New polymer syntheses: 21. LC-poly(ester imide)s prepared from trimellitic acid, α,ω-diaminoalkanes and various hydroquinones or dihydroxynaphthalenes

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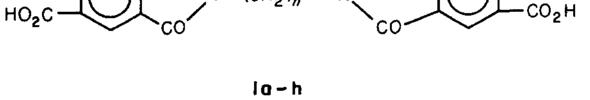
A series of nine α,ω-diaminoalkane bistrimellitimides was prepared from trimellitic anhydride and these were then condensed with the acetyl derivatives of various bisphenols. These bisphenols included hydroquinone, methyl-, chloro-, phenyl- and tetrachlorohydroquinone, 1,5-, 1,4-, 2,7- and 2,6-dihydroxynaphthalenes. Only poly(ester imide)s containing hydroquinone and tetrachlorohydroquinone or 2,6-dihydroxynaphthalene formed a mesogenic melt. Compared with the corresponding poly(ester imide)s built up from 4,4′-dihydroxybiphenyl, the melting points were lower and the temperature range of the mesogenic melt was significantly smaller. WAXS measurements of the solid materials indicated a layered structure with a periodicity corresponding to the length of the monomer units. The poly(ester imide)s were characterized by elemental analyses, viscometry, d.s.c. measurements, polarizing microscopy and thermogravimetric analyses. Furthermore, heat-distortion temperatures were measured under high and low pressure. Most poly(ester imide)s with an even number of methylene groups exhibit heat distortion temperatures close to the melting point, whereas those with an odd number display heat distortion temperatures close to the glass transition.

(Keywords: synthesis; LC-poly(ester imide)s; trimellitic acid; hydroquinone; dihydroxynaphthalene)

INTRODUCTION

In the preceding paper in this series[1], the synthesis and characterization of poly(ester imide)s prepared from α,ω-diaminoalkane bistrimellitimides (**1a**–**h**) and 4,4′-dihydroxybiphenyl were reported. Characteristic properties of this class of LC-polyesters are a relatively broad temperature range of the mesogenic phase (*ca.* 70°C–170°C depending on *n*), a high degree of crystallinity, a high rate of crystallization and consequently high heat distortion temperatures. Such liquid crystalline polyesters (LC-) are of interest, because they have relatively flexible chains and correspondingly low melt viscosities combined with high heat distortion temperatures, and because the properties of the homopolyesters are not affected by transesterification or sequence effects. Therefore, the present work had the purpose of elucidating the influence of various bisphenols on the properties of homopolyesters derived from the diacids **1a**–**h**. In this connection it is noteworthy that a copolyester of diacid **1b**, methylhydroquinone, terephthalic acid and 4-hydroxybenzoic acid was claimed, in a recent patent[2], as a thermotropic material for the production of fibres.



1a–h

1a: $n=5$
1b: $n=6$
1c: $n=7$
1d: $n=8$
1e: $n=9$
1f: $n=10$
1g: $n=11$
1h: $n=12$

EXPERIMENTAL

Materials

Hydroquinone and trimellitic anhydride were kindly gifted by Bayer AG (D-4150 Krefeld-Uerdingen, FRG). Trimellitic anhydride was recrystallized from hot toluene in the presence of acetanhydride. The α,ω-diaminoalkanes methylhydroquinone, chlorohydroquinone, phenylhydroquinone, 1,4-, 1,5-, 2,6- and 2,7-dihydroxy naphthalene were all purchased from the Aldrich Co. (St. Louis, USA) and were used without purification. The hydroquinones and dihydroxynaphthalenes were acetylated with acetic anhydride in boiling toluene. Tetrachlorohydroquinone was prepared by reduction of tetrachlorobenzoquinone (Aldrich Co.) with hydrazine in dioxane[3]. All acetylated hydroquinones and dihydroxynaphthalenes are described in the literature (see *Table 1*). The diacids **1a**–**h** were described in the preceding part and **1b** in ref. 4.

Polycondensations

An α,ω-diaminoalkane bistrimellitimide [**1a**–**h**] (100 mmol), an acetylated hydroquinone or dihydroxynaphthalene (100 mmol) and magnesium oxide (100 mg) were weighed into a cylindrical round bottomed glass

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Table 1 Melting points and literature data for hydroquinone or dihydroxynaphthalene acetates prepared by means of acetic anhydride

Bisphenol	Solvents or reaction media	T_m (°C)	T_m(lit.) (°C)	Reference
Hydroquinone	Toluene	123–124	123–124	5
Chlorohydroquinone	Chlorobenzene	71–72	70–71	6
Tetrachlorohydroquinone	Toluene	244–245	245	7
Methylhydroquinone	Toluene	49–52	48–50	8
Phenylhydroquinone	Toluene	71	71	9
1,4-Dihydroxynaphthalene	Toluene	126–127	128–130	10
1,5-Dihydroxynaphthalene	Toluene	158	159–160	11
2,6-Dihydroxynaphthalene	Acetic anhydride	173–175	175	12
2,7-Dihydroxynaphthalene	Acetic anhydride	127–129	129	13

Table 2 Yields and properties of poly(ester imide)s prepared from α,ω-diaminoalkane bistrimellitimides (**1a**–**h**) and hydroquinone bisacetate

Formula	n	Yield (%)	T_g[a] (°C)	T_{m_1}[a] (°C)	T_{m_2}[a] (°C)	η_{inh}[b] (dl/g)	LC-phase[c] (°C)	Elemental formula (M.wt.)	Elemental analyses	C	H	N
2a	5	92.9	141	295	–	0.39	315–326	$C_{29}H_{20}N_2O_8$	Calcd.	66.41	3.84	5.34
								(524.49)	Found	66.01	3.89	5.55
2b	6	85.6	134	350	406	0.46	350–365	$C_{30}H_{22}N_2O_8$	Calcd.	66.91	4.12	5.20
								(538.52)	Found	66.47	4.40	5.87
2c	7	88.3	117	268	276	0.39	236–264	$C_{31}H_{24}N_2O_8$	Calcd.	67.39	4.38	5.07
								(552.55)	Found	67.18	4.30	5.20
2d	8	95.2	–	348	–	0.54	345–350	$C_{32}H_{26}N_2O_8$	Calcd.	67.84	4.63	4.95
								(566.57)	Found	67.56	4.67	5.10
2e	9	89.7	–	238	256	0.34	234–256	$C_{33}H_{28}N_2O_8$	Calcd.	68.27	4.86	4.83
								(580.60)	Found	68.23	4.95	5.05
2f	10	94.1	–	275	286	0.32	277–282	$C_{34}H_{30}N_2O_8$	Calcd.	68.68	5.09	4.71
								(594.63)	Found	68.53	5.21	4.95
2g	11	88.5	85	216	230	0.71	220–238	$C_{35}H_{32}N_2O_8$	Calcd.	69.07	5.30	4.60
								(608.65)	Found	69.08	5.56	4.96
2h	12	91.3	–	242	266	0.53	232–262	$C_{36}H_{34}N_2O_8$	Calcd.	69.44	5.50	4.50
								(622.68)	Found	69.20	5.79	4.89

[a] From d.s.c. measurements (heating rate 20°C/min)
[b] Measured in dichloromethane/trifluoroacetic acid (4:1 by volume) with $c = 2$ g/l at 20°C
[c] As observed under the polarizing microscope

reactor equipped with stirrer and gas-inlet and outlet tubes. The reaction mixture was heated under nitrogen to 250°C where the condensation started. The temperature was then raised in a stepwise manner until the final reaction temperature was reached (*Tables 1, 2* and *4*). During the last 30 min of the condensation, introduction of nitrogen was halted and a vacuum was applied. After cooling, the resulting polymer was crushed and dissolved in *ca.* 200 ml of a 4:1 mixture (by volume) of dichloromethane and trifluoacetic acid and precipitated using methanol. After isolation by filtration, the polymers were dried *in vacuo* at 80°C.

Measurements

The d.s.c. measurements were conducted using a Perkin–Elmer DSC-4, aluminium pans and a heating rate of 20°C/min.

The viscosities were measured with an automated Ubbelohde viscometer thermostatically controlled at 20°C. A solution of polymer (120 mg) in a 4:1 mixture (50 ml) (by volume) of dichloromethane and trifluoroacetic acid was used in all cases.

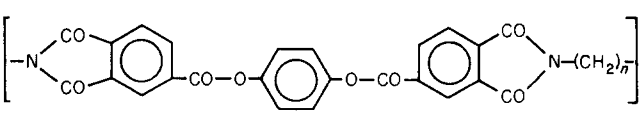
The thermomechanical measurements (penetration method) were conducted using a Perkin–Elmer TMS-2 at a heating rate of 5°C/min at pressures of 0.05 kg mm^{-2} or 1.0 kg mm^{-2}. The thermogravimetric analyses were obtained using a Perkin Elmer TGS-2 at a heating rate of 10°C/min in air.

The wide-angle X-ray scattering (WAXS) curves were measured with a powder diffractometer ‘Siemens D-500’ using Cu-Kα radiation and a Ni-filter. For the set of slits between the radiation source and the scintillation counter, detector angles of 10°, 1°, 0.1° and 0.5°C were chosen. The diagrams were recorded in steps of $\theta = 0.1°$ with a radiation time of 20 s/data point.

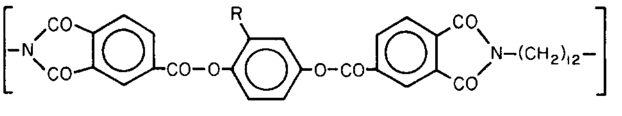
The fibre patterns were measured with a pin-hole camera using Cu-Kα radiation. Fibres of poly(ester imide) **2a** and **5d** were spun from the melt at 280°C.

RESULTS AND DISCUSSION

Poly(ester imide)s derived from hydroquinones

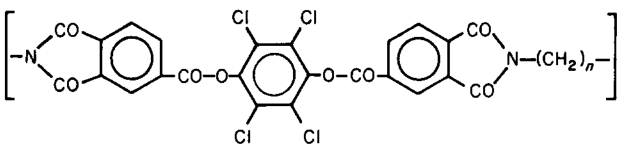


2a–h (n = 5–12)



3a–c

a : R = CH_3
b : R = Cl
c : R = C_6H_5



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One series of poly(ester imide)s, **2a–h**, was prepared from unsubstituted hydroquinone and from the diacids **1a–h**. In the case of **2a–h** the isolated and recrystallized diacids **1a–f** and **1h** were reacted with the acetate of hydroquinone, whereas **2g** was prepared by a 'one pot procedure' from 1,11-diaminoundecane bishydrochloride, trimellitic anhydride and hydroquinone acetate. Yields and various properties of these poly(ester imide)s are summarized in *Table 2*. A second series of poly(ester imide)s, **3a–c** and **4**, was synthesized by condensation of diacid **1h** with the acetates of various substituted hydroquinones. Yields and properties are listed in *Table 2*. The condensations were initiated at 250°C and the temperature was then gradually raised to 320°C. Higher temperatures were avoided as thermal degradation sets in slowly at around 340°C (*Table 3*).

As indicated by the d.s.c. measurements, all poly(ester imide)s of hydroquinones with the exception of **2b**, **d** and **4** possess melting points below 300°C. In these cases, easily stirrable melts were obtained at the final reaction temperature of 320°C, whereas the polyesters **2b**, **d** and **4** solidified in the course of the condensation. In contrast to the analogous poly(ester imide)s derived from 4,4′-dihydroxybiphenyl[1], all poly(ester imide)s derived from substituted or unsubstituted hydroquinones are soluble in mixtures of dichloromethane and trifluoroacetic acid. The inherent viscosities of these poly(ester imide)s are lower than those found for poly(ester imide)s of 2,6-dihydroxynaphthalene (*Table 4*) or those of 4,4′-dihydroxybiphenyl. The main reason is sublimation of the relatively volatile hydroquinone acetates which affects the stoichiometry of the reaction mixture.

D.s.c. measurements conducted at a heating rate of 20°C/min revealed, for several poly(ester imide)s, glass transition temperatures (T_g) in the range 85°C–145°C (*Table 2*). As expected, the T_gs increase with decreasing length of the flexible aliphatic spacer. In some cases (**2d–f** and **2h**) the T_gs could not be measured because neither rapid cooling in the d.s.c. apparatus (−300°C/min) nor quenching using liquid nitrogen produced amorphous samples. In these cases the rate of crystallization is so high that it cannot be suppressed. The same thermal behaviour was found for poly(ester imide)s of 4,4′-dihydroxybiphenyl. This fits in well with the interpretation that the highest rates of crystallization were found for poly(ester imide)s with long aliphatic spacers and preferentially for spacers with an even number of methylene groups. In

Table 3 Yields and properties of LC-poly(ester imide)s prepared from 1,12-diaminodecane bistrimellitimide and various hydroquinones

Hydroquinone	Yield (%)	T_g[a] (°C)	T_{m_1}[a] (°C)	T_{m_2}[a] (°C)	η_{inh}[b] (dl/g)	LC-phase[c] (°C)	Elemental formula (M-wt.)	Elemental analyses	C	H	N	
Unsubstituted methyl	91.3	–	242	266	0.53	232–262	$C_{36}H_{34}N_2O_8$	Calcd.	69.44	5.50	4.50	
							(622.68)	Found	69.20	5.79	4.89	
	90.1	–	215	–	0.32	–	$C_{37}H_{36}N_2O_8$	Calcd.	69.80	5.70	4.40	
							(636.71)	Found	69.71	5.84	4.52	
Chloro	83.3	–	240	–	0.39	–	$C_{36}H_{33}ClN_2O_8$	Calcd.	65.80	5.06	4.26	Cl: 5.40
							(657.12)	Found	65.89	5.19	4.39	Cl: 4.21
Phenyl	88.6	90	–	–	0.39	–	$C_{42}H_{38}N_2O_8$	Calcd.	72.19	5.48	4.01	
							(698.78)	Found	72.25	5.41	4.14	
Tetrachloro	94.8	117	270[d]	323[d]	insol.	335–350	$C_{36}H_{30}Cl_4N_2O_8$	Calcd.	56.86	3.98	3.68	Cl: 18.65
		117	259[e]	371[e]			(760.46)	Found	57.37	3.98	3.87	Cl: 18.16

[a] D.s.c. measurements with a heating rate of 20°C/min
[b] Measured in dichloromethane/trifluoroacetic acid (4:1 by volume) with $c = 2$ g/l at 20°C
[c] As observed under the polarizing microscope
[d] First heating trace
[e] Second heating after rapid cooling

Table 4 Heat distortion temperatures and thermal stability of poly(ester imide)s prepared from α,ω-diaminoalkane bistrimellitimides and hydroquinone

Formula	n	T_{m_1}	Heat-distortion temperatures (°C)[a]	(°C)[b]	Temperatures with the following losses of weight[c] 1%	5%	10%	20%
2a	5	295	285	241	–	–	–	–
2b	6	178	124	–	–	–	–	–
2c	7	268	255	100	354	413	426	438
2d	8	349	330	320	378	429	432	447
2e	9	238	208	103	379	420	434	450
2f	10	275	262	213	355	410	426	443
2g	11	216	205	78	–	–	–	–
2h	12	242	245	217	323	412	432	449

[a] Measured with a pressure of 0.05 kg mm^{-2} at a heating rate of 5°C/min
[b] Measured with a pressure of 1.0 kg mm^{-2} at a heating rate of 5°C/min
[c] Measured with a heating rate of 10°C/min in air

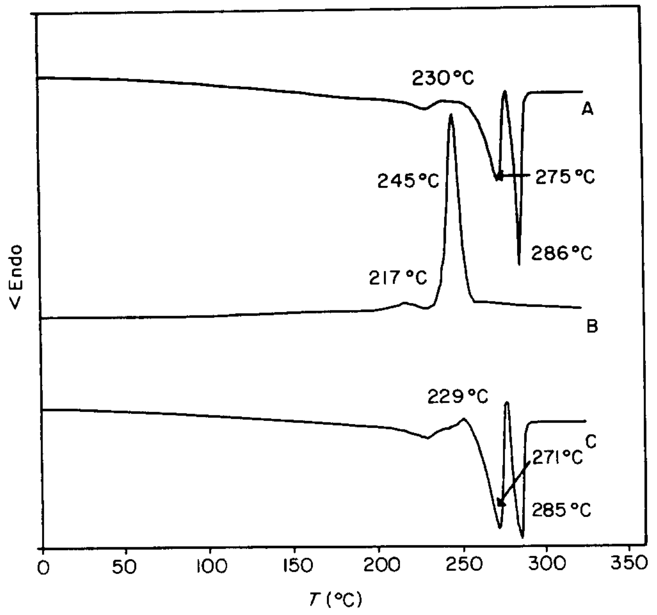
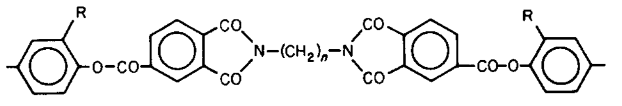


Figure 1 D.s.c. traces (heating and cooling rate 20°C/min) of polyester imide **2f** ($n=10$): (A) first heating, (B) first cooling, (C) second heating

these cases both segmental mobility and the symmetry of three-dimensional packing are optimal.

The d.s.c. measurements also revealed that all poly(ester imide)s of the hydroquinones, with exception of **3c**, are crystalline and possess a relatively sharp melting endotherm (*Figure 1*). In the series **2a–h** the expected odd–even effect is clearly detectable. The poly(ester imide) of phenylhydroquinone **3c** is the only amorphous material, and even prolonged annealing at various temperatures did not induce crystallization. Smaller substituents such as chloro- or methyl groups are still compatible with a crystal lattice, clearly because they do not prevent a coplanar orientation of the hydroquinone and trimellitimide rings. Furthermore, the disordering effect of a random sequence of triads **I–III** is negligible, yet it suffices to suppress formation of a mesogenic melt even in the case of the small methyl group.



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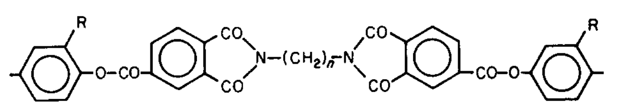

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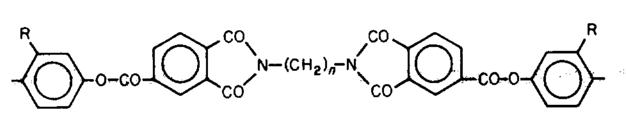


III

The d.s.c. traces of most poly(ester imide)s containing hydroquinones exhibit a second endotherm (T_{m_2} in *Tables 2* and *3*) which indicates the transition from the anisotropic to the isotropic melt (*Figure 1*). Observation under the polarizing microscope confirmed that the two endotherms T_{m_1} and T_{m_2} indeed indicated the temperature limits of the mesogenic phase. The temperatures extracted from d.s.c. measurements and optical observations did not show a satisfactory agreement in all cases. However, it must be taken into account that the T_{m_2} derived from the d.s.c. endotherms represents the peak minimum which does not necessarily indicate the beginning or ending of a phase transition observable under the microscope. Nonetheless, both methods agree that all poly(ester imide)s comprising hydroquinone and tetrachlorohydroquinone form a mesogenic melt. As expected the stability of this mesogenic phase is significantly lower than that of analogous polymers containing 4,4′-dihydroxybiphenyl. In most cases the mesogenic phase only existed over a temperature range of 15°C–25°C. This range is relatively narrow, and thus, unfavourable for reproducible thermoplastic processing from the mesogenic melt.

Despite the narrow temperature range of the anisotropic melt, observation under the microscope with crossed polarizers enabled the detection of a granular texture which fitted better with a smectic rather than with a nematic phase. This texture did not significantly change between T_{m_1} and T_{m_2}. Because the regular primary structure favours a smectic phase, it is clear that a smectic melt is formed at T_{m_1} and immediately changes to the isotropic melt at T_{m_2}.

The WAXS powder and fibre patterns measured at room temperature suggest a nearly perfect layered structure in the solid state. Sharp reflections with a meridional position in the fibre patterns are observable at small angles (*Figure 2*). They are the first and higher order reflection of layered structures with *d*-spacings corresponding to the lengths of the monomer units. As demonstrated by *Figure 3* the *d*-spacings increase with the lengths of the aliphatic spacers. Other research groups[14–16] report similar observations and interpretations for LC-polyesters with regular sequences of mesogenic groups and spacers.

Two aspects of the present WAXS measurements are noteworthy. First, the poly(ester imide)s **2a–d** do not exhibit the meridional first order reflection but only the second and higher order reflections in contrast with **2e–h** and **5d–e** (*Figure 2*). A satisfactory explanation for this

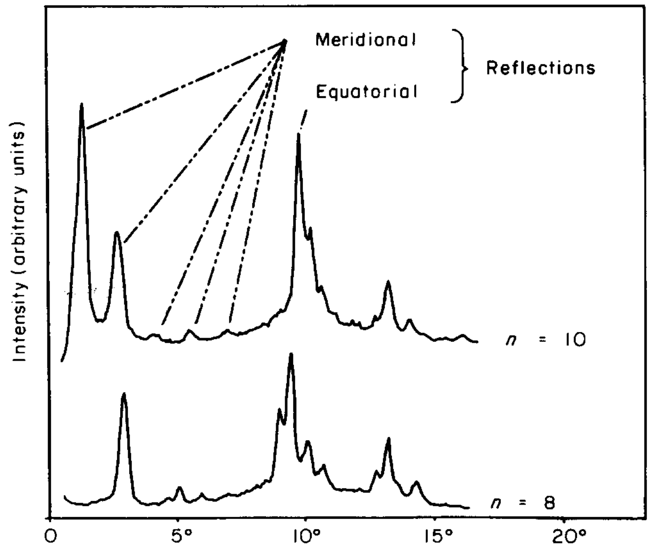


Figure 2 WAXS powder patterns of the hydroquinone containing poly(ester imide)s **2f** ($n=10$) and **2d** ($n=8$)

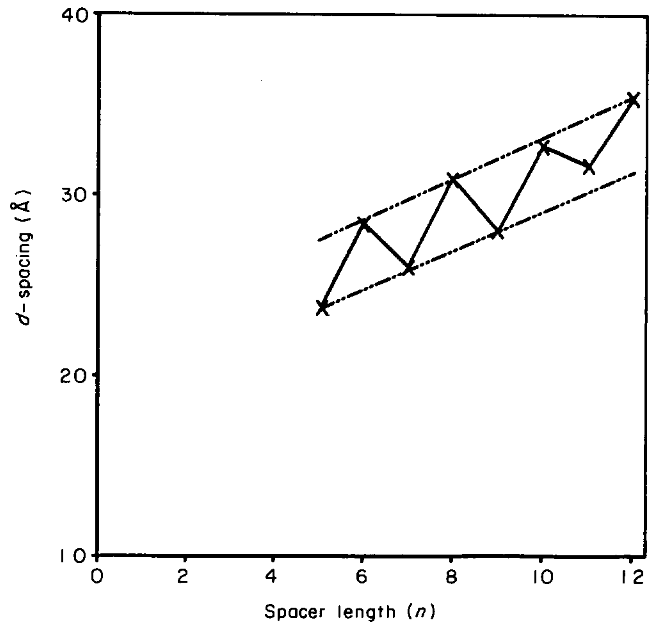


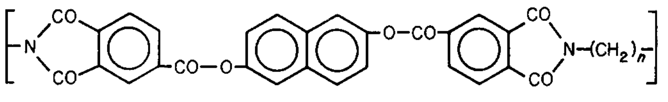
Figure 3 Plot of *d*-spacings calculated from the small-angle reflections in WAXS powder patterns of polyester(ester imide)s **2a–h** *versus* the number of methylene groups in the spacers

phenomenon cannot be offered currently. Second, the *d*-spacings calculated from the second order reflections of **2a–h** display an odd–even effect (*Figure 3*). The *d*-spacings of poly(ester imide)s with odd-spacers are shorter by *ca.* 4.5 Å, a distance comparable with the length of a benzene ring. Similar results were found for the poly(ester imide)s of 4,4'-dihydroxybiphenyl[1]. This strong odd–even effect indicates that the chain packing of the odd members of both series is quite different from that of even members. Interestingly, a shortening of the *d*-spacings by 4.5 Å cannot be explained by different conformations of the spacers alone. Therefore, it is clear that the mesogenic groups of the odd-membered poly(ester imide)s are considerably tilted relative to the layer planes. Such a supermolecular order is known, from low molecular weight mesogens, as the smectic-C phase. A significant tilting of the monomer units against the layer planes has the consequence that overlapping and intermolecular forces between the mesogenic groups (which vary with $1/r^6$) are reduced. In agreement with this hypothesis odd-membered poly(ester imide)s possess lower melting points (T_{m_1}), greater solubilities in organic solvents and poorer mechanical properties (see below) than the even-membered ones.

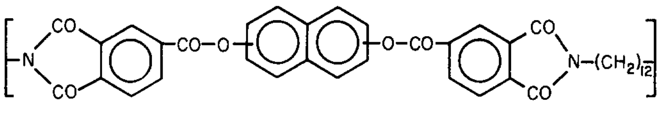
In order to elucidate the influence of crystallinity and rate of crystallization on the heat distortion temperature, thermomechanical analyses (*Figure 4*) were conducted by means of the penetration method. When foils, pressed at *ca.* 350°C and cooled in air, were measured under low pressure (0.05 kg mm^{-2}), the breakdown of the mechanical resistance occurred at temperatures where the melting process begins, i.e. 10°C–20°C below the minimum of the d.s.c. endotherm. The only exception found was for polymer **2b** (*Table 4*). In this case the rate of cooling seemed to be too high for complete crystallization. When the mechanical resistance was measured under high pressure (1 kg mm^{-2}), (nearly identical with the 'Vicat-A' test), a conspicuous reduction in heat-distortion temperature down to values close to T_g was found for most polymers with odd numbers of methylene groups (**2c**, **2e**, **2g**, *Table 4*). In contrast, those poly(ester imide)s with even-membered spacers (**2d**, **2f**, **2h**) maintain a high level of heat-distortion temperature, *ca.* 100°C–200°C (e.g. **2d**) above the glass transition temperature. These different mechanical properties of poly(ester imide)s with even and odd-membered spacers were not observed for poly(ester imide)s of 4,4'-dihydroxybiphenyl[1]. These differing properties might be explained by the differing sizes and perfections of the crystallites in combination with lower degrees of crystallinity. However, a reduced crystallinity was neither detectable by d.s.c. nor by WAXS measurements. Therefore, a different mode of chain packing, as indicated by WAXS measurements, is the more likely explanation.

In any event, the penetration measurements indicated that the crystallites of **2a–h** form a rather stable coherent matrix with the amorphous phase dispersed in the voids. Such a morphology is quite opposite to that for other LC-polyesters, such as the PET/PHB system, where the crystallites are dispersed in the amorphous matrix, so that the heat-distortion temperature never rises above T_g (in the range 80°C–90°C). Thus the present study demonstrates, in agreement with our previous results[1], that even long aliphatic spacers do not necessarily ensure low heat-distortion temperatures.

Poly(ester imide)s containing dihydroxy naphthalenes



5a–e
a : $n = 7$ d : $n = 10$
b : $n = 8$ e : $n = 12$
c : $n = 9$



6a–c
a : 1,4-dihydroxynaphthalene
b : 1,5-dihydroxynaphthalene
c : 2,7-dihydroxynaphthalene

A series of poly(ester imide)s (**5a–e**) was prepared by condensation of the diacids **1c–f** and **1h** with 2,6-bisacetoxynaphthalene. A second series (**6a–c**) was obtained by condensation of diacid **1h** with the acetates of 1,4-dihydroxy, 1,5-dihydroxy- or 2,7-dihydroxynaphthalene. The polyesters of this second series did not show a mesogenic phase upon heating. D.s.c. measurements revealed that these poly(ester imide)s are entirely amorphous with glass transition temperatures of 94°C (**6a**), 101°C (**6c**) and 110°C (**6b**), respectively. Therefore, these polyesters were not further characterized. Despite their crystallinity, all poly(ester imide)s of the first series (**5a–e**) were soluble in mixtures of dichloromethane and trifluoroacetic acid. The inherent viscosities measured in these solvents were slightly higher (*Table 5*) than those obtained for the poly(ester imide)s of the hydroquinones, yet only in one case was the desired order of magnitude above 1.0 gl/g achieved.

Rapid cooling of the poly(ester imide)s **5a–e** rendered all these materials at least partially amorphous, so that glass transition temperatures were detectable by d.s.c. measurements. Clearly the lower degree of symmetry of the 2,6-substituted naphthalene unit compared with hydroquinone entails a lower rate of crystallization. The T_gs display a continuous increase from 95°C to 131°C with decreasing length of the spacer by analogy with the properties of **2a–h**. Despite the few members of series **5a–e**, the melting endotherms (T_{m_1}) suggest that they obey an odd–even effect by analogy with similar poly(ester imide)s (**2a–h** and ref. 1). The melting points as revealed by d.s.c. measurements are comparable with those of the hydroquinone series **2a–h** (*Table 2*). It is well known that the more extended aromatic core of the 2,6-disubstituted naphthalene will give higher clearing temperatures (T_{m_2}, *Table 5*) than a 1,4-substituted benzene. Thus the mesogenic phases of **5a–e** are stable over a broader temperature range than those of **2a–h**.

The broader range of the LC-phase enabled a closer inspection of the textures. Although a classification of mesogenic phases of polymers, exclusively based on textures, is not reliable, comparison with pictures in the literature and with copolyesters forming nematic phases suggests that the mesogenic phases of the poly(ester imide)s **5a–e** is smectic in nature. The texture observed over the whole temperature range between T_{m_1} and T_{m_2} is granular in nature. At T_{m_2}, when the isotropic melt is formed, individual spots may display a kind of 'schlieren texture', yet a coherent phase with this texture was never observed. It seems that the smectic phase changes to the isotropic melt without intermediate formation of a nematic phase. WAXS measurements of the solid poly(ester imide)s **5a–e** exhibit sharp reflections at small angles in close analogy with the WAXS patterns of **2a–h** (*Figure 3*). These reflections indicate the same layered supermolecular structure already discussed for **2a–h** and analogous poly(ester imide)s of 4,4'-dihydroxybiphenyl[1]. The regular sequences of mesogen and spacer and the predominant formation of layered structures in both melt and solid states may explain why the poly(ester imide)s **2a–h** and **5a–e** possess such high rates of crystallization

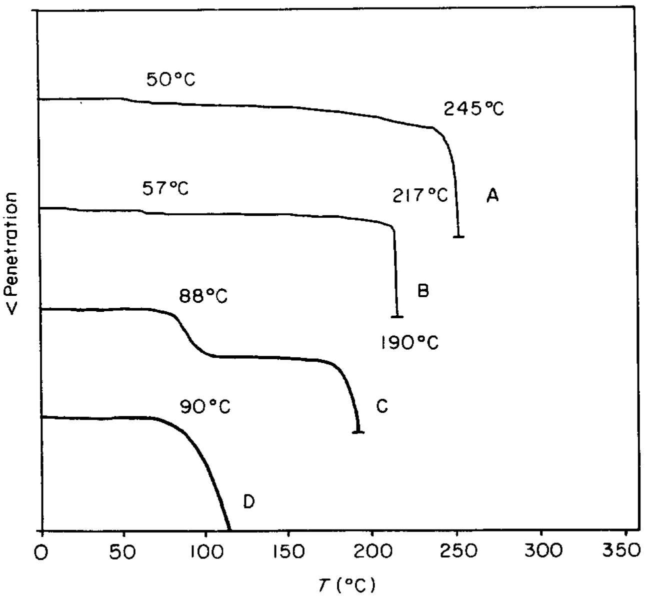


Figure 4 Thermomechanical analyses measured at a heating rate of 5°C/min: (A) poly(ester imide) **2f** ($n = 10$), pressure 0.05 kp mm^{-2}; (B) poly(ester imide) **2f** ($n = 10$), pressure 1.0 kp mm^{-2}; (C) poly(ester imide) **5e** ($n = 12$), pressure 0.05 kp mm^{-2}; (D) poly(ester imide **5e** ($n = 12$), pressure 1.0 kp mm^{-2}

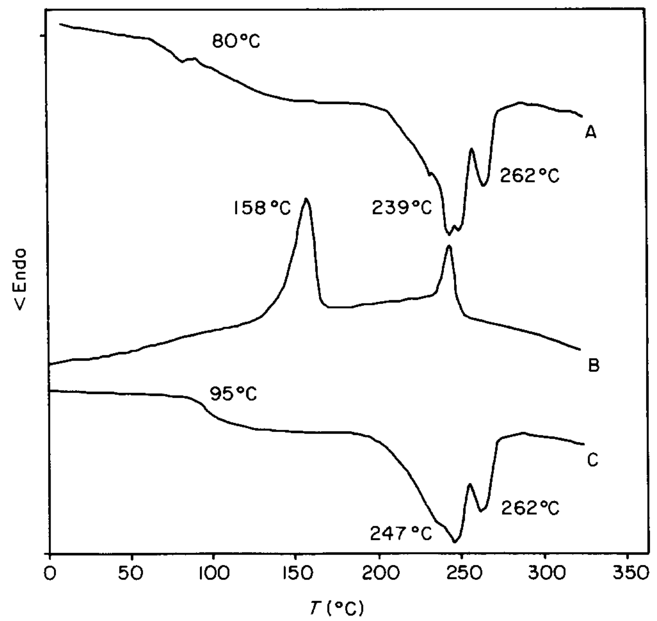


Figure 5 D.s.c. traces (heating and cooling rate 20°C/min) of poly(ester imide) **5e** ($n = 12$): (A) first heating, (B) first cooling, (C) second heating

Table 5 Yields and properties of LC-poly(ester imide)s prepared from 1,12-diaminododecane bistrimellitimide (**1e**) and 2,6-dihydroxy naphthalene

Formula	n	Yield (%)	T_g[a] (°C)	T_{m_1}[a] (°C)	T_{m_2}[a] (°C)	η_{inh}[b] (dl/g)	LC-phase[c] (°C)	Elemental formula (Mwt.)	Elemental analyses			
										C	H	N
5a	7	81.0	131	263	305	insol.	255–290	$C_{35}H_{26}N_2O_8$	Calcd.	69.76	4.35	4.65
								(602.60)	Found	69.85	4.35	4.85
5b	8	87.0	127	359	370	0.61	345–375	$C_{36}H_{28}N_2O_8$	Calcd.	70.12	4.58	4.54
								(616.13)	Found	69.73	4.58	4.68
5c	9	87.3	117	252	270	0.51	255–290	$C_{37}H_{30}N_2O_8$	Calcd.	70.47	4.79	4.44
								(630.66)	Found	70.38	4.88	4.62
5d	10	95.3	106	282	351	1.31	290–340	$C_{38}H_{32}N_2O_8$	Calcd.	70.80	5.00	4.35
								(644.69)	Found	70.79	5.13	4.39
5e	12	85.5	95	239	262	0.60	240–300	$C_{40}H_{36}N_2O_8$	Calcd.	71.42	5.39	4.16

[a] D.s.c. measurements (heating rate 20°C/min)
[b] Measured in dichloromethane/trifluoro acetic acid (4:1 by volume) with $c = 2$ g/l at 20°C
[c] As observed under the polarizing microscope

Table 6 Heat distortion temperature and thermal stability of poly(ester imide)s prepared from α,ω-diaminoalkane bistrimellitimides and 2,6-dihydroxy naphthalene

Formula	n	T_{m_1} (°C)	Heat-distortion temperature (°C)[a]	(°C)[a]	Temperatures with the following losses of weight 1%	5%	10%	20%
5a	7	263	123	118	404	425	336	456
5b	8	359	266	163	390	437	452	468
5c	9	252	104	92	377	432	458	468
5d	10	282	267	106	380	429	442	451
5e	12	239	190	88	326	429	453	474

[a] Measured with a pressure of 0.05 kg mm^{-2} at a heating rate of 5°C/min
[b] Measured with a pressure of 1.0 kg mm^{-2} at a heating rate of 5°C/min
[c] Measured with a heating rate of 10°C/min in air

and high degrees of crystallinity compared with random copolyesters such as those derived from poly(ethylene terephthalate) and 4-hydroxybenzoic acid[1,17] or β-(4-hydroxyphenyl)propionic acid and 4-hydroxybenzoic acid[18].

The thermomechanical analyses were conducted under exactly the same conditions already used for the characterization of polymers **2a–h**. However, in contrast with the results obtained from poly(ester imide)s of hydroquinone or 4,4′-dihydroxybiphenyl, the heat-distortion temperatures of **5a–e** measured under high pressure are all close to the glass transition temperature (*Table 6*). This result indicates a relatively slow and incomplete crystallization compared with **2a–h**, in good agreement with the d.s.c. measurements that revealed a substantial fraction of amorphous phase upon rapid cooling of the samples. Apparently the lower degree of symmetry of the 2,6-substituted naphthalene units compared with hydroquinone has severe consequences for both the rate of crystallization and the degree of crystallinity, and thus, also for the mechanical properties.

Finally, the thermostabilities of the poly(ester imide)s **2a–h** and **5a–e** were studied in air at a heating rate of 10°C/min. It is clear that the thermostability of LC-polymers with aliphatic spacers in the main chain, is considerably lower than that of fully aromatic polyesters, when oxygen is present. Nonetheless, the results listed in *Tables 4* and *6* indicate that even those poly(ester imide)s with the longest aliphatic spacers are stable enough to allow any kind of processing at temperatures up to 360°C. The results in *Tables 4* and *6* also indicate that the thermostability of poly(ester imide)s containing naphthalene rings (**5a–e**) is slightly higher than that for polyesters containing hydroquinone (**2a–h**). Thus, the poly(ester imide)s of 2,6-dihydroxynaphthalene have the advantage of a slightly higher thermostability and of a broader mesogenic phase, which enables processing from the anisotropic melt. On the other hand, these poly(ester imide)s possess poorer mechanical properties and 2,6-dihydroxynaphthalene is considerably more expensive than hydroquinone.

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