New polymer syntheses: 59. Homo- and copolyesters of 4-(4′-hydrophenoxy)benzoic acid

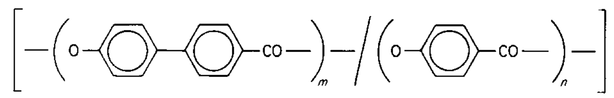
Hans R. Kricheldorf* and Volker Döring
Institut für Technische und Makromolekulare Chemie der Universität, Bundessstrasse 45, 2000 Hamburg 13, Germany
(Received 15 October 1991; revised 23 March 1992; accepted 25 March 1992)

The homopolyester of 4-(4′-hydroxyphenoxy)benzoic acid (poly(4-HPBA)), was prepared under two different reaction conditions and compared with a sample provided by another research group. Depending on the synthetic route, different melting points, d.s.c. traces and crystal lattices were found. However, after repeated heating and cooling, one thermodynamically stable modification with a melting point of 370–375°C can be obtained. Copolyesters of 4-hydroxybenzoic acid and 4-(4′-hydroxyphenoxy)benzoic acid were prepared with various molar ratios either in the melt (condensation in bulk) or in solution. These copolyesters were characterized by elemental analyses, ^{1}H n.m.r. spectroscopy, d.s.c. measurements, wide-angle X-ray scattering measurements at various temperatures, and optical microscopy. Whereas copolyesters prepared in solution do not melt below 500°C, those prepared by polycondensation in bulk show melting points down to approximately 260°C and form a nematic melt.

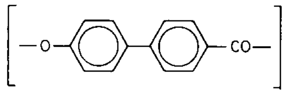
(Keywords: copolyester; polycondensation; crystal structure; nematic melt)

INTRODUCTION

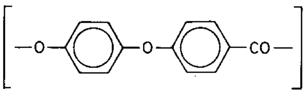
Poly(4-hydroxybenzoic acid) (polyHBA) has attracted much interest for two reasons. First, it possesses complex physical properties because it can adopt several crystal modifications and because it shows interesting phase transitions[1–6]. Second, 4-hydroxybenzoic acid (4-HBA) is a widely used building block of thermotropic polyester, including products of technical interest such as Xydar® and Vectra®. The present work is part of a systematic study of copolyesters derived from 4-HBA and other aromatic hydroxy acids. In two previous papers[7,8] copolyesters derived from 4′-hydroxybiphenyl-4-carboxylic acid (**1**) were described along with the homopolyester of this monomer (**2**). The aim of the present work was to gather information on the homopolyester (**3**) and copolyesters (**4**) of 4-(4′-hydroxyphenoxy)benzoic acid (**5**). The incorporation of an ether group should flexibilize the polymer chain compared to **1** and **2** and the consequences of this for basic properties such as glass transition (T_g), crystallinity melting point (T_m) and stability of mesophases should be evaluated.



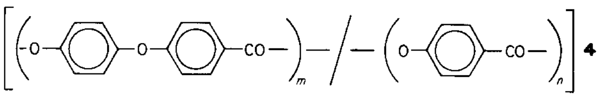
1



2



3



4

EXPERIMENTAL

Materials

4-HBA and ethyl-4-hydroxybenzoate were gifts of Bayer AG (4150 Krefeld-Uerdingen). 4-HBA was acetylated with an excess of acetic anhydride and a catalytic amount of pyridine in refluxing toluene (m.p. 185–188°C; m.p. 185–187, ref. 9). 4-(4′-Hydroxyphenoxy)benzoic acid was prepared from 4-bromoanisol and ethyl-4-hydroxybenzoate according to literature methods[10,11]. The acetyl derivative had a melting point of 151–153°C after recrystallization from toluene/ligroin (m.p. 150°C, ref. 11). Marlotherm-S (a mixture of isomeric dibenzylbenzenes) is a commercial product available from Hüls AG (4370 Marl FRG).

Poly[4-(4′-hydroxyphenoxy)benzoic acid] 3

Polycondensation in bulk. 4-(4′-Acetoxyphenoxy)benzoic acid **5** (50 mmol) and magnesium oxide (10 mg) were heated in a cylindrical glass reactor, equipped with stirrer, and gas inlet and outlet tubes, to 250°C where the condensation started. The temperature was then raised to 300°C in 10°C steps over a period of 2 h. Finally vacuum was applied at 300°C for 20 min. The cold product was powdered and extracted with hot acetone. Yield 94%. Analyses: calculated for $C_{13}H_8O_3$ (212.2): C 73.58, H 3.80; found: C 73.11, H 3.82%.

---

*To whom correspondence should be addressed

0032–3861/92/245321–07

Polycondensation in solution. 4-(4′-Acetoxyphenoxy)benzoic acid **5** (20 mmol) was dissolved in Marlotherm-S (60 ml) and heated with stirring under nitrogen to 260°C for 8 h, 290°C for 18 h and to 320°C for 4 h. After cooling, the precipitated polyester was isolated by filtration and washed with hot acetone. Yield 77%. Analyses: found: C 72.82, H 3.90%.

Copolyester 4

Copolycondensation in bulk. 4-(4′-Acetoxyphenoxy)benzoic acid **5** (25 mmol), 4-acetoxybenzoic acid (25 mmol) and 10 mg magnesium oxide were weighed into a cylindrical glass reactor and heated under stirring to 250°C, where the condensation started. The temperature was then raised to 300°C in 10°C steps over a period of 2.5 h. Finally vacuum was applied at 300°C for 0.5 h. The crude copolyester was mechanically removed from the reactor, powdered and extracted with hot acetone.

Copolycondensation in solution. 4-(4′-Acetoxyphenoxy)benzoic acid **5** (8 mmol) and 4-acetoxybenzoic acid (32 mmol) were rapidly heated in Marlotherm-S (80 ml) to 340°C. The temperature was maintained for 16 h, with stirring and a slow stream of nitrogen. After cooling, the reaction mixture was diluted with chloroform and the precipitated copolyester was isolated by filtration. The crude product was washed with hot acetone and dried at 120°C *in vacuo*.

Measurements

The d.s.c. measurements were conducted on a Perkin-Elmer DSC-4 in aluminium pans at a heating rate of 20°C min^{-1}.

^{1}H n.m.r. spectra at 300 MHz were obtained on a Bruker MSL-300 FT n.m.r. spectrometer. Copolyester (50 mg) was hydrolysed in a mixture of 0.6 ml CD_3OD and 0.4 ml of a 40 wt% $NaOD/D_2O$ solution.

The wide-angle X-ray scattering (WAXS) patterns were recorded on a Siemens D-500 powder diffractometer with Ni-filtered CuKα radiation. Synchrotron radiation measurements ($\lambda = 1.50$ Å) were conducted at HASYLAB (DESY, Hamburg, Germany) at a heating rate of 20°C min^{-1} as described previously[6].

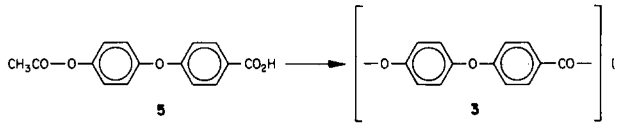
RESULTS AND DISCUSSION

Poly[*4-*(*4*′-hydroxyphenoxy)benzoic acid] *3*

For a better understanding of the structure–property relationships of the copolyesters **4a–g** it seemed advisable to study the homopolyester **3** in more detail. The homopolyester **3** was first synthesized by de Abajo and de la Campa[11], but only a melting range (>400°C) was reported for its characterization. In the present work 4-(4′-acetoxyphenoxy)benzoic acid **5** was prepared as monomer according to the literature[10,11]. Its polycondensation (equation (1)) was conducted in two ways:

sample A: in an inert reaction medium (Marlotherm-S®) at 320°C;
sample B: by condensation in bulk at increasing temperature (250–300°C). In this case magnesium oxide was used as initiator.

For comparison a third sample, sample C, was obtained from de Abajo and de la Campa. This sample was prepared by polycondensation of monomer **5** in diphenylether at 250°C (5 h) and dried after intensive washing with toluene[11].


(1)

All three samples of polyester **3** (A, B and C) were insoluble in common solvents, so that reprecipitation or characterization in solution were not feasible.

Interestingly, samples A and C prepared at temperatures ≤300°C show nearly identical WAXS patterns (*Figure 1A*); these resemble the pattern of modification I of polyHBA[12] which suggests that polyester **3** adopts a similar orthorhombic modification. In contrast, the WAXS powder pattern of sample B (*Figure 1B*) resembles that of the orthorhombic modification III formed by polyHBA in the temperature range[5,6] 340–440°C. When sample A was annealed at 320°C for 2 h, the WAXS pattern changed and was finally identical with that of sample B. In other words the crystal modification of sample B seems to be the thermodynamically stable modification.

The d.s.c. measurements of samples A, B and C yielded three different curves for the first heating run. In the case of sample A, two endotherms were detectable at 311 and 357°C (*Figure 2A*). After annealing at 340°C (20 min) the second heating curve only exhibited one endotherm at 377°C (*Figure 2B*). Again only one endotherm (at 365°C) was detectable in the first heating curve of sample B. These observations suggest that the first endotherm (at 311°C) in the d.s.c. curve of sample A represents an irreversible transition into the more stable modification of sample B, in full agreement with the WAXS patterns.

In the case of sample C, two endotherms again appeared in the first heating curve of the original sample (*Figure 3A*). The first endotherm (305°C) might be identical with that of sample A. Surprisingly, the second endotherm showed up at 414°C, 40°C above the highest endotherm of samples A or B. However, this endotherm

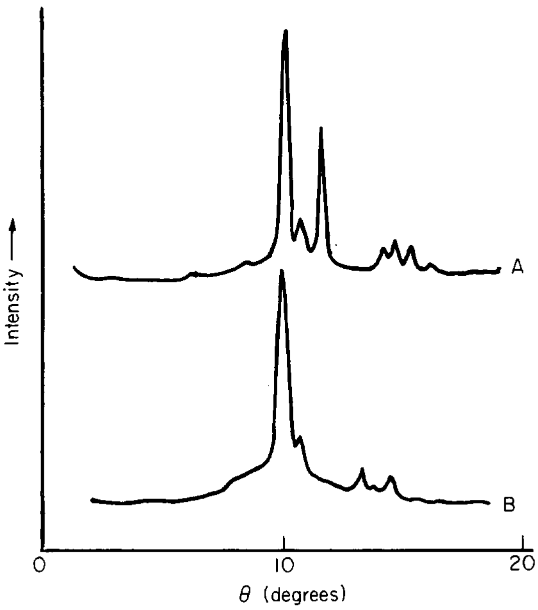


Figure 1 WAXS powder patterns (CuKα radiation at 25°C) of polyester 3. A, Sample A prepared by bulk condensation at 250–300°C; B, sample B prepared in Marlotherm-S at 260–320°C

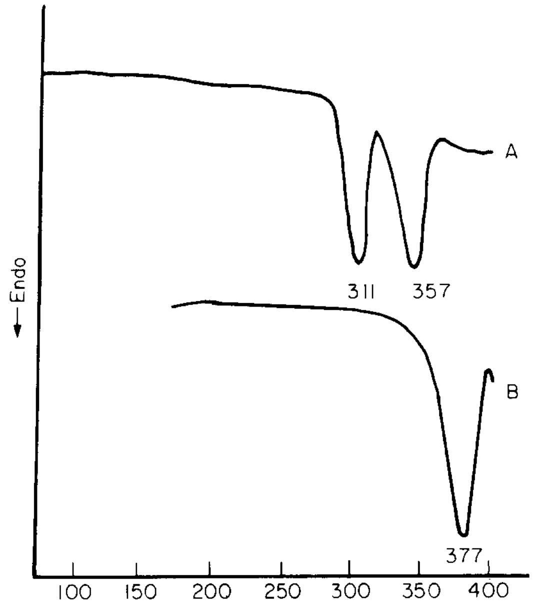


Figure 2 D.s.c. measurements (heating rate 20°C min^{-1}) of polyester 3 sample A. A, First heating of the crude product; B, first heating after annealing at 340°C for 20 min

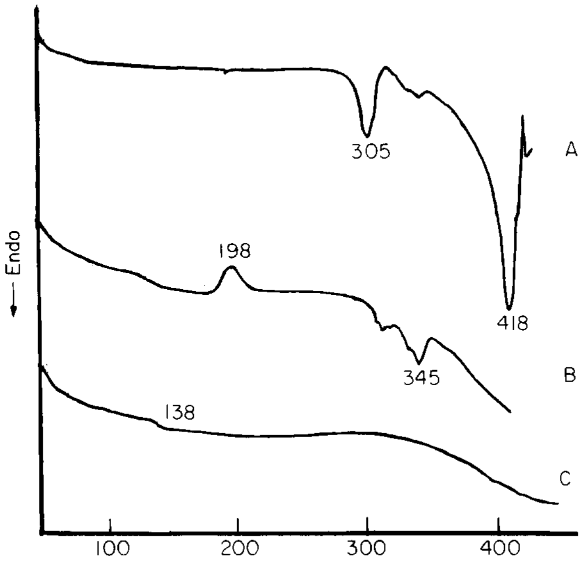
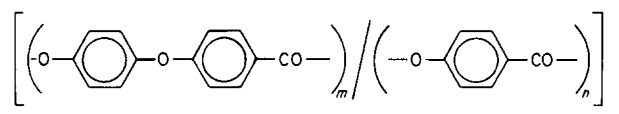


Figure 3 D.s.c. measurements (heating rate 20°C min^{-1}) of polyester 3 sample C. A, First heating; B, second heating after rapid cooling (~200°C min^{-1}) from 430°C; C, second heating of a fresh sample after a first heating to 430°C followed by slow cooling (~20°C min^{-1}) down to 25°C

was not reproducible upon repeated heating and cooling, in contrast to the endotherm of samples A and B. When sample C was rapidly cooled from 430 to 25°C and heated again, a glass transition step at 136°C, a recrystallization exotherm at 198°C and a melting endotherm at 345°C were detectable (*Figure 3B*). This endotherm obviously corresponds to the endotherm of samples A and B. When sample C was slowly cooled from the melt at 430°C, the second heating trace did not show any exotherm or endotherm (*Figure 3C*). Optical microscopy confirmed that polyester **3** begins to decompose in the isotropic melt above 400°C, thus the lack of phase transitions found after slow cooling from 430°C is the result of thermal degradation.

Considered together, the results indicate that the incorporation of an oxygen into the biphenyl unit reduces the melting point by approximately 200°C, when polyesters **2** and **3** are compared. Furthermore, the comparison of three different samples of **3** demonstrates the crystal modifications and thermal properties of this polyester depend largely on the thermal history and thus on the synthetic procedure.

*Copolyesters **4a–g***



4a–g

a : m/n = 1/1
b : m/n = 1/1,5
c : m/n = 1/2
d : m/n = 1/2,3
e : m/n = 1/4
f : m/n = 1/9
g : m/n = 1/19

Syntheses. The copolyesters **4a–g** were prepared by copolycondensation of monomer **5** and 4-acetoxybenzoic acid under various feed ratios. Two series of copolyesters were prepared using different condensation procedures – copolycondensation in bulk or in Marlotherm-S. Copolyesters obtained in bulk are labelled (B): their yields and properties are summarized in *Table 1*. Copolyesters prepared in solution are labelled (S): their properties are listed in *Table 2*.

These different condensation procedures were chosen for the following reasons. First, it was found in the case of the homopolyester **3** that the thermal history has a tremendous influence on the properties of the material. Second, copolycondensation in bulk usually yields copolyesters with nearly random sequences, and molar compositions close to the feed ratio. Different reactivities of the comonomers have a stronger influence on the structure of copolyesters when the copolycondensations are conducted in solution[13]. Third, copolycondensations of monomer mixtures rich in 4-acetoxybenzoic acid usually yield more perfect crystallites when conducted in solution.

Only three copolyesters, namely **4a**(B), **4b**(B) and **4c**(B) were soluble in common organic solvents. In mixtures of $\mathrm{CH_2Cl_2}$ and trifluoroacetic acid (volume ratio 4:1) inherent viscosities of 1.0, 0.6 and 1.2 dl g^{-1} were found. The fact that **4b**(B) possesses a lower glass transition temperature than **4a**(B) and **4c**(B) is consistent with these viscosity values. The insolubility of all other copolyesters in common solvents prevented solution-dependent characterization.

In order to check the molar composition, all copolyesters were hydrolysed in an n.m.r. tube by means of NaOD/$\mathrm{D_2O}$/CDOD, and afterwards 300 MHz ^{1}H n.m.r. spectra of the completely hydrolysed samples were recorded. As demonstrated by the spectrum of *Figure 4*, the signals of both hydroxyacids are sufficiently separated to allow a fairly accurate determination of the composition. The molar ratios obtained in this way show, in most cases, a perfect agreement with the feed ratios, but in some cases 10–15% deviation was detectable. The content of 4-HBA was found to be lower than expected. Furthermore, the synthesis of **4c**(S) was repeated and

Table 1 Yields and properties of copolyesters prepared by copolycondensation of monomer **5** and 4-acetoxybenzoic acid in bulk at temperatures between 250 and 300°C

Polymer	Feed ratio[a]	Composition[b]	Yield (%)	Formula (molecular weight)	Elemental analyses		T_g[c] (°C)	T_{m_1}[c] (°C)	T_{m_2}[c] (°C)	T_i[d] (°C)
					C	H				
4a(B)	1/1.0	1/1.0	92	$C_{30}H_{12}O_5$ (332.1)	Calcd 72.29 Found 71.30	3.64 3.56	120	260 (1H) 288 (2H)	395(1H) 401(2H)	420–450
4b(B)	1/1.5	1/1.5	96	$C_{94}H_{56}O_{24}$ (1569.5)	Calcd 71.94 Found 70.96	3.60 3.58	106	272, 286 284 (2H)	dec.	420–455
4c(B)	1/2.0	1/1.8	97	$C_{27}H_{16}O_7$ (452.4)	Calcd 71.68 Found 70.13	3.56 3.50	118	280	–	450–480
4d(B)	1/2.3	1/2.0	95	$C_{88}H_{52}O_{23}$ (1477.3)	Calcd 71.54 Found 70.49	3.55 3.50	103	258	–	460–490
4e(B)	1/4.0	1/3.5	94	$C_{41}H_{24}O_{11}$ ( )	Calcd 71.10 Found 70.90	3.49 3.43	95	–	–	470–510
4f(B)	1/9.0	1/8.0	94	$C_{76}H_{49}O_{21}$ (1293.2)	Calcd 70.60 Found 69.65	3.43 3.51	–	318	342	dec.[e] >530

[a] Molar ratio of both monomers
[b] Molar composition of the isolated copolyesters as determined by ^{1}H n.m.r. spectroscopy
[c] From d.s.c. measurements with a heating rate of 20°C min^{-1}; T_{m_1} and T_{m_2} symbolize endotherms; 1H = first heating
[d] Isotropization temperature as observed by optical microscopy at a heating rate of 20°C min^{-1}
[e] Thermal decomposition

Table 2 Yields and properties of copolyesters prepared by copolycondensation of monomer **5** and 4-acetoxybenzoic acid in Marlotherm-S at 340°C

Polymer	Feed ratio[a]	Composition[b]	Yield (%)	Formula (molecular weight)	Elemental analyses		T_g[c] (°C)	T_{m_1}[c] (°C)	T_{m_2}[c] (°C)	T_i[d] (°C)
					C	H				
4c(S)	1/2	1/1.9	78	$C_{27}H_{16}O_7$ (452.4)	Calcd 71.68 Found 71.49	3.56 3.48	121	237	–	dec.[e] >500
4e(S)	1/4	1/3.6	74	$C_{41}H_{24}O_{11}$ ( )	Calcd 71.10 Found 71.10	3.49 3.51	120 (2H)	228 (1H) 243 (2H)	293 (1H)	dec.[e] >500
4f(S)	1/9	1/1.0	77	$C_{76}H_{49}O_{21}$ (1293.2)	Calcd 70.60 Found 70.60	3.43 3.50	–	274	–	dec.[e] >500
4g(S)	1/1.9	1/1.9	84	$C_{146}H_{84}O_{41}$ (2494.2)	Calcd 70.31 Found 70.20	3.39 3.37	–	310	–	dec.[e] >500

[a] Molar ratio of both monomers
[b] Molar composition of the isolated copolymers as determined by ^{1}H n.m.r. spectroscopy
[c] From d.s.c. measurements with a heating rate of 20°C min^{-1}; T_{m_1} and T_{m_2} symbolize endotherms; 1H = first heating
[d] Isotropization temperature as observed by optical microscopy at a heating rate of 20°C min^{-1}
[e] Thermal decomposition

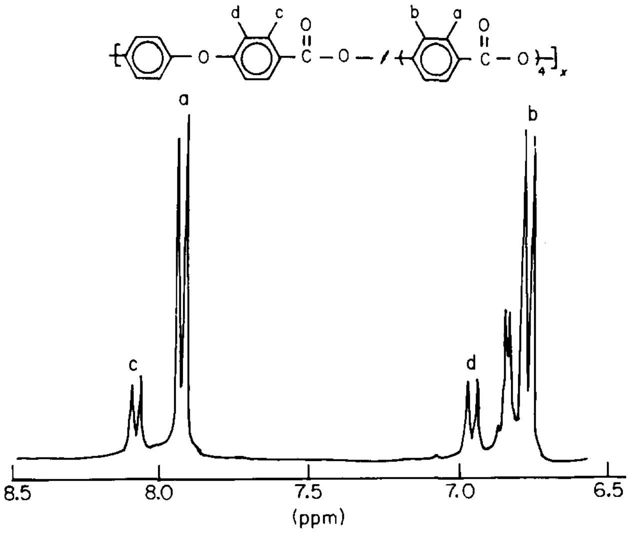


Figure 4 ^{1}H n.m.r. spectrum (300 MHz) of copolyester **4** after hydrolysis in $CD_3OD/NaOD/D_2O$

stopped after a conversion (i.e. yield) of 21%. The molar composition of this sample was identical with that of sample **4c**(S) listed in *Table 2*. Thus the ^{1}H n.m.r. spectroscopic results suggest very similar reactivities of both monomers. The reactivities of the comonomers influence not only the composition of the copolyesters, but also their sequences. In the case of the soluble samples **4a**(B), **4b**(B) and **4c**(B), ^{13}C n.m.r. spectra confirmed the existence of nearly random sequences. The spectrum of **4a** (B) (*Figure 5*) displays the four CO signals of nearly identical intensity expected for an overall randomness of the sequence. Unfortunately, this kind of information was not accessible for the samples prepared in Marlotherm-S (*Table 2*), in as much as ^{13}C n.m.r. cross polarization/magic angle spinning spectra of the solid samples did not give any sequence information.

Properties. For a better understanding of the thermal properties of copolyesters **4a**–**g** it seems advisable to discuss first the WAXS powder patterns. In the case of series **4a**(B)–**4f**(B) the WAXS patterns show a continuous increase of crystallinity with increasing molar fraction of 4-HBA units (*Figure 6*). Powder patterns such as that of **4a**(B) have been observed for several copolyesters of HBA[12,14–16]. This pattern is typical for comonomers with lateral dimensions similar to those of HBA, but with a different length: such comonomers are 4-hydroxyphenylpropionic acid[12], ethylene terephthalate[14], 4′-hydroxybiphenyl-4′-carboxylic acid[8] or

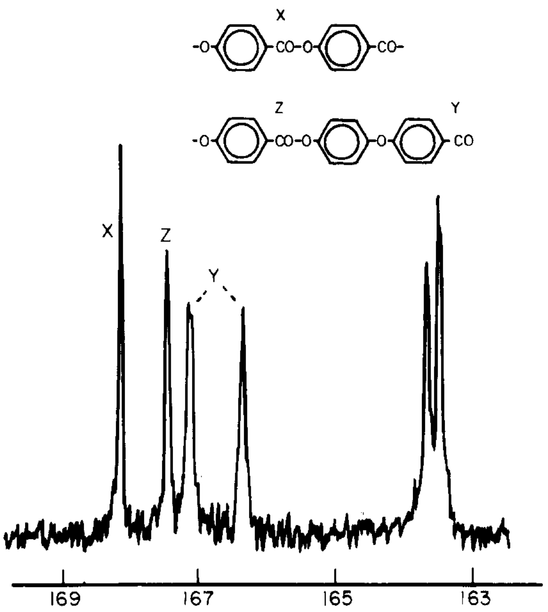


Figure 5 ^{13}C n.m.r. spectrum (75.4 MHz) of copolyester **4a**(B) measured in $CDCl_3$/trifluoroacetic acid (volume ratio 4:1)

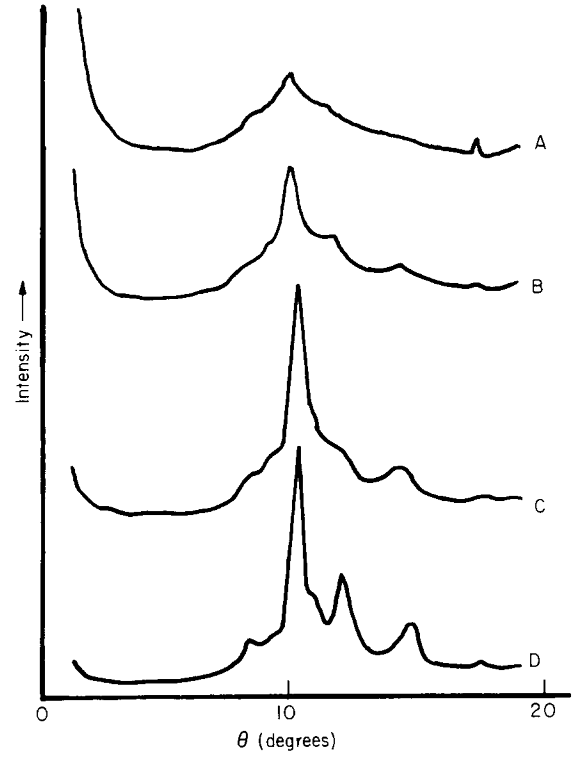


Figure 6 WAXS powder patterns: A, copolyester **4a**(B); B, **4d**(B); C, **4e**(B); D, **4f**(B)

combinations of hydroquinone and imid dicarboxylic acids[15]. The molecular order represented by this WAXS pattern may be described as a columnar mesophase with a more or less broad distribution of lateral distances. This columnar mesophase may include domains with a nearly perfect hexagonal chain packing which are responsible for the reflection at $\theta = 9.6°$. This reflection represents the lateral distance of neighbouring chains (4.6 Å). Increasing molar fraction of HBA units favours the formation of orthorhombic domains, and the WAXS patterns approach that of pure polyHBA, which is shown in *Figure 7D*.

In contrast to the copolyesters of series (B) the WAXS patterns of series (S) indicate a high degree of crystallinity for all copolyesters of this series (*Figure 7*). It is characteristic for copolycondensations in solutions that the fraction and perfection of crystallites is much higher than in the case of copolycondensations in bulk. It has been demonstrated for polyHBA[3,16,17] that oligomers crystallize from the reaction mixture in Marlotherm-S and continue the chain growth in the crystalline state. However, the high crystallinity of **4d**(S)–**4f**(S) compared with **4d**(B)–**4f**(B) also raises the suspicion that the copolyesters prepared in Marlotherm-S possess sequences with a higher degree of blockiness. Different sequences correlated with different degrees of crystallinity have recently been found for copolyesters of HBA and 4-hydroxy-3-phenylbenzoic acid prepared in Marlotherm-S and in bulk, respectively[12].

In agreement with their high crystallinity, the copolyesters of series (S) differ in several properties from those of series (B). For instance, all copolyesters of series (S) are insoluble and infusible. The d.s.c. curves exhibit one endotherm below 400°C. The temperature of this endotherm rises with increasing molar fraction of HBA units (*Figure 8*) and approaches the temperature of the α-transition of pure polyHBA. WAXS powder patterns measured with synchrotron radiation or variable

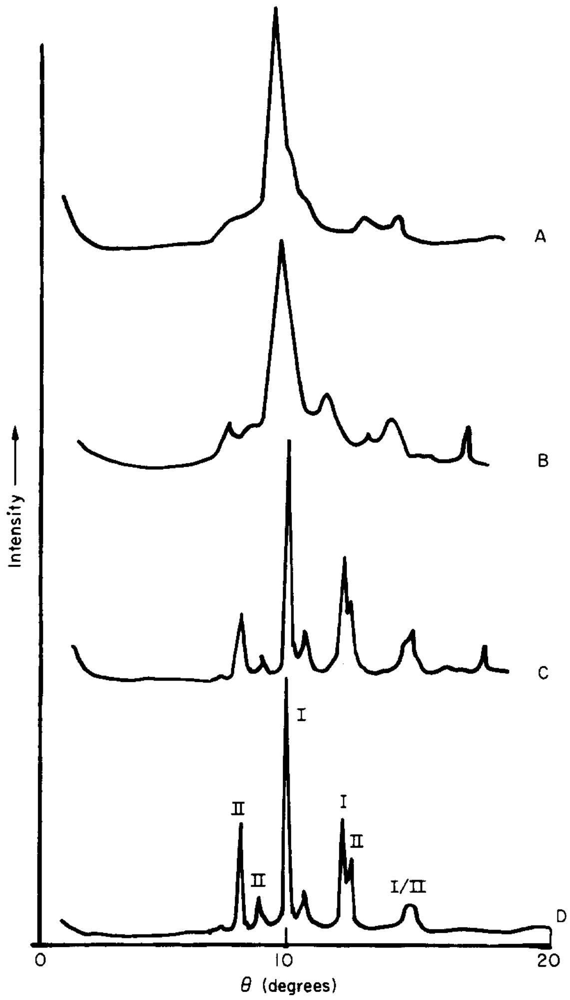


Figure 7 WAXS powder patterns: A, copolyester **4e**(S); B, **4f**(S); C, **4g**(S); D, poly(4-hydroxybenzoate)

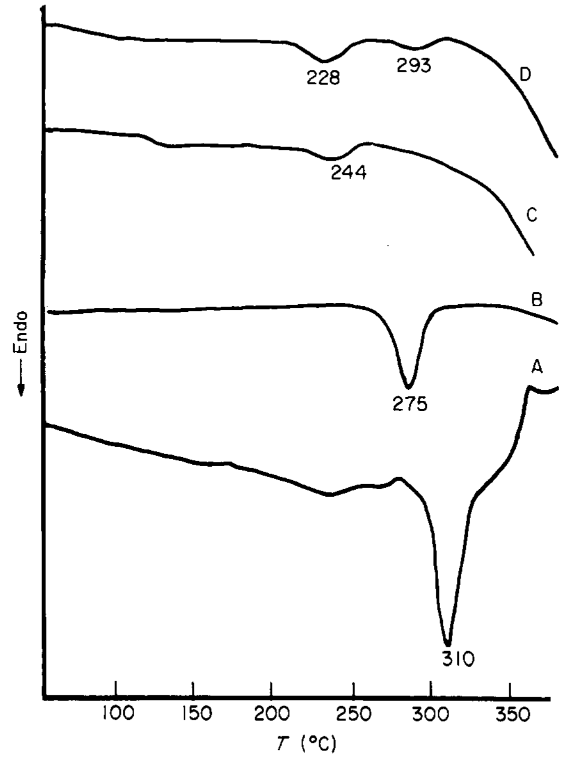


Figure 8 D.s.c. measurements (heating and cooling rate 20°C min^{-1}): A, **4e**(S) first heating; B, **4e**(S) second heating; C, **4f**(S) first heating; D, **4g**(S) first heating

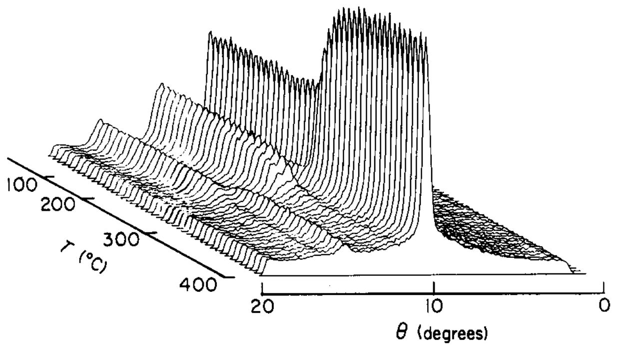


Figure 9 WAXS powder patterns of copolyester **4f**(S) measured with synchrotron radiation ($\lambda = 1.50$ Å) at a heating rate of 20°C min^{-1}

temperature up to 400°C confirm that this endotherm indicates a change to different orthorhombic modifications, in close analogy to pure polyHBA (*Figure 9*).

In this connection is should be emphasized that the temperature of the α-transition (*Figure 8*) and the structure of the WAXS powder patterns (*Figure 7*) change continuously with the molar composition of **4d**(S)–**4g**(S). This observation is a strong argument against a pronounced blockiness of the sequences. Long blocks of HBA units would result in a biphasic character of these copolyesters with two endotherms in the d.s.c. curves, or at least with one endotherm around 330–340°C as typical for polyHBA.

A characteristic of the d.s.c. curves of copolyesters prepared in bulk is the appearance of a glass transition step, which agrees well with the presence of an amorphous phase as indicated by the WAXS powder patterns (*Figure 6*). Furthermore, one or two closely neighbouring endotherms are detectable in the temperature range 250–320°C (*Table 1* and *Figure 10*). A second, weaker endotherm around 400°C shows up in the heating curve of **4a**(B). Optical microscoy with crossed polarizers revealed that copolyesters **4a**(B)–**4e**(B) form a nematic melt in contrast to the copolyesters of series (S). The endotherms in the temperature range 260–320°C indicate the melting process. The isotropization occurs at temperatures above 420°C and extends over a range of 30–40°C, as is typical for random copolyesters. The isotropization process is in all cases affected by thermal decomposition and thus is not reversible. The endotherms observable in the d.s.c. trace of **4f**(B) indicate a change between different orthorhombic modifications analogous to polyHBA[5,8] and not a melting process.

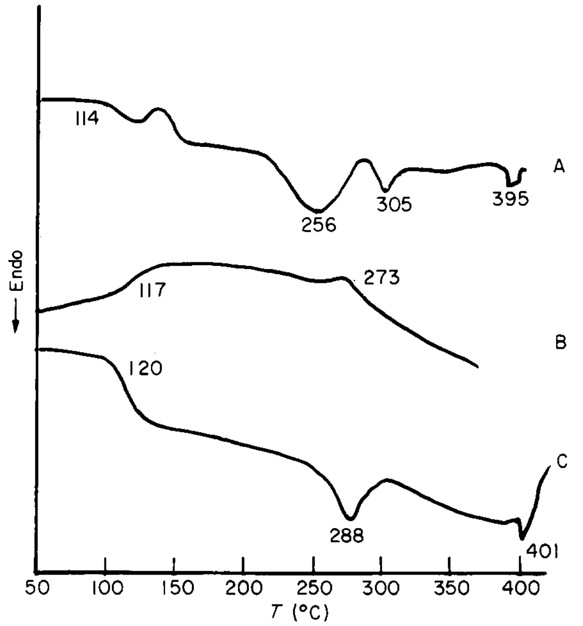


Figure 10 D.s.c. measurements (heating and cooling rate 20°C min^{-1}) of copolyester **4a**(B): A, first heating; B, first cooling; C, second heating

CONCLUSIONS

Random copolyesters of 4-HBA and 4-(4′-hydroxyphenoxy)benzoic acid can be prepared by polycondensation of their acetyl derivatives in bulk. Such copolyesters are thermotropic and form a nematic melt in contrast to the parent homopolyesters. When compared to copolyesters of 4′-hydroxybiphenyl-4-carboxylic acid (**1**) the melting points are 100–120°C lower and the crystallinity and thermostability are lower.

REFERENCES

1 Economy, J., Storm, R. S., Matkovich, V. I., Cottis, S. G. and Nowak, B. E. *J. Polym. Sci., Polym. Chem. Edn* 1976, **14**, 2207

2 Economy, J., Volksen, W., Viney, C., Geiss, R., Siemens, R. and Karis, T. *Macromolecules* 1988, **21**, 2777

3 Lieser, G., Schwarz, G. and Kricheldorf, H. R. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 1599

4 Hanna, S. and Windle, A. *Polym. Commun.* 1988, **29**, 236

5 Yoon, D. Y., Masciocchi, N., Depero, L. E., Viney, C. and Parrish, W. *Macromolecules* 1990, **23**, 1793

6 Kricheldorf, H. R. and Schwarz, G. *Polymer* 1990, **31**, 481

7 Schwarz, G. and Kricheldorf, H. R. *Makromol. Chem. Rapid Commun.* 1988, **9**, 717

8 Kricheldorf, H. R., Ruhser, F. and Schwarz, G. *Macromolecules* 1991, **24**, 4990

9 Kaufmann, A. *Ber. Dtsch Chem. Ges* 1909, **42**, 3480

10 Walker, J. *J. Chem. Soc.* 1942, 347

11 de Abajo, J. and de la Campa, J. *J. Polym. Sci.: Part C, Polym. Lett.* 1988, **26**, 313
12. Lieser, G. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 1611
13 Kricheldorf, H. R. and Ruhser, F. *Polymer* 1992, **33**, 2431
14 Kricheldorf, H. R. and Conradi. A. *J. Polym. Sci. A. Polym. Chem.* 1987, **25**, 489
15 Kricheldorf, H. R. and Pakull, R. *New Polym. Mater.* 1989, **1**, 165
16 Kricheldorf, H. R. and Schwarz, G. *Makromol. Chem.* 1983, **184**, 475
17 Taesler, C., Petermann, J., Schwarz, G. and Kricheldorf, H. R. *Makromol. Chem.* 1991, **192**, 2255