Whiskers. 4. Copolyesters of 4-Hydroxybenzoic Acid and 2-(4′-Hydroxyphenyl)benzoxazole-5-carboxylic Acid

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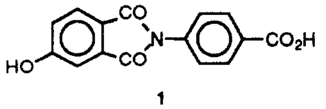
ABSTRACT: Acetylated 2-(4′-hydroxyphenyl)benzoxazole-5-carboxylic acid and 4-acetoxybenzoic acid were polycondensed in high concentration (0.5 mol/L) at 350 °C in a liquid reaction medium. The resulting copolyesters isolated in yields above 90% possess a composition which parallels the feed ratio. Further polycondensations were conducted at 400 °C and low monomer concentrations to yield whisker-like crystals. Yet whiskers were only obtained at a composition of 1:9 in favor of 4-hydroxybenzoic acid (4-HBA). Polycondensation of the silylated monomers yielded thick whiskers also at a composition of 2:8. The WAXS powder patterns indicate that all copolyesters are highly crystalline, but only the whisker-forming copolyesters adopt an orthorhombic crystal lattice similar to that of pure poly(4-HBA). At a composition of 3:7 a hexagonal chain packing prevails. The DSC measurements show that incorporation of the benzoxazole unit into poly(4-HBA) lowers the temperature of all phase transitions.

Introduction

The present work is part of a broader study on copolyesters of 4-hydroxybenzoic acid (4-HBA) and other aromatic hydroxy acids. These copolyesters are of interest for several reasons. First, if meltable and processable, such copolyesters may be useful as thermotropic engineering plastics. Vectra, the copolyester of 6-hydroxy-2-naphthoic acid, is the most intensively studied and commercial example of such materials.[1,2] Second, for a better understanding of poly(4-HBA) it is useful to modify the structure by incorporation of comonomers and to study their influence on chain packing and phase transitions.[3–6] Third, poly(4-HBA) can form needlelike or fibrous crystals, so-called whiskers which are interesting as reinforcing components of fully organic composites.[7–10] Incorporation of comonomers with functional groups or heterocycles is one approach to modify the surface of these whiskers and, thus, their interaction with the surrounding matrix.

In the preceding paper[11] copoly(ester–imide)s of 4-HBA and the isomeric imide monomers 1 and 2 were studied. Whiskers were obtained from all copolyesters of imide monomer 1 but not from those of 2. In the succeeding paper[12] copolyesters of 4-HBA and 2-(4′-carboxyphenyl)-5-hydroxybenzoxazole (3) will be described. The present work was aimed at completing the comparison of stereochemically very similar comonomers by synthesis and characterization of copolyesters of the isomeric benzoxazole monomer 4.



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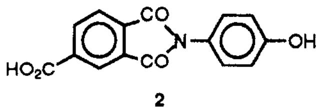

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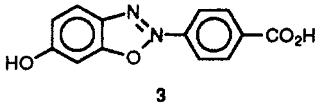

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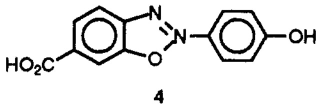

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Experimental Section

Materials. 3-Amino-4-hydroxybenzoic acid (technical grade) was a gift of Bayer AG (w4150 Krefeld–Uerdingen). It was silylated and condensed with 4-acetoxybenzoyl chloride as described previously.[13] 4-Hydroxybenzoic acid (4-HBA) was also a gift of Bayer AG. It was acetylated with an excess of acetic anhydride and a catalytic amount of pyridine in refluxing toluene. The melting point of the resulting 4-acetoxybenzoic acid was 188–190 °C after recrystallization from toluene. The trimethylsilyl derivative was prepared as described previously.[10]

Silylated 2-(4′-Acetoxyphenyl)benzoxazole-5-carboxylic Acid. 2-(4′-Acetoxyphenyl)benzoxazole-5-carboxylic acid (50 mmol) was suspended in toluene (200 mL), trimethylchlorosilane (100 mmol) was added, the reaction mixture was heated with stirring, and triethylamine (100 mmol) was added dropwise. The mixture was refluxed for 5 h, cooled, diluted with ligroin (100 mL), and filtered under exclusion of moisture. After concentration and drying in vacuo, the product was recrystallized from chloroform/ligroin. Yield 60%; mp 290–292 °C. Anal. Calcd for $C_{19}H_{19}NO_5Si$ (369.47): C, 61.77; H, 5.18; N, 3.79. Found: C, 61.24; H, 5.07; N, 3.82. ^1H NMR ($CDCl_3$/TMS): $\delta = 0.41$ (s, 9 H), 2.35 (s, 3 H), 7.75 (dd, 4 H), 7.80 (dd, 2 H), 8.46 (d, 1 H).

Polycondensations. (A) Preparative Method (Table I, Method A). 2-(4′-Acetoxyphenyl)benzoxazole-5-carboxylic acid (25 mmol) and 4-acetoxybenzoic acid (25 mmol) were dissolved in warm Marlotherm-S (100 mL). This solution was heated to 350 °C with stirring under an atmosphere of nitrogen. After 8 h at 350 °C the reaction mixture was cooled, diluted with acetone, and filtered. The isolated polyester was washed several times with hot acetone and dried at 120 °C in vacuo. All other copolyesters (**7b–f**) and the homopolyester **7a** were prepared analogously.

(B) Synthesis of Whiskers (Table II, Method B). 2-(4′-Acetoxyphenyl)benzoxazole-5-carboxylic acid (5 mmol) or a mixture of this monomer and 4-acetoxybenzoic acid (together 5 mmol) was dissolved in Marlotherm-S (100 mL) placed in a metal bath preheated to 330 °C and then rapidly heated to 400 °C. After 4 h the reaction mixture was cooled and worked up as described above.

(C) Silyl Method (Table I, Method C). A mixture of silylated 2-(4′-acetoxyphenyl)benzoxazole-5-carboxylic acid (1 mmol) and silylated 4-acetoxybenzoic acid (4 mmol) was polycondensed as described under B.

Results and Discussion

Syntheses. The monomers used for all but one polycondensation were 4-acetoxybenzoic acid (**5a**) and 2-(4′-acetoxyphenyl)benzoxazole-5-carboxylic acid (**6a**). This latter monomer was prepared from commercial 3-aminobenzoic acid as described previously.[13] For one polycondensation the silylated monomers **5b** and **6b** were used.

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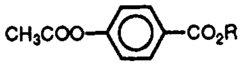
Table I. Reaction Conditions and Results of Polycondensations of 2-(4′-Acetoxyphenyl)benzoxazole-5-carboxylic Acid and 4-Acetoxybenzoic Acid in Marlotherm-S

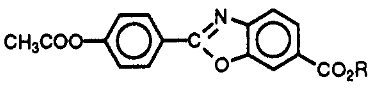
polymer (*m*/*n*)	synthetic method	yield (%)	elem anal.				morphology
				% C	% H	% N	
7a (10/0)	A^a	97	calcd	70.89	2.97	5.90	
			found	69.97	3.16	5.97	
7b (5/5)	A^a	99	calcd	70.59	3.10	3.92	
			found	69.71	3.17	3.98	
7c (4/6)	A^a	88	calcd	70.50	3.14	3.36	
			found	69.05	3.29	3.58	
7d (3/7)	A^a	94	calcd	70.41	3.18	2.71	
			found	70.10	3.24	2.77	
7e (2/8)	A^a	91	calcd	70.29	3.23	1.95	
			found	69.86	3.21	1.97	
7f (1/9)	A^a	91	calcd	70.16	3.29	1.06	
			found	70.13	3.31	1.12	
7a′ (10/0)	B^b	36	calcd	70.89	2.97	5.90	
			found	70.54	2.89	5.84	lamellar
7e′ (2/8)	B^b	38	calcd	70.29	3.23	1.95	short cylindrical crystals
			found	69.87	3.20	2.38	
7e″ (2/8)	C^c	32	calcd	70.29	3.23	1.95	short thick whiskers
			found	69.93	3.21	2.22	
7f′ (1/9)	B^b	41	calcd	70.16	3.29	1.06	needlelike whiskers
			found	70.01	3.31	1.20	

[a] Polycondensation at 350 °C/8 h with a total monomer concentration of 0.5 mol/L. [b] Polycondensation at 400 °C/4 h with a total monomer concentration of 0.05 mol/L. [c] Polycondensation of silylated monomers at 400 °C/4 h with a total monomer concentration of 0.05 mol/L.

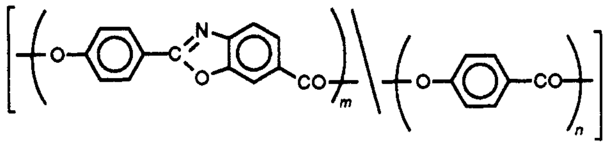
Two series of polycondensations were conducted. For the first ("preparative") series high molar concentrations of monomers (0.5 mol/L) were used and the reaction temperature was limited to 350 °C. For the second ("whisker") series, lower monomer concentration (0.05 mol/L) and a reaction temperature of 400 °C were applied, because these reaction conditions favor the formation of whiskers.[9,11] The products of these "whisker series" are denoted **7a′**,**7e′**, and **7f′**. The copolyester obtained by the polycondensation of silylated monomers (eq 1) is denoted **7e″**. The yields and some properties of all polyesters are summarized in Table I.



5a, R = H
b, R = SiMe$_3$

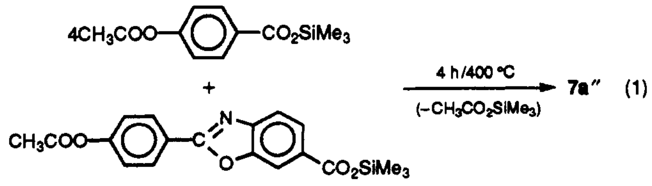


6a, R = H
b, R = SiMe$_3$



7a–f

a, *m*/*n* = 10/0
b, *m*/*n* = 5/5
c, *m*/*n* = 4/6
d, *m*/*n* = 3/7
e, *min* = 2/8
f, *m*/*n* = 1/9



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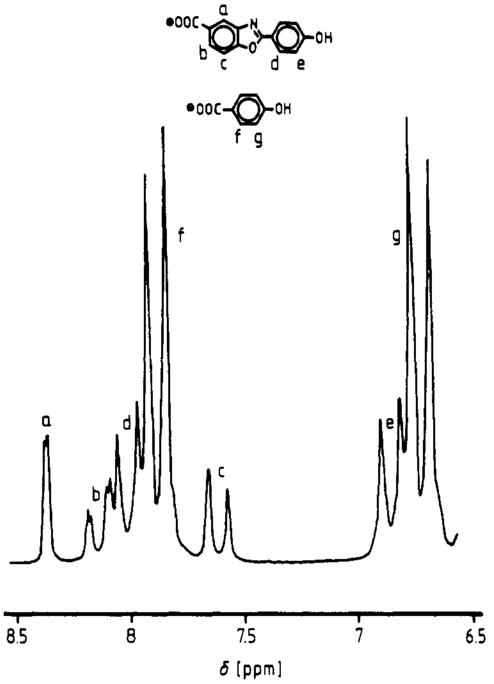

Figure 1. 300-MHz ^{1}H NMR spectrum of copolyester **7e** hydrolyzed in an NMR tube with NaOD/D$_2$O/CD$_3$OD.

The N-elemental analyses of all copolyesters indicate that their molar composition matches the feed ratio. This conclusion is supported by the ^{1}H NMR spectra of copolyesters hydrolyzed in NMR tubes by means of NaOD/D$_2$O and CD$_3$OD (Figure 1). In a more qualitative way the content of the benzoxazole unit can also be estimated from IR spectra. As illustrated by Figure 2, a band at 1625 cm^{-1} originating from a vibration of the oxazole ring parallels the molar concentration of the benzoxazole unit. These results together with the WAXS and DSC measurements discussed below suggest that the comonomers possess nearly identical reactivities and form more or less random sequences at the high reaction temperatures used for all polycondensations. The same observations were also made for all copolyesters of monomers **1**, **2**, and **3**. Unfortunately, a more detailed characterization of polyesters **7a–f** in solution was not feasible, because all polyesters are highly crystalline and insoluble in all nondestructive solvents.

Characterization. When the polyesters of the "preparative series" (**7a–f**) were examined by electron microscopy, needlelike crystals (whiskers) were not detectable. Again, only aggregates of lamellar crystals (no whiskers) were found when the benzoxazole monomer **6**

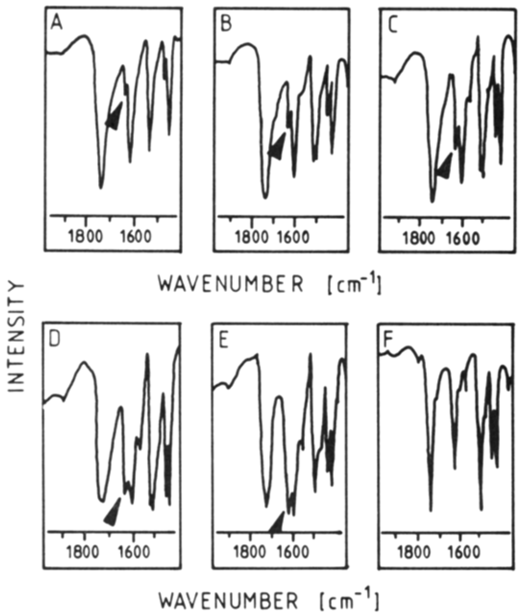

Figure 2. IR spectra (KBr pellets) of copolyesters **7a–f**: (A) **7f**; (B) **7e**; (C) **7d**; (D) **7c**; (E) **7b**; (F) **7a**.

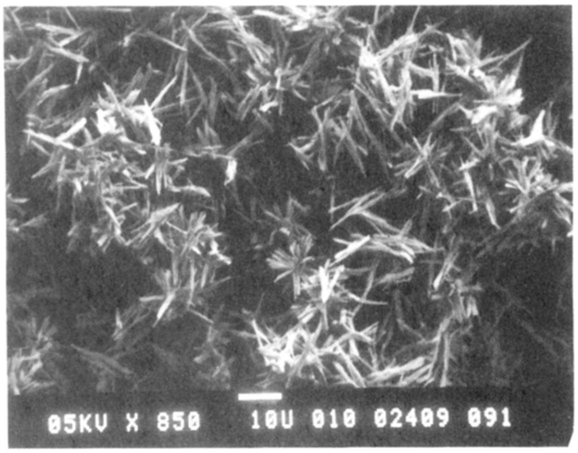

Figure 3. SEM micrograph of the 1/9 copolyester **7f′** prepared at 400 °C/4 h (the white bar has a length of 10 μm).

was polycondensed at low concentration and high temperature (**7a′**). The 2/8 copolyester **7e′** gave short cylindrical crystals, and only the 1/9 copolyesters **7f** yielded whiskers with an aspect ratio of approximately 10:1 and a length of 10–15 μm (Figure 3). Because the polycondensation of silylated carboxylic acids is a cleaner reaction which may favor the formation of whiskers,[10] the synthesis of the 2/8 copolyester was repeated with silylated monomers (eq 1). The resulting crystals of **7e″** look like thick needles with an aspect ratio of approximately 5:1 (Figure 4). This result is certainly not a full success, but it demonstrates that silylation of the monomers may favor the formation of columnar or needlelike crystals.

WAXS powder patterns of all polyesters were recorded at 25 °C. No significant difference was found between the samples of the "preparative series" (**7e,f**) and the "whisker series" (**7e′**,**f′** or **7e″**). A comparison between **7a** (Figure 5A) and **7b** (Figure 5B) reveals that the 5/5 copolyester is still highly crystalline and the crystal lattice is more or less identical with that of homopolyester **7a**. The WAXS pattern of **7c** (Figure 5C) allows two noteworthy conclusions. First, this copolyester contains the highest fraction of amorphous phase (>50%). It will be reported in the succeeding part of this series[12] for copolyesters of the benzoxazole monomer **3** that it is again

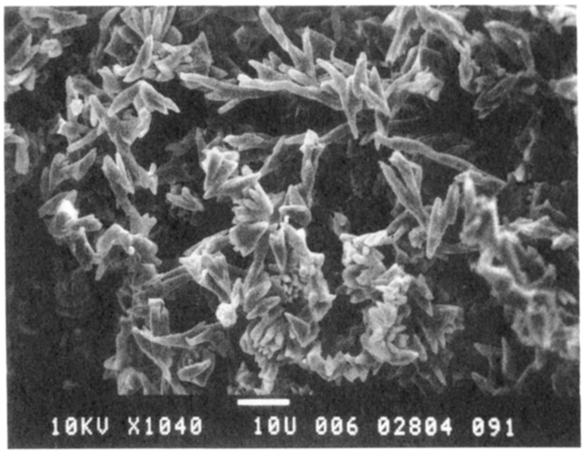

Figure 4. SEM micrograph of the 2/8 copolyester **7e″** prepared from silylated monomers at 400 °C/4 h (the white bar has a length of 10 μm).

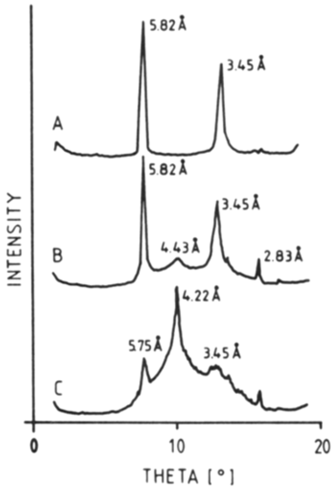

Figure 5. WAXS powder patterns of (A) homopolyester **7a**, (B) copolyester **7b**, (C) copolyester **7c**.

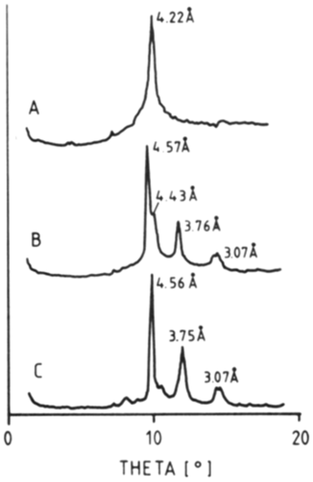

Figure 6. WAXS powder patterns of (A) copolyester **7d**, (B) copolyester **7e**, and (C) copolyester **7f**.

the 4/6 copolyester which contains the largest amorphous fraction. Second, the most prominent reflection appears at 4.22 Å. It is the only reflection of the 3/7 copolyester **7d** (Figure 6A), but it is typical neither for the orthorhombic crystal lattice of the homopolyester **7a** nor for poly(4-HBA). This reflection most likely indicates a hexagonal chain packing (but not hexagonal crystal lattice!). Remarkable is the width of this reflection and the absence of a higher order reflection. Possibly the chains

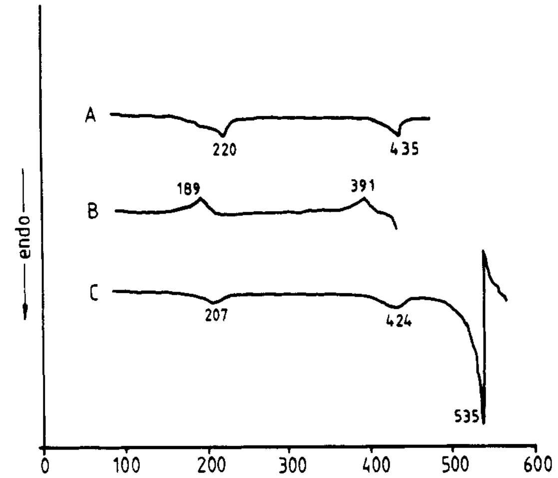

Figure 7. DSC measurements of copolyester **7f** conducted at a heating and cooling rate of 20 °C/min: (A) first heating; (B) first cooling; (C) second heating.

do not maintain exact hexagonal positions but obey a certain distribution function of distances. However, the more likely interpretation is to assume that the chains form an almost exact hexagonal packing with considerable conformational disorder (e.g., noncoplanarity of the 2-phenylenebenzoxazole unit).

The WAXS powder patterns of the 2/8 and 1/9 copolyesters are similar (Figure 6B,C) and indicate that both copolyesters prefer an orthorhombic crystal lattice almost identical with modification I of pure poly(4-HBA).[14] This finding supports the hypothesis that only those copolyesters which can exist in one of the orthorhombic crystal lattices of poly(4-HBA) are able to form whisker-like crystals. Apparently it does not matter whether the copolyesters prefer modification I, as demonstrated in the present work, or modification II, as reported for poly(ester-imide)s of monomer 1 in the preceding part.[11] This conclusion is consistent with the fact that neither modification I nor modification II exists under the reaction conditions used for the preparation of whiskers. As evidenced by WAXS measurements at high temperatures,[15,16] poly(4-HBA) forms a third orthorhombic modification above 350–360 °C. This modification III is characterized by greater lateral distances of the neighboring polyester chains, which ease 180 °C flip motions of the benzene rings.[17] The less densely packed modification III can in turn easier accommodate comonomers with lateral dimensions that slightly deviate from those of 4-HBA. Thus, the compatibility of comonomers with modification I or II is only an indirect but apparently reliable indicator for the ability of copolyesters to form whisker-like crystals.[11,12]

DSC measurements of polyesters **7a–f** conducted at a heating and cooling rate of 20 °C/min gave the following results. The 5/5 copolyester **7b** and the homopolyester **7a** do not display any features in their DSC curves up to 480 °C, where degradation becomes apparent. Again, no endotherms are detectable in the heating curves of **7c** and **7d**. This finding is not surprising, because polyesters with hexagonal chain packing usually do not display any change of modification at higher temperatures.[4,6] The first heating curves of **7e** and **7f** exhibit three endotherms when recorded up to 55 °C in close analogy to the heating curve of pure poly(4-HBA).[15] The endotherm at 530–540 °C represents melting and rapid degradation and is not reversible (Figures 7C and 8C). In the case of **7f**, both endotherms at lower temperatures (Figure 7A) are paralleled by exotherms in the cooling trace (Figure 7B),

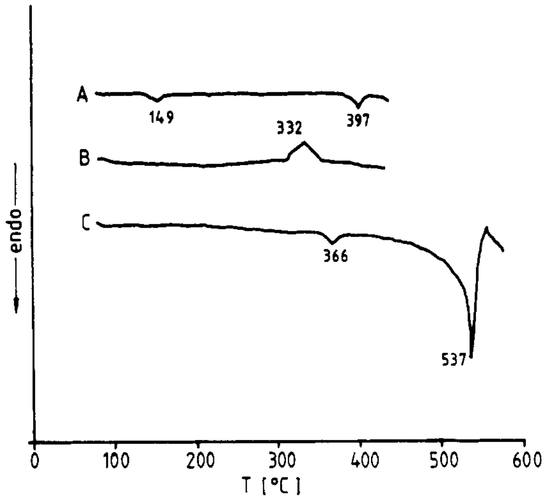

Figure 8. DSC measurements of copolyester **7e** conducted at a heating and cooling rate of 20 °C/min: (A) first heating; (B) first cooling; (C) second heating.

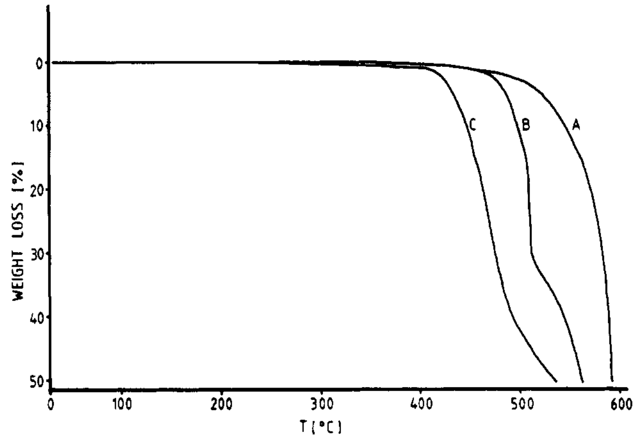

Figure 9. Thermogravimetric analyses conducted at a heating rate of 10 °C/min in air: (A) homopolyester **7a**; (B) copolyester **7b** (5/5); (C) copolyester **7f** (1/9).

whereas in the case of **7e** only one exotherm is detectable (Figure 8B). Obviously, these phase transitions represent similar changes of modification as described for poly(4-HBA) by several authors.[14–17] It is consistent with this interpretation that a comonomer with poor or moderate compatibility of the crystal lattice reduces the temperature of these phase transitions with increasing molar ratio. 3-Substituted 4-hydroxybenzoic acids as comonomers show a similar effect.[3,5] Hence, the WAXS powder patterns exhibiting the reflections of modification I and the DSC traces displaying the typical phase transitions of this modification are in perfect agreement.

Finally, a short study of the thermal stability of polyesters **7a–e** should be mentioned. All samples were heated in air at a heating rate of 10 °C/min. Under these conditions the homopolyester (**7a**) of the benzoxazole monomer 4 exhibits the highest thermostability (Figure 9), and the stability of the copolyester decreases with increasing molar fraction of 4-HBA units. An analogous structure–property relationship was found for copolyesters of the benzoxazole monomer 3. These results indicate that the benzoxazole units possess a remarkable thermostability.

Conclusion

The results of the present and preceding work support the hypothesis that only those copolyesters of 4-HBA which can exist in the orthorhombic modification I or II are able to form whisker-like crystals. The compatibility of monomers 1–4 with one of these crystal modifications decreases in the order 1 ≫ 4 > 3 > 2. However, it is not clear which structural parameters are responsible for the observed significant differences. Obviously, the torsional angle between the phenylene ring and the heterocycle plays an important role, because the coplanarity of the comonomer favors an orthorhombic chain packing. Unfortunately, no information on these torsional angles is currently available.

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