New polymer syntheses: 34. Copoly(ester imide)s of 4-hydroxybenzoic acid and *N*-(4-carboxyphenyl)-4-hydroxyphthalimide

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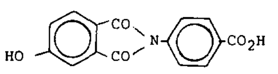
N-(4-Carboxyphenyl)-4-acetoxyphthalimide was prepared from 4-hydroxyphthalic acid, 4-aminobenzoic acid and acetic anhydride. From this monomer a new homopoly(ester imide) was prepared by thermal condensation at 350°C in an inert reaction medium. By condensation with 4-acetoxybenzoic acid at 350°C a series of copoly(ester imide)s with variable composition was prepared. Differential scanning calorimetry measurements indicated a reversible first-order phase transition at temperatures between 340 and 390°C. Wide-angle X-ray scattering measurements revealed that the orthorhombic modification II (known from pure poly(4-hydroxybenzoate)) is predominant at low temperatures, whereas at high temperature a pseudohexagonal chain packing (modification III) is preferred. The isomeric copoly(ester imide)s derived from trimellitic anhydride, 4-aminophenol and 4-hydroxybenzoic acid possess quite different properties. The pseudohexagonal chain packing is adopted even at room temperature, and thus no phase transition occurs upon heating.

(Keywords: copoly(ester imide)s; condensation; pseudohexagonal chain packing; synchrotron radiation)

INTRODUCTION

The copolyesters of 4-hydroxybenzoic acid (4-Hybe) and 6-hydroxy-2-naphthoic acid (Vectra®) demonstrate[1,2] that incorporation of a crankshaft structure into the poly(4-Hybe) chain reduces the melting point (theoretical m.p. 620°C) to such an extent that mechanical processing becomes feasible at temperatures below 400°C. The imide monomers **1** and **2** possess a structure that resembles to some extent the crankshaft structure of 6-hydroxy-2-naphthoic acid. Furthermore a higher thermostability is expected for these imide units. Thus it was of interest to synthesize and characterize copolyesters of imide **1** and 4-Hybe. The properties of these copoly(ester imide)s should be compared with those of the previously described[3] isomeric copoly(ester imide)s derived from **2** and 4-Hybe.



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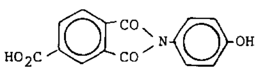

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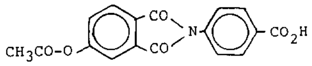
EXPERIMENTAL

Materials

Crude 4-hydroxyphthalic acid prepared from sulphonated phthalic acid was a gift from Bayer AG (Krefeld-Uerdingen, FRG). It was converted to pure 4-acetoxyphthalic anhydride (m.p. 88–90°C)[4] by means of acetic anhydride in boiling dioxane. 4-Hydroxybenzoic acid was purchased from Aldrich Co. (St Louis, USA); and acetylated by means of acetic anhydride in boiling toluene. 4-Aminobenzoic acid was a gift from Bayer AG; it was used without further purification. Marlotherm-S®, a mixture of isomeric dibenzylbenzenes, was a gift from Hüls AG (Marl, FRG).

N-*(4-Carboxyphenyl)-4-acetoxyphthalimide* (**3**)

4-Acetoxyphthalic anhydride (0.5 mol) and 0.4 mol 4-aminobenzoic acid were heated in 500 ml of dry dimethylformamide to 120°C for 1 h. Distilled acetic anhydride (1 mol) was then added and heating to 120°C was continued for an additional hour. Afterwards the reaction mixture was poured into ice–water and the crystallized product was isolated by filtration. After recrystallization from 1,4-dioxane the product was dried at 60°C/12 mbar; yield 95%; the melting point was not measurable because of thermal decomposition.



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Polycondensations

In Marlotherm-S. *N*-(4-Carboxyphenyl)-4-acetoxyphthalimide (50 mmol = 16.3 g) was dissolved and stirred in 100 ml of Marlotherm-S for 8 h at 350°C under nitrogen. After cooling the reaction mixture was diluted with chloroform, and the crystalline polyester was isolated by filtration. The polyester was then washed twice with boiling chloroform and finally dried at 120°C/12 mmHg. The co-condensations were conducted in an analogous manner.

Bulk condensations. 4-Acetoxybenzoic acid (60 mmol), *N*-(4-carboxyphenyl)-4-acetoxyphthalimide (60 mmol) and 10 mg magnesium acetate were heated with stirring under

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Table 1 Yields and elemental analyses of poly(ester imide)s **4** and **7a–g**

Formula no.	Yield (%)	Elem. formula (formula weight)	Elemental analyses			
				C	H	N
4	92	$C_{15}H_7NO_4$	Calc.	67.93	2.66	5.28
		(265.23)	Found	68.07	2.75	5.41
7a	88	$C_{67}H_{32}N_4O_{18}$	Calc.	68.14	2.73	4.74
		(1181.02)	Found	67.81	2.77	4.91
7b	85	$C_{37}H_{18}N_2O_{10}$	Calc.	68.31	2.79	4.31
		(650.56)	Found	68.25	2.61	4.47
7c	75	$C_{22}H_{11}NO_6$	Calc.	68.57	2.88	3.64
		(385.34)	Found	68.22	3.01	3.86
7d	79	$C_{29}H_{15}NO_8$	Calc.	68.91	2.99	2.77
		(505.45)	Found	68.15	3.14	2.68
7e	86	$C_{36}H_{19}NO_{10}$	Calc.	69.12	3.06	2.24
		(625.55)	Found	68.75	3.17	2.28
7f	84	$C_{43}H_{23}NO_{12}$	Calc.	69.26	3.11	1.88
		(745.66)	Found	69.00	3.24	1.70
7g	89	$C_{78}H_{43}NO_{22}$	Calc.	69.59	3.22	1.04
		(1346.21)	Found	69.30	3.26	1.09

a slow stream of nitrogen to 260°C, where the evolution of acetic acid started. The temperature was gradually raised to 350°C and maintained for 1 h after solidification of the reaction mixture.

Measurements

The WAXS powder patterns were measured on a Siemens D-500 diffractometer at room temperature with Cu K_α radiation using a Ni filter. For the set of slits between radiation source and scintillation detector, angles of 10°, 1° and 0.05° were chosen. The patterns were recorded in steps of $\theta = 0.1°$ with a radiation time of 20 s per data point.

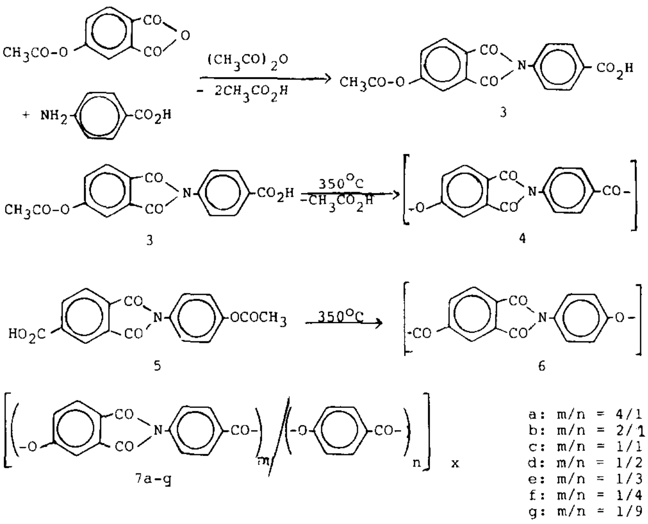
The time-resolved WAXS measurements at elevated temperatures were conducted with a synchrotron radiation beamline ($\lambda = 1.50$ Å) at HASYLAB, DESY Hamburg, by means of a vacuum furnace and a one-dimensional, position-sensitive detector. The heating rate was 20°C min^{-1} and the accumulation time for one spectrum was 15 s. The 75.6 MHz ^{13}C n.m.r. spectra were measured with a Bruker MSL-300 *FT* spectrometer in 10 mm o.d. sample tubes. A pulse width of 45°, 32 000 data points/15 000 Hz spectral width and relaxation delay of 3 or 9 s were used.

RESULTS AND DISCUSSION

Syntheses of monomers and poly(ester imide)s

Crude 4-hydroxyphthalic acid served as starting material for all derivatives of **1** studied in this work. By reaction of the crude dicarboxylic acid with acetic anhydride, pure 4-acetoxyphthalic anhydride was obtained. Its reaction with 4-aminobenzoic acid and acetic anhydride yielded monomer **3**. The polycondensation of monomer **3** was conducted in two ways, either as bulk condensation at temperatures between 250 and 350°C or in an inert reaction medium (Marlotherm-S) at 350°C. The reaction mixture of the bulk condensation turned solid after a short reaction time.

Solidification was also observed when a 1:1 mixture of monomer **3** and 4-acetoxybenzoic acid was condensed at 250–350°C. Higher reaction temperatures led to partial decomposition of the reactants. Thus, the condensation in Marlotherm-S was preferred in all cases. A reaction time of 8 h and a temperature of 350°C were chosen, because a previous study of the condensation of monomer **5** had demonstrated that these reaction conditions are optimum for the synthesis of poly(ester imide) **6**, which is isomeric to **4**.



The co-condensations of monomer **3** and 4-acetoxybenzoic acid gave high yields of copoly(ester imide)s **7a–g** in the form of crystalline powders. The elemental analyses, in particular the nitrogen analyses, indicate that the incorporation of monomer **3** into the polyester chain corresponds to the feed ratio (*Table 1*). This conclusion was confirmed by ^{13}C n.m.r. measurements. Several copoly(ester imide)s were completely hydrolysed in a $CH_3OD/NaOD/D_2O$ mixture and ^{13}C n.m.r. spectra of the resulting solution were recorded. Two different relaxation delays (4 s and 9 s) were applied to compensate the influence of different relaxation rates of quaternary carbons on the signal intensities. The signals of the O-bonded quaternary carbons in 4-hydroxyphthalic acid and 4-hydroxybenzoic acid were evaluated. They showed a satisfactory agreement with the molar ratios derived from the *N*-elemental analyses. The homopolymer **4** and the copolymers **7a–g** were insoluble in all common solvents, and thus characterization in solution was not feasible.

Properties of homopolyesters

Prior to a discussion of the properties of copoly(ester imide)s **7a–g**, the parent homopolyesters need a short description. Most properties of poly(4-Hybe) are well documented[5–11]. However, in connection with the discussion of copoly(ester imide)s **7a–g** it may be useful to recall that poly(4-Hybe) can exist in three crystal modifications. The low-temperature modification I has an orthorhombic cell with dimensions $a = 7.52$ Å, $b = 5.70$ Å and $c = 12.49$ Å[9]. This modification is the sole, or at least the predominant, form when poly(4-Hybe) is prepared by thermal condensation of 4-acetoxybenzoic acid (*Figure 1A*). Modification II (*Figure 1A*) also possesses an orthorhombic cell, but with dimensions $a = 3.77$ Å, $b = 11.06$ Å and $c = 12.89$ Å[9]. This modification may be predominant when poly(4-Hybe) is synthesized by condensation of 4-trimethylsiloxybenzoyl chloride at temperatures ≤300°C[8,12]. Both orthorhombic modifications undergo a reversible first-order transition to the high-temperature modification III (*Figure 1B*), which is characterized by a pseudohexagonal chain packing[9] with a lateral distance of 4.8 Å between neighbouring chains. The polyester chains of modification III possess a considerable degree of segmental mobility, which enables chemical reactions to occur in the solid state[7] and entails a significantly higher ductility of compact samples[5].

The poly(ester imide)s **4** and **6** have several properties in common. They are insoluble in all common solvents. No melting process is detectable up to temperatures around 480 ± 10°C, where thermal degradation prevents further observation. The d.s.c. traces do not show any phase transition; even a glass transition step is lacking. The WAXS powder patterns are largely similar, but differ significantly from those of poly(4-Hybe) (*Figure 2*). The reflections of the poly(ester imide)s **4** and **6** and those of poly(4-Hybe) are listed in *Table 2*.

Copoly(ester imide)s of 4-hydroxyphthalic acid

D.s.c. measurements of copoly(ester imide)s **7a–g** were conducted at a heating and cooling rate of 20° min^{-1} under nitrogen. In the case of **7a** (4:1 composition) only a barely detectable flat endotherm was found around 400°C. A strong endotherm appeared at 387°C in the heating trace of **7b** and the corresponding exotherm in the cooling trace (*Figure 3A*). Similar endotherms and exotherms were detectable in the d.s.c. traces of **7c–g** as demonstrated in *Figures 3B* and *3C* and *4A* and *4B* for **7c, d** and **7e, g**.

Three aspects of these d.s.c. measurements are of particular interest. First, the temperature of the endotherm decreases continuously from ~400°C to 340°C —the value of pure poly(4-Hybe)—with decreasing molar fraction of the imide monomer. Secondly, the temperature difference between endotherm and exotherm has a non-linear relationship. In the case of poly(4-Hybe) (*Figure 4C*) the hysteresis effect is only of the order of 20–25°C, yet it reaches nearly 70°C in the case of **7d** and **7e** (*Figures 3C* and *4A*). Thirdly, the exotherm is a double peak in the copolymers, and the intensity ratio of both peaks varies with the molar fraction of imide monomer. The intensity of the low-temperature peak increases with decreasing percentage of imide unit.

At first glance the temperature dependence of the phase transition of **7a–g** might be interpreted in terms of strong dipole–dipole interactions of imide and ester carbonyl groups. Dipole–dipole interactions decrease with distance as $1/r^6$, and thus the strong dipoles of the imide groups favour in principle the more densely packed orthorhombic crystal lattice at the expense of the pseudohexagonal chain packing. However, this simple explanation does not fit in with the properties of the copoly(ester imide)s **8a–g** discussed below. In this connection it is

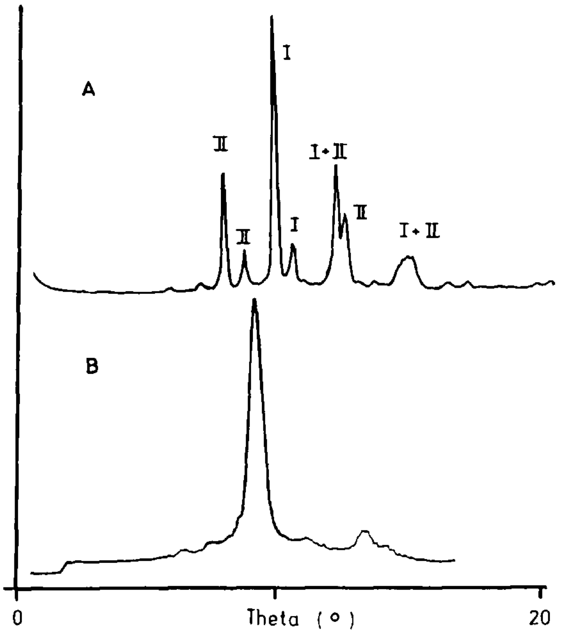


Figure 1 WAXS powder patterns of poly(4-hydroxybenzoate). (A) Sample obtained by polycondensation of 4-acetoxybenzoic acid for 16 h at 320°C in Marlotherm-2: modifications I + II measured at 20°C. (B) The same sample measured at 340°C: modification III (pseudohexagonal chain packing)

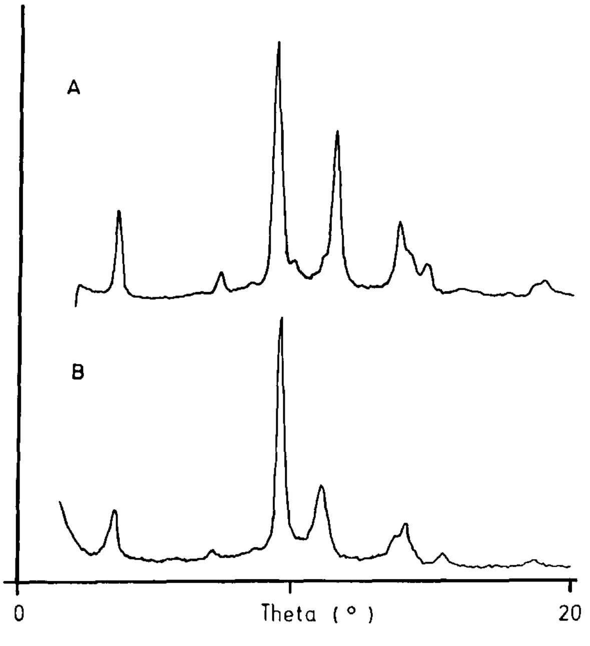


Figure 2 WAXS powder patterns of: (A) poly(ester imide) **4**; (B) poly(ester imide) **6**

Table 2 List of WAXS reflections of various homo- and copolyesters

Formula no.	Angle θ (deg) of the reflection (intensity)[a]						
Poly(4-Hybe) mod. I	9.8 (s)	10.5 (m)	12.1 (s)	14.7 (m)			
Poly(4-Hybe) mod. II	8.1 (s)	8.8 (m)	12.1 (w)	12.4 (m)	14.7 (m)		
Poly(ester imide) 4	3.7 (m)	7.4 (w)	9.5 (s)	10.0 (w)	11.5 (s)	13.9 (m)	14.9 (w)
Poly(ester imide) 6	3.6 (m)	7.2 (w)	9.7 (s)	11.1 (m)	13.8 (w)	14.2 (m)	15.5 (w)
Poly(ester imide) 7	7.8 (s)	8.6 (m)	12.2 (s)	14.0 (w)	14.5 (m)		
Poly(ester imide) 8	9.9 (s)	13.9 (w)	14.3 (w)				

[a] s = strong, m = medium, w = weak

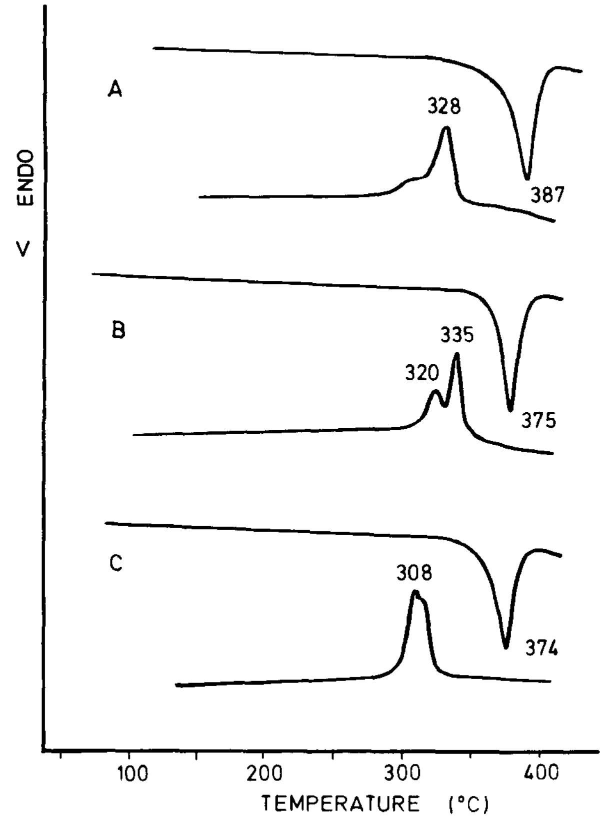


Figure 3 D.s.c. measurements conducted at a heating and cooling rate of 20°C min^{-1}: (A) heating and cooling traces of copoly(ester imide) **7b**; (B) heating and cooling traces of copoly(ester imide) **7c**; (C) heating and cooling traces of copoly(ester imide) **7d**

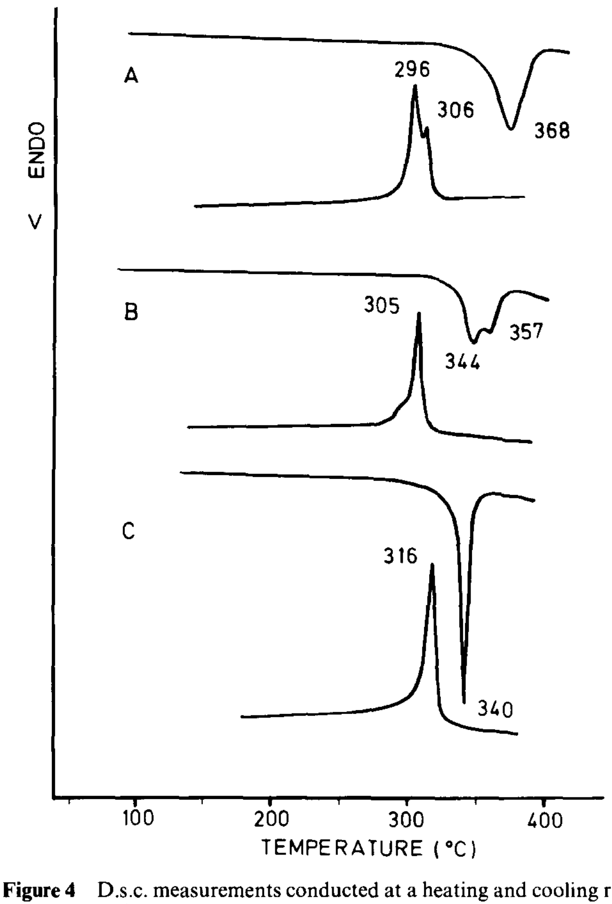


Figure 4 D.s.c. measurements conducted at a heating and cooling rate of 20°C min^{-1}: (A) heating and cooling traces of copoly(ester imide) **7e**; (B) heating and cooling traces of copoly(ester imide) **7g**; (C) heating and cooling traces of poly(4-hydroxybenzoate)

noteworthy that at least two classes of copolyesters of 4-Hybe exist which undergo similar phase transitions at lower temperatures, namely copolyesters of 4-mercaptobenzoic acid[13] and copolyesters of 3-chloro-4-hydroxybenzoic acid[14]. Thus at the current state of research it can only be stated that two classes of copolyesters exist, those with high-temperature phase transitions relative to poly(4-Hybe) and those with low-temperature phase transitions. A third class of crystalline copolyesters of 4-Hybe are, of course, those where the comonomer suppresses any phase transition (see discussion below).

The double-peak phenomenon of the phase transition was also observed for copolyesters of 4-Hybe and 4-mercaptobenzoic acid, and also for pure poly(4-Hybe) when it was prepared from 4-trimethylsiloxylbenzoyl chloride[7]. In the latter case the presence of both low-temperature modifications (I+II) might be responsible for the occurrence of two phase transitions. However, the WAXS powder patterns of **7a–g** suggest that this explanation does not hold for these copoly(ester imide)s.

The WAXS powder patterns of **7a–g** display an interesting sequence of changes as demonstrated for **7a**, **c**, **f**, **g** in *Figures 5* and *6*. Incorporation of only 20 mol% 4-Hybe into the chain of poly(ester imide) **4** (copolyester **7a**) causes a considerable change of the WAXS pattern (*Figure 5A*). Most reflections (in particular the most prominent one) agree with those of modification II of pure poly(4-Hybe). Increasing molar ratio of 4-Hybe intensifies the reflections of modification II, whereas the reflections representing the crystal lattice of homopoly(ester imide) **4** gradually disappear (*Figures 5B* and *6A*). The powder patterns of **7d**, **e**, **f** represent the pure modification II (*Figure 6A*). Further incorporation of 4-Hybe leads to an almost complete change from modification II to I (*Figure 6B*). The most interesting result of these X-ray measurements is the finding that incorporation of imide monomer **1** into poly (4-Hybe) entails a stabilization of modification II, which in the case of pure poly(4-Hybe) is less stable than I. In this connection it should be

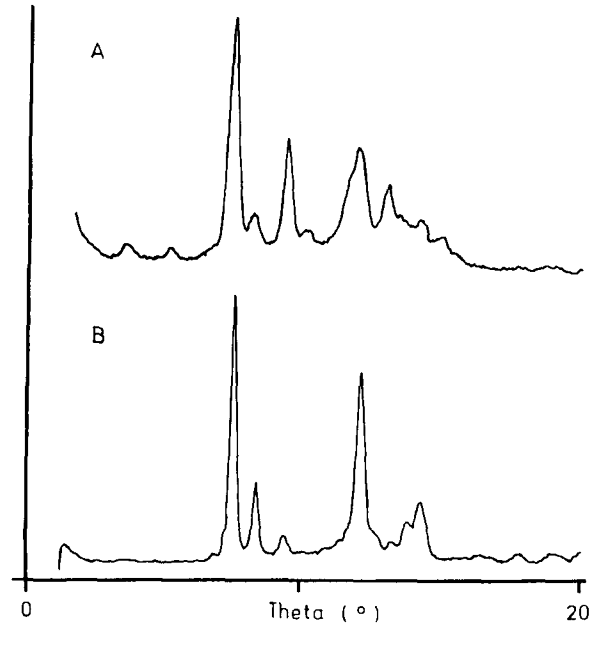


Figure 5 WAXS powder patterns of: (A) copoly(ester imide) **7a** (4:1); (B) copoly(ester imide) **7c** (1:1)

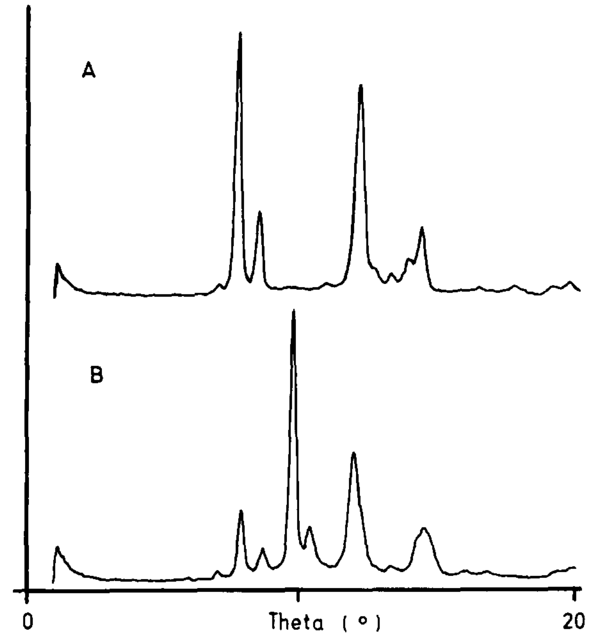


Figure 6 WAXS powder patterns of: (A) copoly(ester imide) **7f** (1:4); (B) copoly(ester imide) **7g** (1:9)

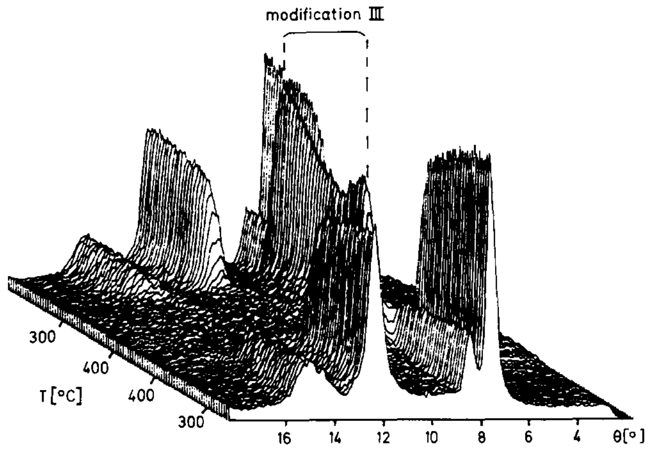


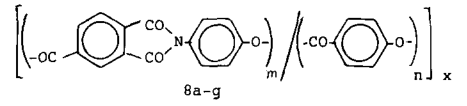
Figure 7 WAXS powder patterns of copoly(ester imide) **7c** (1:1) measured with synchrotron radiation at a heating rate of 20°C min^{-1} at time intervals of 15 s

emphasized that modification II is never predominant when pure 4-acetoxybenzoic acid is condensed under conditions used for the synthesis of **7a–g**.

Finally, the WAXS powder pattern of **7c** was measured at variable temperature using synchrotron radiation of wavelength 150 Å. The sample was heated (to 430°C) and cooled at a rate of 20°C min^{-1} and a WAXS pattern was recorded every 15 s. *Figure 7* demonstrates that the reflections of modification II disappear around 360°C and one strong reflection at $\theta = 9.8°$ shows up. This reflection is characteristic of the pseudohexagonal structure (modification III) of poly(4-Hybe) (*Figure 1B*). The only difference between the high-temperature WAXS patterns of poly(4-Hybe) and copoly(ester imide) **7d** is a weak reflection at $\theta = 13.6 \pm 1°$ in the pattern of the homopolymer (*Figure 1B*). Nonetheless the WAXS measurements of *Figure 7* clearly prove that the phase transition of copoly(ester imide)s **7a–g** has the same character as that of poly(4-Hybe) and does not represent a melting process.

Copoly(ester imide)s of trimellitic acid

Syntheses of the copoly(ester imide)s **8c–f** were described in a previous part of this series[3]. For this work the series was completed with syntheses of copoly(ester imide)s **7a, b, g**. All these copoly(ester imide)s have in common that they are highly crystalline and insoluble in all common solvents. No melting process is detectable upon microscopic observation up to temperatures in the range 450–480°C, where thermal degradation takes place. Furthermore, the d.s.c. traces do not show any phase transition between 40 and 440°C, in sharp contrast to the d.s.c. curves of the isomeric copolymers **7a–g**.



8a-g

a : m/n = 4/1
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 = 1/8

WAXS powder patterns recorded at room temperature provided a satisfactory explanation of this conspicuous difference. The sole or at least the strongest reflections in the powder patterns of the copoly(ester imide)s **8a–f** are those of the pseudohexagonal structure (modification III) known from poly(4-Hybe) (*Figures 8* and *9*). Only in the case of copolymer **8g** are the signals of modification I predominant (*Figure 9B*) in close analogy to the powder pattern of **7g** (*Figure 6B*). Thus, it is obvious that incorporation of monomer **2** into the chain of poly(4-Hybe) stabilizes modification III even at room temperature. The formation of modification III at lower temperature was also observed for other copolyesters of 4-Hybe[12,15,16]. Yet in all other cases reported so far modification III was accompanied by substantial fractions of amorphous material. Anyway, the most conspicuous result of this work is that two isomeric comonomers favour two quite different crystal modifications in copolyesters of 4-Hybe. A satisfactory explanation for this difference cannot be offered. However, it is conceivable that the imide units are to some extent compatible with two crystal lattices of poly(4-Hybe)

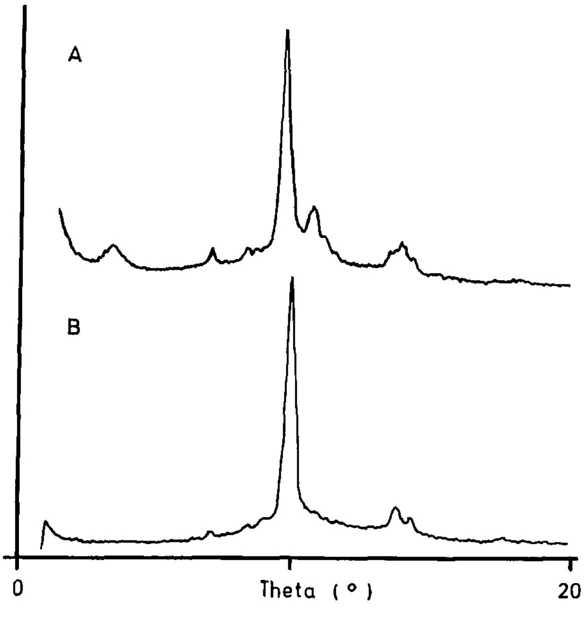


Figure 8 WAXS powder patterns of: (A) copoly(ester imide) **8a** (4:1); (B) copoly(ester imide) **8c** (1:1)

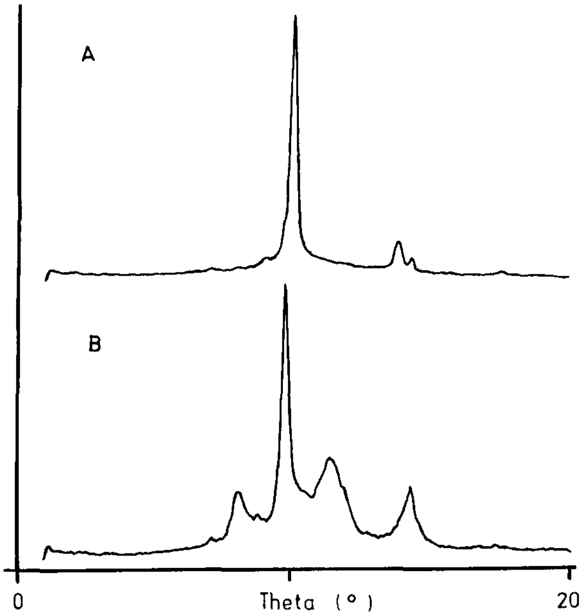


Figure 9 WAXS powder patterns of: (A) copoly(ester imide) **8f** (1:4); (B) copoly(ester imide) **8g** (1:8)

because the length of the inside units is nearly identical with that of dimeric 4-Hybe.

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