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Liquid-Crystalline Polyimides. 3. Fully Aromatic Liquid-Crystalline Poly(ester imide)s Derived from *N*-(4-Carboxyphenyl)trimellitimide and Substituted Hydroquinones

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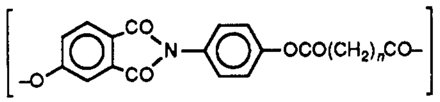
ABSTRACT: Three imidodicarboxylic acids were prepared from trimellitic anhydride and 4-aminobenzoic acid, 2-chloro-4-aminobenzoic acid, or 3-chloro-4-aminobenzoic acid. These dicarboxylic acids were condensed with acetyl derivatives of methyl-, chloro-, bromo-, or phenylhydroquinone, with mono- or bis(phenylthio)-hydroquinone, or with 2,5-diphenoxyhydroquinone. The resulting poly(ester imide)s were characterized by elemental analyses, ^{13}C NMR spectra, inherent viscosities, and DSC and WAXS measurements by optical microscopy with polarized light and by thermogravimetric analyses; polyesters derived from methyl-, chloro-, and bromohydroquinone have melting points in the temperature range 345–365 °C, but their birefringent melt does not flow. Polyesters derived from phenyl- and (phenylthio)hydroquinone are also semicrystalline but form a mobile nematic melt. Polyesters derived from 2,5-bis(phenylthio)- or 2,5-diphenoxyhydroquinone are amorphous and only form an isotropic melt. The chlorine substituents in the imidodicarboxylic acid reduce both crystallinity and stability of the mesophases. In addition to homopolyesters, three copolyesters containing two different hydroquinones were synthesized and characterized.

Introduction

In a previous[1] and in a future part[2] of this series, syntheses and properties of poly(ester imide)s 1 and 2 are reported. Both polymer classes have in common that they form a crystalline solid state with a layered supermolecular order, a so-called crystalline smectic state. Yet, whereas poly(ester imide)s 1 form a broad nematic phase above their melting points (T_m), poly(ester imide)s 2 form two crystalline and one glassy smectic phases. These results allow two important conclusions. First, the imide monomers 3 and 4 are good mesogens. Second, isomeric classes of poly(ester imide)s may possess largely differing properties. In this connection it seems to be worthwhile to synthesize and study fully aromatic poly(ester imide)s based on monomers 3 and 4. Whereas poly(ester imide)s derived from monomer 3 and substituted terephthalic acids were described in the preceding paper,[3] the present work was aimed at studying poly(ester imide)s derived from the dicarboxylic acid 4 and various substituted hydroquinones.



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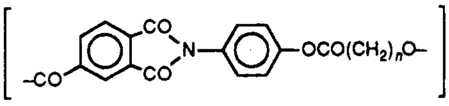

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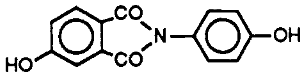

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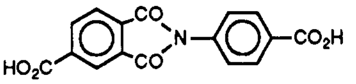

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In this connection a recent patent should be mentioned[4] that describes fully aromatic copolyesters containing monomer 4. However, these copolyesters consist of five or six different monomer units, and the molar fraction of 4 is only on the order of 10–20%. These copolyesters are thermally stable and thermotropic even without the presence of 4. In other words, incorporation of 4 does not seem to have a significant influence on the properties of these copolyesters.

Experimental Section

Materials. Trimellitic anhydride was a gift of Bayer AG (Krefeld-Uerdingen, FRG). It was recrystallized from dioxane-containing acetic anhydride. 1,4-Benzoquinone, methylhydroquinone, chlorohydroquinone, phenylhydroquinone, thiophenol, and 2-chloro- and 3-chloro-4-aminotoluene were purchased from Aldrich Chemical Co. (St. Louis, MO) and used without further purification. Bromohydroquinone was prepared by bromination of hydroquinone;[5] (phenylthio)- and 2,5-bis(phenylthio)-hydroquinone were synthesized by addition of thiophenol onto 1,4-benzoquinone,[6] and 2,5-diphenoxyhydroquinone was obtained from 2,5-dibromo-1,4-dimethoxybenzene and phenol by an Ullmann reaction.[7,8] Acetylation of all hydroquinones was achieved by heating in pure acetic anhydride (10-fold molar excess) for 2 h to ca. 100 °C. The diacetates were recrystallized from ethanol or ethanol/water mixtures. Melting points and properties of all acetylated hydroquinones have been reported in the literature.[9-15] 4-Aminobenzoic acid was a gift of Bayer AG (Krefeld-Uerdingen, FRG) and was used without purification. 2-Chloro- and 3-chloro-4-aminobenzoic acid were prepared from 2- and 3-chlorotoluidine by N-acetylation and oxidation with $KMnO_4$ according to the literature.[16-18]

Imidodicarboxylic Acids 4–6. Trimellitic anhydride (0.3 mol) and 4-aminobenzoic acid (0.3 mol) were heated in 400 mL of dry *N,N*-dimethylformamide to 120 °C for 2 h. After cooling, acetic anhydride (0.4 mol) was added and heating to 120 °C was continued for 2 h. The cooled reaction mixture was then poured into ice water and the precipitated product was isolated by filtration. After drying at 60 °C in vacuo the crude dicarboxylic acid was recrystallized from 1,4-dioxane.

Dicarboxylic acid 4: yield 81%, mp 376 °C (DSC). Anal. Calcd for $C_{16}H_9NO_6$ (311.249): C, 61.69; H, 2.91; N, 4.50. Found: C, 61.50; H, 2.81; N, 4.39 (mp 377–381 °C[19]).

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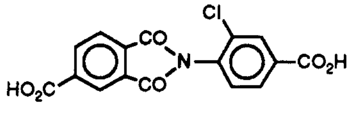

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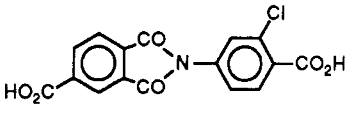

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Dicarboxylic acid 5: yield 88%; mp 316 °C (DSC). Anal. Calcd for $C_{16}H_8ClNO_6$ (345.70): C, 55.59; H, 2.33; N, 4.05; Cl, 10.26. Found: C, 55.09; H, 2.27; N, 4.15; Cl, 10.43.

Dicarboxylic acid 6: yield 89%; mp 332 °C (DSC). Anal. Calcd for $C_{16}H_8ClNO_6$ (345.70): C, 55.59; H, 2.33; N, 4.05; Cl, 10.26. Found: C, 55.66; H, 2.28; N, 4.12; Cl, 10.25.

Polycondensations. An imidodicarboxylic acid (50 mmol), the diacetate of a substituted hydroquinone (50 mmol), and magnesium oxide (10 mg) were weighed into a round-bottomed cylindrical glass reactor equipped with gas inlet and outlet tubes. The reaction mixture was heated with stirring to a temperature of 260 °C, where condensation slowly started. The temperature was then gradually raised to 330 °C. The liberated acetic acid was removed with a slow stream of nitrogen. After 20 h, vacuum was applied and heating was continued for 30 min. With the exception of poly(ester imide)s **7a–c**, stirrable melts were obtained and long fibers could be drawn from the melt at the end of the polycondensation. The cold polycondensates were mechanically removed from the reactor, dissolved in CH_2Cl_2/trifluoroacetic acid (4:1 by volume) and precipitated into cold methanol. After drying at 110 °C for 24 h in vacuo the crude polymers were characterized. The results are listed in Tables I and II. The polyesters **7a–c**, insoluble in CH_2Cl_2/trifluoroacetic acid, were extracted with hot dioxane and dried.

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer at 20 °C. Solutions of 100 mg of polymer in 50 mL of a 4:1 CH_2Cl_2/TFA mixture were used in all cases except for polymers **7a–c**. DSC measurements were conducted with a Perkin-Elmer DSC-4 in aluminum pans at a heating and cooling rate of 20 °C/min.

WAXS powder patterns were measured on a Siemens D-500 diffractometer with Ni-filtered Cu Kα radiation at 20 °C. The synchrotron-radiation measurements were conducted with a beam line (λ = 1.50 Å) of HASYLAB, DESY at Hamburg.[20]

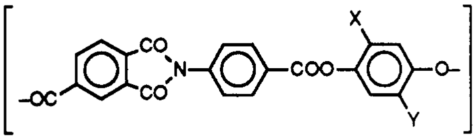
The thermogravimetric analyses were conducted with a Perkin-Elmer TSG-2 at a heating rate of 10 °C/min in air.

The thermomechanical analyses were conducted with a Perkin-Elmer TMS-2 at a heating rate of 10 °C/min with loads of 0.05, 0.5, and 1.0 kg/mm². IR spectra were measured from KBr pellets on a Nicolet 20 SXB FT spectrometer.

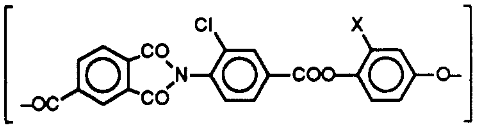
Results and Discussion

Syntheses. The dicarboxylic acid 4 was prepared from trimellitic anhydride and 4-aminobenzoic acid according to a modified procedure reported in the literature.[19] For reasons discussed below the chloro-substituted dicarboxylic acids 5 and 6 were also of interest. They were synthesized similarly from chloro-substituted 4-aminobenzoic acids and trimellitic anhydride. The 2- and 3-chloro-4-aminobenzoic acids were prepared in a three-step procedure starting from commercial 2- and 3-chlorotoluidine.[16-18]

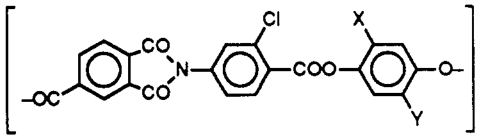
The substituted hydroquinones used as reaction partners for the condensation of monomers **4–6** were either commercially available (methyl-, chloro-, and phenylhydroquinone) or synthesized by addition of thiophenol to 1,4-benzoquinone[6] or bromination of hydroquinone.[5] 2,5-Diphenoxyhydroquinone was prepared from 2,5-dibromo-1,4-dimethoxybenzene and sodium phenoxide by an Ullmann reaction.[7,8] The acetylated hydroquinones were condensed with the dicarboxylic acids in the presence of catalytic amounts of magnesium oxide at temperatures between 270 and 320 °C. In the case of methyl-, chloro-, or bromohydroquinone, no melt was obtained, even when the temperature was raised to 340 °C. The high melting points of monomer 4 (T_m = 376 °C by DSC) and monomer 6 (T_m = 332 °C by DSC) and the high melting points of the resulting polyesters **7a–c** (Table I) prevented the formation of a melt during the polycondensation. Nonetheless, the condensation proceeded in the form of the sintering process. The high crystallinity and insolubility in common solvents also prevented purification by reprecipitation. Thus, in the case of **7a–c**, only crude, presumably low molecular weight materials were obtained. Yields and properties of poly(ester imide)s **7a–g** are summarized in Table I and those of poly(ester imide)s **8a–c** and **9a–d** in Table II.



7a: X = CH_3; Y = H
b: X = Cl; Y = H
c: X = Br; Y = H
d: X = C_6H_5; Y = H
e: X = SC_6H_5; Y = H
f: X = SC_6H_5; Y = SC_6H_5
g: X = OC_6H_5; Y = OC_6H_5



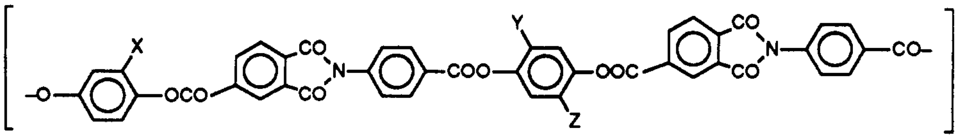
8a: X = C_6H_5
b: X = SC_6H_5



9a: X = C_6H_5; Y = H
b: X = SC_6H_5; Y = H
c: X = Y = SC_6H_5

Finally, three copolymers **10–12** were synthesized by condensation of dicarboxylic acid 4 with equimolar mixtures of two different hydroquinones. Their properties are listed in Table III.

Detection of Crystalline and Liquid-Crystalline Phases. All poly(ester imide)s were subjected to DSC measurements at a heating and cooling rate of 20 °C/min. The DSC traces of all samples displayed a glass transition



10: X = Cl; Y = SC_6H_5; Z = H
11: X = Cl; Y = SC_6H_5; Z = SC_6H_5
12: X = C_6H_5; Y = SC_6H_5; Z = H

Table I
Yields and Properties of Poly(ester imide)s Prepared from Dicarboxylic Acid 4 and Various Substituted Hydroquinones

polym formula	yield, %	η_{inh},[a] dL/g	elem. formula (formula wt)		elem anal.			T_g,[b] °C	T_m,[b] °C	T_i,[c] °C
					C	H	N			
7a		insol	$C_{28}H_{13}NO_6$	calcd	69.18	3.28	3.51	175	351	>480
			(399.36)	found	68.32	3.36	3.44			(dec)
7b		insol	$C_{22}H_{10}NO_6Cl$	calcd	62.95	2.40	3.34[e]	177	362	>510
			(419.79)	found	63.25	2.31	3.46			(dec)
7c		insol	$C_{22}H_{10}NO_6Br$	calcd	56.92	2.17	3.02	180	347	>460
			(464.24)	found	57.20	2.30	3.21			(dec)
7d	97	1.14	$C_{28}H_{15}NO_6$	calcd	72.88	3.28	3.04	196	263	460–480
			(461.43)	found	71.53	3.33	3.02		(weak)	
7e	96	1.06	$C_{28}H_{15}NO_6S$	calcd	68.15	3.06	2.84	168	307/326[d]	500
			(493.49)	found	66.48	3.09	2.87			
7f	93	0.73	$C_{34}H_{19}NO_6S_2$	calcd	67.88	3.18	2.33[f]	151	230	isotropic
			(601.66)	found	67.42	3.19	2.39		(weak)	
7g	63	6.70	$C_{34}H_{19}NO_8$	calcd	71.70	3.36	2.46	166	amorph	isotropic
			(569.53)	found	71.09	3.35	2.57			

[a] Measured with $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (4:1 by volume) at 20 °C. [b] From DSC measurements with a heating rate of 20 °C min. [c] From optical microscopy with a heating rate of 20 °C/min. [d] Depending on annealing. [e] Calcd: Cl, 8.45. Found: Cl, 8.39. [f] Calcd: S, 10.66. Found: S, 10.85.

Table II
Yields and Properties of Poly(ester imide)s Prepared from Dicarboxylic Acids 5 or 6 and Various Substituted Hydroquinones

polym formula	yield, %	η_{inh},[a] dL/g	elem. formula (formula wt)		elem anal.			T_g,[b] °C	T_m,[b] °C	T_i,[c] °C
					C	H	N			
8a	91	0.72	$C_{28}H_{14}NO_6Cl$	calcd	67.82	2.85	2.82	183		430–440
			(495.88)	found	67.14	2.88	2.97			
8b	96	0.80	$C_{34}H_{18}NO_6ClS$	calcd	63.70	2.67	2.65[d]	160	199	400–410
			(527.94)	found	63.39	2.65	2.85		(weak)	
9a	92	0.60	$C_{28}H_{14}NO_6Cl$	calcd	67.82	2.85	2.82	152		420–430
			(495.88)	found	67.14	2.73	2.94			
9b	98	0.76	$C_{28}H_{14}NO_6ClS$	calcd	63.70	2.67	2.65[e]	132		420–430
			(527.94)	found	63.24	2.66	2.78			
9c	95	0.30	$C_{34}H_{18}NO_6ClS_2$	calcd	64.20	2.85	2.20	130		
			(636.11)	found	63.32	2.80	2.27			

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (4:1) by volume. [b] From DSC measurements with a heating rate of 20 °C/min. [c] From optical microscopy with a heating rate of 20 °C/min. [d] Calcd: Cl, 6.72; S, 6.07. Found: Cl, 6.84; S, 5.96. [e] Calcd: Cl, 6.72; S, 6.07. Found: Cl, 6.94; S, 5.88.

Table III
Yields and Properties of Copoly(ester imide)s 10–12 Prepared from Diacid and Equimolar Amounts of Two Different Hydroquinones

polym formula	yield, %	η_{inh},[a] dL/g	elem. formula (formula wt)		elem anal.			T_g,[b] °C	T_m,[b] °C	T_i,[c] °C
					C	H	N			
10	>90	insol	$C_{50}H_{25}QN_2O_{12}S$	calcd	65.76	2.76	3.07	180		300–420
			(913.28)	found	65.55	2.79	3.17			
11	>90	insol	$C_{56}H_{29}ClN_2O_{12}S_2$	calcd	67.98	2.95	2.83	165		340–460
			(989.38)	found	66.35	2.83	2.86			
12	92	0.81	$C_{56}H_{30}N_2O_{12}S$	calcd	70.44	3.17	2.93	167	245	440–460

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (4:1) by volume. [b] From DSC measurements with a heating rate of 20 °C/min. [c] From optical microscopy with a heating rate of 20 °C/min.

step with a glass transition temperature (T_g) in the range of 150–200 °C for poly(ester imide)s **7a**–**g** (Table I). The highest T_g (196 °C) was found for the polyester of phenylhydroquinone (7d). The T_g's of polyesters derived from the chloro-substituted dicarboxylic acids 5 and 6 are lower than those derived from 4 (Table II).

The poly(ester imide)s prepared from methyl-, chloro-, and bromohydroquinone have in common that both DSC (Figure 1) and WAXS measurements (Figures 2 and 3) indicate a semicrystalline character. The endotherms in the range of 345–365 °C (Table I) are weak and barely detectable in the DSC curves (Figure 1). However, microscopic observation with crossed polarizers revealed a softening effect at the temperatures of the listed endotherms (Table I). Furthermore, WAXS measurements of **7c** conducted with synchrotron radiation at variable temperature (Figure 3) clearly confirmed the existence of reversible melting/crystallization around 350 °C. The melting process was not clearly detectable under the microscope, because the melts were highly viscous and did not flow. Upon heating above 420 °C all three samples turned gradually black and neither formation of a mobile nematic melt nor a mobile isotropic melt was detectable. Possibly thermal degradation entails cross-linking of polyesters **7a**–**e**. The strong endotherms observable in the DSC traces of all three poly(ester imide)s (Figure 1) presumably represent the isotropization process, but because of thermal degradation microscopic observation did not allow a clear-cut decision.

Both DSC and WAXS measurements indicate that the polyester of phenylhydroquinone is normally an amorphous material. Only after long annealing (≥2 h) at 180 or 200 °C is a weak, broad endotherm detectable at a round 230 °C. Nonetheless this poly(ester imide) formed a mobile nematic melt above T_g with a typical threaded "schlieren texture". The nematic phase is stable up to temperatures above 500 °C, where rapid thermal degradation takes place.

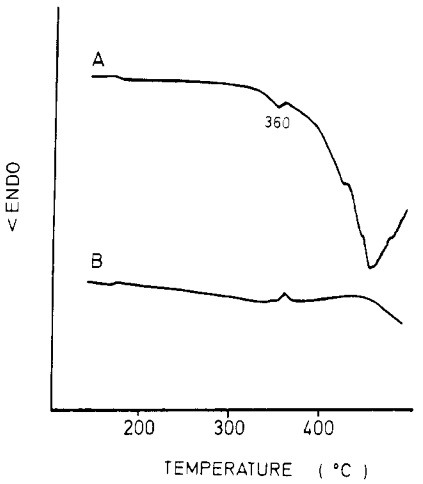


Figure 1. DSC measurements of poly(ester imide) **7c** conducted at a heating and cooling rate of 20 °C/min: (A) first heating; (B) first cooling.

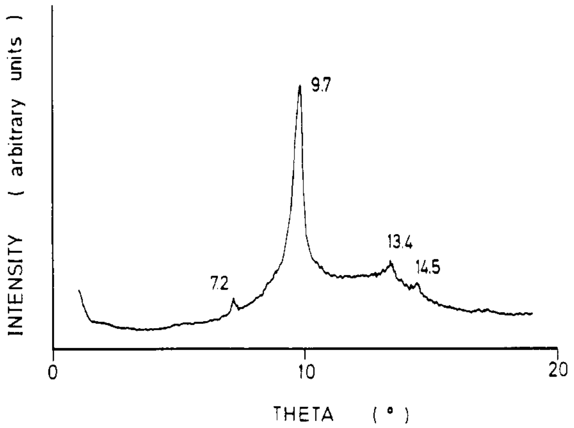


Figure 2. WAXS powder pattern of poly(ester imide) **7b** measured with Cu Kα radiation at 20 °C.

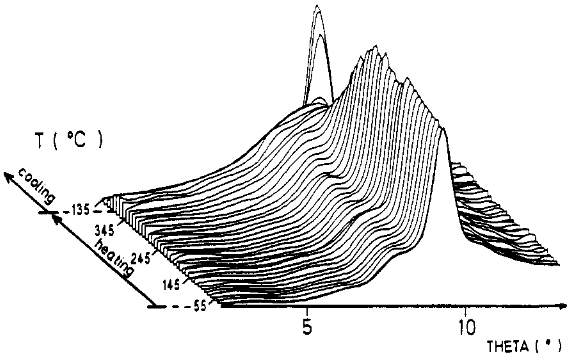


Figure 3. WAXS powder patterns of poly(ester imide) **7c** measured with synchrotron radiation at a heating rate of 20 °C/min.

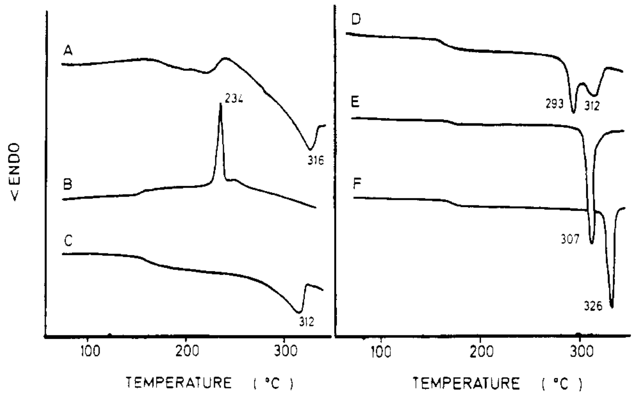


Figure 4. DSC measurements of poly(ester imide) **7e** measured at a heating and cooling rate of 20 °C/min: (A) first heating; (B) first cooling; (C) second heating; (D) heating after annealing 0.5 h at 260 °C; (E) after annealing for 16 h at 260 °C; (F) after annealing 1 h at 300 °C.

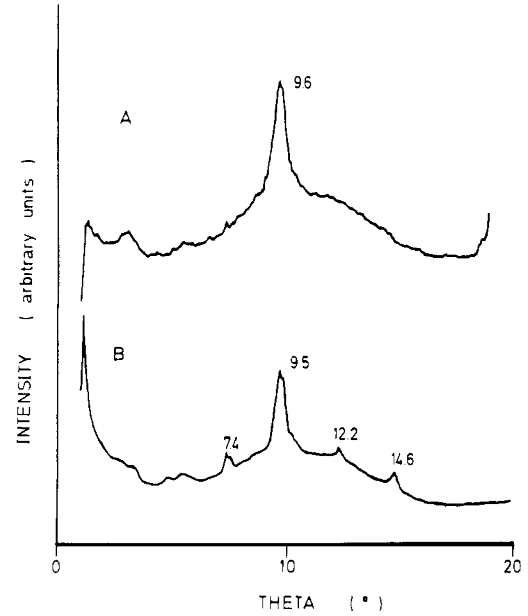


Figure 5. WAXS powder patterns of poly(ester imide) **7e** measured with Cu Kα radiation at 20 °C: (A) sample dried at 120 °C; (B) sample annealed at 300 °C (1 h).

In analogy with **7d** the poly(ester imide) of (phenylthio)hydroquinone **7e** forms a mobile nematic phase, which is stable up to ca. 500 °C. Yet in contrast to **7d**, poly(ester imide) **7e** is a rapidly crystallizing material. The DSC measurements revealed a strong endotherm around 316 °C in the heating trace and an exotherm in the cooling trace (Figure 4A–C). Annealing at 260 °C shifts the endotherm to lower temperatures (Figure 4D,E), whereas annealing at 300 °C shifts it to 320 °C. WAXS patterns display the appearance of several weak reflections upon annealing at 300 °C, whereas the main reflection at ϑ = 9.5° remains unchanged (Figure 5). These results suggest a gradual perfection of crystallites upon annealing, rather than coexistence of two modifications. However, a detailed X-ray study of this material was beyond the scope of this work.

The high tendency of **7e** to crystallize is a consequence of radius and bond angle of the sulfide group. The bond angles of aromatic sulfides are on the order of 110°[21,22] and allow the phenyl side chain to adopt a conformation parallel to the main chain. Such a parallel position, which is not possible in the case of phenylhydroquinone, favors crystallization and stabilization of the nematic phase. Similar observations were reported for liquid-crystalline polyesters derived from (arylthio)terephthalic acid.[23-25]

Both DSC and WAXS measurements of poly(ester imide)s derived from 2,5-disubstituted hydroquinones **7f** and **g** prove that they are neither crystalline nor liquid crystalline. This result is surprising because both hydroquinones are highly symmetrical when compared with the monosubstituted ones. Apparently the combination of an asymmetrical dicarboxylic acid with a symmetrical diphenol may be less favorable for the formation of crystalline and liquid-crystalline phases than the combination of two asymmetrical monomers. This interpretation is supported by further observations. Also poly(ester imide) **9c** derived from the chloro-substituted dicarboxylic acid **6** and bis(phenylthio)hydroquinone is amorphous

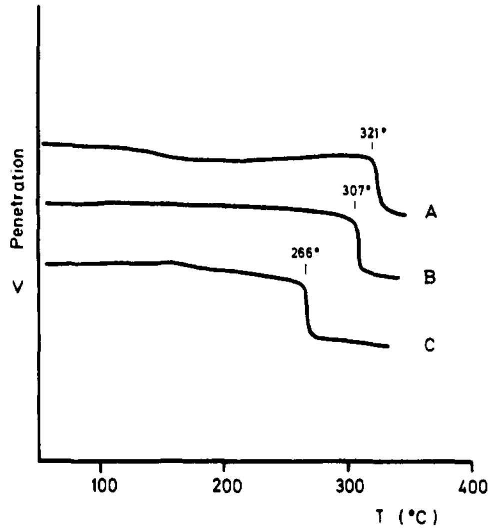
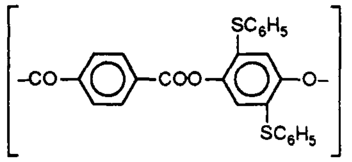


Figure 6. Penetration measurements of annealed poly(ester imide) **7e** conducted with a heating rate of 10 °C/min: (A) load 0.05 kg/mm^2; (B) load 0.5 kg/mm^2; (C) load 1 kg/mm^2.

and isotropic (Table II). On the other hand, a polyester prepared from terephthalic acid and bis(phenylthio)hydroquinone (**13**) was found to be highly crystalline (T_m =



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380 °C by DSC) and to form a mesophase above T_m (due to decomposition >400 °C, the texture could not be identified). Thus, the structure–property relationships found here for the combination of symmetrical and asymmetrical monomers is an interesting new aspect, which deserves further investigation.

Furthermore, the properties of poly(ester imide)s **8a,b** and **9a,b** need to be discussed. Introduction of one chlorine into the para-substituted phenyl ring reduces the symmetry of the entire monomer. In this case the observed properties are a logical consequence of the lower symmetry, because poly(ester imide)s **8a,b** and **9a,b** show a lower stability of the nematic phase than in the case of **7d** and **7e** (Tables I and II). Furthermore, polyester **9b** derived from (phenylthio)hydroquinone is amorphous in contrast to **7c**, and in the case of **8b** a low degree of crystallinity is only detectable after annealing.

Finally, the copoly(ester imide)s **10–12** need a short comment. Both copolyesters derived from chlorohydroquinone (**10** and **11**) have in common that only a fraction is soluble in mixtures of dichloromethane and trifluoroacetic acid. The insoluble fraction contains more chlorine than the soluble fraction. Furthermore, optical microscopy revealed a nematic more or less mobile melt above 350 °C, but this melt was biphasic and contained an isotropic part. The nematic fraction gradually decreased upon heating to 500 °C where rapid degradation took place. These results indicate a considerable degree of chemical heterogeneity.

A homogeneous melt and a completely soluble solid were obtained in the case of copolyester **12**. This copolyester forms a homogeneous nematic phase in close analogy to its parent homopolyesters **7d** and **7e**. Interestingly, this copolyester is crystalline and exhibits strong melting endotherms in the DSC heating trace. Upon annealing this endotherm shifts from 218 to 245 °C. Thus the properties of **12** are in between those of **7d** and **7e** and suggest that in this case a homogeneous material with a nearly random sequence was formed.

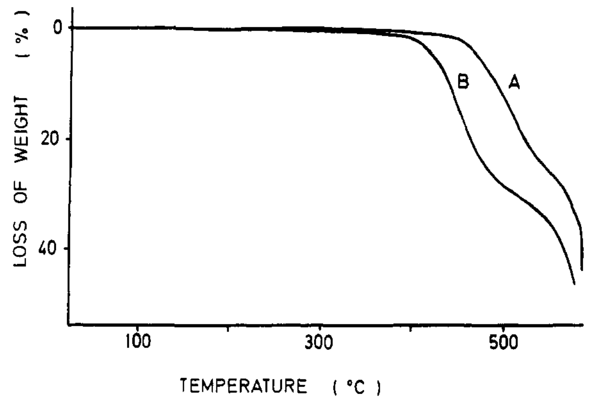

Figure 7. Thermogravimetric analyses conducted at a heating rate of 10 °C/min in air: (A) poly(ester imide) **8a**; (B) poly(ester imide) **9b**.

Table IV
Thermogravimetric Analyses Conducted at a Heating Rate of 10 °C/min in Air

polymer formula	loss of wt (%) at given temp					
	2	5	10	20	45	50
7d	420	442	456	471	528	541
7e	400	437	454	479	600	
8a	448	470	490	522	585	
8b	420	438	456	490	579	
9a	412	436	460	491	578	585
9b	404	425	442	465	575	

Heat Distortion Temperatures and Thermostability. In order to obtain basic information on heat distortion temperatures (HDT), two poly(ester imide)s, **7d** and **7e**, were subjected to penetration measurements. In the case of **7d** a film pressed at 300 °C (and rapidly cooled) was measured with loads of 0.05, 0.1, 0.5, and 1 kg/mm^2. As expected for an entirely amorphous material, HDT approached T_g with increasing load. A different situation is presented by the semicrystalline sample **7e**. The film pressed at 350 °C was annealed for 10 min at 300 °C. When this film was measured with a low load of 0.05 kg/mm^2, an HDT of 322 °C was found in perfect agreement with the melting endotherm observed in the DSC heating trace (Figure 6). With higher loads the HDT decreases to 265 °C (Figure 6). Nonetheless, even this value is nearly 100 °C higher than T_g.

Thermogravimetric analyses of several poly(ester imide)s were conducted at a heating rate of 10 °C/min in air. The results obtained for weight losses of 2, 5, 10, 20, and 50% are listed in Table IV. The TGA curves of the samples with the lowest and highest thermostability are displayed in Figure 7. When a loss of weight of 5% is taken as standard for comparison of the various samples, it turns out that poly(ester imide) **9b** is the least stable material, with a temperature of 420 °C, and sample **8a** the most stable material, with a temperature of 470 °C. All other poly(ester imide)s show 5% loss of weight around 440 °C. These values, although satisfactory, are not better than those measured under identical conditions for other thermotropic aromatic polyesters, in particular, for poly(4-hydroxybenzoate).[26]

References and Notes

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Registry No. **4**, 7702-03-6; **5**, 131458-58-7; **6**, 131458-59-8; **7a** (copolymer), 131458-63-4; **7b** (copolymer), 131458-64-5; **7c** (copolymer), 131458-65-6; **7d** (copolymer), 131458-66-7; **7e** (copolymer), 131458-67-8; **7f** (copolymer), 131458-68-9; **7g** (copolymer), 131458-69-0; **8a** (copolymer), 131458-70-3; **8b** (copolymer), 131458-71-4; **9a** (copolymer), 131458-72-5; **9b** (copolymer), 131458-73-6; **9c** (copolymer), 131458-74-7; **10** (copolymer), 131458-75-8; **11** (copolymer), 131489-36-6; **12** (copolymer), 131489-37-7; **13** (copolymer), 131458-76-9; **13** (SRU), 131458-61-2; MgO, 1309-48-4; trimellitic anhydride, 552-30-7; 4-aminobenzoic acid, 150-13-0.