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Whiskers. 6. Poly(ester–amide)s Derived from 4-Hydroxybenzoic Acid and 4-Aminobenzoic Acid

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ABSTRACT: A new method for the synthesis of poly(ester–amide)s derived from 4-hydroxybenzoic acid (4-HBA) and 4-aminobenzoic acid (4-ABA) was elaborated. The silylated 4-aminobenzoic acid was acylated with 4-acetoxybenzoyl chloride under mild conditions, and the resulting dimer was polycondensed in an "one-pot procedure" at 350 or 400 °C. In another experient, *N*-(4-acetoxybenzoyl)-4-aminobenzoic acid was isolated and afterwards polycondensed. Both methods gave crystalline poly(ester–amide)s of different morphology. The one-pot procedure yielded crystals looking like shavings which were characterized by elemental analyses, IR spectroscopy, wide-angle X-ray scattering, and electron microscopy. The results of these measurements suggest that the products of the one-pot procedure possess a predominantly alternating sequence, whereas the products of the two-step procedure possess a more blocky sequence. Furthermore, cocondensations with 4-acetoxybenzoic acid or its trimethylsilyl ester were conducted, and the morphology of the resulting copoly(ester–amide)s was studied. Whiskerlike crystals were only obtained from copoly(ester–amide)s containing 90 mol % 4-HBA units.

Introduction

In a patent and paper of Toyobo Co.[1,2] and in previous parts of this series,[3–8] the synthesis and characterization of columnar or fibrous whiskers of poly(4-hydroxybenzoic acid) and several copolyesters were reported. Such whiskers are of interest for two reasons. First, they are usually single crystals with a high degree of chemical and physical perfection. Second, they may be useful as reinforcing fillers (or fibers) for other amorphous or semicrystalline matrix polymers. A basic problem of their application as reinforcing fibers is the weak cohesion between matrix and whiskers. One approach to improve the cohesion (but not the only one) consists of a modification of the surface by incorporation of comonomers with polar groups, functional groups, or H-bond forming groups. From this point of view, the synthesis of whiskers containing amide groups is of particular interest because a better cohesion with a polyamide matrix may be expected. In this connection, the purpose of the present work was to elaborate a new synthetic approach yielding aromatic poly(ester–amide)s with a whiskerlike morphology.

Experimental Section

Materials. 4-Hydroxybenzoic acid (4-HBA), 4-aminobenzoic acid (4-ABA), and chlorotrimethylsilane were gifts of BAYER AG (Krefeld). They were used without further purification. 4-Acetoxybenzoyl chloride (mp 30 °C) was prepared as described in the literature[9]) and purified by distillation in vacuo. *N*,*O*-Bis(trimethylsilyl)-4-aminobenzoic acid (mp 82–84 °C; lit.[10] mp 83–84 °C) was prepared by silylation of 4-aminobenzoic acid with chlorotrimethylsilane and triethylamine in refluxing toluene and purified by distillation in vacuo. Marlotherm-S is a commercial product of Hüls AG (Marl, FRG). It was used without further purification, because it has been found that distillation does not improve the results.

***N*-(4-Acetoxybenzoyl)-4-aminobenzoic Acid.** 4-Aminobenzoic acid (0.1 mol) was suspended in dry chloroform (500 mL), chlorotrimethylsilane (0.2 mol) was added at once, and triethylamine (0.2 mol) was added dropwise at 60 °C under stirring. The reaction mixture was refluxed for 3 h and cooled with ice, and 4-acetoxybenzoyl chloride (0.1 mol) was added. After stirring for 20 h at 20 °C, the reaction mixture was washed with water, and the crystalline precipitate was isolated by filtration, washed again with water, and recrystallized from 1,4-dioxane: yield 72%. Anal. Calcd for $C_{16}H_{13}NO_5$ (299.28): C, 64.21%; H, 4.38%; N, 4.68%. Found: C, 63.90%; H, 4.53%, N, 4.91%.

Polycondensations. (A) "Silyl Acetate Method". All reaction mixtures were prepared in an atmosphere of dry N_2. *N*,*O*-Bis(trimethylsilyl)-4-aminobenzoic acid (25 mmol) and 4-acetoxybenzoyl chloride (25 mL) were weighed into a round-bottom flask equipped with gas inlet and outlet tubes. Marlotherm-S (50 mL) was added, and the reaction mixture was stirred at 20 °C for 20 h. Marlotherm-S (75 mL) was then added again, and the temperature was raised to 100 °C for 1 h and finally (without stirring) to 350 °C for 16 h. After cooling, the crystalline

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precipitate was isolated by filtration, extracted with acetone in a Soxhlet apparatus, and dried at 120 °C in vacuo.

In the case of cocondensations, trimethylsilyl 4-acetoxybenzoate was added when the temperature reached 100 °C.

(B) "Acetate Method". A mixture of *N*-(4-acetoxybenzoyl)-4-aminobenzoic acid and Marlotherm-S (125 mL) was heated to 350 °C for 16 h under a slow stream of nitrogen. After cooling, the precipitated product was worked up as described above.

Measurements. The DSC measurements were conducted on a Perkin-Elmer DSC-4 at a heating rate of 20 °C/min in aluminum pans under nitrogen.

The WAXS powder patterns were recorded with a Siemens D-500 diffractometer using Ni-filtered Cu Kα radiation.

The IR spectra were recorded from KBr pellets with a Nicolet SXB-20 FT-IR spectrometer.

The SEM micrographs were obtained on a Leitz AMR 1600 T instrument with an acceleration potential of 10 kV. All samples were coated with gold on a Balzers SC-040 instrument. The white bar in Figures 3 and 4 represents 10 μm.

Results and Discussion

Synthetic Methods. Several attempts were made to prepare more or less random copoly(ester–amide)s by cocondensations of 4-acetoxybenzoic acid and *N*-acetyl-4-aminobenzoic acid. These cocondensations were conducted with equimolar amounts of both monomers in Marlotherm-S or *m*-terphenyl at temperatures in the range 250–350 °C. Furthermore, the reaction time was varied from 4 to 20 h. Regardless of the reaction conditions, only oligomers were obtained because of the low reactivity of the *N*-acetyl group under these reaction conditions. This conclusion is based on the observation that homopolycondensations of *N*-acetyl-4-aminobenzoic acid were not feasible in contrast to homopolycondensations of 4-acetoxybenzoic acid. The oligomeric character of the reaction products was ascertained by ^{1}H NMR spectroscopic evaluation of the acetyl signal after dissolution in D_2SO_4.

Because of the failure to produce polymers, a new approach was conducted based on the synthesis of silylated *N*-(4-acetoxybenzoyl)-4-aminobenzoic acid (**3**) from the known starting materials **1** and **2** (eq 1) (Scheme 1). The acylation of the silylated aminobenzoic acid (eq 1) needs to be conducted at moderate temperatures for several hours to give high yields and to avoid side reactions. This silylated monomer (**3**) was never isolated. It was either directly subjected to polycondensation ("one-pot procedure", eqs 1 and 3) or it was alcoholyzed or hydrolyzed (eq 2), and the free *N*-(4-acetoxybenzoyl)-4-aminobenzoic acid (**4**) was isolated.

The polycondensation of monomer **3** yields the poly(ester–amide) **5a** with elimination of trimethylsilyl acetate (eq 3). This one-pot procedure is thus called the "silyl acetate method" throughout this work (Tables 1 and 2). This new synthetic approach is based on the previously described polycondensation of silylated 4-acetoxybenzoic acid[5]) or 6-acetoxynaphthoic acid.[11] The polycondensation of monomer **4** (a two-step procedure, including its synthesis) proceeds with elimination of acetic acid and is called the "acetate method" in this work. The resulting poly(ester–amide), **6a**, has in principle the same formula as **5a**, but its properties are different from those of **5a**, which justifies a different formula number.

When the polycondensation of **3** was conducted in three different solvents (numbers 1–3, Table 1) almost identical elemental analyses and morphologies were obtained. Because of the higher yield and the lower costs of Marlotherm-S, this solvent was used for all further polycondensations. The relatively low reactivity of the silyl ester/phenol acetate system prevents satisfactory polycondensations in solution below 320 °C. A temperature of 350 °C (±10 °C) was found to be the optimum reaction temperature. Higher temperatures did not yield better results. The characteristic crystals ("shavings", see below) initially formed even at 400 °C finally lost their shape, and the products turned brown due to thermal degradation. A similarly negative result was found when monomer **4** was polycondensed at 400 °C. Therefore, all further polycondensations (Table 2) were conducted at 350 °C.

In analogy to the synthesis of **5a**, a series of copoly(ester–amide)s was prepared by addition of silylated 4-acetoxybenzoic acid to the solution of **3** prior to heating (eq 5). The resulting copoly(ester–amide)s **5b–e** are characterized by an increasing molar fraction of 4-HBA units. An analogous series of poly(ester–amide)s (**6b–e**) was prepared by cocondensation of monomer **4** with 4-acetoxybenzoic acid (eq 6).

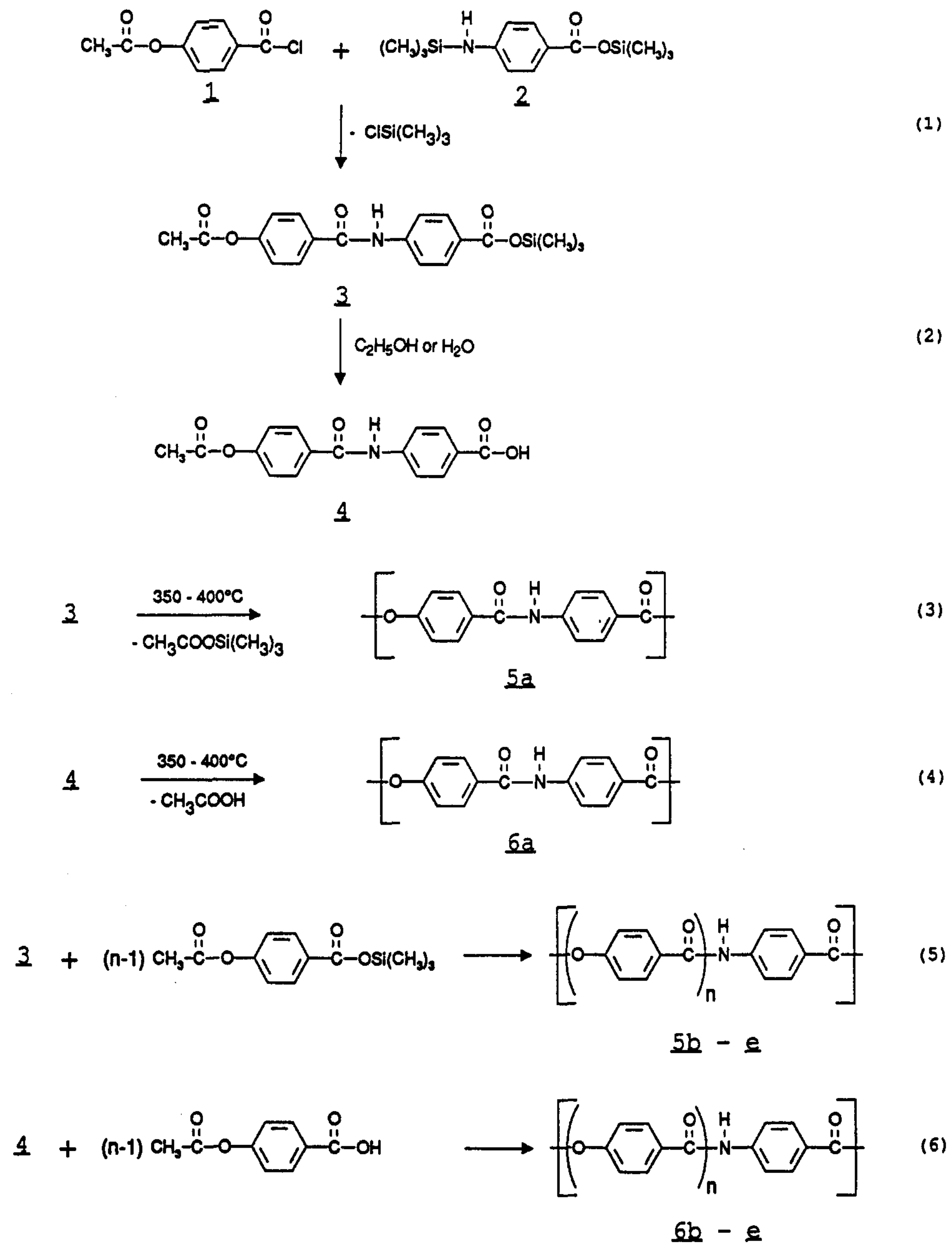
Characterization of Poly(ester–amide)s. All poly(ester–amide)s of this work proved to be insoluble in common inert solvents. Dissolution in hot concentrated sulfuric acid is accompanied by chemical degradation. Thus, no characterization in solution was feasible. The N-elemental analyses allow a crude comparison of molar composition and feed ratio of 4-HBA and 4-ABA. The data listed in Table 2 indicate that both **5a** and **6a** contain somewhat more 4-ABA units than expected from the feed ratio. In other words, their microstructure, i.e., the alternating sequence, is not absolutely perfect for all chains, with the greater deviation in the case of **6a**. In contrast, the deviation from the feed ratio is slightly greater in the case of **5b–e**, when compared to **6b–e**. The origin of this difference is difficult to explain because side reactions are more likely in the cases of **6b–e** due to the catalytic influence of acidic protons.

The IR spectra (Figures 1 and 2) confirm the variation of the molar composition by the intensity ratios of the ester and amide CO bands at 1735 ± 1 and 1660 ± 2 cm^{-1}. In the case of **5a** and **6a**, the intensity ratio of both CO bands is almost identical (Figure 1), but the region of N–H stretching vibrations (3000–3500 cm^{-1}) is more different. Similar differences were found when **5b** and **6b** or **5c** and **6c** were compared. These differences in the IR spectra suggest that the microstructure and/or the morphology of both poly(ester–amide) series is somewhat different. This suggestion is indeed confirmed by other analytical methods.

SEM micrographs revealed that the morphology depends on two parameters: the synthetic method and the molar composition. The shavings of Figure 3A are characteristic for **5a** prepared at 350 °C. This synthesis was repeated several times, and the morphology of the crystals proved to be reproducible. When the molar fraction of 4-HBA units increases, the morphology changes completely and small crystallites of irregular shape are formed (**5b–d**). With 90 mol % 4-HBA units (**5e**), short whiskers with an aspect ratio around 10 were formed (Figure 3B). These whiskers form lateral aggregates which in some cases have a faint resemblance to fern leaves.

A particularly interesting aspect of these findings is the fact that no gradual transition takes place between the morphology of **5a** and the whiskers of **5e** (or neat poly(4-HBA)). This finding may be interpreted as evidence for a nearly perfect alternating sequence of **5a** which is responsible for the characteristic morphology called shavings. This hypothesis is supported by the properties of **6a–e** (see below) and by the properties of poly(ester–amide)s prepared from silylated 4-aminobenzoic acid and 6-acetoxy-2-naphthoic acid (to be reported in a future

Scheme 1



a: n = 1.0 (HBA/ABA = 5/5)
b: n = 1.5 (HBA/ABA = 6/4)
c: n = 2.3 (HBA/ABA = 7/3)
d: n = 4.0 (HBA/ABA = 8/2)
e: n = 9.0 (HBA/ABA = 9/1)

Table 1. Reaction Conditions and Results of Polycondensations Yielding Poly(ester-amide)s 5a via the "Silyl Acetate Method" or 6a via the "Acetate Method"

						elemental anal.[b]			
expt	synth[a] method	reactio medium	temp, °C	time, h	yield, %	C	H	N	morphology
1	Sil-Ac	*m*-terphenyl	350	16	77	69.36	4.08	7.31	"shavings" (Figure 1)
2	Sil-Ac	Therminol-66	350	16	73	69.28	4.25	7.00	"shavings" (Figure 1)
3	Sil-Ac	Marlotherm-S	350	16	83	69.54	4.04	6.54	"shavings" (Figure 1)
4	Sil-Ac	Marlotherm-S	380	8	74	70.09	4.11	6.75	irregular aggregates
5	Sil-Ac	Marlotherm-S	400	8	85	70.64	4.11	6.90	irregular aggregates
6	Sil-Ac	Marlotherm-S	400	4	75	70.47	4.13	7.06	irregular aggregates
7	acetate	Marlotherm-S	350	16	80	70.65	4.23	6.86	shish kebabs (Figure 2)
8	acetate	Marlotherm-S	400	4	82	70.12	4.19	7.18	irregular aggregates

[a] Sil-Ac: polycondensations of 3. Acetate: polycondensations of 4. [b] Calculated for $C_{14}H_9NO_3$ (239.23): C, 70.29; H, 3.79; N, 5.86%.

paper). Again no transition was found between the whiskers of neat poly(6-hydroxy-2-naphthoic acid) and the shavings of the alternating poly(ester–amide).

In contrast, poly(ester–amide) 6a prepared at 350 °C/16 h possesses a shish-kebab-like morphology (Figure 4A). This morphology gradually disappears when the molar

Table 2. Yields and Properties of Copoly(ester-amide)s 5a–e and 6a–e Prepared by Polycondensations in Marlotherm-S at 350 °C/16 h

polymer	feed ratio[a]	yield, %	molar[b] comp	elem. formula (fw)	elemental anal.	C	H	N	morphology
5a	5/5	83	5/5.6	$C_{14}H_9NO_3$ (239.23)	calcd	70.29	3.79	5.86	shavings
					found	69.54	4.04	6.54[c]	
5b	6/4	82	6/4.6	$C_{35}H_{22}N_2O_8$ (598.56)	calcd	70.23	3.70	4.68	irregular crystallites
					found	69.92	4.00	5.37[c]	
5c	7/3	83	7/4.1	$C_{70}H_{43}N_3O_{17}$ (1198.11)	calcd	70.17	3.62	3.51	irregular crystallites
					found	59.89	3.71	4.77[c]	
5d	8/2	85	8/2.1	$C_{35}H_{21}NO_9$ (599.55)	calcd	70.12	3.52	2.34	irregular crystallites
					found	70.59	3.51	2.50	
5e	9/1	78	9/1.3	$C_{70}H_{41}NO_{19}$ (1200.08)	calcd	70.06	3.44	1.17	whiskers
					found	70.17	3.64	1.51	
6a	5/5	80	5/5.9	$C_{14}H_9NO_3$ (239.23)	calcd	70.29	3.79	5.86[c]	shish kebab structures
					found	70.65	4.23	6.86	
6b	6/4	82	6/4.5	$C_{35}H_{22}N_2O_8$ (598.56)	calcd	70.23	3.70	4.68[c]	irregular crystallites
					found	70.10	3.88	5.23	
6c	7/3	88	7/3.0	$C_{70}H_{43}N_3O_{17}$ (1198.11)	calcd	70.17	3.62	3.51	irregular crystallites
					found	70.38	3.80	3.53	
6d	8/2	85	8/2.0	$C_{35}H_{21}NO_9$ (599.55)	calcd	70.12	3.53	2.34	irregular crystallites
					found	69.78	3.57	2.29	
6e	9/1	86	9/1.0	$C_{70}H_{41}NO_{19}$ (1200.08)	calcd	70.06	3.44	1.17	short columnar whiskers
					found	69.68	3.55	1.08	

[a] Molar ratio of 4-acetoxybenzoic acid and monomer 4 or silylated 4-acetoxybenzoic acid and monomer 3. [b] Molar ratio of the copoly(ester–amide)s as calculated from N elemental analyses. [c] Average of four analyses based on two separately prepared samples.

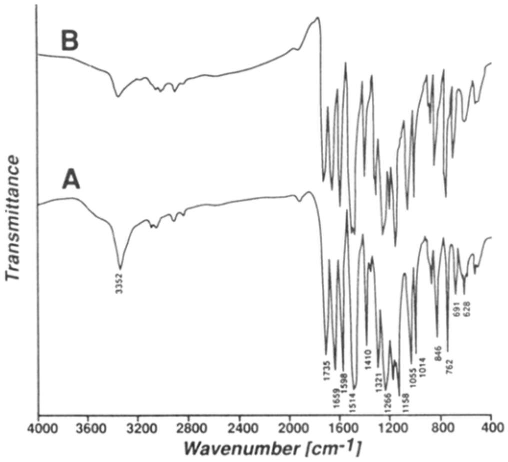


Figure 1. IR spectra (KBr pellets) of poly(ester–amide)s: (A) **5a**, (B) **6a**.

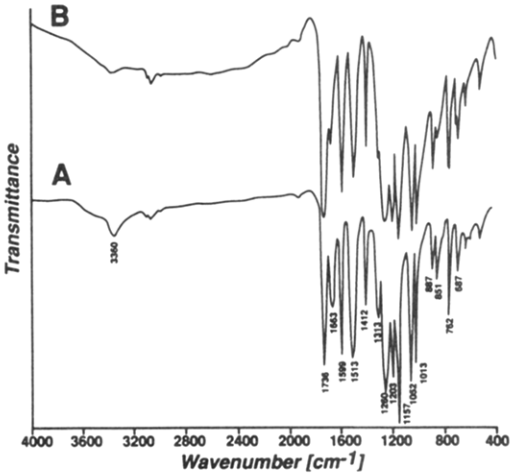


Figure 2. IR spectra (KBr pellets) of poly(ester–amide)s: (A) **5c**, (B) **5e**.

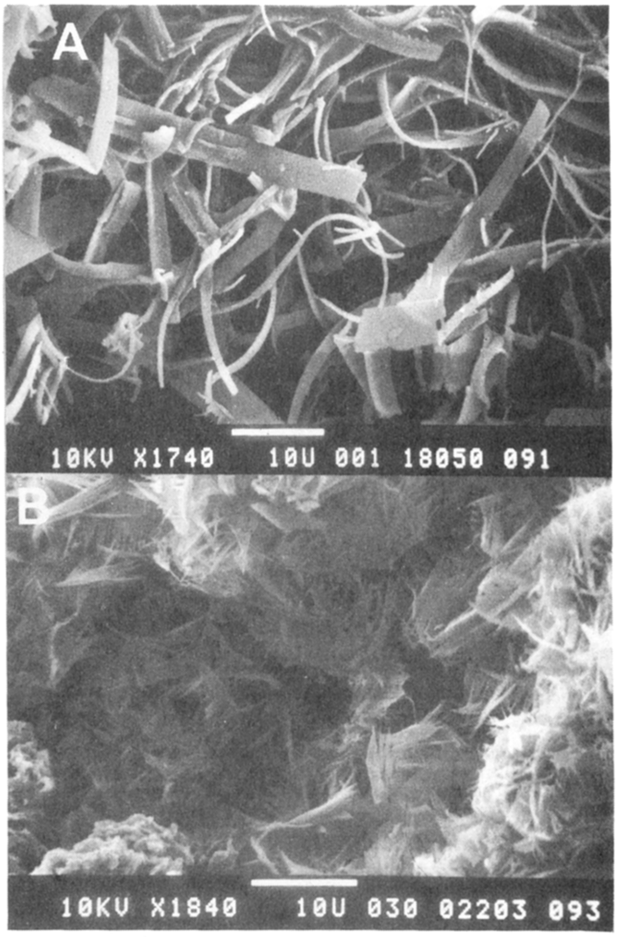


Figure 3. SEM micrographs of (A) poly(ester–amide) **5a** prepared in Marlotherm-S at 350 °C/16 h and (B) poly(ester–amide) **5e**.

fraction of 4-HBA increases (**6b** and **6c**). Shish-kebab-like morphologies were also observed for poly(4-HBA) when reaction mixtures were rapidly cooled after short reaction times.[3] In this case, oligomers soluble in the hot reaction mixture crystallized on the surface of long whiskers upon cooling. Therefore, the work-up procedure was varied, for instance, by injection of the hot reaction mixture into a large volume of hot dioxane or acetone. However, the morphology remained unchanged. Obviously, the shish kebab structures represent a thermodynamically stable situation after the long reaction time of

Figure 4. SEM micrographs of (A) poly(ester-amide) **6a** prepared in Marlotherm-S at 350 °C/16 h and (B) poly(ester-amide) **6d**.

16 h. When the fraction of 4-HBA increases further, columnar whiskers (aspect ratios 6–10) are formed in the case of **6e** (Figure 4B). This latter result is reasonable, because the polycondensation of pure 4-acetoxybenzoic acid under the same conditions yields columnar whiskers with aspect ratios in the range 20–40. Taken together, these results demonstrate that the morphologies of the poly(ester-amide)s **6a–e** are different from those of **5a–e**. The most conspicuous difference is to be found between samples **5a** and **6a**.

Another characteristic difference between the poly(ester-amide) series **5a–e** and **6a–e** was revealed by DSC measurements. The DSC heating curves of **5a–d** are featureless up to temperatures of around 450 °C, where rapid thermal degradation sets in. Even in the case of **5e**, no endotherm is detectable between 300 and 370 °C despite the presence of relatively long blocks of 4-HBA units. An endotherm at this temperature is characteristic for whiskers of poly(4-HBA)[2,4,5] and would be expected for a copolyester containing such a high fraction of 4-HBA units. Obviously, the 4-aminobenzoic acid suppresses effectively the change of crystal modifications which is typical for poly(4-HBA).[11-16] This finding is noteworthy because the dimensions of 4-aminobenzoic acid are almost identical with those of 4-hydroxybenzoic acid. In the case of copolyesters of 4-HBA with other hydroxy acids, the comonomers suppress the solid–solid phase transitions only, if their dimensions differ largely from those of 4-HBA.[17-21] Hence, it seems that in the case of poly(ester-amide)s **5a–e**, the H-bond of the amide group is the main hindrance for a change of modifications.

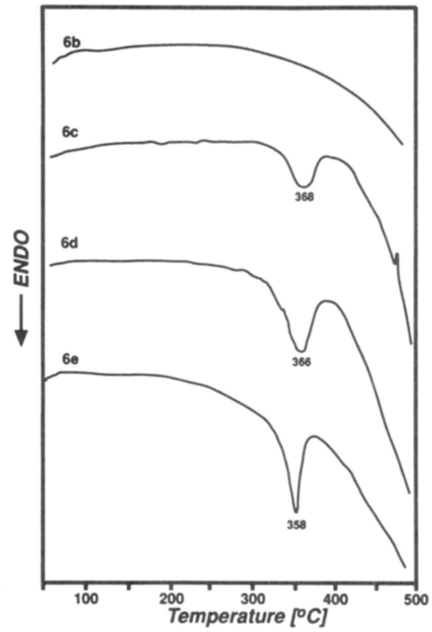


Figure 5. DSC heating curves (heating rate 20 °C/min) of poly(ester-amide)s (A) **6b**, (B) **6c**, (C) **6d**, and (E) **6e**.

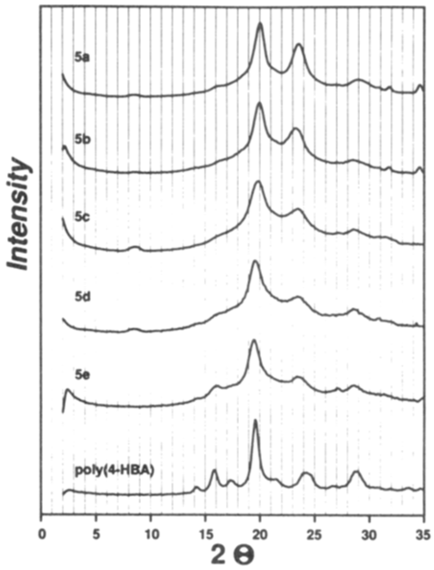


Figure 6. WAXS powder patterns of poly(ester-amide)s **5a–e** and poly(4-HBA).

On the other hand, the DSC curves of **6c–e** (Figure 5) display endotherms in the range 358–368 °C which are absent in the DSC curves of **5c** and **5d**. These endotherms may be interpreted as indicators of a highly blocky sequence resulting from proton-catalyzed transesterification. This interpretation has the advantage that the different morphologies of **5a–e** and **6a–e** could be explained by a reduction in the extent of transesterification in the case of the silyl acetate method.

The WAXS powder patterns of **5a–e** (Figure 6) and **6a–e** (Figure 7) illustrate a number of interesting points and provide tentative confirmation of the foregoing discussion. Firstly, the copolyesters all appear to adopt structures which may be indexed according to the orthorhombic unit cell of modification I of pure poly(4-HBA),[16] although the presence of modification II[16] is detectable in all WAXS patterns of **6a–e**. Secondly, the percentage crystallinity is reduced as the mole fraction of 4-HBA decreases. Thirdly, and importantly, samples **6a–e** possess considerably higher crystallinity than the copolymers **5a–e**. Taken together with the assumption that the DSC

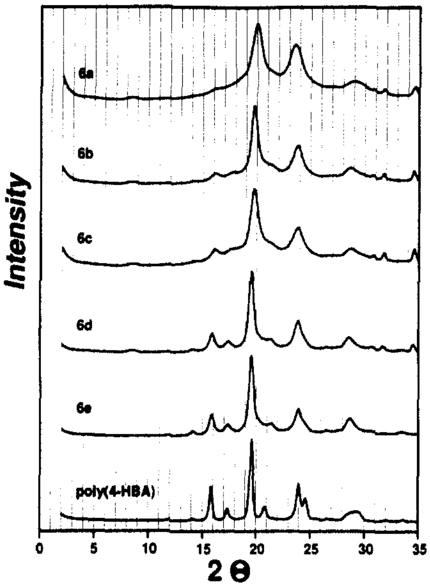


Figure 7. WAXS powder patterns of poly(ester–amide)s **6a–e** and poly(4-HBA).

endotherms in Figure 5 indicate the presence of long blocks of poly(4-HBA), this suggests that the formation of larger and more perfect crystallites in these samples may be attributed to increased levels of blockiness.

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