Copolyesters of 4-hydroxy-3-phenylbenzoic acid and 4-hydroxybenzoic acid

Hans R. Kricheldorf and Frank Ruhser
Institut für Technische und Makromolekulare Chemie der Universität, Bundesstr. 45, 2000 Hamburg 13, Germany

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Crystalline poly(3-phenyl-4-hydroxybenzoic acid) was prepared by polycondensation of 4-acetoxy-3-phenylbenzoic acid in solution at 320°C. Differential scanning calorimetry (d.s.c.) and wide angle X-ray scattering (WAXS) measurements indicate that this homopolyester forms a nematic melt between 345°C and 465°C. Five copolyesters of 4-hydroxybenzoic acid (HBA) and 4-hydroxy-3-phenylbenzoic acid (3-PhHBA) with varying molar composition were prepared by polycondensation in solution. One additional copolyester was prepared by polycondensation in bulk. ^{1}H n.m.r. spectroscopy revealed a significantly lower reactivity of the phenyl-substituted acetoxybenzoic acid. The influence of the molar composition on crystallinity, phase transitions and stability of the nematic mesophase was studied by d.s.c. and WAXS measurements and by optical microscopy. Heat distortion temperatures were determined by the penetration method. It was found that the copolyesters prepared in bulk and in solution possess quite different properties. Only the copolyester prepared in bulk forms a nematic melt above its melting point at 205 ± 3°C.

(Keywords: 4-hydroxy-3-phenylbenzoic acid; 4-hydroxybenzoic acid; copolyesters)

INTRODUCTION

Poly(4-hydroxybenzoic acid) [poly (HBA)], the parent homopolyester of numerous thermotropic copolyesters, does not melt without decomposition[1] and is thus, difficult to process. Incorporation of small substituents, such as methyl, methoxy or chlorine atoms, does not suffice to bring about a meltable homopolyester[2–4]. Longer substituents, such as alkyl or aralkyl side chains, render poly(HBA) meltable[5,6], but these side chains are sensitive to oxidation and are unstable above 300°C. Therefore, the polyesters of 2- or 3-phenyl-4-hydroxybenzoic acid are of interest, because these monomers should form thermostable polyesters which can be processed from the melt.

Poly(4-hydroxy-3-phenylbenzoic acid) [poly(3-PhHBA)] was first described by Takekoshi in a patent claim[7], but the formation of a mesophase was not detected and investigated. Furthermore, several ternary and quaternary copolyesters containing 3-phenyl-4-hydroxybenzoic acid (3-PhHBA) were claimed to be thermoplastic thermotropic engineering plastics[8] and yet only one binary copolyester of 3-PhHBA and HBA (molar ratio 2:3) was described in a patent[9]. The present work deals with a more detailed characterization of poly(3-PhHBA) and copolyesters of 3-PhHBA and HBA. It is part of a broader study of copolyesters of HBA and various aromatic hydroxy acids.

EXPERIMENTAL

Materials

HBA and 3-PhHBA were gifts from Bayer AG (Krefeld, Germany). They were acetylated (without additional purification) by an excess of acetic anhydride and a catalytic amount of pyridine in refluxing toluene. Marlotherm-S® (a commercial mixture of isomeric dibenzylbenzenes) was a gift from Hüls AG (Marl, Germany).

Polycondensations

In Marlotherm-S®. 4-Acetoxybenzoic acid (30 mmol), 4-acetoxy-3-phenylhydroxybenzoic acid (30 mmol) and Marlotherm-S® (100 ml) were heated under stirring in a 350 ml three-necked reaction vessel. The temperature was maintained at 320°C for 16 h, whereby the evolved acetic acid was removed with a low stream of nitrogen. After cooling the reaction mixture was diluted with acetone (200 ml) and filtered. The isolated crystalline copolyester was twice washed with hot acetone and dried at 65°C *in vacuo*. The homopolyester **1** and the copolyesters **2a**–**d** were prepared analogously.

In bulk. 4-Acetoxybenzoic acid (50 mmol), 4-acetoxy-3-phenylbenzoic acid (50 mmol) and magnesium oxide (10 mg) were weighed into a cylindrical glass reactor equipped with stirrer and gas inlet and outlet tubes. The reaction mixture was rapidly heated to 260°C, where the condensation started. The temperature was then gradually raised to 320°C and kept there for 30 min. Vacuum was then applied for an additional 30 min. The cold reaction product was mechanically removed from the glass reactor, washed with hot acetone and dried at 65°C *in vacuo*.

Measurements

Differential scanning calorimetry (d.s.c.) curves were obtained from a Perkin–Elmer DSC-4 in aluminium pans under nitrogen.

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Wide angle X-ray scattering (WAXS) powder patterns were measured at 20°C with a Siemens D-500 diffractometer using Ni-filtered CuKα radiation. The synchrotron radiation measurements were conducted at a wavelength of 1.50 Å with an one-dimensional position-sensitive detector at HASYLAB, DESY, Hamburg, Germany[10]. A heating rate of 20°C min^{-1} (in a vacuum furnace) and an accumulation time of 10 s for one powder pattern were used.

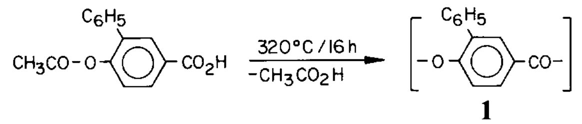
The 300 MHz ^1H n.m.r. spectra were recorded with a Bruker MSL 300 FT spectrometer in 5 mm o.d. sample tubes. The copolyesters (50 mg samples) were hydrolysed in the n.m.r. tubes with a mixture of 0.7 ml CD_3OD and 0.3 ml of 40 wt% $NaOD/D_2O$.

The penetration measurements were conducted with a Perkin–Elmer TMS-2 under a load of 1 kg mm^{-2} at a heating rate of 10°C min^{-1}. In the case of copolyester **2f** a 25 MHz ^{13}C n.m.r. spectrum was measured with a Bruker AC-100 FT spectrometer in a 10 mm o.d. sample tube. A mixture of $CDCl_3$ and trifluoroacetic acid (10:1 v/v) with internal tetramethylsilane served as solvent.

RESULTS AND DISCUSSION

Poly(4-hydroxy-3-phenylbenzoic acid)

It was shown in a previous paper[8] that high molecular weight polyesters of substituted and unsubstituted HBAs can be obtained by condensation of the corresponding acetyl derivatives in Marlotherm-S® at 320°C. Because the melting point of poly(3-PhHBA) **1** seemed to be higher than this reaction temperature[7], the same procedure was used for the polycondensation of 4-acetoxy-3-phenylbenzoic acid (equation (1)). The poly(3-PhHBA) **1** obtained in this way was a crystalline powder with correct elemental analyses (see Experimental). Hydrolysis in $NaOD/CD_3OD$ followed by ^1H n.m.r. spectroscopy showed the presence of a low concentration of acetate groups. From the signal intensity of this former end group an average degree of polymerization of 300 was estimated. Due to side reactions of the acetate end groups this value may only be considered as a rough estimate. D.s.c. measurements conducted with a heating and cooling rate of 20°C min^{-1} revealed for the reprecipitated sample dried at 60°C a glass transition at 240–250°C immediately followed by a recrystallization endotherm (*Figure 1A*). The melting endotherm appears at 343°C. The cooling trace displays an exotherm and the second heating trace again shows the melting endotherm at a somewhat lower temperature. However, when the heating is continued to temperatures around 500°C where slow thermal degradation begins, a second endotherm becomes detectable at 490°C (curve D in *Figure 1*). Optical microscopy with crossed polarizers confirmed that the first endotherm represents a melting process leading to a nematic phase with typical 'schlieren texture'. In the temperature range of the second endotherm (440–470°C) isotropization takes place. WAXS powder patterns measured with synchrotron radiation at a heating rate of 20°C min^{-1} confirmed that a nematic melt is formed in the temperature range of 350–370°C. All reflections disappear in this temperature range (*Figure 2*).



$$CH_3CO{-}O{-}C_6H_3(C_6H_5){-}CO_2H \xrightarrow[-CH_3CO_2H]{320°C/16h} \left[{-}O{-}C_6H_3(C_6H_5){-}CO{-}\right] \quad (1)$$

1

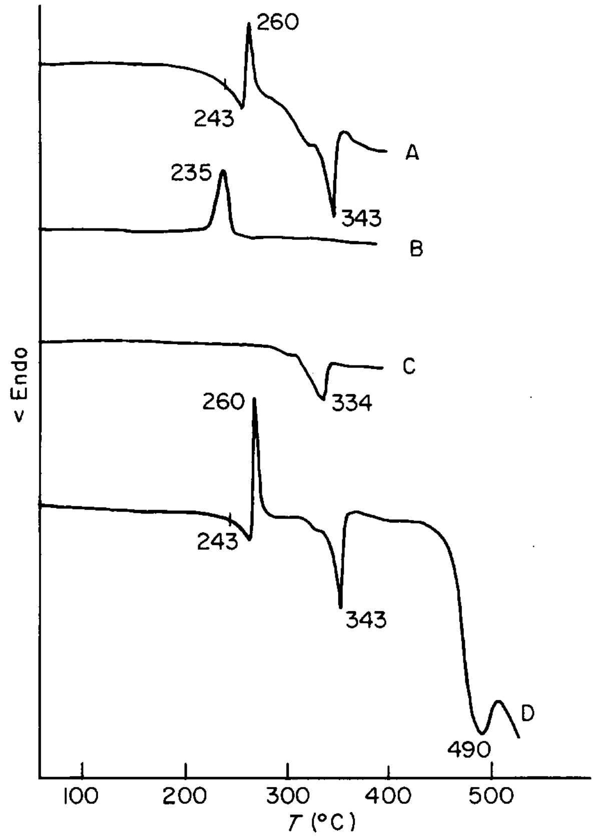


Figure 1 D.s.c. measurements (heating and cooling rate: 20°C min^{-1}) of **1**: (A) first heating; (B) first cooling; (C) second heating; (D) first heating of a fresh sample

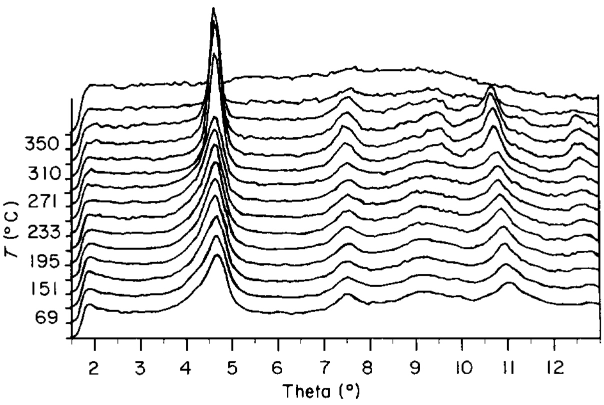


Figure 2 WAXS powder patterns of **1** measured with synchrotron radiation at a heating rate of 20°C min^{-1}

Synthesis of copolyesters

Five copolyesters (**2a**–**e**) with variable molar composition were prepared by cocondensation of 4-acetoxy-3-phenylbenzoic acid (3-PhABA) and 4-acetoxybenzoic acid (ABA) in Marlotherm-S® at 320°C. In order to investigate the influence of the reaction conditions on the composition of the copolyesters the synthesis of a copolyester with a feed ratio of 1:1 was repeated by condensation in bulk. This copolyester is denoted **2f**. Yields and properties of all the copolyesters are summarized in *Table 1*.

Table 1 Yields and properties of copolyesters prepared by polycondensation of 4-acetoxybenzoic acid and 4-acetoxy-3-phenylbenzoic acid in Marlotherm-S® at 320°C

Copolymer	Feed ratio[a]	Molar composition[b]	Yield (%)	M_n[c]	Elemental formula (weight)	Elemental analyses		
							C	H
2a	5:95	5:140	85	35000	$C_{209}H_{120}O_{58}$	Calc.	70.53	3.39
					(3449.25)	Found	70.15	3.58
2b	10:90	10:140	81	20000	$C_{111}H_{64}O_{30}$	Calc.	71.01	3.44
					(1877.73)	Found	70.54	3.80
2c	20:80	20:100	86	50000	$C_{48}H_{28}O_{12}$	Calc.	72.36	3.54
					(796.75)	Found	71.48	3.80
2d	30:70	30:90	89	60000	$C_{34}H_{20}O_{8}$	Calc.	73.38	3.62
					(556.53)	Found	73.08	3.92
2e	50:50	50:65	50	–	$C_{221}H_{132}O_{46}$	Calc.	75.34	3.78
					(3523.49)	Found	75.01	3.65
2f	50:50	50:55	60	65000	$C_{20}H_{12}O_{4}$	Calc.	75.94	3.82
					(316.32)	Found	75.23	3.76

[a] Molar ratio of acetyl PhHBA and acetyl HBA

[b] Molar ratio of 3-PhHBA/HBA units as determined by ^1H n.m.r. spectroscopy of hydrolysed copolyesters

[c] As determined from ^1H n.m.r. end group analyses of hydrolysed copolyesters

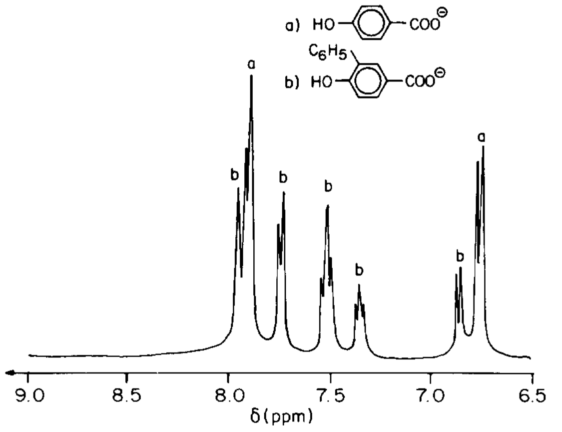
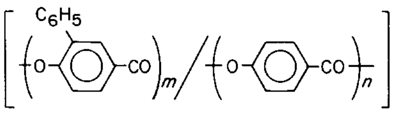


Figure 3 300 MHz ^1H n.m.r. spectrum of hydrolysed copolyester **2e** in $NaOD/D_2O/CD_3OD$

The molar composition of all copolyesters was determined by ^1H n.m.r. spectroscopy. Because the copolyesters rich in HBA units were insoluble in all common solvents, all copolyesters were hydrolysed in n.m.r. tubes using $NaOD/CD_3OD$. The ^1H n.m.r. signals of the resulting homogeneous solutions were assigned by comparison of solutions prepared from free HBA and 3-PhHBA (*Figure 3*). The results indicate that the rate of incorporation of 3-PhABA is significantly lower than that of HBA (*Table 1*). This difference is obviously a normal consequence of the steric hindrance caused by the phenyl group *ortho* to the acetoxy group. The different reactivities are less conspicuous when the polycondensation is conducted in the molten state (**2f**).

The ^1H n.m.r. spectroscopy of the hydrolysed copolyesters also allowed a crude estimation of the number average molecular weights (M_n). These were calculated from the signal intensities of the hydrolysed acetate end groups. The accuracy of this analytical approach is limited by side reactions of the acetate groups in the course of the polycondensation[11]. A more accurate method does not exist, due to the insolubility of most copolyesters. For the same reason sequence analyses by means of ^{13}C n.m.r. spectroscopy were not feasible in the case of **2a–e**. However, ^{13}C n.m.r. measurements of **2f** in a mixture of $CDCl_3$ and trifluoroacetic acid (1:1 v/v) revealed a splitting of the O–C signal of 3-PhHBA at 152 ppm. This splitting obviously represents the sequence effect of the two dyads HBA-3-PhHBA and 3-Ph-HBA-3-PhHBA. The almost identical intensities of both peaks suggest the formation of a nearly random sequence. This conclusion agrees with other properties discussed below.



2a–f

For information on **a**, **b**, **c**, **d**, **e** and **f** see *Table 1*.

Properties of copolyesters

WAXS powder patterns demonstrate that all the copolyesters are more or less crystalline (*Figures 4* and *5*). The crystallinity decreases from ~90–95% (**2a**, *Figure 4A*) to <20% (crude **2f**, *Figure 5A*) with increasing molar fraction of 3-PhHBA units. The relatively sharp reflections in the powder patterns of **2a–e** agree with those of poly(HBA) suggesting that crystallites of chain segments rich in HBA units are present. This interpretation agrees with the different reactivites of both monomers and the assumption of blocky sequences. The low degree of crystallinity observed for **2f** agrees in turn with the assumption of a nearly random sequence as suggested by the ^{13}C n.m.r. spectrum. The low degree of crystallinity of **2f** also fits in with the significantly improved solubility, when compared to **2e**.

D.s.c. measurements of all copolyesters were conducted with a heating and cooling rate of 20°C min^{-1} (*Figures 6* and *7*). The d.s.c. curves of copolyesters **2a–e** show three characteristic features. First, a glass transition step is not detectable. Second, a reversible first-order transition occurs at temperatures between 197°C and 297°C depending on the molar composition (*Figure 6* and *Table 2*). Third, a second irreversible transition is evident from an endotherm in the temperature range of

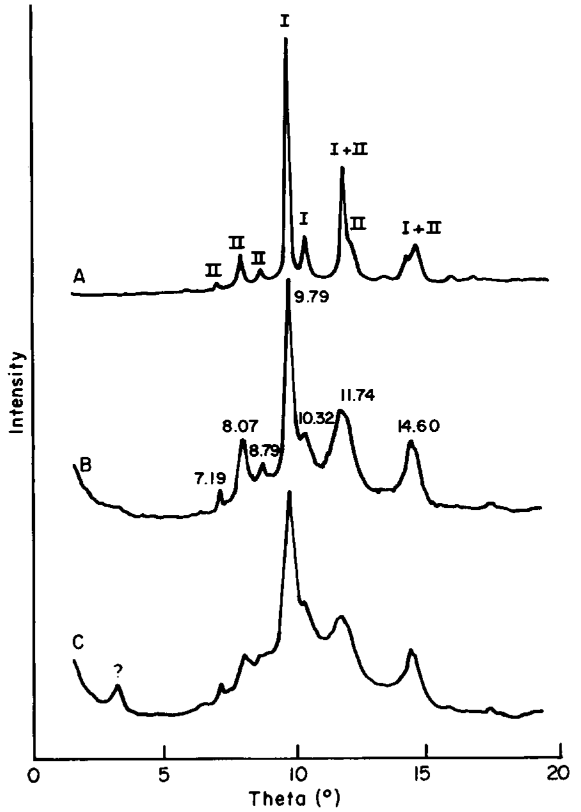


Figure 4 WAXS powder patterns measured with CuKα radiation at 20°C: (A) copolyester **2a**; (B) copolyester **2c**; (C) copolyester **2d**

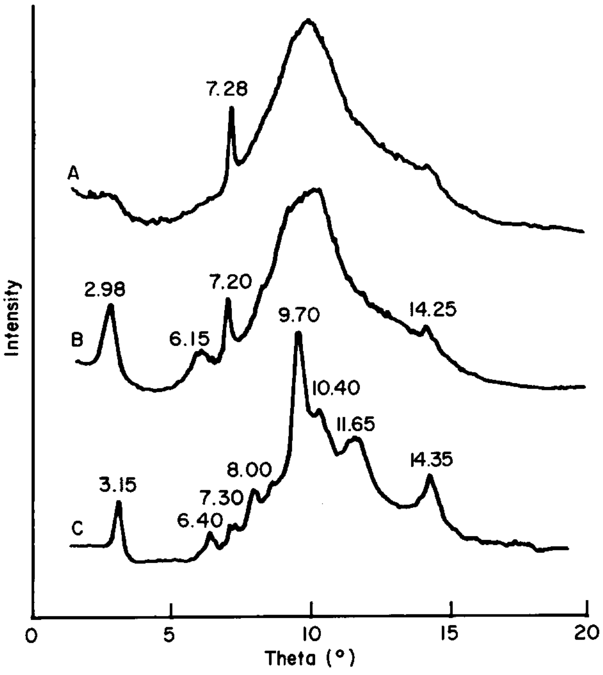


Figure 5 WAXS powder pattern measured with CuKα radiation at 20°C: (A) copolyester **2f**; (B) copolyester **2f** after annealing for 20 h at 170°C; (C) copolyester **2e**

490–520°C. Optical microscopy with crossed polarizers revealed that this 'high-temperature endotherm' represents a combined melting and decomposition process (so called γ-transition). The same process was found at 520–530°C in the case of pure poly(HBA)[1].

Optical microscopy also revealed that copolyesters **2a**—**e** do not form a mobile nematic melt below 500°C.

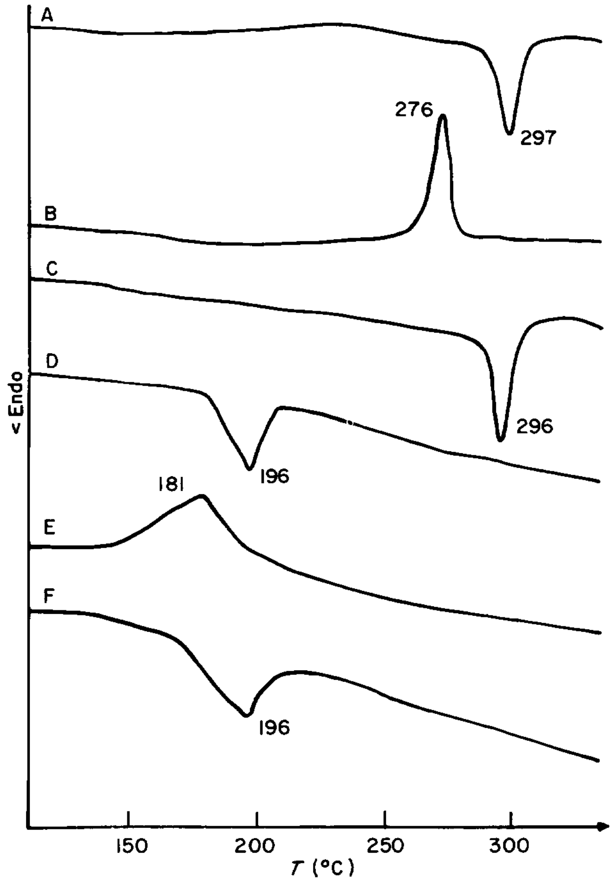


Figure 6 D.s.c. measurements (heating and cooling rate: 20°C min^{-1}) of copolyester **2a**: (A) first heating; (B) first cooling; (C) second heating, and of copolyester **2d**: (D) first heating; (E) first cooling; (F) second heating

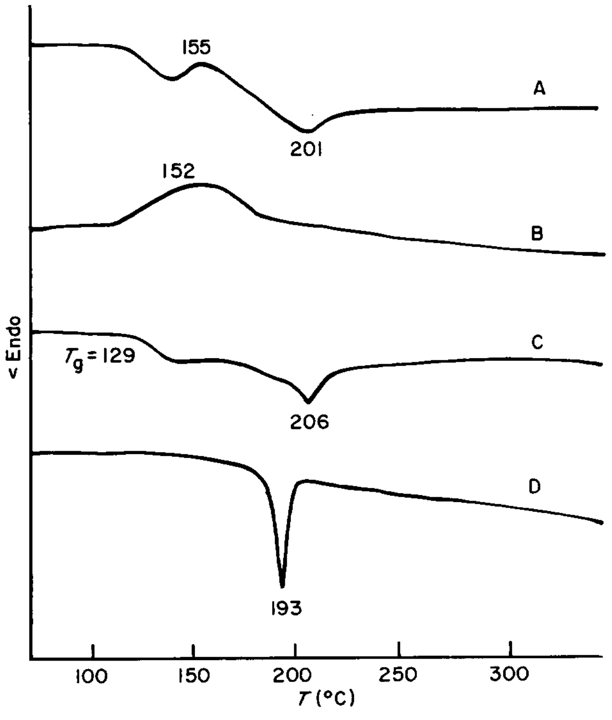


Figure 7 D.s.c. measurements (heating and cooling rate: 20°C min^{-1}) of crude copolyester **2f**: (a) first heating; (B) first cooling; (C) second heating; (D) first heating after annealing at 170°C for 20 h

Table 2 Thermal properties of copolyesters **2a–f**

Polymer formula	T_{ss}[a] (°C)	T_m[b] (°C)	T_m[c] (°C)	T_i[d] (°C)	T_i[e] (°C)
2a	297	515	515–520	–	–
2b	247	515	515–525	–	–
2c	196	510	510–520	542	540
2d	196	495	500–510	541	540
2f	–[f]	201	205–210	465	420–450

[a] Solid–solid phase transition (d.s.c. at 20°C min^{-1})
[b] Formation of the nematic melt (d.s.c. at 20°C min^{-1})
[c] Formation of the nematic melt (optical microscopy at 20°C min^{-1})
[d] Isotropization temperature (d.s.c. at 20°C min^{-1})
[e] Isotropization temperature (optical microscopy at 20°C min^{-1})
[f] Glass transition: 143°C first heating, 130°C second heating

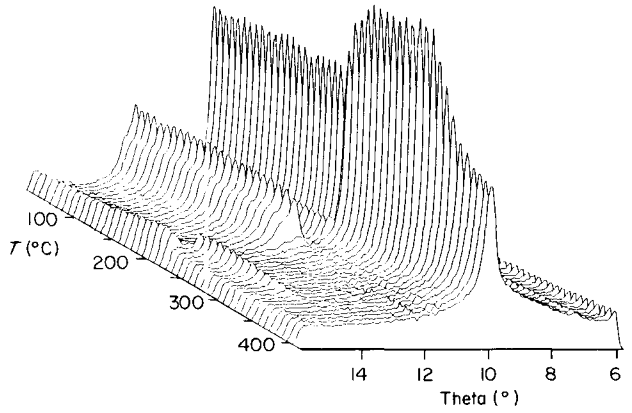


Figure 8 WAXS powder patterns of copolyester **2b** measured with synchrotron radiation at a heating rate of 20°C min^{-1}

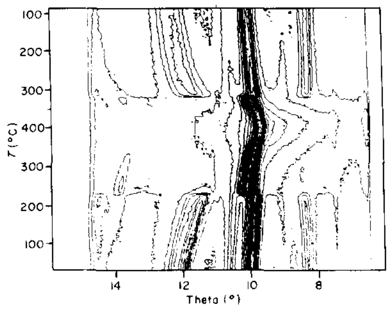


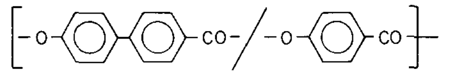
Figure 9 Contour map of the WAXS powder patterns of copolyester **2b** as obtained by synchrotron radiation (heating and cooling rate: 20°C min^{-1})

The melting process and the nematic melt observed at ≥500°C (*Table 2*) are, of course, affected by thermal degradation.

The nature of the first-order phase transition below 300°C was elucidated by WAXS measurements conducted with synchrotron radiation at a heating and cooling rate of 20°C min^{-1} (*Figures 8* and *9*). In close analogy with poly(HBA) the copolyesters **2a–e** undergo a reversible change between two orthorhombic modifications[1,12] (so called α-transition). In contrast to the less sensitive d.s.c. measurements the WAXS synchrotron measurements also reveal that a second reversible transition occurs at a temperature between 350°C and 450°C (depending on molar composition). This so-called β-transition is characterized by a change of the orthorhombic modification III to a hexagonal chain packing. This hexagonal chain packing is characterized by a strong reflection around $\vartheta = 9.5°$ representing the direct distance between neighbouring chains. A weak reflection at $\vartheta = 6.9°$ represents the length of a dimeric unit (0 0 2 reflection) and indicates a kind of layer structure. As discussed for poly(HBA)[13] this hexagonal chain packing is a consequence of the columnar shape of the polyester chains which is the result of rotational motions of phenylene rings around their *para* axis. In other words, this hexagonal chain packing resembles a smectic B structure with rotational freedom of the mesogens. This is consistent with the interpretation that an increasing molar fraction of 3-PhHBA units lowers the temperature, where this rotational freedom unfreezes.

The thermal properties of copolyester **2f** are quite different from those of **2a–e**. The d.s.c. curves exhibit a glass transition around 130°C (*Figure 7*). Furthermore, a flat endotherm is detectable in the temperature range of 200–210°C.

Optical microscopy confirmed that this endotherm is a true melting process (T_m). A nematic melt with typical threaded 'schlieren texture' is formed above T_m and isotropization occurs in the temperature range of 420–450°C. When a film of **2f** was pressed at 200°C and subjected to penetration measurements, a heat distortion temperature (HDT) of 175°C was found under a load of 1 kg mm^{-2}. After annealing at 170°C for 20 h, a higher crystallinity (*Figure 5B*) and a higher HDT (186°C) were found. A comparison of these mechanical properties with those of the isomeric copolyester **3** have been discussed



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previously[14]. The largely differing properties of samples **2e** and **2f** suggest the following conclusion. The lower reactivity of 3-PhABA (as indicated by ^{1}H n.m.r. spectroscopy, *Table 1*) not only entails a lower rate of incorporation but also the formation of a blocky sequence. In Marlotherm-S® crystalline oligomers grow to crystalline polymers as described for poly(HBA)[15,16] so that transesterification between chain segments is slow or absent. In the molten state a higher rate of incorporation of 3-PhABA may be combined with a high rate of transesterification catalysed by MgO, with the consequence of a more or less random sequence. The combined effect of different compositions and sequences explain all the effects discussed above.

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