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LC-POLYIMIDES. 33. POLY(ESTER-IMIDE)S OF 4,4′-DIAMINODIPHENYL ETHER BISTRIMELLITIMIDE

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ABSTRACT

The dichloride of 4,4′-diaminodiphenyl ether bistrimellitimide was polycondensed with numerous diphenols or diols in hot 1-chloronaphthalene. The resulting poly(ester-imide)s were characterized by elemental analyses, inherent viscosities, ^{1}H NMR spectroscopy, DSC and X-ray measurements. When hydroquinone, methylhydroquinone, 2,7-dihydroxynaphthalene, 4,4′-dihydroxybiphenyl or 4,4′-dihydroxydiphenyl ether were used as building blocks, the poly(ester-imide)s decomposed before a mobile melt was obtained. Typical nematic Schlieren textures were observed with tert-butylhydroquinone or phenylhydroquinone monomers. A diphenol containing an aliphatic spacer yielded a smectic LC-phase, which was characterized by X-ray measurements with synchroton radiation up to 300°C. Attempts to obtain cholesteric poly(ester-imide)s by incorporation of isosorbide failed. The resulting chiral poly(ester-imide)s were isotropic. Further poly(ester-imide)s were prepared from diphenols and 4,4′-diaminodiphenylmethane bistrimellitimide or 4,4′-diaminodiphenylsulfone bistrimellitimide. All these poly(ester-imide)s formed isotropic melts. The pertinent structure-property relationships are discussed.

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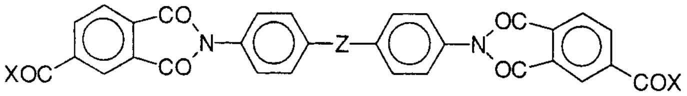
INTRODUCTION

Previous systematic studies of numerous poly(ester-imide)s [1-5], poly(carbonate-imide)s [6-8], and poly(ether-imide)s [9, 10] have revealed that highly symmetrical imide moieties, such as pyrromellitdiimide (PMDI), naphthalene, 1,4,5,8-tetracarboxylic imide or 3,3′,4,4′-biphenyltetracarboxylic imide are relatively poor mesogens. Nonsymmetrical imide structure such as those derived from trimellitic anhydride (TMA) or 4-hydroxyphthalic anhydride are more favorable [11]. A straightforward explanation of this phenomenon allowing a simple prediction or calculation of the mesogenic character of imide moieties is still lacking in as much as the structure of the comonomers plays an important role [12].

The present work was aimed at studying the mesogenicity of the dicarboxylic acids 1-3 which can easily be synthesized from TMA and commercial aromatic diamines. Considering symmetry, these dicarboxylic acids represent an intermediate case between the TMA derivative 4 and the highly symmetrical PMDI derivatives. Several papers and patents describing liquid-crystalline (LC)-poly(ester-imide)s PEI derived from 1a-3a have recently been published [13-16]. However, those LC-PEI's containing three or four comonomers favoring a LC-character, so that the mesogenic properties of 1a-3a are difficult to evaluate. Therefore, the present work was mainly concerned with synthesis and characterization of homo PEI's derived from the dicarboxylic acids 1a, 2a or 3a and one diphenol or diol, to obtain a deeper insight into the mesogenic character of these monomers.



1a : Z = O; X = OH
2a : Z = CH_2; X = OH
3a : Z = SO_2; X = OH

1b : Z = O; X = Cl
2b : Z = CH_2; X = Cl
3b : Z = SO_2; X = Cl

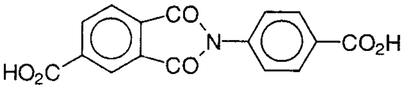


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Table 1. Yields and Properties of the Imide Dicarboxylic Acids 1a, 2a, and 3a, and their Dichlorides 1b, 2b and 3b

Imide No	Yield (%)	melting point (°C)	
1a	92	378 - 379	(Lit: m.p.: 378 [20])
1b	86	240 - 241	(Lit: m.p.: 238 - 239 [21])
2a	91	362 - 364	(Lit: m.p.: 360 [20])
2b	88	263 - 265	(Lit: m.p.: 254 [20])
3a	89	365 - 367	(Lit: m.p.: 364 [20])
3b	94	282 - 283	(Lit: m.p.: 250 - 252 [22])

EXPERIMENTAL

Materials

Trimellitic anhydride, 4,4′-diaminodiphenylether, 4,4′-diaminodiphenylmethane, hydroquinone, 2,7-dihydroxynaphthalene, and 1-chloronaphthalene were gifts of Bayer AG (Leverkusen, Germany) and were used as received. 4,4′-Diamino-diphenylsulfone, methylhydroquinone, *tert*-butylhydroquinone, phenylhydroquinone, 4,4′-dihydroxybiphenyl, 4,4′-dihydroxydiphenyl ether, isosorbide, 1,6-hexandiol, 1,12-dodecandiol and adipoylchloride were purchased from Aldrich Co. (Milwaukee, Wisc.) and used as received.

The three dicarboxylic acids needed in this work (1a, 2a, 3a) were prepared from trimellitic anhydride and 4,4′-diaminodiphenylether, or 4,4′-diaminodiphenyl-methane or 4,4′-diaminodiphenylsulfone in refluxing *m*-cresol. The corresponding dichlorides (1b, 2b, 3b) were prepared by refluxing in thionyl chloride with dropwise addition of dimethylformamide. The yields, melting points and the literature data are summarized in Table 1.

Polycondensations

A typical synthesis of a PEI was performed as follows: 4,4′-Diaminodiphenyl ether bistrimellitimide (10 mmol) and the hydroquinone or another diol (10 mmol) were weighed into a cylindrical glass reactor equipped with gas-inlet and outlet tubes. 1-Chloronaphthalene (5 ml) was added. The reaction vessel was placed into an oil bath preheated to 150°C, and the reaction mixture was homogenized with a mechanical stirrer. The temperature was then rapidly raised to 230°C and maintained for 8 hours. Finally, the PEI was dissolved in a mixture of CH_2Cl_2 and trifluoroacetic acid (volume: 4:1) and precipitated into methanol.

Measurements

Inherent viscosities were measured with an Ubbelohde viscosimeter thermostated at 20°C. DSC measurements were conducted with a Perkin-Elmer DSC-7 in aluminum pans under nitrogen. The 100 MHz ^1H NMR spectra were recorded with a Bruker AC-100 FT NMR spectrometer in 5 mm o.d. sample tubes at 25°C.

The X-ray measurements were conducted with a Siemens D-500 using Ni-filtered Cu K_α radiation.

Furthermore, X-ray measurements were conducted with synchroton radiation (λ = 1.50Å) at HASYLAB (DESY), Hamburg. A heating rate of 10°C/min, and a one-dimensional position sensitive detector were used.

RESULTS AND DISCUSSION

Syntheses

All PEI's were prepared by polycondensation of the dicarboxylic acid chlorides 1b, 2b or 3b (Table 1) with the corresponding diphenols or diols in 1-chloronaphthalene. This procedure avoids problems with high melting temperatures and high melt viscosities which may affect polycondensation in bulk. On the other hand, polycondensations in an inert reaction medium may be affected by an early precipitation of insoluble oligomers. All the polymers were soluble in 1-chloronaphthalene at the reaction temperature of 230-240°C. The yields and properties of the homoPEI's 5a-5i derived from 1b are summarized in Table 2.

The yields and properties of the PEI's 6a, b and 7a, b prepared from 2b and 3b, respectivly are compiled in Table 3.

In addition to these homoPEI's, two series of chiral copoly(ester-imide)s 8a -d and 9a-e were synthesized. The purpose of their syntheses was to obtain chol-

Table 2. Yields and Properties of Copoly(ester-imide)s Containing Different Diols

Polym. Form.	Yield (%)	η_{inh} [a] (dl/g)	Elem. Form. (Form weight)	Elemental Analyses				T_g [b] (°C)	T_i [c] (°C)	Texture
					C	H	N			
5a	98	0,36	$C_{36}H_{18}N_2O_9$ (622,545)	Calcd Found	69,46 69,88	2,91 3,15	4,50 4,46	--	--	not meltable before degradation
5b	96	0,41	$C_{37}H_{20}N_2O_9$ (636,572)	Calcd Found	69,81 70,23	3,17 3,42	4,40 4,34	--	--	not meltable before degradation
5c	98	0,48	$C_{40}H_{26}N_2O_9$ (678,653)	Calcd Found	70,79 71,33	3,86 4,25	4,13 4,12	189	300 - 310	nematic Schlieren texture
5d	96	1,18	$C_{42}H_{22}N_2O_9$ (698,643)	Calcd Found	72,21 72,46	3,17 3,31	4,01 3,92	212	> 400	nematic Schlieren texture
5e	97	0,42	$C_{42}H_{22}N_2O_{10}$ (714,642)	Calcd Found	70,59 70,83	3,10 3,78	3,92 3,73	--	--	not meltable before degradation
5f	96	0,44	$C_{40}H_{20}N_2O_9$ (672,605)	Calcd Found	71,43 71,87	3,00 3,11	4,17 4,03	246	--	not meltable before degradation
5g	98	0,86	$C_{42}H_{22}N_2O_9$ (698,643)	Calcd Found	72,21 72,56	3,17 3,23	4,01 3,96	232	--	not meltable before degradation
5h	97	0,55	$C_{54}H_{46}N_2O_{11}$ (898,965)	Calcd Found	72,15 72,93	5,16 5,33	3,12 3,20	--	265 - 275	smectic texture
5i	96	1,29	$C_{42}H_{42}N_2O_9$ (694,781)	Calcd Found	70,18 70,71	5,89 5,49	3,90 3,82	105	--	isotropic

a) measured at 20°C, with c = 2 g/l in CH_2Cl_2 / trifluoroacetic acid (volume ratio 4 : 1)
b) DSC measurements with a heating rate of 20°C / min
c) isotropization observed by optical microscopy at a heating rate of 10°C / min

Table 3. Yields and Properties of the Isotropic Copoly(ester-imide)s Containing Different Diols and Isosorbide

Polym. Form.	Yield (%)	η_{inh} [a] (dl/g)	Elem. Form. (Form weight)	Elemental Analyses	C	H	N	S	T_g [b] (°C)	T_m [c] (°C)
6a	97	0,54	$C_{41}H_{28}N_2O_8$ (676,681)	Calcd Found	72,77 73,02	4,17 4,28	4,14 4,02		160	--
6b	98	0,64	$C_{55}H_{48}N_2O_{10}$ (896,993)	Calcd Found	73,65 73,93	5,39 5,57	3,12 3,06		125	245
7a	96	0,38	$C_{40}H_{26}N_2O_{10}S$ (726,716)	Calcd Found	66,11 66,46	3,61 3,74	3,85 3,81	4,41 4,20	179	--
7b	97	0,50	$C_{54}H_{46}N_2O_{12}S$ (947,028)	Calcd Found	68,49 68,68	4,90 4,77	2,96 3,02	3,39 3,16	140	--

a) measured at 20°C, with c = 2 g/l in CH_2Cl_2 / trifluoroacetic acid (volume ratio 4 : 1)
b) DSC measurements with a heating rate of 20°C / min
c) melting and isotropization as observed by optical microscopy at a heating rate of 10°C / min

Table 4. Yields and Properties of the Isotropic Copoly(ester-imide)s 8a-d Containing Adipic Acid, Tert-butylhydroquinone and Isosorbide

Polym. Form.	Yield (%)	η_{inh} [a] (dl/g)	Elem. Form. (Form weight)	Elemental Analyses	C	H	N	T_g [b] (°C)
8a	97	0,91	$C_{374}H_{252}N_{18}O_{86}$ (6374,170)	Calcd Found	70,47 70,85	3,99 4,13	3,96 3,85	205
8b	98	0,59	$C_{372}H_{250}N_{18}O_{87}$ (6364,131)	Calcd Found	70,21 70,57	3,96 4,03	3,96 3,88	202
8c	97	0,50	$C_{326}H_{240}N_{14}O_{76}$ (5569,528)	Calcd Found	70,30 70,89	4,34 4,73	3,52 3,29	174
8d	99	0,44	$C_{324}H_{238}N_{14}O_{77}$ (5559,489)	Calcd Found	70,00 70,36	4,32 4,46	3,53 3,48	162

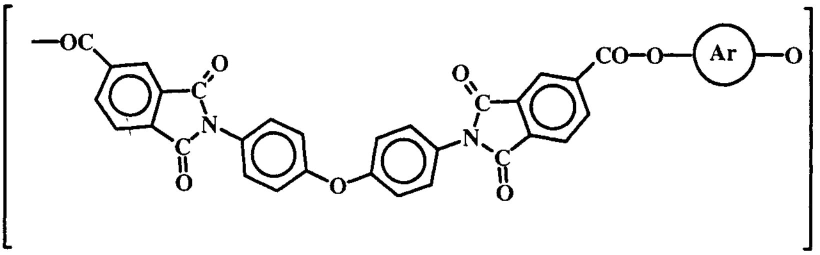
a) measured at 20°C, with c = 2 g/l in CH_2Cl_2 / trifluoroacetic acid (volume ratio 4 : 1)
b) DSC measurements with a heating rate of 20°C / min

Table 5. Yields and Properties of the Isotropic Copoly(ester-imide)s 9a- e Containing Tert-butylhydroquinone and Isosorbide in the Molar Ratio 95/5

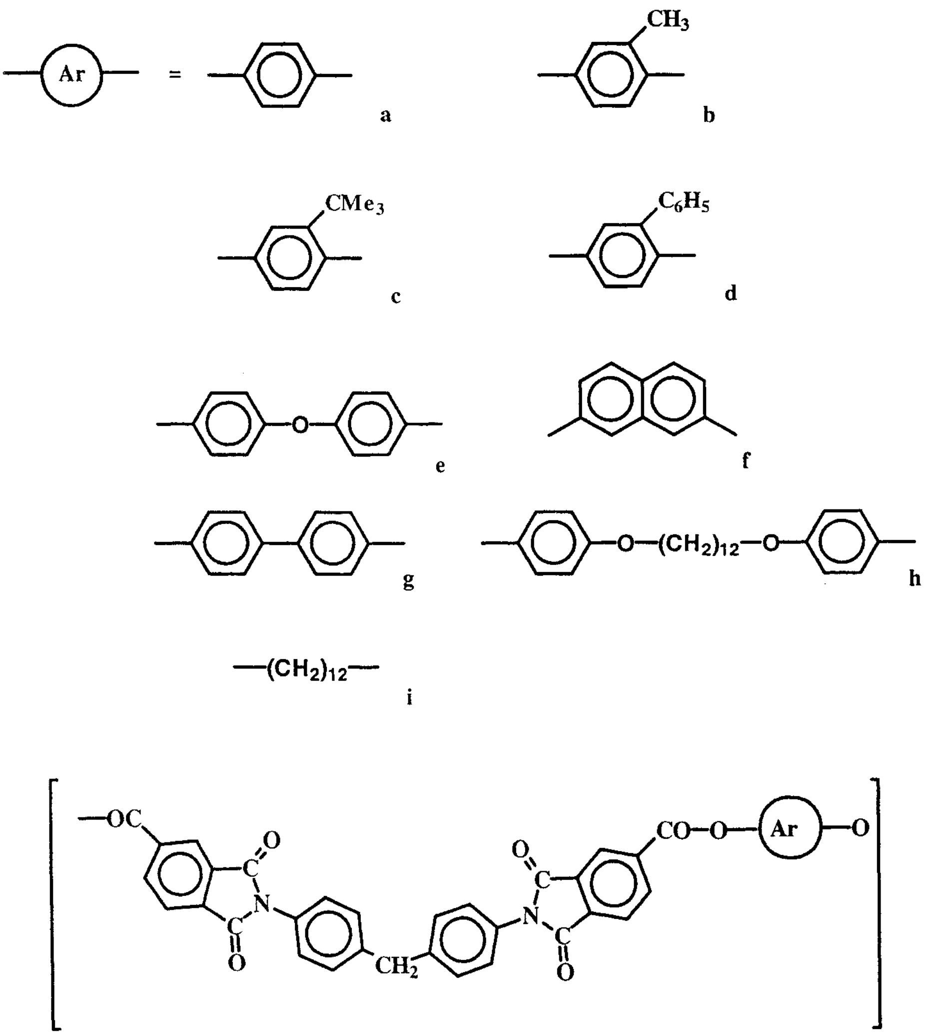
Polym. Form.	Yield (%)	η_{inh} [a] (dl/g)	Elem. Form. (Form weight)	Elemental Analyses	C	H	N	T_g [b] (°C)
9a	97	0,28	$C_{398}H_{258}N_{20}O_{91}$ (6776,491)	Calcd	70,54	3,84	4,13	177
				Found	70,77	4,01	4,05	
9b	97	0,21	$C_{394}H_{258}N_{20}O_{91}$ (6728,447)	Calcd	70,33	3,87	4,16	172
				Found	70,67	3,96	4,07	
9c	96	0,29	$C_{390}H_{258}N_{20}O_{91}$ (6680,403)	Calcd	70,12	3,89	4,19	174
				Found	70,43	3,97	4,15	
9d	97	0,30	$C_{386}H_{258}N_{20}O_{91}$ (6632,359)	Calcd	69,90	3,92	4,22	178
				Found	70,02	4,04	4,19	
9e	98	0,26	$C_{382}H_{258}N_{20}O_{91}$ (6584,315)	Calcd	69,68	3,95	4,25	157
				Found	69,84	4,05	4,19	

a) measured at 20°C, with c = 2 g/l in CH_2Cl_2 / trifluoroacetic acid (volume ratio 4 : 1)
b) DSC measurements with a heating rate of 20°C / min

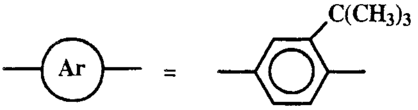
esteric PEI's capable of forming a Grandjean texture [17, 18]. A Grandjean texture is of great interest for its optical properties [19], and cholesteric polymers capable of yielding a stable Grandjean texture may be of interest as organic pigments. The chiral PEI's 8a-d and 9a-e were characterized by inherent viscosities and elemental analyses (Tables 4 and 5). In the case of 8a-d and 9a-e, the incorporation of the aliphatic comonomers according to the feed ratio was confirmed by ^1H NMR spectroscopy. As illustrated by the spectrum of Figure 1, all copolyesters possessed the expected structure.



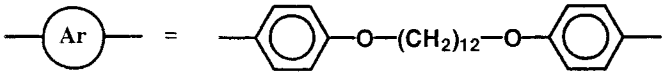
5a - i

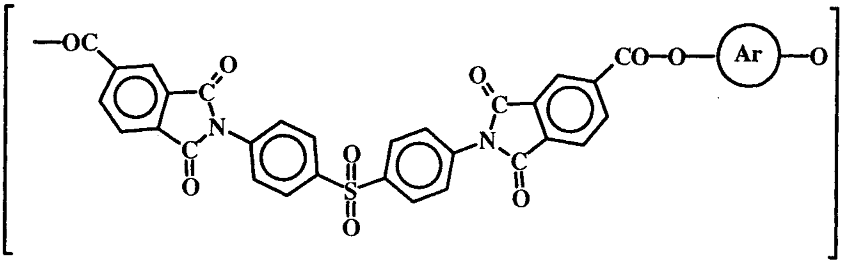

Ar
=
CH3
a
b
CMe3
c
C6H5
d
O
e
f
g
O—(CH2)12—O
h
—(CH2)12—
i
—OC
O
C
N
C
O
CH2
O
C
N
C
O
CO—O—
Ar
—O

6a:

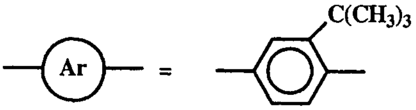

Ar
=
C(CH3)3

6b:

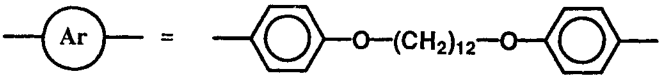

Ar
=
O—(CH2)12—O

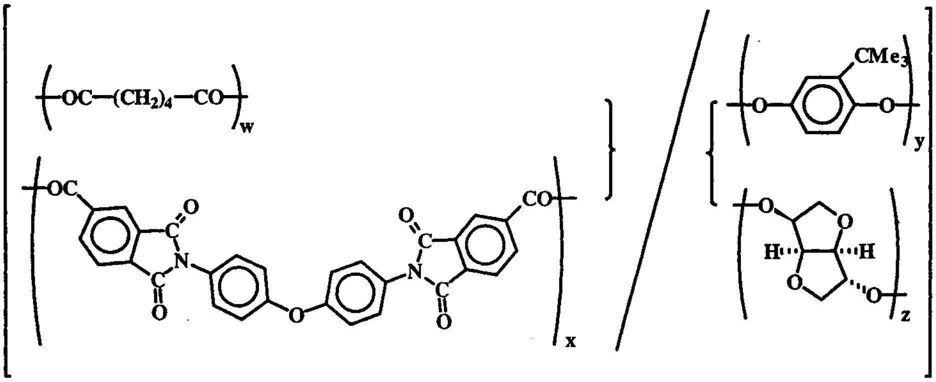


7a:



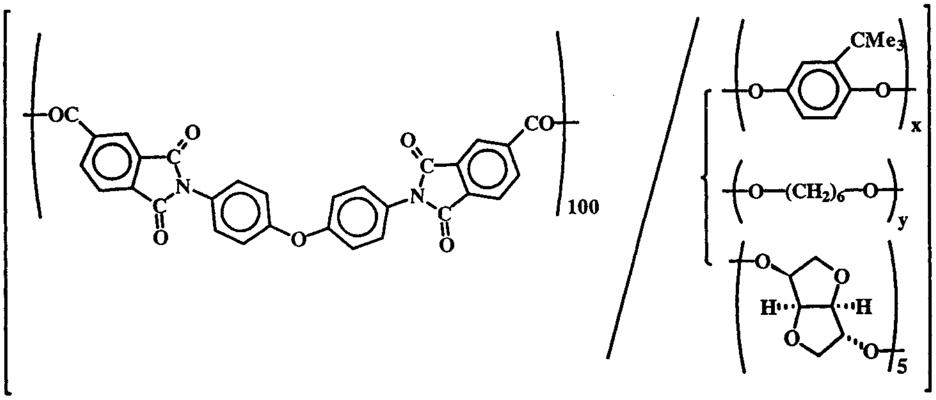
7b:





8a - d

a: w / x / y / z = 10 / 90 / 95 / 5
b: w / x / y / z = 10 / 90 / 90 / 10
c: w / x / y / z = 30 / 70 / 95 / 5
d: w / x / y / z = 30 / 70 / 90 / 10



9a - e

a: x / y = 95 / 0
b: x / y = 85 / 10
c: x / y = 75 / 20
d: x / y = 65 / 30
e: x / y = 55 / 40

Thermal Properties

All homo and coPEI's were examined by optical microscopy with crossed polarizers and DSC measurements to study the formation of LC-phases.

In the case of PEI 's 5a and 5b, no melting process was detectable. Both polymers began to decompose slowly above 400°C, and more rapidly above 450°C without forming a mobile melt. The WAXS powder patterns (Figure 2A) showed that both PEI's were highly crystalline. No glass-transition temperatures were detectable in the DSC traces.

When larger substituents are attached to the hydroquinone, the properties of the resulting PEI's 5c and 5d changed completely. These PEI's were not crystalline and the glass-transition temperatures (T_g's see Table 2) were clearly detectable in the DSC curves. Both PEI's formed a nematic phase above their T_g's. The nematic phase of 5c vanished above 300°C, so that in this case a reversible isotropization was observed. In the case of 5d, the nematic phase was stable up to temperatures above 400°C, where the isotropization was affected by thermal degradation. The PEI's 5e-5g were crystalline and did not melt below 400°C. Above 400°C, thermal degradation prevented the formation and characterization of a stable melt, analogous to 5a and 5b. PEI 5h was semicrystalline. Its WAXD powder pattern was nearly identical with that of 6b, (Figure 2B). It was found to be capable of forming an enantiotropic smectic LC-phase, whereas the PEI 5i was amorphous forming an isotropic melt above the T_g of 105°C. Thus, these results demonstrate that the properties of polyesters derived from the dicarboxylic acid 1a may vary over an extremely broad range, and LC-phases may be found in examples with suitable diphenols.

The characterization of the polyesters 6a and 6b (derived from 1b) gave the following results. The PEI 6a was found to be an amorphous material yielding an isotropic melt above its T_g at 160°C. PEI 6b had a crystalline smectic structure and exhibited an isotropic melt at 245°C (discussed below). Both polyesters 7a and 7b were found to be amorphous and isotropic.

These results allow the conclusion that the tendency to form a liquid-crystalline or crystalline phase decreases in the following order:

$$1a > 1b > 1c$$

However, even the dicarboxylic acid 1a is a relatively poor mesogen. This classification is not only based on the isotropic character of polyester 5i, it also became evident from the observation that the chiral copolyesters (8a-d and 9a-e) were isotropic. The above order of mesogenicity is in perfect agreement with previous studies of polyesters derived from the diphenols 10a-c [23] and with studies of poly(ester-imide)s derived from the tetracarboxylic anhydrides 11a-c [24].

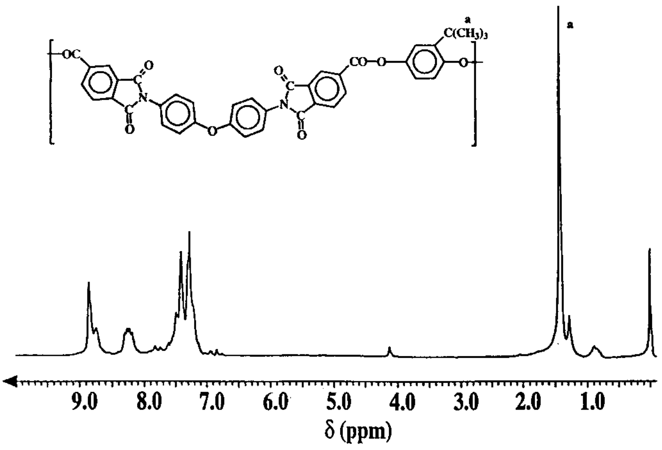


Figure 1. 100 MHz ^1H NMR spectrum of the copoly(ester-imide) 5c.

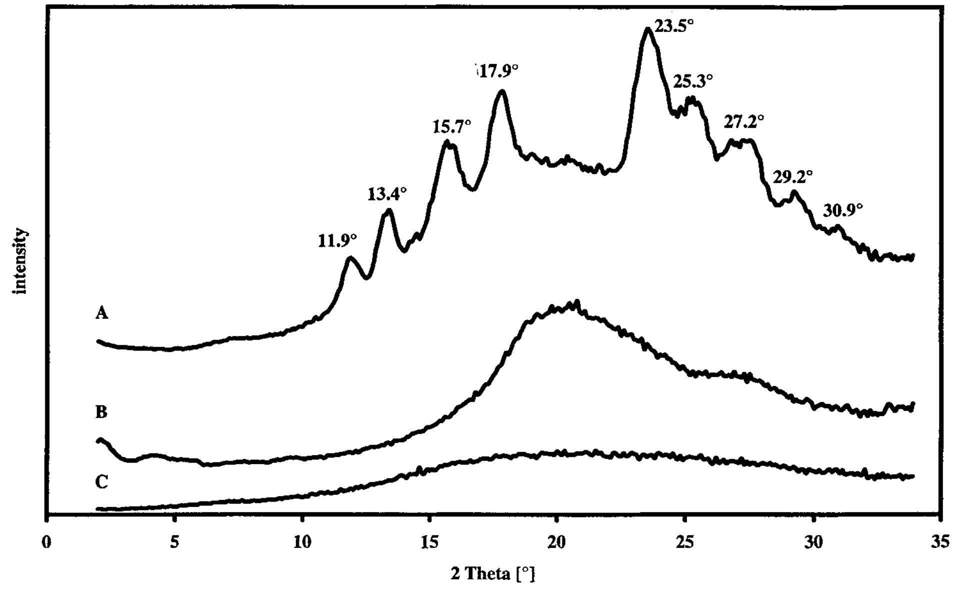
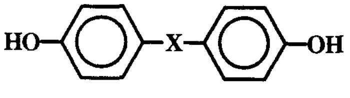


Figure 2. WAXS powder patterns of the poly(ester-imide)s 5b (A), 6b (B) and 7b (C).

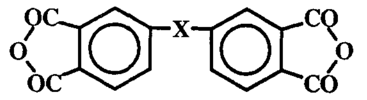
The following orders of decreasing mesogenicity were found:

10a >10b > 10c and 11a > 11b > 11c

The reasons for these orders are twofold. Firstly, the bond angle decrease in this order from approximately 125° to 100° [23], and a smaller bond angle means a greater deviation from linearity. Secondly, a diphenyl ether unit has a higher tendency (for steric and electronic reasons [24]) to adopt a nearly coplanar conformation of both phenyl rings. Such a coplanar conformation favors electronic interactions between neighboring chain segments (which decrease with the sixth power of the distance), and thus, stabilizes a nematic order.



10a: X = O
10b: X = $C(CH_3)_2$
10c: X = SO_2



11a: X = O
11b: X = $C(CF_3)_2$
11c: X = SO_2

Properties of the Poly(ester-imide)s 5h, 6b and 7b

For the PEI 5h, the existence of smectic phases was detected, and the X-ray measurements indicated a rather complex "phase behavior". A full elucidation of the supermolecular structure and the phase transitions of 5h was not intended in this work. Nonetheless, a short description of the basic features and problems should be given in this work as a preliminary characterization used as a basis for future more detailed studies.

The DSC measurements conducted of 5h with a heating and cooling rate of 20°C/min revealed a broad glass-transition between 170 and 200°C, along with one strong endotherm around 267°C (Figure 3). These thermal properties were reproducible in the second heating trace. Optical microscopy with crossed polarizers revealed that the endotherm at 267°C represents the isotropization process. This assignment entails in turn that the DSC curves do not carry any information about a melting/crystallization process. The absence of wide-angle reflections in the X-ray powder and fiber patterns confirmed that 5h is non-crystalline, if not annealed for a long time. Polarized optical microscopy also revealed that 5h forms a bâtonnet texture upon cooling from the isotropic melt (Figure 4), typical of a smectic-A phase. Polarized optical microscopy did allow the detection of additional phase transitions (e.g. smectic-A --> smectic-C) upon further cooling. These results demonstrate that the PEI 5h forms at least one smectic LC-phase and a solid state which is a frozen smectic phase, a so-called smectic glass.

When WAXD powder patterns of 5h were recorded in the temperature range of 30-300°C (Figures 5 and 6), the following puzzling results were obtained.

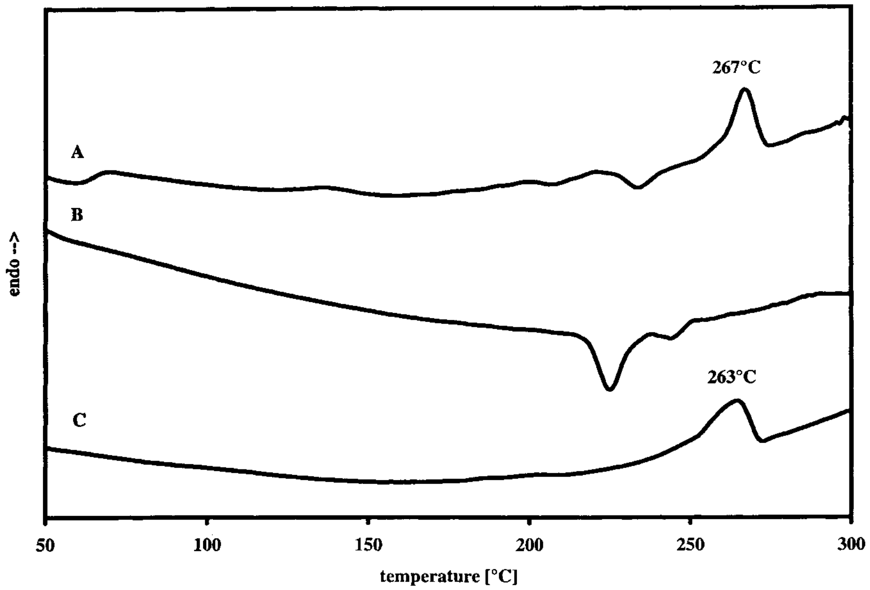


Figure 3. DSC measurements (heating and cooling rate 20°C/min) of poly(ester-imide) 5 h: A) 1st heating, B) 1st cooling, C) 2nd heating.

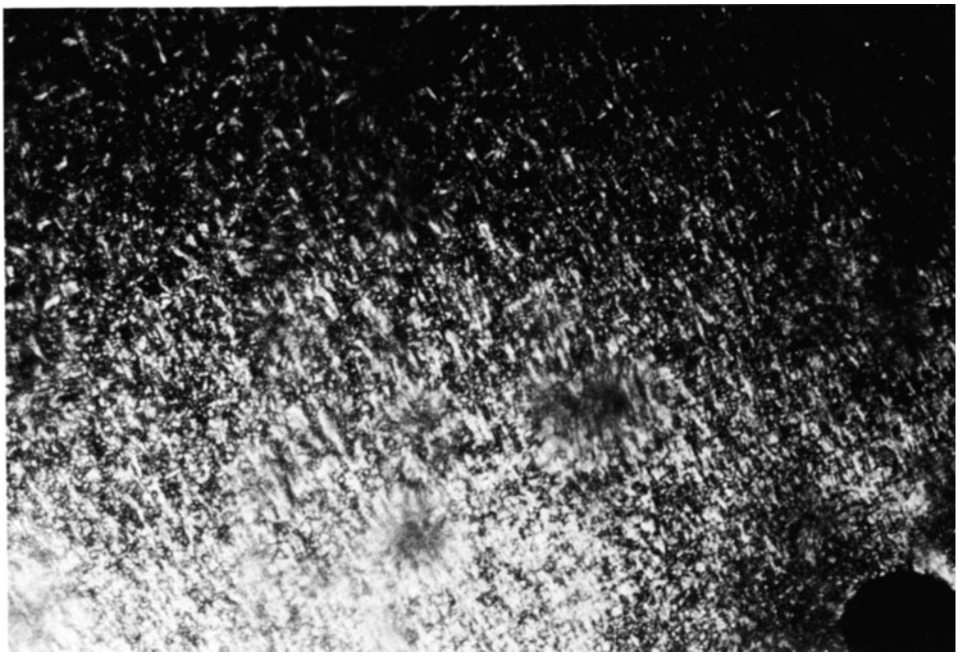


Figure 4. Bâttonet texture of the poly(ester-imide) 5h formed upon cooling from the isotropic melt below 250°C.

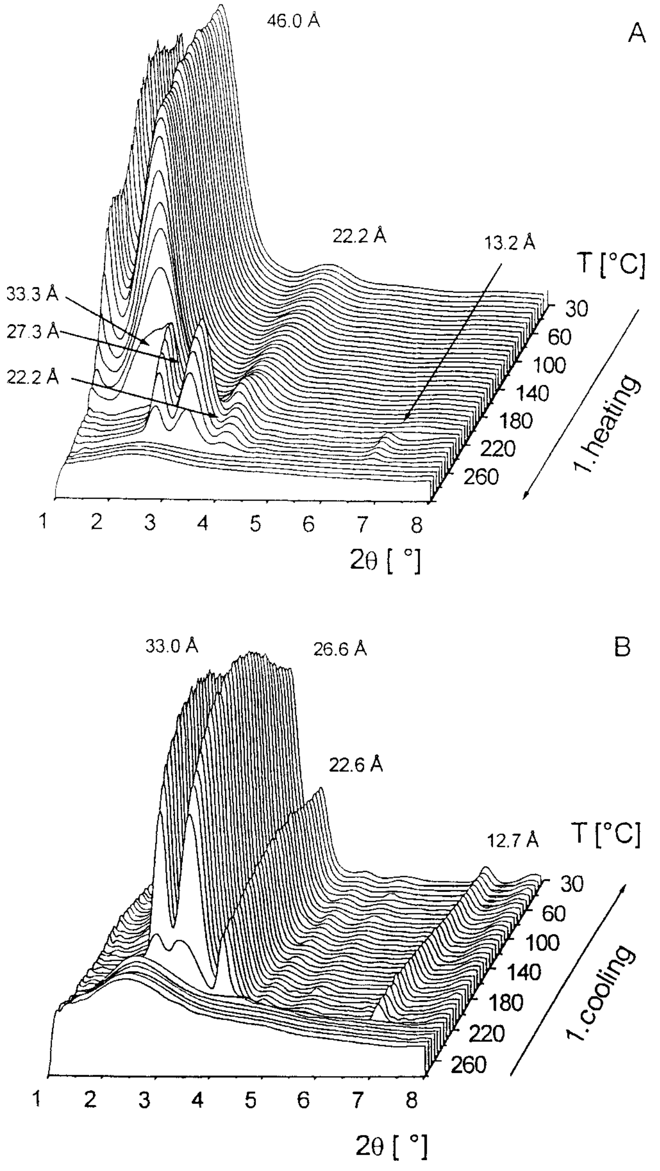


Figure 5. X-ray synchrotron radiation measurements of 5h conducted with a heating and cooling rate ot 10°C min: A) 1st heating of a sample precipitated into methanol and dried at 110°C, B) 1st cooling of the same sample.

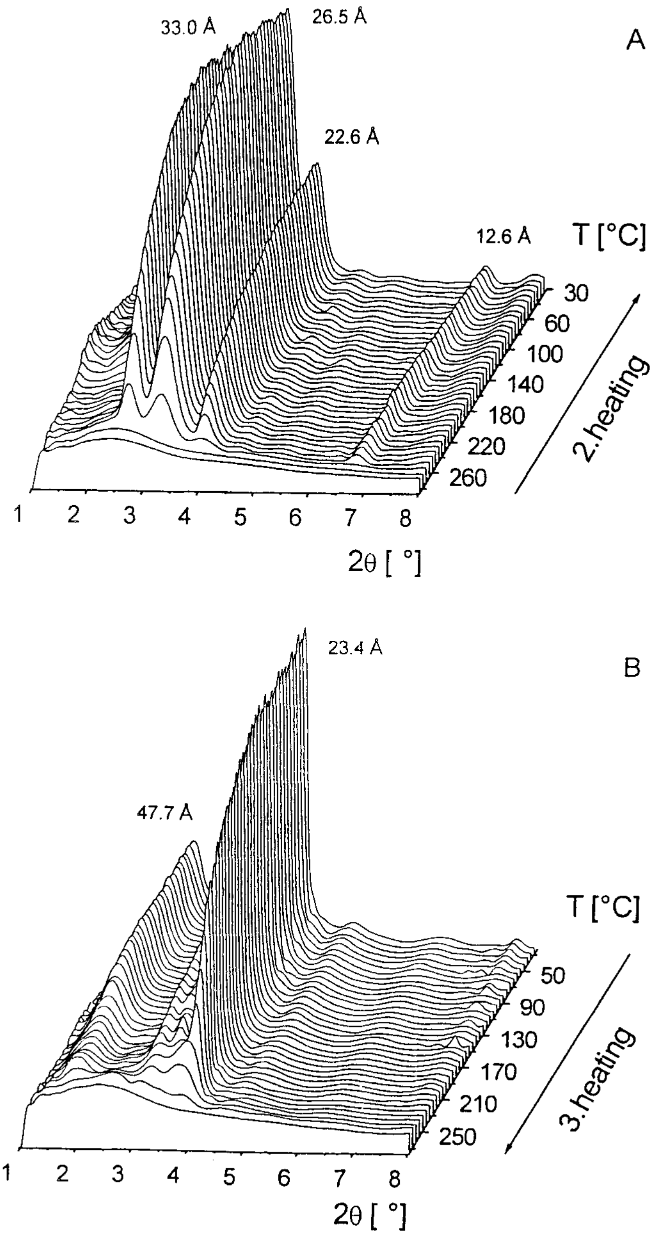


Figure 6. X-ray synchrotron radiation measurements of 5h: A) 2nd heating, B) 3rd heating after quenching from the isotropic melt.

The first heating (Figure 5A) was conducted with a sample precipitated from methanol and dried at 110°C *in vacuo*, i.e. below the glass-transition temperature (T_g). In this case, a strong middle-angle reflection (MAR) was found corresponding to an atomic distance (d-spacing) of 46 Å. Above T_g, the MAR shifted to shorter d-spacings, and around 220°C, four new reflections appeared at 33.3, 27.3, 22.2, and 13.2 Å. Above 260°C, all reflections disappeared in agreement with the isotropization observed by optical microscopy. The four MAR's observed at higher temperatures in the first heating trace reappeared upon cooling from the isotropic melt (Figure 5 B), and remained unchanged in the second heating (Figure 6A). Therefore, it may be concluded that the four MAR's corresponding to d-spacings around 33.0, 26.5 , 22.5, and 13.0 Å represent the thermodynamically stable situation. When the WAXD powder patterns were recorded after quenching from the isotropic melt, again a different picture was obtained (Figure 6B). This means that the supermolecular structure of 5h is extremely sensitive to the thermal history. This is particularly surprising, because no changes of crystal modification are involved.

Finally, a fiber pattern was recorded from fibers cooled down from the isotropic melt (Figure 7). Two sharp MAR's corresponding to d-spacings of 22.0 and 11.2 Å were found on the meridian. Furthermore, a four-point pattern was detected indicating the presence of a frozen smectic-C phase. Considering a d-spacing of 27.5 Å and a tilt angle of 57-58°, this four-point diagram allows the calculation of a layer distance around 52 Å. This distance agrees well with the length of the repeating unit with a predominance of tt-conformations of the alkane spacer. Thus, the fiber pattern clearly demonstrates that two different layer structures were frozen-in in the fiber. A straightforward interpretation of the MAR's at 47, 33, 22 and 12 ± 1 Å observed in the various X-ray patterns presented in Figures 5 and 6 cannot be presented at this time.

The solid state and the melting process of the polyester 6b was also examined by synchrotron radiation measurements. Wide angle reflection and the microscopic observation of spherulites confirmed the existence of a crystalline phase. However, a strong MAR also proved the existence of a layer structure (Figure 8). When the original sample precipitated into methanol and dried at 110°C (below the T_g) was heated, it showed initially a MAR (and its 2nd order reflection) corresponding to d-spacing of 45 Å. Between 170 and 175°C, a solid-solid transition took place yielding a layer structure with a d-spacing of 38-39 Å (Figure 8A). This second layer structure is the thermodynamically stable phase which was formed again upon cooling and reheating (Figure 8B). An endothermic transition

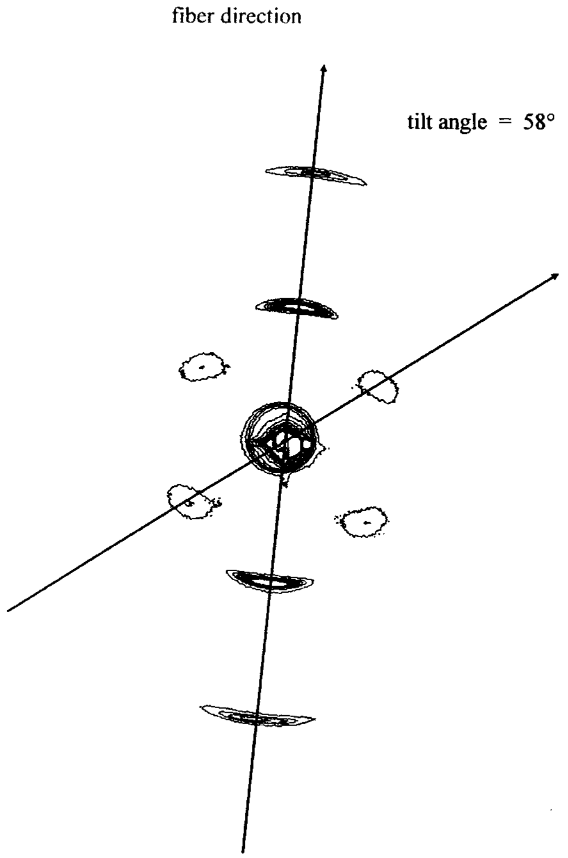


Figure 7. Fiber pattern of 5h (the fiber was hand-drawn from the isotropic melt).

between 140 and 170°C in the 1st heating curve and its absence during the 2nd heating of the DSC measurements (Figure 9) agree well with the synchrotron radiation measurements. The endotherms in the range of 230-245°C represent the melting process which depends on the perfection of the crystallites, and thus, on the thermal history.

Considering a length of 51 ± 1 Å for the fully extended, upright repeating unit, a d-spacing of 38 Å indicates a significant tilt relative to the layer plane quite analogous to polyester 5h.

However, it should be emphasized that 6b in contrast to 5h does not form an enantiotropic LC-phase.

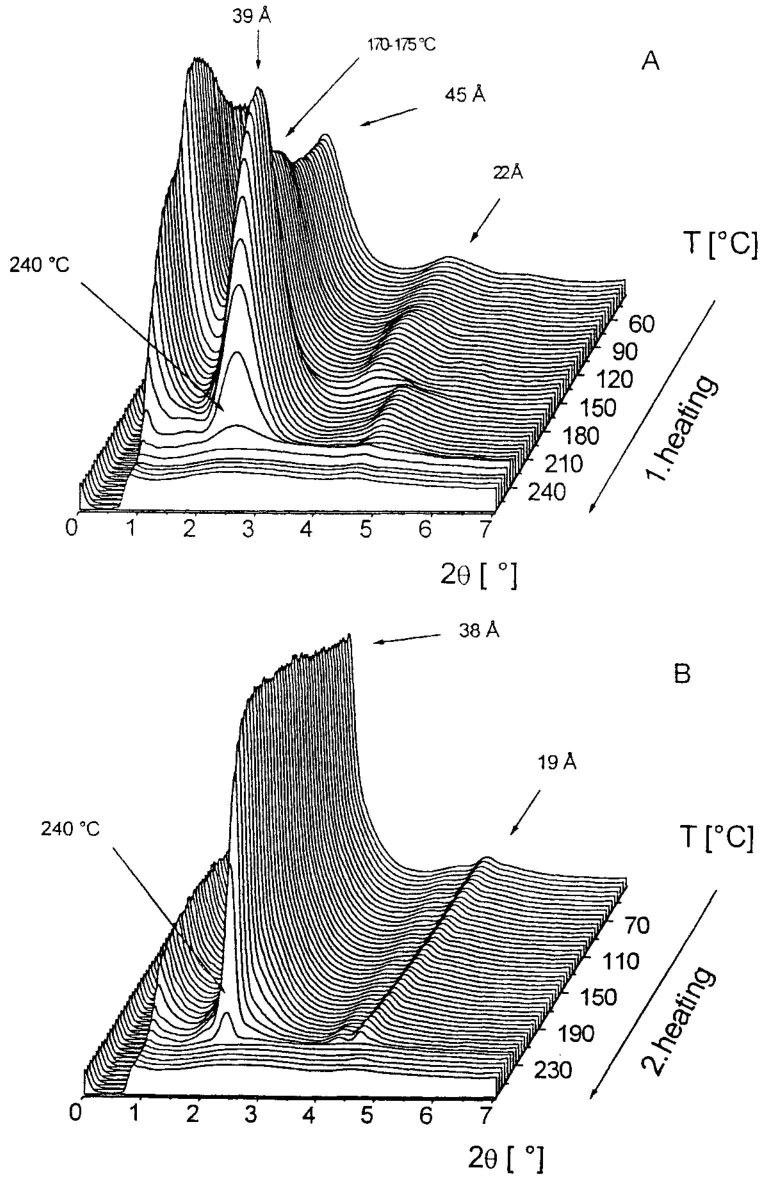


Figure 8. X-ray synchrotron radiation measurements of polyester 6b (middle angle reflections only): A) 1st heating after precipitation and drying at 110°C, B) 2nd heating.

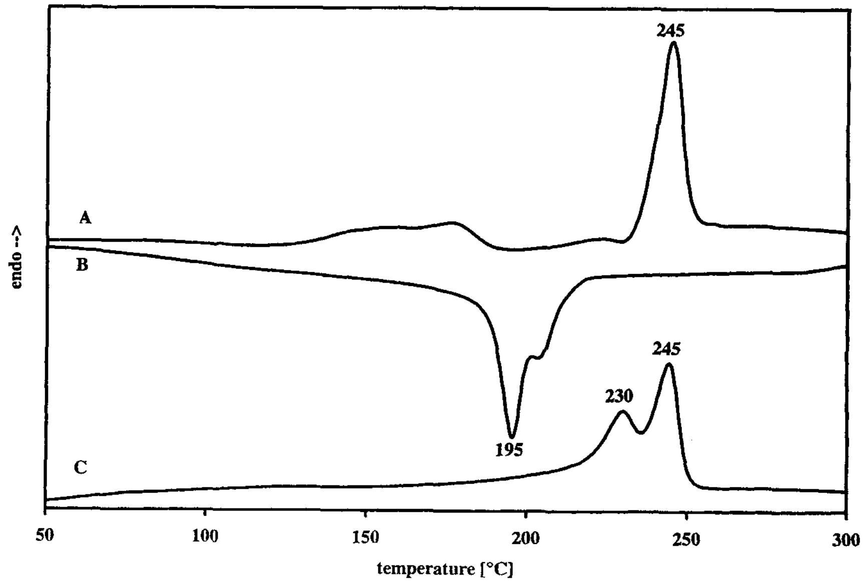


Figure 9. DSC measurements (heating/cooling rate 20°C/min) of PEI 6b: A) 1st heating, B) 1st cooling, C) 2nd heating

CONCLUSION

Numerous poly(ester-imide)s were prepared from various diphenols and three different imide dicarboxylic acids. These dicarboxylic acids were synthesized from trimellitic anhydride and 4,4′-diaminodiphenyl ether (1a), 4,4′-diaminodiphenyl methane (1b) or 4,4′-diaminodiphenyl sulfone (1c). The thermal properties of the poly(ester-imide)s were characterized with the purpose to elucidate the mesogenic character of the three imide dicarboxylic acids 1a-1c. The results of this work, combined with those of previous studies concerning polyesters derived from 10a-c and 11a-c, allow the conclusion that the tendency to form layer structures and/or LC-phases decreases in the following order:

1a > 1b > 1c

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