a regular sequence of polar and nonpolar units along the main chain⁹⁻¹¹. The crystallization of the mesogenic groups inside their layers is not a prerequisite for the stabilization of the layers in contrast to low molar mass smectic compounds⁹. In agreement with this hypothesis, polar oligoether spacers which are more or less compatible with the imide units destabilize the layer structures¹⁰. Nonetheless, the PEIs **2a, b** still can form a smectic layer structure in the solid and in the molten state but the temperature range of the LC-phase is narrower than in the case of **1c**¹³.

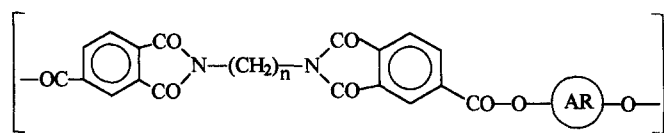
Taken together, polyimides containing aliphatic spacers were found to be useful substrates to study relationships between chemical structure and layered supermolecular structures on a broader basis. In this connection it was the purpose of the present work to synthesize PEIs of a structure closely related to that of **1a-c** and **2a, b**, but with branched aliphatic spacers (i.e. structures **3a, b** and **4a, b**). The influence of branched spacers on the formation of LC-phases of other thermotropic polyesters has also been studied by other research groups¹⁴⁻²¹, but LC-polyimides were never included in those studies.

EXPERIMENTAL

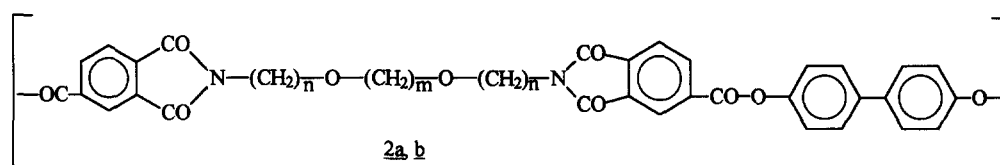
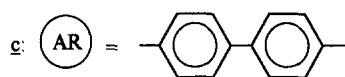
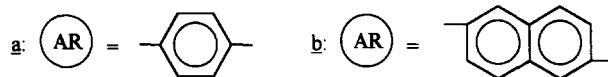
Materials

Trimellitic anhydride, was a gift of Glasurit S.A. (Guadalajara, Spain) and it was used as received. 3-Methyl-1,5-diaminopentane was a gift of DuPont de Nemours (Bad Homburg, Germany). The equimolar mixture of 4,4-dimethyl-2-methyl-1,6-diaminohexane and 2,2-dimethyl-4-methyl-1,6-diaminohexane was purchased from Hüls AG (Marl, Germany). 2,6-Dihydroxynaphthalene and 4,4'-dihydroxybiphenyl were purchased from Aldrich Co. (Milwaukee, WI, USA). They were

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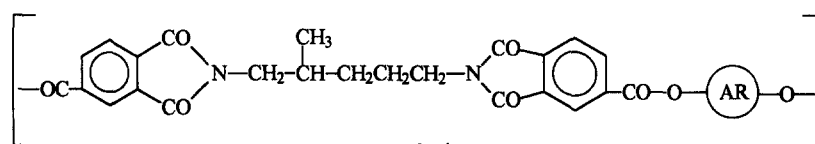


1a-h (n = 4-12)

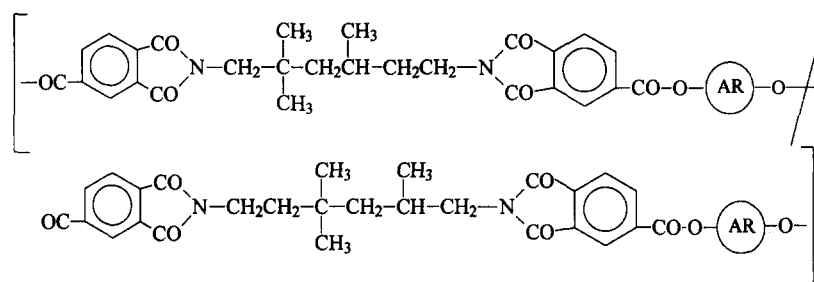
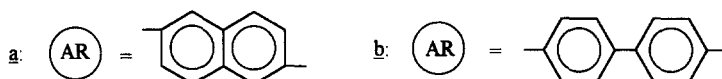


2a, b

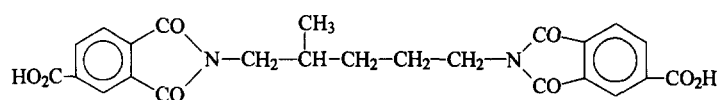
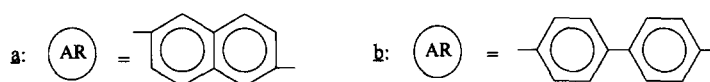
a: n = 2, m = 2 b: n = 3, m = 4



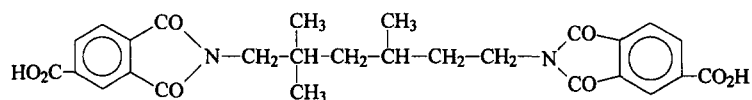
3a, b



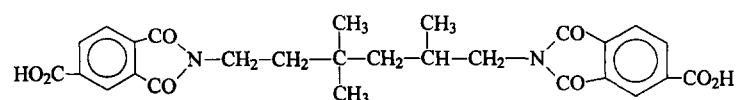
4a, b



5



equimolar mixture



6

Table 1 Yields and properties of the poly(ester-imide)s **3a**, **b** and **4a**, **b**

Polym. No.	Yield (%)	η_{inh}^a (dl g ⁻¹)	Elem. formula (form. weight)	Elemental analyses			
					C	H	C
3a	95	0.78	C ₃₄ H ₂₄ N ₂ O ₈ (588.6)	Calcd.	69.38	4.11	4.76
				Found	69.45	4.08	4.57
3b	93	0.47	C ₃₆ H ₂₆ N ₂ O ₈ (614.6)	Calcd.	70.35	4.26	4.56
				Found	70.00	4.13	4.52
4a	95	0.64	C ₃₇ H ₃₀ N ₂ O ₈ (630.6)	Calcd.	70.47	4.79	4.44
				Found	70.07	4.68	4.29
4b	90	0.52	C ₃₉ H ₃₂ N ₂ O ₈ (656.7)	Calcd.	71.33	4.91	4.27
				Found	71.20	5.17	4.48

^a Measured at 25°C with $c = 2 \text{ g l}^{-1}$ in CH₂Cl₂/trifluoroacetic acid (volume ratio 4/1)

acetylated as described in the literature²² and recrystallized from toluene/ligroin.

Imide dicarboxylic acids **5** and **6**

Trimellitic anhydride (0.2 mol) was dissolved in hot acetic acid (600 ml). Upon cooling of this solution a diamine (0.1 mol) was added dropwise (under cooling), so that the temperature did not raise above 25°C. After stirring for 1 h at 20–25°C the temperature was raised to 120°C and maintained at this temperature for 4 h. After cooling the reaction mixture was poured into cold water, and the crude product was isolated by filtration.

5 was recrystallized from dioxane: Yield 69%, m.p. 258–260°C. Analyses calcd. for C₂₄H₂₀N₂O₈ (464.4): C 62.01, H 4.34, N 6.03, found C 62.23, H 4.34, N 6.00%.

6 was recrystallized from acetic acid/water: Yield 65%, m.p. 215–217°C. Analyses calcd. for C₂₇H₂₆N₂O₈ (506.5): C 64.02, H 5.17, N 5.53, found C 64.03, H 5.35, N 5.60%.

Polycondensations

An imide dicarboxylic acid (30 mmol), an acetylated diphenol (30 mmol) and MgO (10 mg) were weighed into a cylindrical glass reactor equipped with stirrer and gas inlet and outlet tubes. The reactor was placed into an oil bath preheated to 100°C and the temperature was then raised rapidly to 245–250°C where a homogeneous melt was obtained in all cases. The melt was stirred for 2 h at 250°C and then for 1 h at 260°C. The evolved acetic acid was removed with a slow stream of nitrogen. Finally, the melt was stirred at 280°C for 0.5 h *in vacuo*. After cooling the crude polyesters were dissolved in a mixture of CH₂Cl₂/trifluoroacetic acid (volume ratio 4/1), precipitated into methanol and dried at 120°C *in vacuo*.

Measurements

The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 25°C.

The d.s.c. measurements were conducted with a Perkin Elmer DSC-7 in aluminium pans under nitrogen.

The 100 MHz ¹H n.m.r. spectra were recorded with a Bruker AC-100 FT n.m.r. spectrometer in 5 mm o.d. sample tubes using a 4/1 (by volume) mixture of CDCl₃/trifluoroacetic acid as solvent.

The WAXS powder patterns were recorded at 25°C with a Siemens D-500 powder diffractometer using Ni-filtered CuK_α radiation. The synchrotron radiation measurements were conducted with a wavelength of

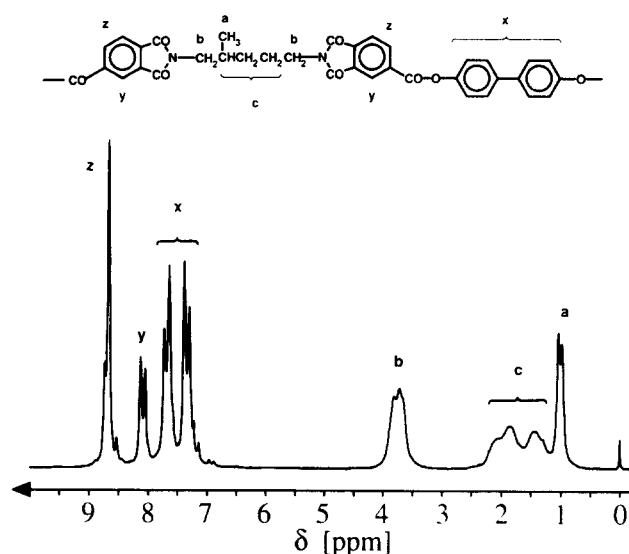


Figure 1 100 MHz ¹H n.m.r. spectrum of poly(ester-imide) **3b**

$\lambda = 1.50 \text{ \AA}$ at HASYLAB (DESY, Hamburg). A one-dimensional position sensitive detector and a heating rate of 20°C min⁻¹ were used for all measurements.

RESULTS AND DISCUSSION

Syntheses

The poly(ester-imide)s **3a**, **b** and **4a**, **b** were prepared by polycondensations of the imide dicarboxylic acids **5** or **6** with acetylated 2,6-dihydroxynaphthalene or acetylated 4,4'-dihydroxybiphenyl. These polycondensations were conducted in bulk with magnesium oxide as transesterification catalyst. The yields and inherent viscosities of the PEIs **3a**, **b** and **4a**, **b** are summarized in *Table 1*. The new dicarboxylic acids **5** and **6** were synthesized in a conventional way by heating the corresponding diamines with trimellitic anhydride in acetic acid. The chemical structures of all new monomers and PEIs were characterized by elemental analyses (see *Table 1*), by i.r. and by ¹H n.m.r. spectroscopy. The i.r. spectra displayed the 'CO-bands' typical for an aromatic imide structure (1775 ± 5 and 1735 ± 5 cm⁻¹). The ¹H n.m.r. spectra showed the expected signals and confirmed the correct ratios of aliphatic and aromatic protons as exemplified by the spectrum of *Figure 1*.

Chain packing and thermal properties

All four PEIs were annealed at 160°C (for 16 h), a

temperature above the glass-transition step (T_g) of all four samples. WAXS powder patterns of the annealed samples were recorded at room temperature. The powder patterns of the PEIs **4a** and **4b** are nearly identical, therefore only three WAXS patterns are displayed in *Figure 2*. These WAXS patterns show in all four cases two or three middle angle reflections (MARs) in the range of $2\theta = 3-11^\circ$. The reflection around $2\theta = 6-7$ or $10-11^\circ$ are the 2nd and 3rd order reflections of the first reflection. These reflections clearly indicate that the PEIs **3a**, **b** and **4a**, **b** form smectic layer structures in the solid state quite analogous to the related PEI's **1a-h** and **2a**, **b**.

The layer distances (d -spacings) were calculated from the MARs by means of the Bragg equation (*Table 2*). They are larger than those determined for the PEIs having unsubstituted spacers (**1b**, **c**). This finding suggests that due to the steric demands of the methyl groups a stretching of the spacers takes place so that less gauche and more trans conformations are present when compared to the parent PEIs **1a-h**²³. From the parent PEIs it is also known^{1,22} that in the case of odd spacers the mesogens are tilted relative to the layer plane. In the

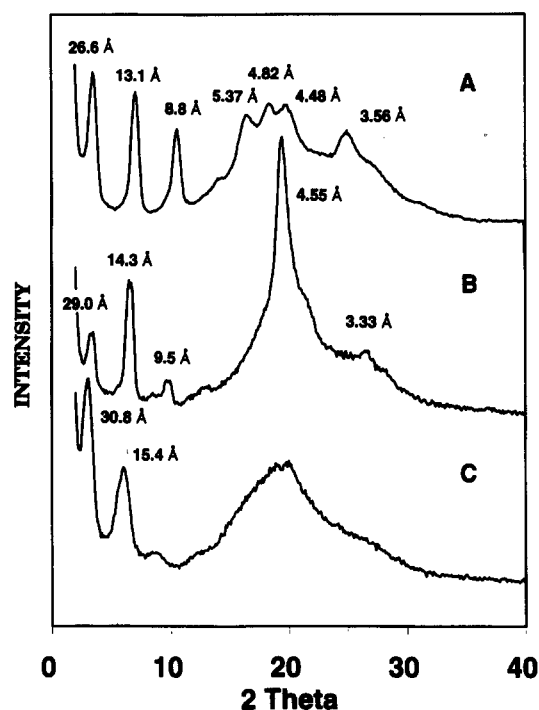


Figure 2 WAXS powder patterns of the poly(ester-imide)s **3a**, **3b** and **4b**

case of even spacers the mesogens adopt an almost upright position at least in the solid state. The experimental d -spacings found in this work suggest that quite analogous to **1b** the PEIs **3a** and **3b** possess tilted mesogens, whereas the mesogens of **4a** and **4b** are nearly in an upright position relative to the layer planes in analogy to **1c**.

The wide angle reflections (WARs) revealed a significant difference between **3a**, **b**, on the one hand, and **4a**, **b** on the other hand. The PEIs **3a** and **3b** show WARs indicating the existence of crystalline smectic phases whereas in the case of **4a**, **b** the 'halo' indicates a smectic glassy state. In the case of **3a** the WARs suggest that the lateral array of the mesogens corresponds to an orthorhombic type of order. Considering a tilting of the mesogens this layer structure may be denoted smectic-H. Interestingly, the lateral order of **3b** is somewhat different from that of **3a** favouring a hexagonal array which fits in with the steric demands of the biphenyl unit. Taking into account a tilted array of mesogens the layer structure of **3b** corresponds more or less to a smectic F or G phase. In the case of **4a** and **4b** the layer distance calculated from the MARs suggest an upright position of the mesogens in analogy to **1c**. Taking into account the total lack of a lateral order inside the layer of the mesogens the solid state of **4a** and **4b** may be labelled 'frozen smectic-A phase'.

In order to confirm this interpretation based on WAXS powder patterns, several attempts were made to obtain fibre patterns of all PEIs. Unfortunately, no sufficient orientation was found in the case of **3a** and **3b**, whereas satisfactory fibre patterns were obtained from **4a** and **4b**. The fibre pattern of **4a** displays a broad halo on the equator and five sharp reflections exactly on the meridian. Four out of these five reflections are the higher orders of the basic MAR. Thus, this fibre pattern agrees well with a frozen smectic-A phase having a high perfection of the layer structure, which did not change upon heating up to 200°C .

When fibres of **4b** were measured at various temperatures, a more complex result was found. Again an amorphous halo appears on the equator and small sharp reflections on the meridian. These meridional reflections represent up to the 9th order of a MAR representing a frozen smectic-A phase. However, in addition to these meridional reflections the 1st and 2nd order MARs exhibit two maxima off the meridian. In other words a 'four point pattern' is observable (*Figure 3A*) which indicates the existence of domains with tilted mesogens. The tilt angle is small with 26° relative to the normal on

Table 2 Thermal properties

Polym. No.	T_g^a ($^\circ\text{C}$)	T_{m1}^a ($^\circ\text{C}$)	T_{m2}^a ($^\circ\text{C}$)	T_i^a ($^\circ\text{C}$)	T_i^b ($^\circ\text{C}$)	Texture	δ -Spacing	
							Exp. ^c	Unsubst. ^d
3a	130	245–265	280–285	320–330	340–350	Nematic	26.6	24.6 (1b)
3b	155	–	365–370	(dec.)	>400	Nematic + smectic	28.5	
4a	133	–	–	309–315	310–320	Nematic	30.2	28.8 (1c)
4b	128	–	–	–	>400	Nematic	30.8	

^a D.s.c. measurements with a heating rate of $20^\circ\text{C min}^{-1}$

^b Optical microscopy with a heating rate of $10^\circ\text{C min}^{-1}$

^c WAXS measurements of annealed samples recorded at 25°C (see *Figures 2* and *7*)

^d Experimental values of the unsubstituted PEIs **1b** and **1c**

the layer plane at 25°C. Upon heating the tilt angle increases to $30 \pm 1^\circ$ at 100°C and decreases again to $26 \pm 1^\circ$ around 200°C. Finally, the 'four point pattern' disappears between 200 and 240°C (Figure 3B) whereas the meridional reflections of smectic-A phase exist up to higher temperatures. Obviously, a frozen smectic-C can be formed along with the frozen smectic-A phase depending on the thermal history. This interpretation is supported by the synchrotron radiation measurements discussed below.

Thermal properties

When the four PEIs were subjected to d.s.c. measurements with a heating and cooling rate of $20^\circ\text{C min}^{-1}$, glass-transition steps were detected in all cases indicating

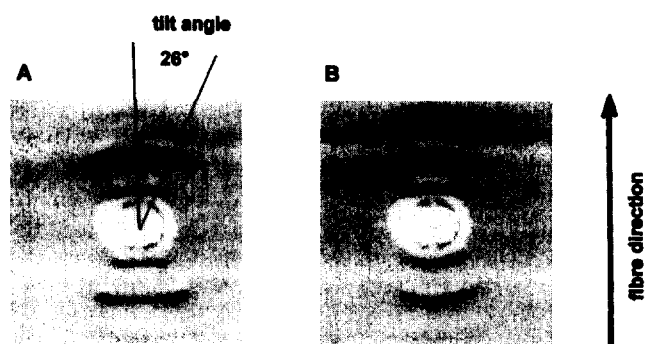


Figure 3 Fibre patterns of poly(ester-imide) 4b: (A) at 25°C; (B) at 230°C

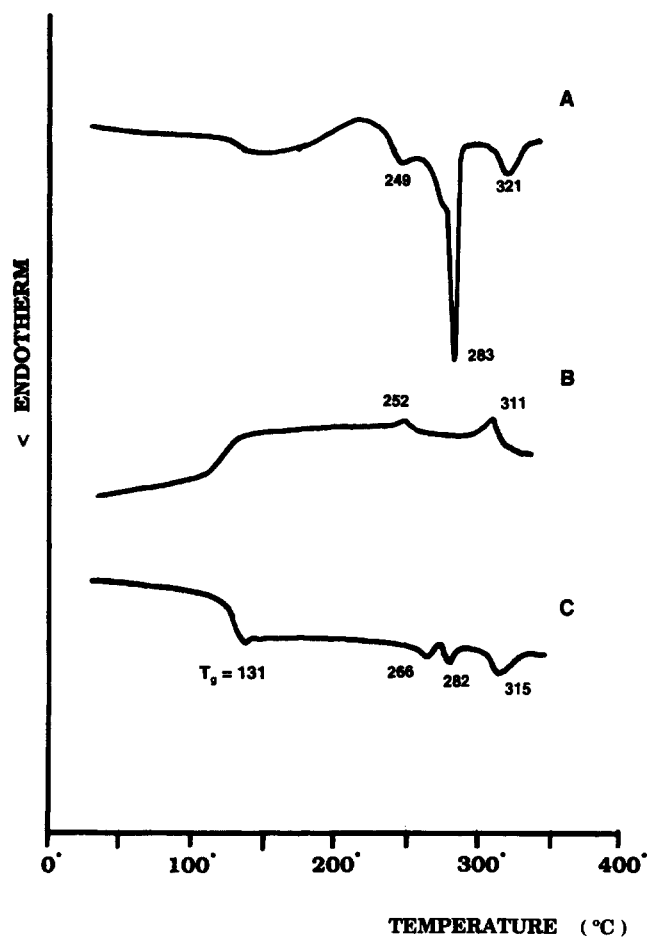


Figure 4 D.s.c. measurements (heating and cooling rate $20^\circ\text{C min}^{-1}$) of poly(ester-imide) 3a

a rather low degree of crystallinity in good agreement with the WAXS powder patterns. In the case of 3a three endotherms were detectable in the heating trace (Figure 4A), but only two exotherms in the cooling trace (Figure 4B). The optical microscopy with crossed polarizers revealed that the endotherm at the highest temperature (320–330°C) represents the isotropization process of a highly mobile LC-phase. Due to its typical threaded schlieren texture this LC-phase was unambiguously identified as nematic phase. The stronger endotherm around (283°C represents the melting of the smectic-H phase and the strong super-cooling effect of the low temperature exotherm (-30°C in Figure 4C) agrees well with the interpretation as a crystallization process. The weak endotherm at 249°C disappears upon annealing at 260°C, and may result from smaller and less perfect crystallites.

In the case of PEI 3b the d.s.c. curves displayed only one weak exotherm around 370–380°C. The optical microscopy revealed the highly mobile threaded schlieren texture of a nematic melt above 380°C (Figure 5,

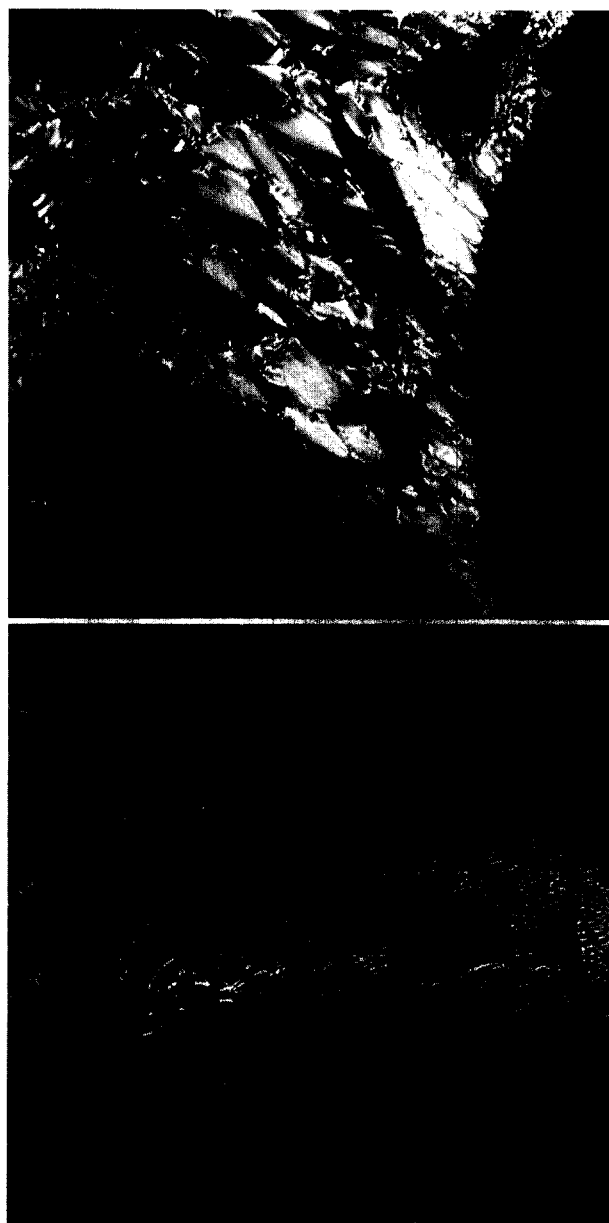


Figure 5 Textures of the poly(ester-imide) 3b: fan-shaped smectic texture at 340°C (above), nematic schlieren texture at 380°C (below)

lower texture). The isotropization occurred above 400°C and was affected by rapid thermal degradation. Interestingly, this PEI formed a viscous but mobile fan-shaped texture below 370°C (Figure 5, upper texture) which may represent a smectic-A or a smectic-C phase. Therefore, it is clear that the endotherm at 370–380°C indicates a transition between a liquid smectic and a nematic phase. Surprisingly, the solidification of the smectic melt which occurs below 200°C was not clearly detectable in the d.s.c.-curves. A weak endotherm is observable in the heating trace around 170°C, but it is directly connected with the glass-transition step. In the case of **3b** synchrotron radiation measurements of the MARs were conducted between 50 and 400°C (Figures 6 and 7). The intensity of the MARs begin to decrease above 155°C (Figure 6) in agreement with the assumed transition from the solid to the liquid smectic phase. The intensity of the MARs decreases continuously up to 390°C where they vanish in agreement with the formation of a nematic phase. Furthermore, the weak MARs

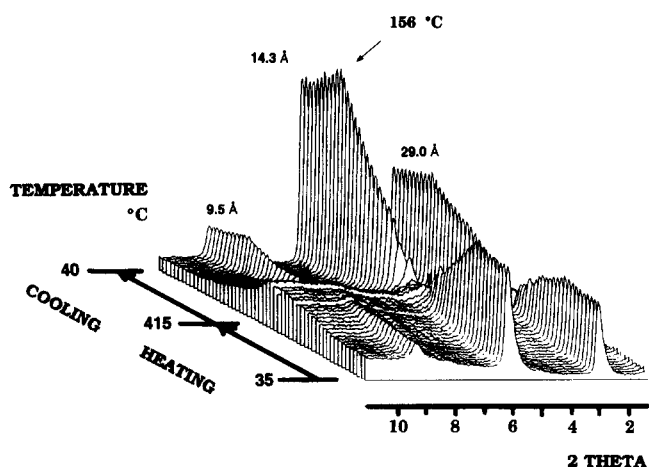


Figure 6 Synchrotron radiation measurements (middle angles only) of poly(ester-imide) **3b** conducted with a heating rate of 10°C min⁻¹. The three reflections represent the 1st, 2nd and 3rd order of the layer reflection

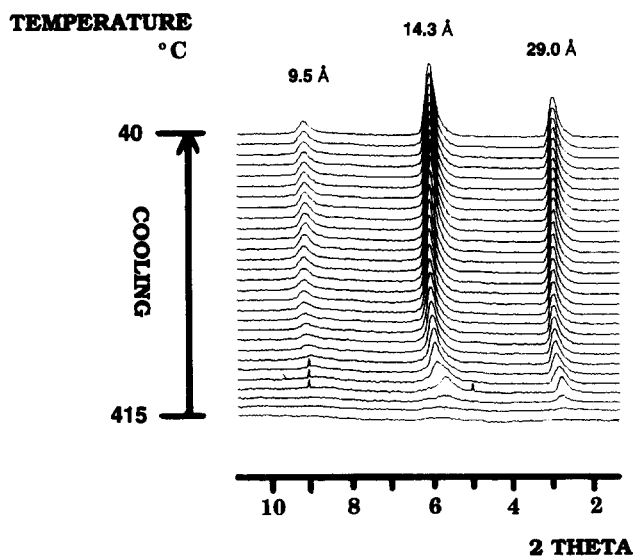


Figure 7 Synchrotron radiation measurements (middle angles only) of poly(ester-imide) **3b** conducted with a heating rate of 10°C min⁻¹

shift to lower scattering angles (greater *d*-spacings) between 370 and 390°C (Figure 7). This change may be interpreted as a transition from a smectic-C phase to a smectic-A phase. Unfortunately, the textures do not give a clearcut confirmation of this hypothesis. Interestingly, the *d*-spacing does not change between 25 and 350°C. Thus, the synchrotron radiation measurements support the hypothesis that **3b** forms a smectic-F or -G like solid state with tilted mesogens which melts into a smectic-C phase above 180°C which finally changes to a smectic-A and a nematic phase above 350°C.

At first glance the d.s.c. measurements and microscopic results of **4a** and **4b** proved to be simpler than those of **3a, b**. Only a nematic phase was detectable by optical microscopy. A reversible isotropization around 320°C was observed for **4a**. This isotropization was also evident from an endotherm at 315°C in the d.s.c. heating curve of **4a**. The isotropization of **4b** occurred above 400°C with rapid thermal degradation quite analogous to the isotropization of **3b**. Therefore, the isotropization is not evident from the d.s.c. curves.

Surprisingly, the d.s.c. traces of both PEIs did not exhibit a well defined endotherm for a transition of a smectic melt into the nematic melt. Obviously, the nematic melt is gradually formed above the glass transition of the frozen smectic-A phase. This assumption was confirmed by synchrotron radiation measurements (Figure 8). A strong MAR was present above the

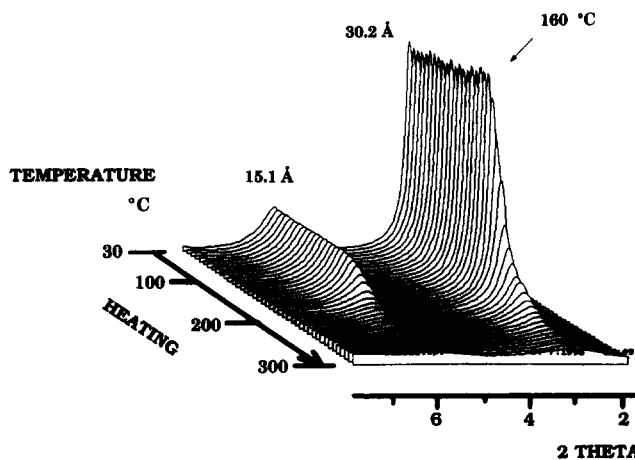


Figure 8 Synchrotron radiation measurement (middle angles only) of poly(ester-imide) **4a** conducted with a heating rate of 10°C min⁻¹

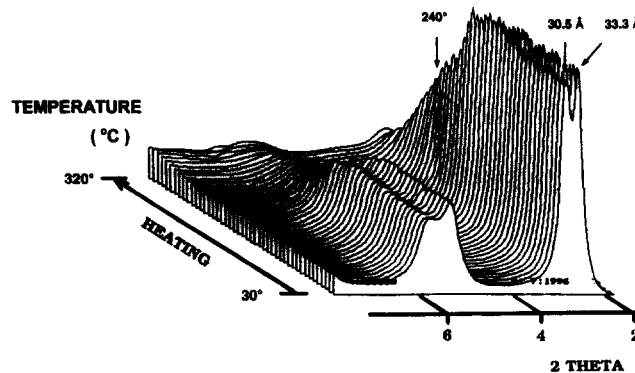


Figure 9 Synchrotron radiation measurements (middle angle reflection only) of poly(ester-imide) **4b**: first heating conducted with a heating rate of 10°C min⁻¹

T_g up to approximately 160°C. Its intensity gradually decreased at higher temperatures and completely vanishes around 190°C. Above this temperature a highly mobile threaded schlieren texture of a nematic phase was observable up to 320°C.

The d.s.c. trace of **4b** exhibited a weak, barely detectable flat endotherm between 250 and 280°C. The optical microscopy showed a viscous almost solid phase below this temperature, whereas a highly mobile threaded schlieren texture was found above 275°C. It seems that a smectic phase persists at least partially up to 260–270°C. Again this interpretation of the d.s.c. measurements and optical microscopy was confirmed by synchrotron radiation measurements. Strong MARs indicating the existence of a layer structure were detectable up to the T_g displayed in the d.s.c. curve. The intensity of these MARs decreased continuously up to temperatures around 280°C, where it completely vanished (Figure 9). However, these MARs differ from those of **4a** in that the 1st and 2nd order MAR show a splitting into two peaks which differ by 2 Å (Figure 9). This splitting is only detectable when samples precipitated from methanol and dried at $\leq 120^\circ\text{C}$ were measured. After heating to the nematic melt and cooling one pair of MARs was irreversibly lost. The remaining series of MARs correspond to the existence of a smectic-A phase in the molten and in the solid state. The additional MARs with shorter d -spacings suggest the coexistence of a thermodynamically less stable smectic-C phase in the solid state. Thus, these synchrotron radiation measurements agree perfectly with the above interpretation of the fibre patterns of **4b** (Figure 3). The finding that the smectic-A phase of **4b** is more stable in the molten state agrees with the thermal properties of **4a**.

CONCLUSION

The present study reveals an interesting relationship between the structure of the spacers and the chain packing of the poly(ester-imide)s under investigation. The substitution of the spacers with methyl groups destabilizes the layer structures in two ways, which are characteristic for polyimides with a regular sequence of polar imide groups and nonpolar spacers. Three methyl substituents prevent, as demonstrated by the PEIs **4a** and **4b**, a lateral ordering of the mesogens so that the solid state is a smectic glass. Apparently the diameter or, in other words, the cross section of the spacers is so large that the dipole–dipole interactions and van der Waals forces, which decrease with the sixth power of the distances, cannot enforce a perfect lateral order of the mesogens. The finding that layers were formed despite the total lateral disorder of the mesogens supports our previously formulated hypothesis¹⁰ that the formation of a smectic layer structure is mainly a kind of phase separation on the molecular level.

The steric influence of the spacers is also illustrated by the observation that one methyl substituent alone does not suffice to prevent the formation of highly ordered, quasi crystalline smectic layers in the solid state.

However, even one methyl group has enough destabilizing influence on the LC-phase to favour a nematic phase at higher temperatures. Such a strong influence of modified alkane spacers on smectic LC-main chain polymers has not been demonstrated before. In contrast to low molar LC-materials it is obviously not correct to ascribe the supermolecular structure of LC-main chain polymers mainly or exclusively to the structure of the mesogens. This present and previous studies^{10,23} suggest that the influence of the spacer on the formation and order of smectic phases may be nearly as strong as that of the mesogens. These conclusions are particularly true for relatively short mesogens. Mesogens with a greater length/diameter ratio show, of course, the tendency to stabilize smectic phases^{15–17}.

ACKNOWLEDGEMENT

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