New Polymer Syntheses. 48. Thermotropic Copolyesters of 4′-Hydroxybiphenyl-4-carboxylic Acid and 4-Hydroxybenzoic Acid or 3-Chloro-4-hydroxybenzoic Acid

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ABSTRACT: 4′Acetoxybiphenyl-4-carboxylic acid and 4-acetoxybenzoic acid were condensed in the molten states at various molar ratios. Monomer mixtures with a high molar fraction of 4-acetoxybenzoic acid were also condensed in an inert reaction medium. Analogous condensations were conducted with 3-chloro-4-acetoxybenzoic acid. In addition to these copolyesters, the homopolyesters of 4,4′-hydroxybiphenylcarboxylic and 3-chloro-4-hydroxybenzoic acid were synthesized and characterized. The copolyesters were characterized by elemental analyses, ^{1}H NMR spectroscopy, DSC measurements, penetration measurements, and WAXS measurements at 20 °C or at temperatures up to 450 °C. Furthermore, a 1:1 copolyester of 3-phenyl-4-hydroxybenzoic acid and 4-hydroxybenzoic acid was synthesized and compared with other copolyesters of the latter monomer. All copolyesters are more or less crystalline and show their lowest melting point at a content of 70 mol % 4-hydroxybenzoic acid (T_m = 380 °C) or at ca. 50 mol % 3-chloro-4-hydroxybenzoic acid (T_m = 338 °C). WAXS measurements and optical microscopy revealed a nematic phase above these melting points.

Introduction

In the past decade several thermotropic aromatic polyesters were commercialized by various chemical companies. Most of these liquid-crystal (LC) polyesters are copolyesters of 4-hydroxybenzoic acid; e.g., Xydar (Amoco Co.), Vectra (Celanese Co.), Ultrax (BASF AG), Victrex SRP (ICI plc.), or Econol (Sumitomo Co.). Poly(4-hydroxybenzoate) (poly(HBA)) itself is highly crystalline with a melting point around 530 °C,[1] is insoluble in all common solvents and, thus, difficult to process.[2,3] Incorporation of comonomers is mainly for the purpose of reducing the melting point below 400 °C or still better 350 °C, so that processing from the melt becomes feasible. The best documented technical LC polyester that meets these requirements is a binary copolymer of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA), the so-called Vectra.[4-12]

In this copolyester HNA exerts two structural functions. First, due to its kink (or crankshaft) structure it disturbs the lateral distances of neighboring chains. Second, due to its greater length compared to HBA it also disturbs the perfect array of van der Waals and dipole forces along an individual chain. In order to obtain a better understanding of the influence of comonomers on the crystal structure and properties of poly(HBA), we previously launched a systematic study of copolyesters containing various aromatic hydroxycarboxylic acids.[13-17] The present work was aimed at synthesizing and characterizing copolyesters of 4′-hydroxybiphenyl-4-carboxylic acid (HBCA). In this connection it is noted that ternary copolyesters consisting of HBA, HNA, and HBCA were described in a patent of Celanese Co.[4]

Experimental Section

Materials. 3-Phenyl-4-hydroxybenzoic acid and 4-hydroxybenzoic acid were gifts of Bayer AG (5090 Leverkusen, FRG) and were used without purification. 3-Chloro-4-hydroxybenzoic acid was purchased from Aldrich Co. (St. Louis, MO). It was dried at 110 °C in vacuo. All hydroxy acids were then acetylated with excess acetic anhydride and 1 mL of pyridine in refluxing toluene. 4′-Acetoxybiphenyl-4-carboxylic acid was prepared as described previously.[18,19] All monomers were recrystallized prior to polycondensation. Marlotherm-S, a mixture of isomeric benzylbenzenes, was a gift of Hüls AG (Marl, FRG).

Polycondensations. (A) Condensation in Solution. A mixture of two acetylated hydroxy acids (ca. 8 g) dissolved in Marlotherm (100 mL) was heated in a metal bath to 350 °C with stirring. The liberated acetic acid was removed with a slow stream of nitrogen; the temperature was maintained for 16 h. After being cooled, the reaction mixture was diluted with acetone, and the crystalline copolyester was isolated by filtration and extracted with refluxing acetone.

(B) Bulk Condensation. A mixture of two acetylated hydroxy acids (ca. 15 g) and 10 mg of magnesium oxide was weighed into a cylindrical, round-bottomed glass reactor equipped with stirrer, gas inlet, and outlet tubes. The reaction mixture was rapidly heated to 260 °C (by means of a metal bath) and then gradually to 330 °C (total time ca. 3 h). Finally, the temperature of 330 °C was maintained for 0.5 h in vacuo. The cold reaction product was mechanically powdered, extracted with refluxing acetone, and dried in vacuo.

Cocondensation of 4-Acetoxybenzoic Acid and 3-Phenyl-4-acetoxybenzoic Acid. The cocondensation of 4-acetoxybenzoic acid (50 mmol) and 3-phenyl-4-acetoxybenzoic acid (50 mmol) was conducted by analogy with procedure B with the following heating program: 1 h/260 °C, 1 h/300 °C, 1 h/320 °C, and 1 h/320 °C in vacuo. The stirrable melt solidified upon cooling. It was dissolved in a mixture of dichloromethane and trifluoroacetic acid (4:1 by volume) and precipitated into methanol. After filtration the product was dried at 110 °C in vacuo. Yield 57%; T_g = 129; T_m = 202 °C (by DSC). Anal. Calcd for $C_{20}H_{12}O_4$ (316.23): C, 75.94; H, 3.82. Found: C, 75.23; H, 3.76.

Measurements. DSC measurements were conducted with a Perkin-Elmer DSC-4 apparatus in aluminum pans under nitrogen.

Penetration (HDT) measurements were obtained on a Perkin-Elmer TGS-2 at a heating rate of 10 °C/min under a load of 1 kg/mm^2. The films used for these measurements were pressed at a temperature 20 °C above the melting point.

^{1}H NMR measurements (molar composition and end-group analyses) were conducted in such a way that 20 mg of a copolyester was hydrolyzed in 0.4 mL of 4 N NaOH and 0.6 mL of CD_3OD in a 5-mm-o.d. NMR tube. The NMR measurements were performed on a Bruker MSL 300 or a Bruker AC 100 spectrometer.

WAXS power patterns were measured at room temperature on a Siemens D-500 apparatus with Ni-filtered Cu Kα radiation. Temperature-dependent WAXS measurements were conducted

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Table I
Result of Copolycondensations of 4′-Acetoxybiphenyl-4-carboxylic Acid and 4-Acetoxybenzoic Acid in Marlotherm-S (16 h at 350 °C) or in Bulk

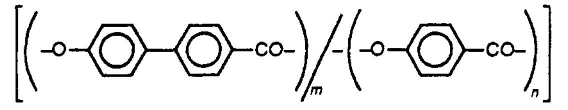
polymer formula	HBCA/HBA[a]	reaction medium	yield, %	T_m,[b] °C	elemental analyses	C	H
1a	5:95	Marlotherm	85[c]	531	calcd:	70.76	3.42
					found:	71.35	3.46
1b	10:90	Marlotherm	82[c]	533	calcd:	71.47	3.47
					found:	71.50	3.85
(**1c**)	20:80	Marlotherm	*d*				
(**1d**)	30:70	Marlotherm	*d*				
1c	20:80		89	415	calcd:	72.78	3.58
					found:	72.00	3.53
1d	30:70		87	380	calcd:	73.96	3.67
					found:	73.53	3.61
1e	40:60		96	387	calcd:	74.99	3.75
					found:	74.51	3.71
1f	50:50		90	412	calcd:	75.94	3.83
					found:	75.35	3.68
1g	75:25		90	487	calcd:	77.96	3.98
					found:	77.52	3.88

[a] Feed ratio of 4′-hydroxybiphenylcarboxylic acid and 4-hydroxybenzoic acid. [b] From DSC measurements with a heating rate of 20 °C/min. [c] M_n approximately 32 000 by ^{1}H NMR end-group analyses. [d] The initially generated oligomers formed a molten mass, which could not be separated from the glass walls.

with synchrotron radiation (λ = 1.50 Å) at HASYLAB, DESY (Hamburg)[20] at a heating rate of 20 °C/min under vacuum.

Results and Discussion

Syntheses of Copolyesters. Copolyesters of 4′-hydroxybiphenyl-4-carboxylic acid (HBCA) and 4-hydroxybenzoic acid (HBA) were prepared by cocondensation of the corresponding acetoxy derivatives. Two condensation procedures were applied. A first attempt to synthesize copolyesters **1a–d** was carried out in such a way that the comonomers were condensed in an inert reaction medium (Marlotherm-S) at 350 °C. In analogy to the synthesis of pure poly(HBA), the copolyesters **1a** and **1b** were obtained as a suspension of crystalline powders. However, in the case of **1c** and **1d**, a solid mass separated on the walls of the reactor, and separation of the insoluble copolyester from the glass wall proved to be difficult. Obviously the melting points of the initially formed cooligomers were so low that they separated in the form of a melt on the surface of the glass reactor.



1a, m:n = 5:95
b, m:n = 10:90
c, m:n = 20:80
d, m:n = 30:70
e, m:n = 40:60
f, m:n = 50:50
g, m:n = 75:25

Therefore, copolyesters **1c–g** were prepared according to a second procedure, namely, by cocondensation in the molten state. However, in all cases the reaction products solidified at high conversions despite a maximum reaction temperature of 330 °C. The results of all cocondensations are summarized in Table I.

In order to determine the composition of the copolyesters, or in other words, the rates of incorporation, the copolyesters were hydrolyzed in NaOH/H_2O/CD_3OD and subjected to ^{1}H NMR measurements. Unfortunately, complete hydrolysis was only achieved in the case of **1a** and **1b**. ^{1}H NMR spectra revealed that the molar composition corresponds to the feed ratio (Figure 1). These results suggest that the reactivities of both comonomers were nearly identical under these reaction conditions. In order to check this suggestion two additional syntheses of **1b** were conducted in such a way that the condensations were stopped at low conversion. The resulting copolyesters isolated with yields of 29 and 43% showed again a composition identical with the feed ratio. These results support the conclusion that both monomers possess almost equal reactivities. Since a deviation from these reactivities is still less likely for cocondensations in the molten state, it may be concluded that all copolyesters **1a–g** possess a composition matching the feed ratio. This conclusion is supported by the C and H elemental analyses (Table I). The ^{1}H NMR spectra of hydrolyzed copolyesters **1a** and **1b** also allowed the determination of $\bar{M}_n$ by end-group analyses as demonstrated for poly(HBA).[21] $\bar{M}_n$'s around 32 000 were found in both cases.

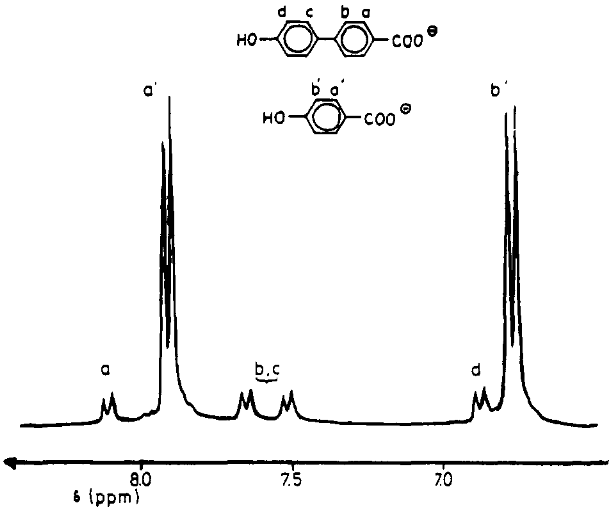
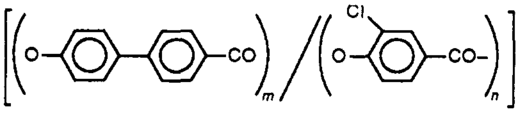


Figure 1. 300-MHz ^{1}H NMR spectrum of copolyester **1b** hydrolyzed in CD_3OD containing 4 N NaOD/D_2O.

Four copolyesters (**2a–d**) of HBCA and 3-chloro-4-hydroxybenzoic acid (ClHBA) were synthesized by bulk cocondensations of the corresponding acetoxybenzoic acid



2a, m:n = 30:70
b, m:n = 40:60
c, m:n = 50:50
d, m:n = 70:30

Table II
Results of Copolycondensations of 4′-Acetoxybiphenyl-4-carboxylic Acid and 3-Chloro-4-acetoxybenzoic Acid

polymer formula	HBCA/ClHBA[a]	yield, %	T_m,[b] °C		elemental analyses C	H	Cl	HBCA/ClHBA[c]
2a	30:70	92	378	calcd:	63.27	2.71	14.86	35:65
				found:	65.31	2.81	13.60	
2b	40:60	98	355	calcd:	65.94	2.94	12.42	42:58
				found:	66.32	2.96	11.67	
2c	50:50	93	338	calcd:	68.49	3.16	10.11	51:49
				found:	68.53	3.08	9.64	
2d	70:30	96	379	calcd:	73.22	3.57	5.80	69:31
				found:	71.55	3.52	6.11	

[a] Feed ratio of 4′-acetoxybiphenyl-4-carboxylic acid and 3-chloro-4-acetoxybenzoic acid. [b] From DSC measurments with a heating rate of 20 °C/min. [c] Molar ratio of comonomers as determined from Cl analysis of isolated copolymers.

Table III
Reaction Conditions and Results of Polycondensation of 4′-Acetoxybiphenylcarboxylic Acid or 3-Chloro-4-acetoxybenzoic Acid in Marlotherm-S

polyester	temp, °C	time, h	yield, %	elem form. (form. wt)		elemental analyses C	H	Cl
poly(HBCA)	320	16	89	$C_{13}H_8O_2$	calcd:	79.58	4.11	
				(196.21)	found:	79.43	4.25	
poly(HBCA)	350	8	60	$C_{13}H_8O_2$	calcd:	79.58	4.11	
				(196.21)	found:	78.68	4.27	
poly(HBCA)	400	4	47	$C_{13}H_8O_2$	calcd:	79.58	4.11	
				(196.21)	found:	77.93	4.34	
poly(3-ClHBA)	320	16	74	$C_7H_3ClO_2$	calcd:	54.40	1.96	22.94
				(154.55)	found:	58.50	2.54	19.77
poly(3-ClHBA)	350	8	25	$C_7H_3ClO_2$	calcd:	54.40	1.96	22.94
				(154.55)	found:	58.81	2.45	18.70
poly(3-ClHBA)	400	4	0	$C_7H_3ClO_2$	calcd:			
				(154.55)	found:			

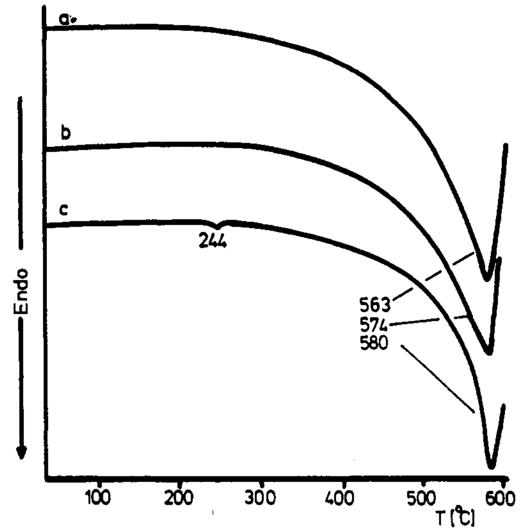
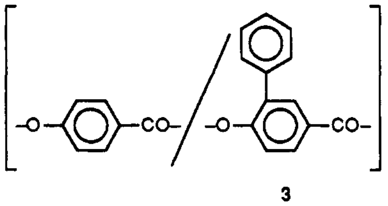


Figure 2. DSC heating curves (rate 20 °C/min) of poly(4′-hydroxybiphenyl-4-carboxylate) (A) prepared at 300 °C, (B) prepared at 350 °C, and (C) prepared at 400 °C.

derivatives. These copolyesters also could not be hydrolyzed in NMR tubes. Nonetheless, a crude determination of their composition was feasible on the basis of the Cl elemental analyses. Again, compositions close to the feed ratios were found (Table II). The insolubility of all copolyesters (**1a–g** and **2a–d**) in common solvents allowed neither physicochemical molecular weight measurements nor NMR sequence analyses. Nonetheless, the WAXS and DSC measurements discussed below suggest that random copolyesters were fomred in all cases, in agreement with equal reactivity ratios in the comonomers.

Finally, the synthesis of a copolyester of 3-phenyl-4-hydroxybenzoic acid (**3**) was conducted for comparison with **1e** and **4**. Yield and properties of this copolyester are reported in the Experimental Section. It should be mentioned that copolyesters of HBA and 3-phenyl HBA (molar composition 3:2) were claimed as thermotropic engineering plastics in a recent patent.[22] A more detailed study of copolyesters of 4-HBA and 3-phenyl-HBA will be reported in a future part of this series.



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Syntheses and Properties of Homopolyesters. For a better understanding of structure/property relationships of copolymers it is advisable to know the properties of the parent homopolymers. Whereas numerous studies were published on the syntheses and properties of poly(HBA), relatively little is known about poly(HBCA)[19] and poly(3-chloro-4-hydroxybenzoic acid) (poly(3-ClHBA)).[16] It was shown in the case of poly(HBA)[24,25] and poly(HNA)[26] that high reaction temperatures (up to 400 °C) favor the perfection of crystallites. Therefore, poly(HBCA) and poly(3-ClHBA) were prepared at three different temperatures (Table III). However, in the case of poly(3-ClHBA), side reactions (evolution of CO_2 was detected by barium hydroxide) prevented the formation of a polyester at 400 °C.

The WAXS powder patterns of all three samples of poly(HBCA) were nearly identical. They indicate, as reported previously,[19] that this polymer prefers a hexagonal chain packing even at room temperature, whereas poly(HBA) prefers orthorhombic modifications below 440 °C.[1,27–29] There are at least two reasons for this difference. First, poly(HBA) possesses a higher concentration of carbonyl groups, which favor the closer packing of an orthorhom-

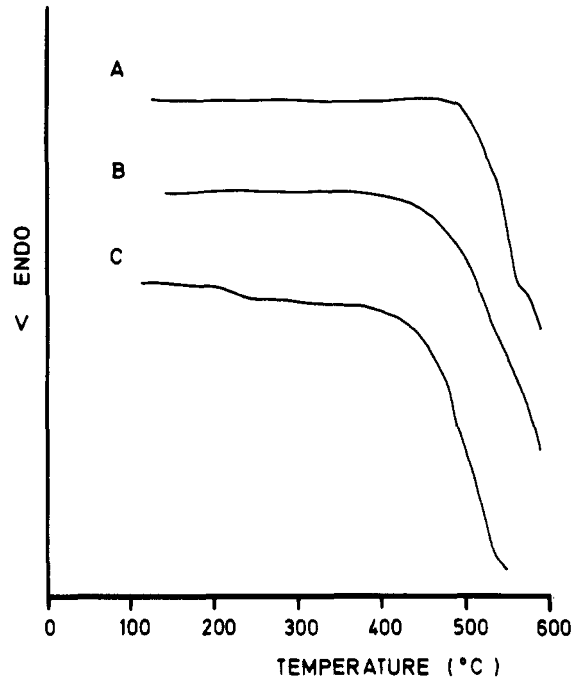
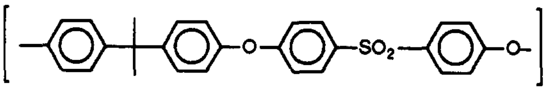


Figure 3. DSC heating curves (heating rate 20 °C/min) of (A) poly(ether sulfone) **4**, (B) polyimide **5**, and (C) poly(ester imide) **6**.

bic cell. Second, the phenyl rings of HBCA units are not coplanar due to an unfavorable interaction of the "ortho protons". The "twisted" biphenyl unit favors a columnar shape of the polyester chain and, thus, a hexagonal chain packing. Since no change of modification occurs upon heating, the DSC trace of poly(HBCA) displays only one endotherm between 550 and 600 °C, which represents simultaneous melting and decomposition. The temperature of this endotherm shifts upward with the increasing reaction temperature used for the preparation of poly(HBCA) (Figure 2). Obviously, higher reaction temperatures favor increasing size and perfection of the crystallites.

The question as to what extent the endotherm results from a melting or decomposition process cannot be answered precisely. By analogy with poly(HBA) and poly(HNA), optical microscopy revealed that poly(HBCA) remains crystalline up to approximately 550 °C, but loses its crystalline shape and decomposes at higher temperatures. Furthermore, it should be taken into account that amorphous polymers such as the poly(ether sulfone) **4**, the polyimide **5**, and the poly(ester imide) **6**, which suffer thermal degradation in the molten state, do not exhibit endotherms in their DSC traces (Figure 3). Therefore, it may be concluded that at least part of the enthalpy change in the DSC trace of poly(HBCA) results from a breakdown of the three-dimensional order. The role of thermal degradation will be discussed below in more detail.



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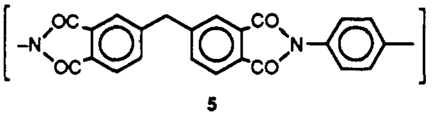

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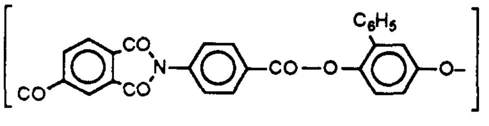

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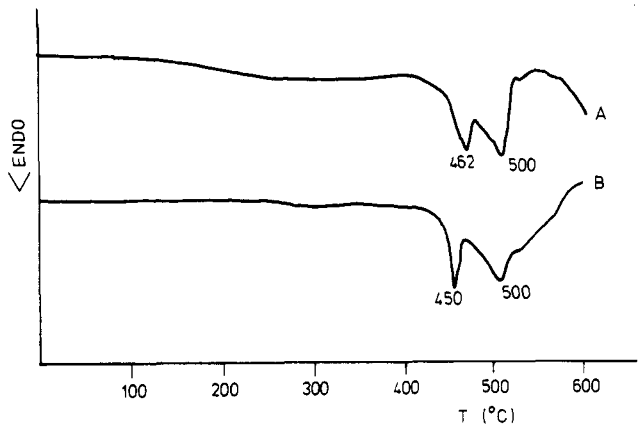


Figure 4. DSC heating curves (heating rate 20 °C/min) of poly(3-ClHBA). (A) Sample prepared at 320 °C/16 h in Marlotherm-S; (B) sample prepared at 350 °C/8 h in Marlotherm-S.

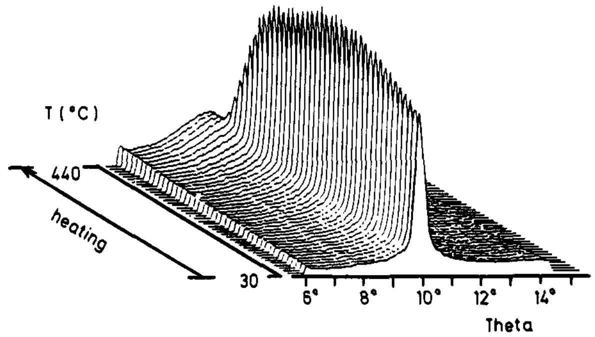


Figure 5. WAXS measurements of copolyester **1f** conducted with synchrotron radiation ($\lambda = 1.50$ Å) at a heating rate of 20 °C/min.

In the case of poly(3-ClHBA) the WAXS patterns of both samples (Table III) were again nearly identical and indicate an orthorhombic or monoclinic crystal lattice.[16] The DSC traces of both samples display two endotherms, although at slightly different temperatures (Figure 4). Because WAXS measurements above 460 °C were not feasible in the course of this work, no reliable interpretation of these DSC traces can be offered. However, by analogy with the DSC traces reported for poly(HBA) and poly(HNA),[1,28] they suggest that the first endotherm of poly(3-ClHBA) results from a change of modification, whereas the second endotherm represents the melting and decomposition process.

Crystallinity and Melting of Copolyesters. WAXS powder patterns taken at 20 °C show that copolyesters **1a–c** contain crystallites with orthorhombic and hexagonal chain packing, whereas **1d–g** exclusively prefer the hexagonal chain packing even at room temperature (Figure 5). The molar fraction of the orthorhombic modification I decreases with higher content of HBCA and is almost negligible in the case of **1c**. Nonetheless, its presence indicates a certain degree of chemical heterogeneity. In other words, the distribution of HBCA units over all chains and along individual chains is not absolutely uniform. However, such a chemical heterogeneity including a certain block length distribution is well-known and quite normal even for an overall random copolymerization of two monomers. The hexagonal chain packing of copolyesters **1c–g** is not a hexagonal crystal lattice and, thus, not a true crystalline state, because any order in the direction of the chain axis is lacking. However, if this columnar mesophase is called quasi-crystalline, it may be said that copolyesters

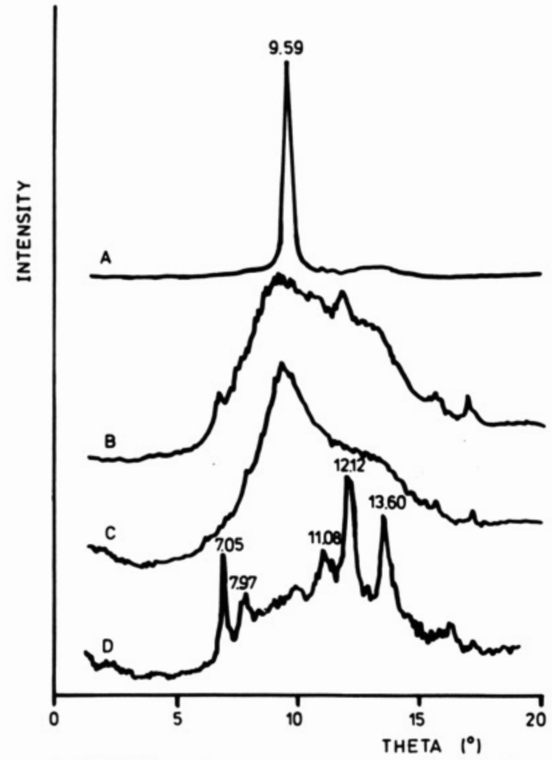


Figure 6. WAXS powder patterns measured at 25 °C with Cu Kα radiation. (A) Copolyester **2d**, (B) copolyester **2c**, (C) copolyester **2b**, (D) copolyester **2a**.

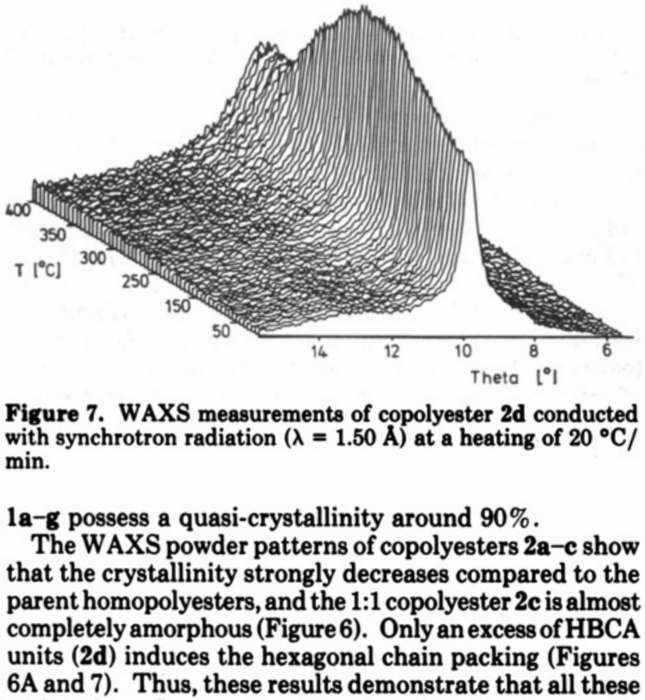
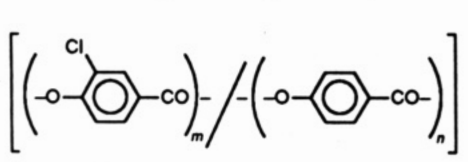


Figure 7. WAXS measurements of copolyester **2d** conducted with synchrotron radiation (λ = 1.50 Å) at a heating of 20 °C/min.

1a–g possess a quasi-crystallinity around 90%.

The WAXS powder patterns of copolyesters **2a–c** show that the crystallinity strongly decreases compared to the parent homopolyesters, and the 1:1 copolyester **2c** is almost completely amorphous (Figure 6). Only an excess of HBCA units (**2d**) induces the hexagonal chain packing (Figures 6A and 7). Thus, these results demonstrate that all these series of copolyesters **1a–g**, **2a–d**, and **7a–i** possess quite different relationships between chemical composition, crystal lattice, and degree of crystallinity.



$$\left[\left(-O-C_6H_3(Cl)-CO-\right)_m/\left(-O-C_6H_4-CO-\right)_n\right]$$

7a, $m{:}n$ = 5:1
b, $m{:}n$ = 2:1
c, $m{:}n$ = 1:1
d, $m{:}n$ = 1:2
e: $m{:}n$ = 1:3
f, $m{:}n$ = 1:4
g, $m{:}n$ = 1:5
h, $m{:}n$ = 1:7
i, $m{:}n$ = 1:10

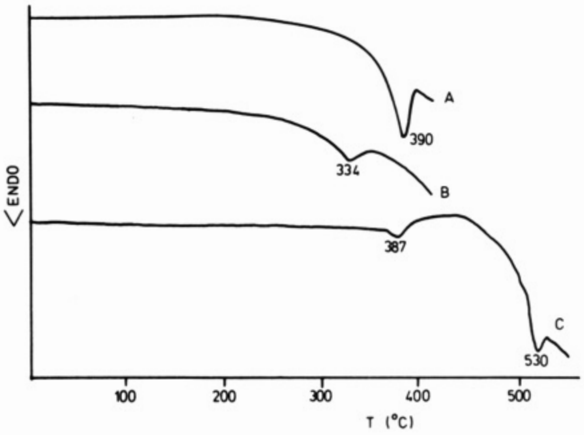


Figure 8. DSC measurements (heating rate 20 °C/min) of copolyester 1. (A) First heating, (B) second heating after rapid cooling from 440 to 200 °C and annealing for 30 min/200 °C, (C) first heating of a another sample of **1e**.

In agreement with the predominance of the hexagonal chain packing of copolyesters **1b–g**, their DSC traces do not display any endotherm resulting from a change of modification. However, such an endotherm is detectable for **1a** at 330 °C in analogy to the DSC traces of poly(HBA). Endotherms indicating a true melting process are detectable in the DSC traces of **1c–f**. These endotherms are reproducible in a second heating curve, when the sample was rapidly cooled from the nematic melt and shortly annealed above the glass transition temperature (curves A and B in Figure 8). Similar DSC traces were obtained for copolyesters **2a–d**, but the endotherm of **2c** is barely detectable.

Optical microscopy revealed the formation of a birefringent tough melt above these endotherms. Isotropization was not detectable up to 560–600 °C, where thermal degradation prevents further observation of the melt (see below). WAXS measurement conducted with synchrotron radiation at a heating rate of 20 °C/min confirm that a nematic melt was formed by both series of copolyesters (Figures 5 and 7). The DSC curves of copolyesters **1b** and **g** reflect the melting process only in the form of a shoulder. Obviously the melting process of copolyesters extends over a broader temperature range than that of the parent homopolyesters and is affected by thermal degradation at temperatures above 450 °C. A comparison of the melting points of copolyesters **1a–g**, **2a–d**, and **7a–i** demonstrates that HBCA units reduce the melting point (T_m) of poly(HBA) to a similar extent as 3-ClHBA units (Figure 9). The low melting point of copolyester **3** (205 °C) shows that a more space filling substituent will cause a further strong reduction of T_m. In contrast, a combination of HBCA and 3-ClHBA units does not significantly lower T_m (Table II) compared to copolyesters **7a–i**. Its main effect is the reduction of crystallinity (Figure 6).

Thermal Degradation of Copolyesters. It is known from poly(HBA)[1,19] and partially from poly(HNA)[28] that thermal degradation is significantly accelerated above 500 °C, i.e., in the temperature range of the strongest endotherm. Various methods, including pyrolysis/mass spectroscopy, have revealed that CO, CO$_2$, phenol, and derivatives of diphenyl ether are formed as volatile fragments in the case of poly(HBA).[3,29,30] Furthermore, Fries rearrangement and formation of a cross-linked material with a low content of ester groups was detected.[1]

In this connection the thermal degradation of copolyesters, such as **1c–f** and **2a–d**, is of interest because they exist in the molten state above 500 °C in contrast to the

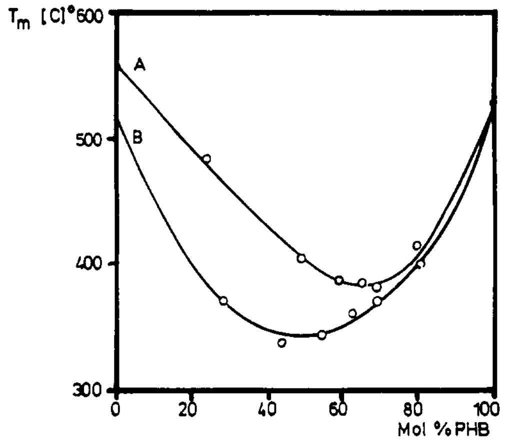
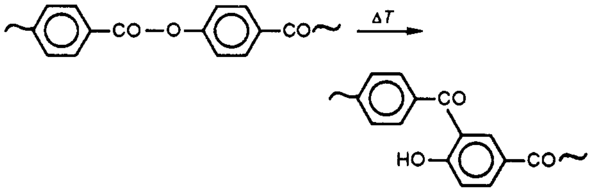


Figure 9. Plot of melting points of copolyesters **1a–g** (A) and **7a–i** (B) versus molar fraction of HBA.

parent homopolyesters. DSC measurements conducted up to 600 °C (curve C, Figure 8) display in all cases an endotherm between 530 and 570 °C. Since this endotherm cannot result from a melting process, it indicates either the isotropization of the nematic phase or a special degradation process. Optical microscopy revealed that the birefringence persists up to 600 °C (technical limit of the hot stage). Furthermore, it was observed that the tough melt formed above T_m became less viscous upon heating until a temperature of 530 ± 10 °C was reached. The melt then solidified within a narrow temperature range of 10–20 °C identical with the endotherm of the DSC curve.

IR spectra of samples heated to 500 °C and quenched do not show a significant change compared to the starting material (Figure 10A). However, when heating is continued above the endotherm, the chemical structure completely changes. This change is, for instance, evident from the reduction of the "ester carbonyl band" at 1730 cm^{-1} and the appearance of a new carbonyl band at 1690 cm^{-1} (Figure 10B). The same observations were reported for poly(HBA) and poly(HNA).[1,26] These results may be interpreted in the following way. At temperatures of 550 ± 20 °C a rapid degradation process occurs with a major contribution from Fries rearrangements. Since the Fries rearrangement yields trifunctional monomer units (eq 1) it also provides the basis for the cross-linking process.



(1)

The detection of a rapid endothermic cross-linking process in a relatively dense nematic melt is not only of interest for the interpretation of endotherms at temperatures above 500 °C, it may also provide an explanation for the low inflammability of thermotropic aromatic polyesters. The formation of a rather thermostable cross-linked material above 550 °C reduces the evolution of flammable gases, the access of hot gases and oxygen to the interior of the material, and the transport of heat from the surface to the interior. In this connection it should be mentioned that the thermal degradation of other aromatic polymers such as the poly(ether sulfone) **4** or the polyamide **5** does not result in cross-linking. Decreasing viscosity of the melt was observed up to 600 °C. This difference may be considered as further support for the hypothesis that the Fries rearrangement plays a major role in the thermal degradation of aromatic polyesters.

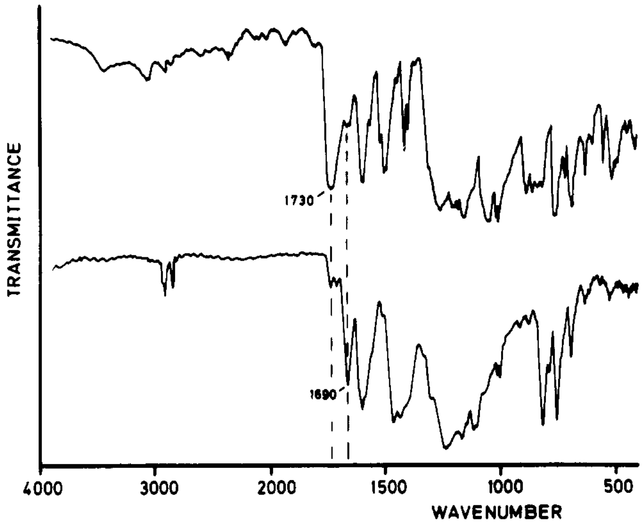


Figure 10. IR spectra (KBr pellets) of copolyester **1d**. (A, upper) After heating to 500 °C (with 20 °C/min) and quenching to 20 °C. (B, lower) After heating to 590 °C.

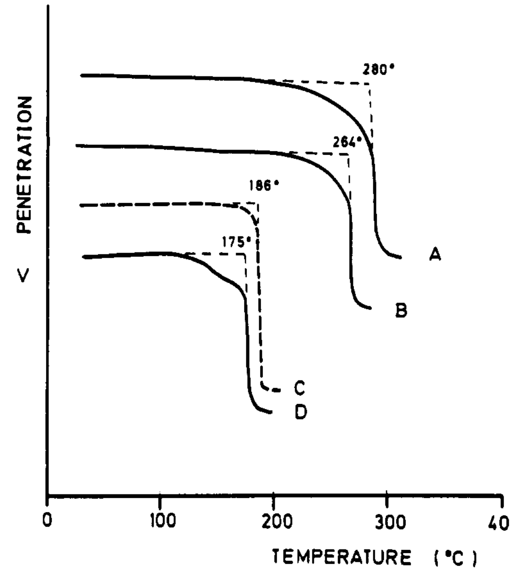


Figure 11. Heat distortion temperature measured by the penetration method at a heating rate of 10 °C/min with a load of 1 kg/mm^2. (A) Copolyester **1e**, (B) copolyester **7c**, (C) copolyester **3** after annealing, (D) copolyester **3** without annealing.

Heat Distortion Temperatures of Copolyesters. Finally, three copolyesters (**1e**, **7c**, and **3**) were selected to elucidate the correlation between chain packing and melting points, on the one hand, and heat distortion temperature on the other hand. Films pressed 20 °C above T_m were subjected to penetration measurements under a load of 1 kg/mm^2. Part of each film was annealed at 200 °C and measured again. In the case of copolyesters **1e** and **7c**, original films and annealed films gave nearly identical results (curves A and B in Figure 11). The HDTs are considerably lower than the melting points. In the case of copolyester **3**, the HDT of the annealed film was significantly higher (curve C) than that of the original film (curve D). These results also demonstrate that substituents with increasing steric demands considerably reduce the HDT. Thus, from the viewpoint of HDT copolyesters of 4′-hydroxybiphenyl-4-carboxylic acid are superior to those of 3-substituted 4-hydroxybenzoic acid, whereas the substituted copolyesters are more attractive from the viewpoint of processability.

References and Notes

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Registry No. (3)(HBA) (copolymer), 134847-96-4; HBCA (homopolymer), 132978-25-7; HBCA (SRU), 118168-46-0; ClHBA (homopolymer), 90385-55-0; ClHBA (SRU), 85609-98-9; (AcOC$_6$H$_4$-*p*-CO$_2$H)[AcO(C$_6$H$_4$-*p*-)$_2$CO$_2$H] (copolymer), 118338-26-4; (AcO(C$_6$H$_4$-*p*-)$_2$CO$_2$H)(3-chloro-4-acetoxybenzoic acid) (copolymer), 134847-95-3.