BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 8, pp. 1697-1705, 1995

0032-3861/95/\$10.00+0.00

Whisker 11. Poly(ester–amide)s derived from vanillic acid and 4-aminobenzoic acid

Hans R. Kricheldorf* and Gerd Löhden
Institut für Technische und Makromolekulare Chemie der Universität, Bundesstrasse 45, D-20146 Hamburg, Germany
(Received 27 1994)

N,O-Bistrimethylsilyl-4-aminobenzoic acid was selectively acylated at the amino group with 4-acetoxy-3-methoxybenzoyl chloride. The resulting dimer with silylated carboxyl group was polycondensed *in situ* at 300 or 350°C using Marlotherm-S as an inert reaction medium. In an alternative approach the silylester group of the dimer was hydrolysed and the resulting *N*-(4′-acetoxy-3-methoxybenzoyl)-4-aminobenzoic acid was polycondensed at 300 or 350°C. Furthermore, copolyesters rich in vanillic acid units were prepared by co-condensations with 4-acetoxy-3-methoxybenzoic acid or its trimethylsilylester. Elemental analyses and ^{1}H nuclear magnetic resonance spectra indicate that the vanillic acid units partially decompose at 350°C, whereas at 300°C the composition of the copolyesters agrees well with the feed ratio. Infra-red spectra support this conclusion. Wide-angle X-ray diffraction powder patterns indicate that the crystallinity increases with higher molar fractions of vanillic acid. The 1:1 copolymers are nearly amorphous. The copoly(ester–amide)s obtained from the monomers with free carboxyl groups form globular aggregates regardless of composition. In contrast, the silylated monomers yield columnar particles with lengths of 10–15 μm and aspect ratios $\geqslant 10$ for copoly(ester–imide)s with a 6:4 and 5:5 composition. Transmission electron microscopy revealed ordered structures in these columnar particles, but the 'crystal growth' cannot yet be interpreted.

(Keywords: poly(ester–amide)s; vanillic acid; 4-aminobenzoic acid)

INTRODUCTION

The present work is part of a broader study of polycondensates based on aromatic hydroxy and amino acids[1–6]. 4-Hydroxybenzoic acid, vanillic acid and 4-aminobenzoic acid are part of the human metabolism (albeit in small quantities), and thus are non-toxic monomers or degradation products. From this point of view, whisker-like or fibrous crystals built up of such monomers might be of interest as components of biodegradable composites. Furthermore, the crystal growth of whisker-like crystals may yield single crystals with interesting physical properties[7–10], and the crystal growth mechanism is itself a matter of controversial discussion[11–15]. Previous, non-published attempts to prepare whisker-like crystals of poly(vanillic acid) were not successful. In this connection the present work was aimed at studying the synthesis and properties of copoly(ester–amide)s derived from vanillic and 4-aminobenzoic acids. Analogous copoly(ester–amide)s based on 4-hydroxybenzoic acid were recently described in a previous part of this series[7].

EXPERIMENTAL

Materials

Vanillic acid was purchased from Aldrich Co. (Milwaukee, WI, USA) and used without further purification. 4-Aminobenzoic acid was a gift from Bayer AG (Leverkusen, Germany). It was silylated with chlorotrimethylsilane and triethylamine in refluxing toluene. *N,O*-Bistrimethylsilyl-4-aminobenzoic acid was isolated by distillation *in vacuo* (f.p. found: 82–84°C; lit.[16]: 83–84°C). Marlotherm-S, a commercial solvent from Hüls AG (Marl, Germany), was distilled *in vacuo* prior to use.

4-Acetoxy-3-methoxybenzoyl chloride

Vanillic acid (0.5 mol) and distilled acetic anhydride (0.7 mol) were refluxed with pyridine (5 ml) in dry toluene (400 ml) for 3 h. The reaction mixture was then concentrated *in vacuo*, the residue was diluted with toluene, and this mixture was concentrated again to remove all acetic acid. Finally, the acetylated vanillic acid was completely crystallized by portion-wise addition of ligroin, and recrystallized from toluene (yield 71%; m.p. found: 139–141°C; lit.[17]: 141–142°C). This product (0.35 mol) was refluxed in freshly distilled thionyl chloride until the evolution of SO_2 and HCl had almost ceased. The resulting acid chloride was then isolated by distillation *in vacuo* (yield 89%; m.p. found: 57–58°C; lit.[18]: 57°C).

Silylation of 4-acetoxy-3-methoxybenzoic acid

4-Acetoxy-3-methoxybenzoic acid (0.25 mol) and hexamethyldisilazane (0.15 mol) were refluxed in dry toluene until the evolution of NH_3 had ceased (~3 h). The reaction mixture was then concentrated *in vacuo* and the product isolated by distillation over a short-path apparatus (yield 90%; m.p. 28–29°C). Elemental analysis

---

* To whom correspondence should be addressed

for $C_{13}H_{18}O_5Si$ (282.4): calculated C, 55.30%; H, 6.43%. Found: C, 56.00%; H, 6.12%.

N-(*4-Acetoxy-3′-methoxybenzoyl*)-*4-aminobenzoic acid*

N,*O*-Bistrimethylsilyl-4-aminobenzoic acid (0.1 mol) was dissolved in dry toluene (150 ml) and 4-acetoxy-3-methoxybenzoyl chloride (0.1 mol) was added. The reaction mixture was stirred for 24 h at 20–25°C, and filtered. The crystalline silylated monomer was dissolved in ethanol (500 ml) and stirred for 24 h at 20–25°C. The resulting crystalline precipitate was isolated by filtration and recrystallized from dimethylformamide/water (yield 75%; m.p. 264–266°C (polycond.)). Elemental analysis for $C_{17}H_{15}NO_6$ (329.3): calculated C, 62.00%; H, 4.59%; N, 4.25%. Found: C, 61.98%; H, 4.70%; N, 4.32%.

Polycondensations

'Silylacetate method'. *N*,*O*-Bis(trimethylsilyl)-4-aminobenzoic acid and an equimolar amount of 4-acetoxy-3-methoxybenzoyl chloride were weighed into a round-bottomed flask containing Marlotherm-S (100 ml). A variable amount of trimethylsilyl-4-acetoxy-3-methoxybenzoate was added in some cases (see *Tables 3* and *4*). The quantity of all monomers was adjusted to a total concentration of $0.2\,mol\,l^{-1}$ of aromatic units (or rings). The reaction mixture was heated either to 300°C for 16 h or to 350°C for 8 h. The liberated trimethylsilylacetate was removed with a slow stream of nitrogen without stirring. After cooling, the precipitated product was isolated by filtration and extracted with hot acetone.

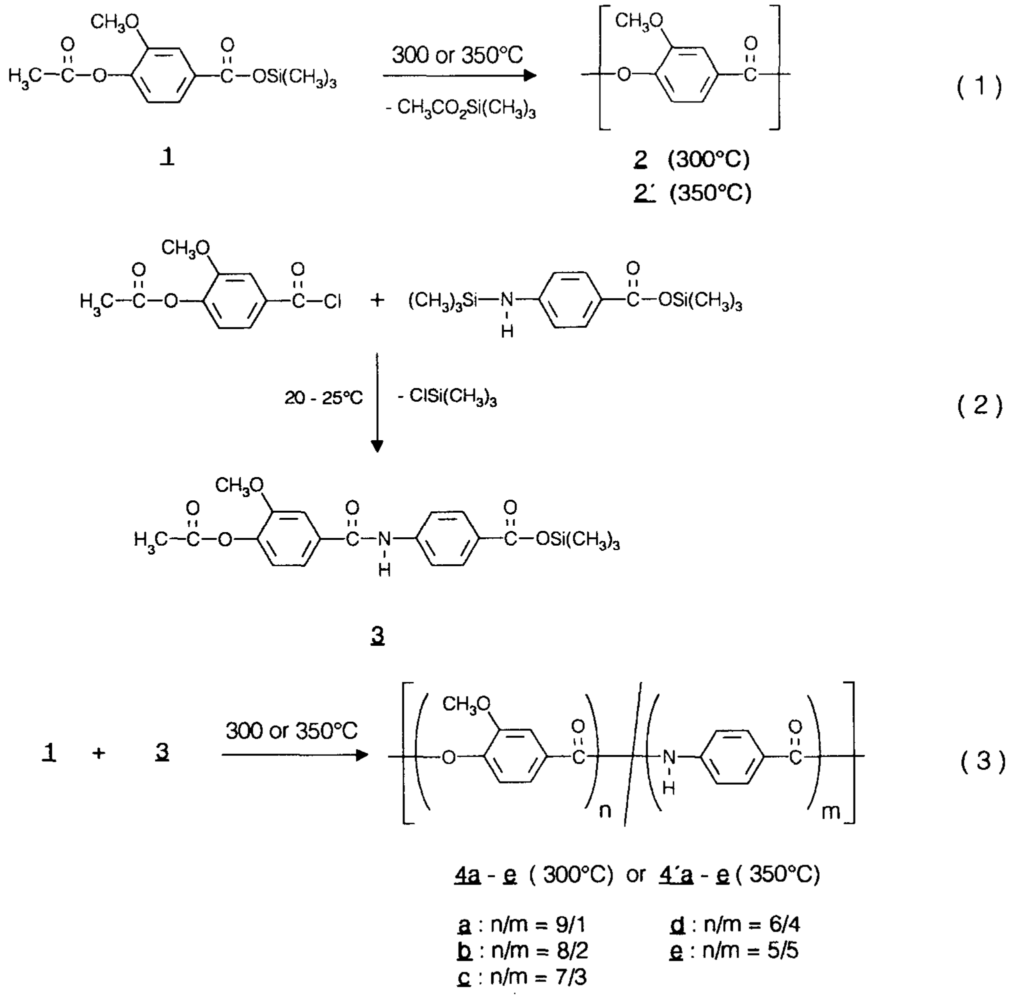
'Acetate method'. *N*-(4′-Acetoxy-3-methoxybenzoyl)-4-aminobenzoic acid and 4-acetoxy-3-methoxybenzoic acid were weighed into a round-bottomed flask and Marlotherm-S was added so that a total concentration of aromatic monomer units of $0.2\,mol\,l^{-1}$ was obtained. The reaction vessel was placed in a metal bath preheated to 150°C and the temperature was rapidly raised to 300 or 350°C. This temperature was maintained for 16 h (300°C) or 8 h (350°C). The evolved acetic acid was removed with a slow stream of nitrogen, but without stirring. After cooling the precipitated product was filtered off, and extracted with hot acetone.

Measurements

Infra-red (i.r.) spectra were recorded with a Nicolet SXB-20 FTIR spectrometer using KBr pellets.

^1H nuclear magnetic resonance (n.m.r.) spectra were obtained at 100 MHz on a Bruker AC 100 FT NMR spectrometer in 5 mm o.d. sample tubes. The copolyesters were hydrolysed with a mixture of 40% (by weight) NaOD in D_2O and CD_3OD (volume ratio 3:7).

Wide-angle X-ray diffraction (WAXD) powder patterns



Scheme 1 Polycondensations via the 'silylacetate method'

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

Scanning electron microscopy (SEM) was performed using a Leitz AMR 1600 T instrument with an acceleration potential of 10 kV. All samples were sputtered with gold using a Balzers SC-040 apparatus. Transmission electron microscopy (TEM) was carried out with a Phillips 400 T instrument operating at 100 kV.

RESULTS AND DISCUSSION

Polycondensations via the 'silylacetate method'

The polycondensations of this work are based on two different condensation methods. The approach discussed first involves the reaction of silylated carboxyl groups with acetylated phenol groups as illustrated by the homopolycondensation of trimethylsilyl-4-acetoxy-3-methoxybenzoate, **1** (*Scheme 1*, equation (1)). Since trimethylsilylacetate is liberated in the course of these polycondensations, this approach is labelled the 'silylacetate method'. The second approach involves the reaction of free carboxylic acid and generates acetic acid. Therefore, it is called the 'acetate method'. The characteristic feature of this approach is the presence of acidic protons which may catalyse side reactions. Whatever the reason, it has been demonstrated in previous studies that both methods may give different yields, crystallinities and morphologies of the resulting polyesters.

From previous syntheses of polyesters in general and whiskers in particular, it was known that reaction temperatures below 300°C are not useful. The lower thermal stability of vanillic acid, compared with that of 4-aminobenzoic acid, suggested that temperatures above 350°C should be avoided. Therefore, two series of

Table 1 Copolycondensations of vanillic acid and 4-aminobenzoic acid by the 'silylacetate method' at 300°C

Polymer	Feed ratio[a]	Yield (%)	Composition[b]	Composition[c]	Elemental analysis			
						C	H	N
2	10:0	43	(100:0)	–	Calc.	64.00	4.82	–
					Found	64.32	4.73	–
4a	9:1	40	87:13	88:12	Calc.	64.54	4.04	0.95
					Found	65.19	4.24	1.08
4b	8:2	26	77:23	–	Calc.	65.09	4.06	1.95
					Found	67.06	4.28	2.41
4c	7:3	27	53:47	–	Calc.	65.67	4.08	2.98
					Found	65.16	4.27	4.93
4d	6:4	43	43.57	(59:41)[d]	Calc.	66.28	4.10	4.07
					Found	66.37	4.17	6.00
4e	5:5	55	35:65	(52:48)[d]	Calc.	66.91	4.12	5.20
					Found	67.52	4.30	6.76

[a] Molar feed ratio of vanillic acid and 4-aminobenzoic acid units
[b] Molar composition of the isolated copolymers calculated from the N elemental analyses
[c] Molar composition of the hydrolysed copolymers as determined by ^{1}H n.m.r. spectroscopy
[d] Molar composition of the soluble fraction

Table 2 Copolycondensations of vanillic acid and 4-aminobenzoic acid by the 'silylacetate method' at 350°C

Polymer	Feed ratio[a]	Yield (%)	Composition[b]	Composition[c]	Elemental analysis			
						C	H	N
2'	10:0	8	(100:0)	100:0	Calc.	64.00	4.82	–
					Found	65.83	4.67	–
4'a	9:1	28	88:12	85:15	Calc.	64.54	4.04	0.95
					Found	64.67	4.15	1.07
4'b	8:2	32	58:42	–	Calc.	65.09	4.06	1.92
					Found	65.42	4.13	4.31
4'c	7:3	34	53:47	–	Calc.	65.67	4.08	2.98
					Found	66.32	4.05	4.91
4'd	6:2	40	51:49	–	Calc.	66.28	4.10	4.07
					Found	65.45	4.55	5.02
4'e	5:5	55	52:48	–	Calc.	66.91	4.12	5.20
					Found	67.22	4.19	5.62

[a] Molar ratio of vanillic and 4-aminobenzoic acid units
[b] Molar composition of the isolated copolymers calculated from the N elemental analyses
[c] Molar composition of the hydrolysed copolymers as determined by ^{1}H n.m.r. spectroscopy

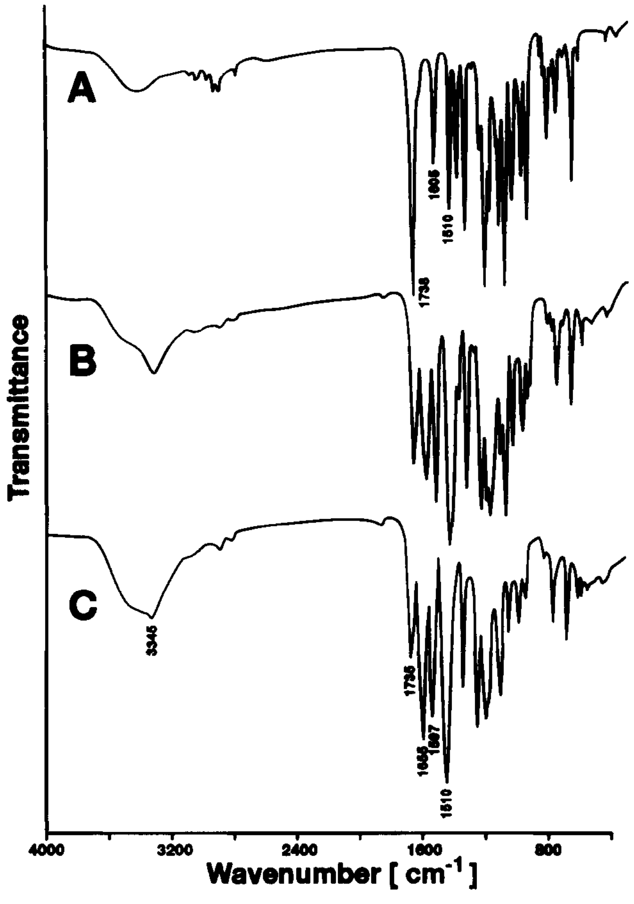


Figure 1 I.r. spectra (KBr pellets) of polyesters prepared by the 'silylacetate method' at 300°C (*Table 1*): (A) poly(vanillic acid), **2**; (B) poly(ester–amide), **4b**; (C) poly(ester–amide), **4e**

polycondensations were conducted: the first at 300°C (summarized in *Table 1*) and the second at 350°C (summarized in *Table 2*). All polycondensations were conducted in a commercial inert reaction medium (Marlotherm-S). The homopolycondensation of silylated 4-acetoxy-3-methoxybenzoic acid (**1**) was studied first. Despite the relatively low yield of the homopolyester **2′** obtained at 350°C (*Table 2*), both its elemental analysis and i.r. spectrum agreed with those of the polyester **2** prepared at 300°C. Therefore, copoly(ester–amide)s were also prepared at the higher temperature.

The copoly(ester–amide)s were synthesized in a 'one-pot procedure' comprising two steps. The first step consists of an acylation of *N*,*O*-bistrimethylsilyl-4-aminobenzoic acid with 4-acetoxy-3-methoxybenzoyl chloride (*Scheme 1*, equation (2)). The silylation of 4-aminobenzoic acid has four advantages in this connection: (i) it improves the solubility; (ii) it protects the carboxyl group against acylation below 100°C; (iii) it enhances the nucleophilicity of the aromatic amino group; and (iv) it prevents the formation of HCl. In consequence, a clean and almost quantitative acylation is feasible below 100°C and heating of the intermediately formed monomer **3** up to 300 or 350°C initiates its polycondensation (*Scheme 1*, equation (3)). When monomer **1** was added prior to the heating above 100°C, copoly(ester–amide)s with increasing molar fraction of vanillic acid were formed (**4a**–**e** at 300°C, or **4′a**–**e** at 350°C). Interestingly, the yields of the copoly(ester–amide)s prepared at 300°C and 350°C fell into the same order of magnitude (*Tables 1* and *2*).

The characterization of the isolated copoly(ester–amide)s suffered from their low solubility in common organic solvents. The i.r.-spectra exhibit a 'CO band' at 1735 cm^{-1} for the ester group and 'CO bands' at 1658 and 1510 cm^{-1} for the amide groups. As illustrated in *Figure 1*, the intensity ratio of these CO bands parallels the molar compositions of the copoly(ester–amide)s. More quantitative information was obtained from the N elemental analyses (see tables) which were repeated to check their reproducibility. Within the margin of error typical for elemental analyses, the compositions calculated from the N values show a satisfactory agreement with the feed ratios at a reaction temperature of 300°C.

Further information on both composition and sequence of the copoly(ester–amide)s was obtained by ^{1}H n.m.r. spectroscopy. Several samples dissolved in a mixture of $NaOD/D_2O$ (40% by weight) and CD_3OD (volume ratio 3:7), with complete hydrolysis of the ester bonds. These hydrolyses were conducted directly in n.m.r. sample tubes, and the ^{1}H n.m.r. spectroscopic evaluation of the crude reaction mixtures showed a satisfactory agreement with the feed ratios.

The ^{1}H n.m.r. spectra of the partially hydrolysed samples **4e** and **4′e** proved to be particularly interesting, because they indicated that all polycondensations involved intensive ester–amide exchange reactions. As illustrated in *Figure 2*, two sharp singlet signals of the OCH_3 group are detectable when **4e** or **4′e** is hydrolysed. By comparison with hydrolysed polyester **2** (*Figure 2*) and hydrolysed monomer **3**, these signals may be attributed to vanillic acid ($\delta = 4.02$ ppm) and *N*-(4′-hydroxy-

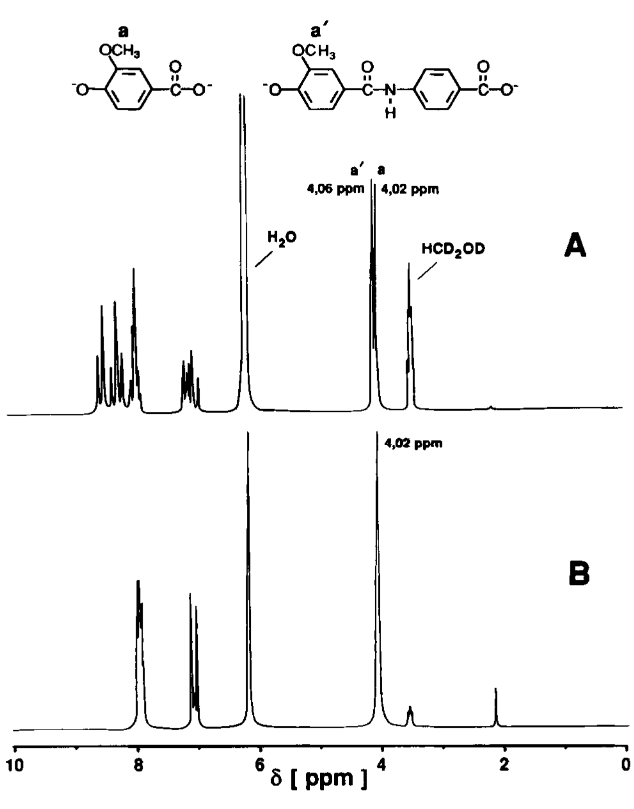
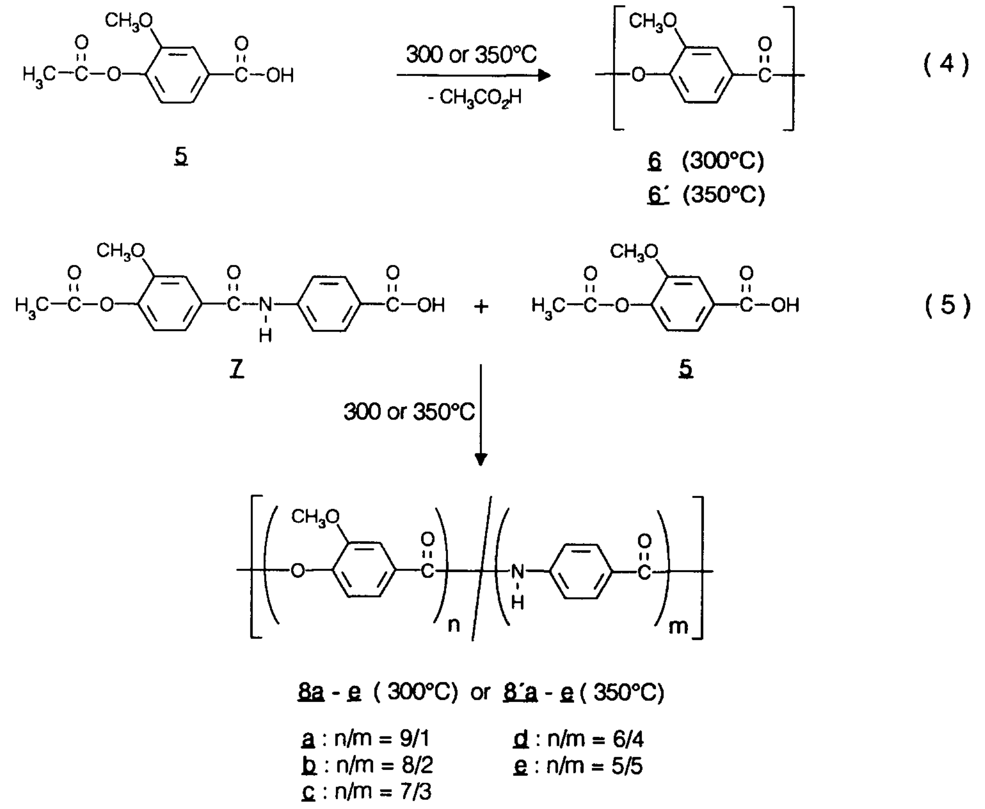


Figure 2 100 MHz ^{1}H n.m.r. spectra of: (A) poly(ester–amide) **4e** hydrolysed in a mixture of $NaOD/D_2O$ (40% by weight) and CD_3OD (volume ratio 3:7); (B) hydrolysed polyester **2**



Scheme 2 Polycondensations via the 'acetate method'

Table 3 Copolycondensations of vanillic acid and 4-aminobenzoic acid by the 'acetate method' at 300°C

Polymer	Feed ratio[a]	Yield (%)	Composition[b]	Composition[c]		Elemental analysis C	H	N
6	10:0	95	-	-	Calc.	64.00	4.82	-
					Found	64.11	4.76	-
8a	9:1	60	90:10	87:13	Calc.	64.54	4.04	0.95
					Found	63.18	4.34	1.01
8b	8:2	63	77:23	77:23	Calc.	65.09	4.06	1.95
					Found	65.37	4.37	2.21
8c	7:3	56	70:30	(68:32)[d]	Calc.	65.67	4.08	2.98
					Found	65.52	4.04	3.03
8d	6:4	50	60:40	(57:43)[d]	Calc.	66.28	4.10	4.07
					Found	65.56	4.31	4.09
8e	5:5	57	48:52	(52:48)[d]	Calc.	66.91	4.12	5.20
					Found	65.98	4.21	5.52

[a] Molar ratio of vanillic and 4-aminobenzoic acid units
[b] Molar composition of the isolated copolymers calculated from the N elemental analyses
[c] Molar composition of the hydrolysed copolymers as determined by ^{1}H n.m.r. spectroscopy
[d] Molar composition of the soluble fraction

3-methoxybenzoyl)-4-aminobenzoic acid ($\delta = 4.06$ ppm). In the case of a perfectly alternating sequence only the latter signal should be detectable. The existence of short polyester blocks (yielding vanillic acid upon hydrolysis) agrees well with the existence of an insoluble fraction which, according to N analyses, contains >50 mol% of 4-aminobenzoyl units. Taking into account intensive ester-amide exchange reactions, it is no longer trivial that feed ratios and compositions are in good agreement.

Polycondensations via the 'acetate method'

The polycondensations of monomers with free carboxyl groups ('acetate method') were conducted exactly parallel to those of the 'silylacetate method'. First, acetylated vanillic acid (**5**) was polymerized at 300°C (**6**) and 350°C (**6'**) (*Scheme 2*, equation (4)). High yields were obtained in both experiments, the i.r. spectra and elemental analyses of both samples (**6** and **6'**) agreeing with each other and with those of the poly(vanillic acid)s **2** and **2'**.

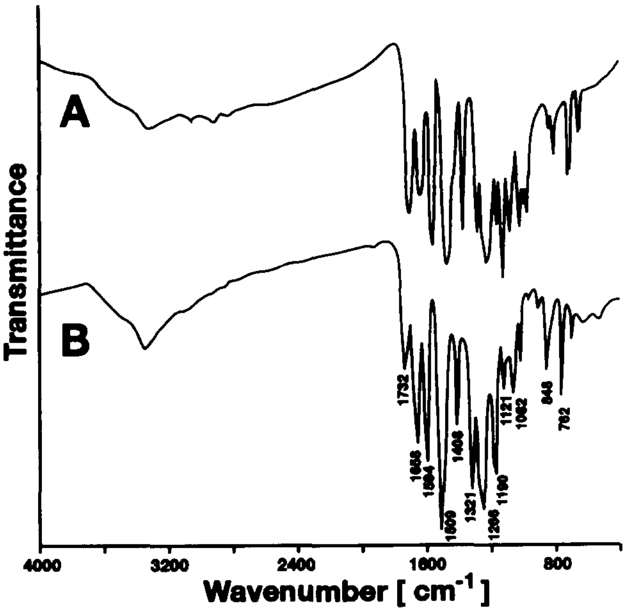


Figure 3 I.r. spectra (KBr pellets) of poly(ester–amide)s prepared by the 'acetate method' : (A) poly(ester–amide) **8e** (prepared at 300°C); (B) **8'e** (prepared at 350°C)

Table 4 Copolycondensations of vanillic acid and 4-aminobenzoic acid by the 'acetate method' at 350°C

Polymer	Feed ratio[a]	Yield (%)	Elemental analysis	C	H	N
6'	10:0	90	Calc.	64.00	4.82	–
			Found	66.73	4.48	–
8'a	9:1	16	Calc.	64.54	4.04	0.95
			Found	65.17	4.25	1.61
8'b	8:2	23	Calc.	65.09	4.06	1.95
			Found	66.74	4.19	2.89
8'c	7:3	15	Calc.	65.67	4.08	2.98
			Found	68.86	3.76	4.53
8'd	6:4	28	Calc.	66.28	4.10	4.07
			Found	67.06	5.23	7.01
8'e	5:5	43	Calc.	66.91	4.12	5.20
			Found	67.78	5.11	6.79

[a] Molar ratio of vanillic and 4-aminobenzoic acid units

In other words, there is no indication of thermal degradation, even at 350°C.

The copoly(ester–amide)s **8a–e** (polycondensed at 300°C) and **8'a–e** (polycondensed at 350°C) were prepared from monomer **7** (*Scheme 2*, equation (5)). This monomer was isolated in crystalline form after selective hydrolysis of monomer **3**. Its co-condensation with acetylated vanillic acid (**5**) yielded copoly(ester–amide)s rich in vanillic acid. The polycondensations conducted at 300°C in Marlotherm-S (*Table 3*) gave yields which were slightly higher than those of the 'silylacetate method' but lower than the homopolycondensations of **5**. The elemental analyses clearly demonstrate that the composition is almost identical with the feed ratio, and the i.r. spectrum (*Figure 3A*) confirms this conclusion. In contrast, low yields resulted from the polycondensations at 350°C (*Table 4*), and the N elemental analyses indicate a considerable loss of vanillic acid. The i.r. spectrum confirms the deficiency of ester groups (*Figure 3B*). Whatever the nature of the side reaction involved in this polycondensation, the results make clear that the 'acetate method' is not useful for a controlled synthesis of poly(ester–amide)s of vanillic acid at temperatures ⩾350°C. This result revealed a remarkable differences between the 'acetate' and 'silylacetate' methods.

WAXD powder patterns allowed another interesting comparison. As illustrated in *Figure 4*, the poly(ester–amide) **4a** still adopts the crystal lattice of poly(vanillic acid). A higher molar fraction of 4-aminobenzoic acid results in nearly amorphous materials, **4b–d**. Finally, in the case of **4e**, three weak, broad reflections become detectable which are characteristic of the crystal lattice of poly(4-aminobenzamide). Due to the hydrogen bonds between the amide groups it is reasonable that the amide groups of the 4-aminobenzoyl units dominate the chain packing. However, surprising is the comparison with series **8a–e** (*Figure 5*). Not only **8a** but also **8b** and **8c** possess the crystal lattice of poly(vanillic acid), albeit that the amorphous fraction increases in this order. Furthermore, **8c** does not exhibit the reflection typical for poly(1,4-aminobenzamide).

These differences are conspicuous because the reaction conditions and the molar compositions were the same in both series. Obviously, the sequences of vanilloyl and 4-aminobenzoyl units must be different in both series. The crystallinities of **8c–e** suggest that longer blocks of vanilloyl units are formed by the 'acetate method'. This

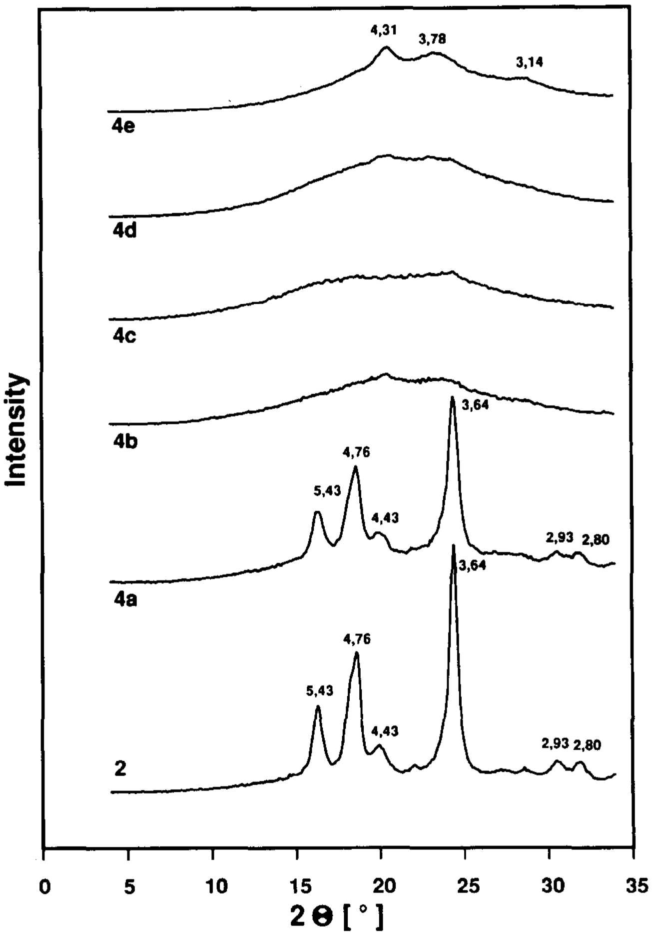


Figure 4 WAXD powder patterns of poly(ester–amide)s prepared by the 'silylacetate method' at 300°C

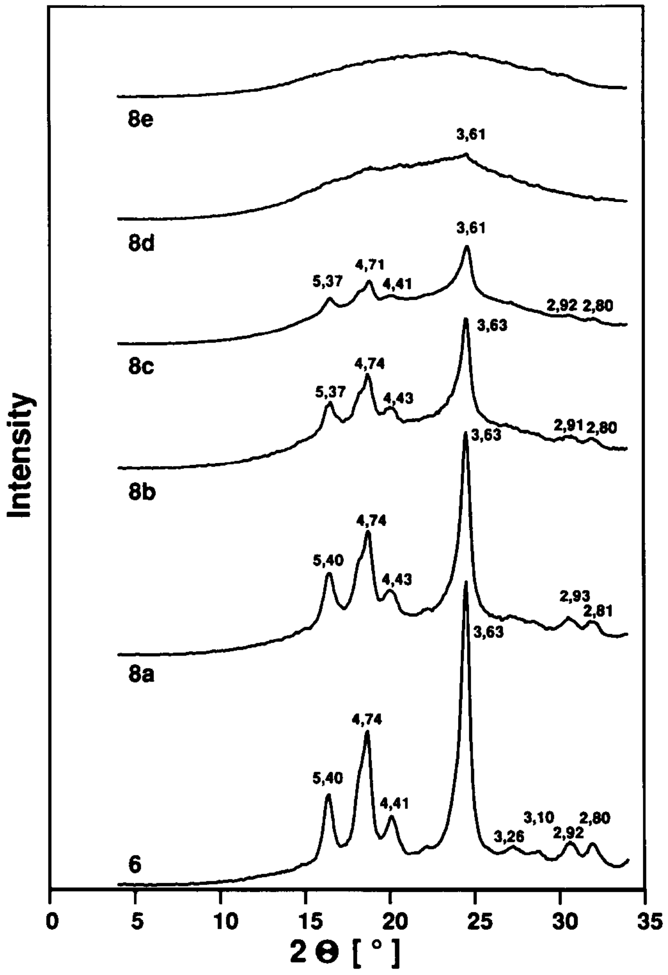


Figure 5 WAXD powder patterns of poly(ester–amide)s prepared by the 'acetate method' at 300°C

Figure 6 SEM micrograph of **8a** (the white bar represents 10 μm)

suggestion is supported by two observations. Firstly, when copoly(ester–amide)s of 4-hydroxy- and 4-aminobenzoic acid were prepared under the same conditions, both WAXD and differential scanning calorimetry (d.s.c.) measurements indicated the formation of crystalline blocks of 4-hydroxybenzoate units, as a result of the 'acetate method'[7]. D.s.c. measurements are not informative in the case of **4a–e** or **8a–e** because the phase transitions typical for crystalline poly(4-hydroxybenzoate) do not exist for poly(vanillic acid). Even glass transition steps were not detectable in the d.s.c. curves. Secondly, polyesters possess in general a higher kinetic and thermodynamical tendency to crystallize than polyamides of analogous structure. For instance, poly(hydroquinone terephthalate) is >90% crystalline whereas poly(*p*-phenylenediamine terephthalamide) is at best 60% crystalline. The same correlation holds for poly(4-hydroxybenzoate) and poly(4-aminobenzamide). Thus, it is conceivable that crystallites of 4-hydroxybenzoate or vanilloyl units are detectable, provided that the poly(ester–amide)s possess blocky sequences.

Morphological studies

All poly(ester–amide)s listed in *Tables 1–3* were examined by SEM. Not unexpectedly, conspicuous differences were found for samples prepared by the 'acetate' or 'silylacetate method'. As shown in *Figures 6* and *7*, the 'acetate method' yielded more or less globular particles. In the case of **8a** ball-like aggregates of thin lamellar crystals were seemingly formed, whereas the particles of **8e** do not show any fine structure. In contrast, fibrous or needle-like particles were obtained from the 'silylacetate method' at 300°C (*Figures 8* and *9*), the length being of the order of 10–20 μm and the aspect ratio ≈ 10. At 350°C the morphology is somewhat different again (*Figures 10* and *11*). The particles look like shavings or agave leaves. Their surface is relatively rough because

Figure 7 SEM micrograph of **8e** (the white bar represents 10 μm)

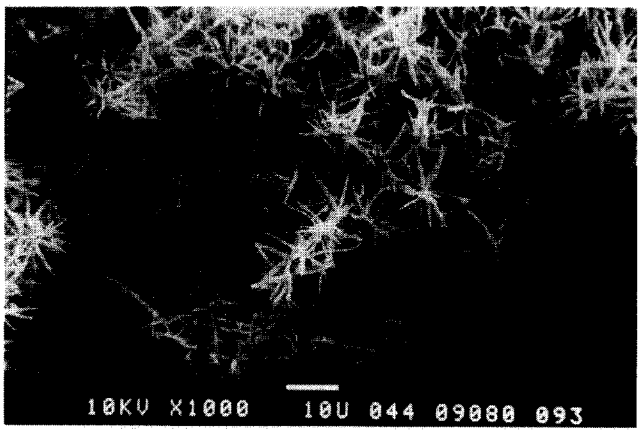


Figure 8 SEM micrograph of **4b** (the white bar represents 10 μm)

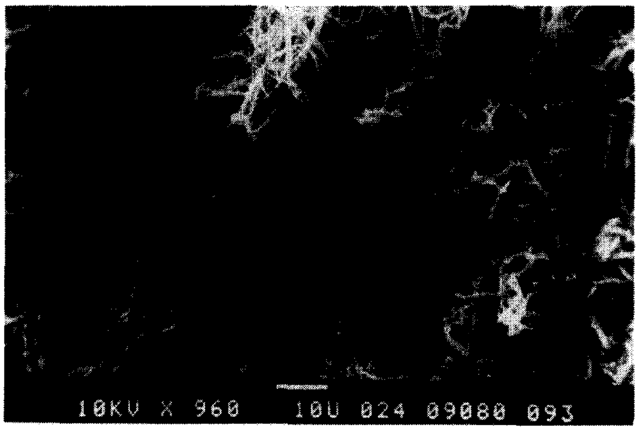


Figure 9 SEM micrograph of **4e** (the white bar represents 10 μm)

numerous tiny crystallites grow on or from their surface. In this connection it should be noted that poly(4-aminobenzamide) or the poly(ester-amide)s of 4-hydroxy- and 4-aminobenzoic acid prepared under similar conditions form particles looking exactly like long shavings. Their morphology is somewhat different from that of **4′b–e** and considerably different from that of **4b–e**.

The whiskers of poly(4-hydroxybenzoate) prepared in Marlotherm-S at 300 or 350°C were found to be single crystals or bundles of long single crystals[12,14] with >90% crystallinity. In the case of **4c–e** or **4′c–e** the situation is completely different because these materials are mainly amorphous. TEM showed an interesting morphology as exemplified for **4e** (*Figure 12*). The cylindrical particles possess a rather plain and smooth surface when examined at moderate magnification (*Figure 12a*). Furthermore, a striation parallel to the surface is detectable which suggests a certain degree of molecular order. However, fine structure consisting of individual

Figure 10 SEM micrograph of **4′d** (the white bar represents 10 μm)

Figure 11 SEM micrograph of **4′e** (the white bar represents 10 μm)

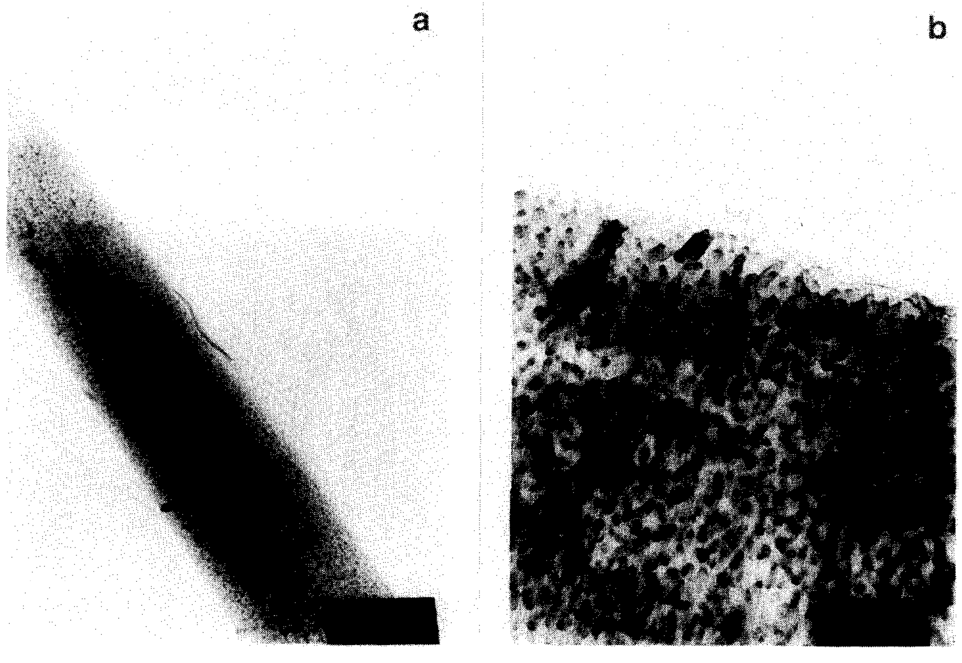


Figure 12 TEM micrographs of **4e** at different magnifications: (a) black bar = 570 nm; (b) black bar = 160 nm

crystallites or fibres is not detectable even at high magnification (*Figure 12b*). At this magnification the surface looks rough, but individual crystallites are not detectable. The phase separation of a completely amorphous polymer should not yield the characteristic anisotropic particles shown in *Figures 8, 9* and *10*. Apparently the low degree of molecular order which is present according to the WAXD patterns (*Figure 4*) plays an important role for the morphology. According to the WAXD patterns, this molecular order is mainly based on interaction between 4-aminobenzoyl units via hydrogen bonds. Nonetheless, it is an interesting mystery at the current stage of research how the observed anisotropic morphology can be formed by a mainly amorphous material. It is hoped that ongoing research will provide a better understanding of this aspect.

REFERENCES

1 Kricheldorf, H. R., Zang, Q. Z. and Schwarz, G. *Polymer* 1982, **23**, 1821
2 Kricheldorf, H. R. and Schwarz, G. *Makromol. Chem.* 1983, **184**, 475
3 Kricheldorf, H. R. and Conradi, A. *J. Polym. Sci., Part A, Polym. Chem.* 1987, **25**, 489
4 Kricheldorf, H. R., Ruhser, F. and Schwarz, G. *Macromolecules* 1991, **24**, 4990
5 Kricheldorf, H. R. and Thomsen, S. A. *J. Polym. Sci., Part A, Polym. Chem.* 1991, **29**, 1751
6 Kricheldorf, H. R., Döring, V. and Schwarz, G. *J. Polym. Sci., Part A, Polym. Chem.* 1993, **31**, 3021
7 Kricheldorf, H. R., Löhden, G. and Wilson, D. J. *Macromolecules* 1994, **27**, 1669
8 Kricheldorf, H. R. and Löhden, G. *Macromolecules* in press
9 Kricheldorf, H. R. and Schwarz, G. *Polymer* 1990, **31**, 481
10 Schwarz, G. and Kricheldorf, H. R. *Macromolecules* 1991, **24**, 2829
11 Kricheldorf, H. R., Schwarz, G., Adebahr, T. and Wilson, D. J. *Macromolecules* 1993, **26**, 6622
12 Taesler, C., Petermann, J., Kricheldorf, H. R. and Schwarz. G. *Makromol. Chem.* 1991, **192**, 2255
13 Kricheldorf, H. R. and Adebahr, T. *High Perf. Polym.* 1994, **6**, 109
14 Yamashita, Y., Kato, K., Kimura, K. and Endo, S. *Makromol. Chem. Rapid. Commun.* 1988, **9**, 687
15 Kimura, K., Endo, S., Kato, Y. and Yamashita, Y. *Polymer* 1993, **34**, 1054
16 Kozyukov, V. P., Mironova, N. V. and Mironov, V. F. *Zh. Obsh. Khim.* 1978, **48**, 2541
17 Gray, G. W. and Iones, B. *J. Chem. Soc.* 1954, 678
18 Rosenmund, V. W. and Zetsche, F. *Chem. Ber* 1923, **56**, 1482