Macromolecules **1995,** *28,* 3911–3917

Whiskers. 12. Whisker-like Crystals of Poly(4′-hydroxybiphenyl-4-carboxylic acid)

Gert Schwarz and Hans R. Kricheldorf*

Institut für Technische und Makromolekulare Chemie der Universität Hamburg, Bundesstrasse 45, D-20146 Hamburg, FRG

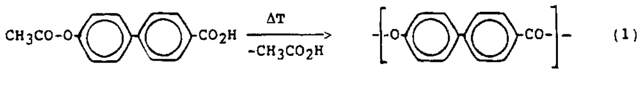
Received February 21, 1994; Revised Manuscript Received February 27, 1995[⊗]

ABSTRACT: 4′-Acetoxybiphenyl-4-carboxylic acid (4′-ABCA) was polycondensed under six different reaction conditions. In 1-chloronaphthalene at 235 °C, oligomers with a degree of polymerization (DP) of 3–4 were obtained. Polycondensation in bulk at 270 °C yielded fibrous oligomers with a DP > 10. Polycondensation of 4′-ABCA in Marlotherm-S at 320 °C yielded a poly(4′-hydroxybiphenyl-4-carboxylic acid), poly(4′-HBCA), without marked morphology. At 400 °C and low monomer concentration, whisker-like crystals were obtained. These whiskers possess an orthorhombic crystal lattice at room temperature which undergoes a reversible change to another orthorhombic smectic-E-like crystal lattice around 245 °C. This transition includes a volume expansion. Around 410 °C a second phase transition to a smectic-B-like phase occurs. At 585 °C simultaneous melting and degradation take place, which mainly involves a Fries rearrangement.

Introduction

This work is part of a broader study dealing with the synthesis and characterization of whisker-like crystals based on organic polymers. In these studies whiskers are defined as elongated crystals with an aspect ratio of at least 10:1. Furthermore, true whiskers are single crystals or bundles (aggregates) of single crystals. Previous studies have shown that only a few polyesters are capable of forming whisker-like crystals: poly(4-hydroxybenzoic acid) [poly(4-HBA)],[1–4] poly(6-hydroxy-2-naphthoic acid) [poly(HNA)],[2,5,6] and poly[*N*-(4-carboxyphenyl)-4-hydroxyphthalimide].[7,8] Furthermore, studies of numerous copolyesters have revealed that the crystal growth of whiskers is sensitive to variations and deformations of the orthorhombic crystal lattices characteristic for the aforementioned homopolyesters.[8–11] Moreover, it was found that the crystal growth of whiskers is highly sensitive to the presence of di- or multifunctional impurities or reaction byproducts. Even 1% of a free hydroxy acid which escaped from acetylation may be detrimental for the formation of whiskers although the polycondensation itself is not hindered at all.[8,12] Hence, if a polyester does not form whisker-like crystals, it is difficult to decide whether its crystal lattice is unfavorable for this particular type of crystal growth or if the purity of the monomer and reaction medium is not high enough.

An interesting candidate for the formation of whiskers is the polyester of 4′-hydroxybiphenyl-4-carboxylic acid (4′-HBCA). This polyester was for the first time synthesized by us[13,14] via polycondensation of 4′-acetoxybiphenyl-4-carboxylic acid (eq 1). Despite a broad variation of the reaction conditions, true whiskers were never obtained, although short cylindrical crystals were isolated in a couple of experiments. Another study in this direction was recently reported by Geil and coworkers.[15] These authors obtained at least one sample containing single crystals with sharp tips and *l*/*d* ratios around 5. Unfortunately, no information on the molecular weight was given. The low reaction temperatures suggest the formation of oligomers rather than polymers. The present work was aimed at studying the synthesis and properties of whiskers of poly(4′-HBCA) in more detail.



(1)

Experimental Section

Materials. 4-Hydroxybiphenyl was a gift of Bayer AG (Leverkusen, FRG) and used without further purification. 4′-Hydroxybiphenyl-4-carboxylic acid was prepared from 4-hydroxybiphenyl as described previously.[13,14,16] 1-Chloronaphthalene (Aldrich Chemical Co., Milwaukee, WI) and Marlotherm-S (gift of Hüls AG, Marl, FRG) were distilled in vacuo prior to use.

4′-Acetoxybiphenyl-4-carboxylic Acid (4′-ABCA). 4′-Hydroxybiphenyl-4-carboxylic acid (0.1 mol), distilled acetic anhydride (0.2 mol), and pyridine (1 mL) were refluxed in toluene for 4 h. The reaction mixture was then concentrated in vacuo, and the residue was diluted with dry toluene, concentrated again, and crystallized overnight. The isolated monomer was further purified by sublimation in vacuo at 200 °C.

Polycondensations. (A) In 1-Chloronaphthalene. A round-bottom flask containing recrystallized 4′-ABCA (10 mmol) and 1-chloronaphthalene (100 mL) was placed into a metal bath preheated to 150 °C. The temperature was then rapidly raised to 235 °C, and the evolved acetic acid was removed with a slow stream of nitrogen. After 12 h the reaction mixture was cooled to 20 °C and filtered The isolated product was twice washed with hot acetone and dried at 120 °C in vacuo.

(B) In bulk. Recrystallized 4′-ABCA (20 mmol) was weighed into a cylindrical glass reactor equipped with a stirrer and gas-inlet and -outlet tubes. The reactor was placed into a metal bath preheated to 150 °C and the temperature was rapidly raised to 270 °C. After 18 h the cold product was mechanically powdered, twice extracted with hot acetone, and dried at 120 °C in vacuo.

(C) In Marlotherm-S. Recrystallized 4′-ABCA (30 mmol) and Marlotherm-S (100 mL) were weighed into a cylindrical glass reactor equipped with a stirrer and gas-inlet and -outlet tubes. The reaction vessel was placed into a metal bath preheated to 150 °C, and the temperature was rapidly raised to 350 °C (ca. 15 min). The evolved acetic acid was removed by a slight stream of nitrogen. After 16 h the reaction mixture was cooled, diluted with acetone, and filtered. The product was twice washed with hot acetone and dried at 120 °C in vacuo. In a second experiment sublimed 4′-ABCA (10 mmol)

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1995.

0024-9297/95/2228-3911$09.00/0

Table 1. Reaction Conditions and Results of Polycondensations of 4′-Acetoxybiphenyl-4-carboxylic Acid

sample no.	reaction medium	temp (°C)	time (h)	conc[a] (mol/L)	yield (%)	T_g[b] (°C)	T_m[b] (°C)	morphology
1	1-chloronaphthalene	235	12	0.1	38			aggregates of lamellar crystals
2	in bulk	270	2		78[c]			
3	in bulk	270	18		65[c]		380–400, 570	Fibers (Figure 4)
4	Marlotherm-S	320	16	0.3	86		410, 570	(Figure 5)
5	Marlotherm-S	400	4	0.1	58	127	305, 400–410, 580	aggregates of tin whiskers (Figure 6)
6	Marlotherm-S	400	16	0.05	41	133	244, 585	whiskers (Figures 7 and 8)

[a] Molar monomer concentration at 20 °C. [b] From DSC measurements at a heating rate of 20 °C/min. [c] The losses resulted from sublimation of monomer and byproducts.

was polycondensed for 4 h at 400 °C, and in a third experiment sublimed 4-ABCA (5 mmol) was heated for 16 h at 400 °C.

Measurements. The DSC measurements were conducted with a Perkin-Elmer DSC-7 in aluminum pans under nitrogen. The IR spectra were recorded from KBr pellets using a Nicolet SXB-20 FT NMR spectrometer. WAXD powder patterns were recorded at 25 °C with a Siemens D-500 diffractometer using Ni-filtered Cu *K*α radiation. The synchrotron radiation measurements were conducted at HASYLAB (DESY, Hamburg) using a wavelength of 1.50 Å and a heating rate of 10 °C/min. Furthermore, a one-dimensional position-sensitive detector was used. The 75.4 MHz ^{13}C NMR CP/MAS spectra were recorded with a Bruker MSL 300 FT spectrometer. Double-bearing ZrO_2 rotors were used at a spinning rate of 4 kHz. All measurements were conducted with a contact time of 1 ms and a repetition time of 3 s.

Results and Discussion

Oligoesters of 4′-Hydroxybiphenyl-4-carboxylic Acid (4′-HBCA). In a recent paper of Geil and coworkers,[15] polycondensation of 4′-ABCA at 235 °C in 1-chloronaphthalene or at 270 °C in bulk was studied. Unfortunately, any information on the monomer concentration and workup procedure is lacking, and even a systematic listing of the reaction times was not given. Therefore, an exact reproduction of the reaction conditions is not feasible. In the present work 4′-ABCA was polycondensed in 1-chloronaphthalene at 235 °C using a concentration of 0.1 mol/L (no. 1, Table 1). Even after a reaction time of 12 h (mentioned in ref 15), the reaction mixture was clear and no product had precipitated. This observation represents clear-cut evidence for the absence of poly(4′-HBCA), because this polyester is insoluble in all common solvents. Upon cooling, oligoesters of 4′-HBCA crystallized from the reaction mixture.

A crude determination of the DP of these oligoesters was obtained by IR spectroscopy (Figure 1) and ^{13}C NMR CP/MAS spectroscopy (Figure 3). The IR spectrum of the monomer 4′-ABCA exhibits two well-separated "CO bands" of the acetate and of the carboxyl group (Figure 1A). The IR spectrum of the oligoester no. 1 (Table 1) shows a strong band of the aromatic ester groups at 1730 cm^{-1} but the "CO bands" of the acetate (1748 cm^{-1}) and of the CO_2H group (1685 ± 1 cm^{-1}) are still present. The spectrum of sample no. 1 is nearly identical with that of sample no. 2 prepared in bulk at 270 °C/2 h (Figure 1B). The ^{13}C NMR CP/MAS spectra of sample nos. 1 and 2 display the CH_3 signal of the acetate end groups at 20 ppm (Figure 3B). A comparison with the spectrum of the monomer (Figure 3A) suggests that the DP of oligoester no. 1 is on the order of 3–4 and around 4 in the case of sample no. 2. The morphology of the crystals of sample no. 1 may be described as aggregates of lamellar crystals. Oligoesters of 4-hydroxybenzoic acid (4-HBA) form similar lamellar crystals, amd micrographs of such crystals have been published several times.[17–19] Taken together, these results demonstrate that polycondensations of 4′-ABCA in 1-chloronaphthalene at 235 °C are not suited to produce high molecular weight poly(4′HBCA).

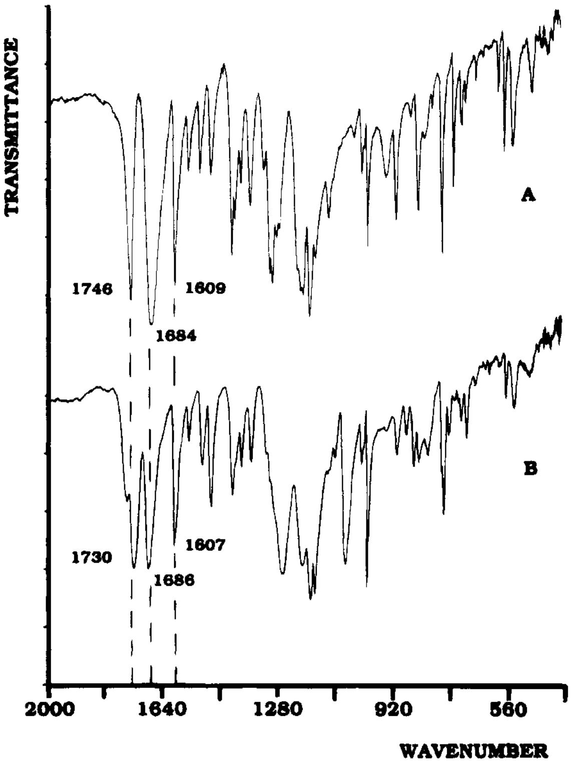


Figure 1. IR spectra (KBr pellets) of (A) 4′-acetoxybiphenyl-4-carboxylic acid and (B) oligo(4′-HBCA) prepared in bulk, 2 h/270 °C (no. 2).

More successful in this regard are polycondensations in bulk at 270 °C. When the reaction time was extended from 2 to 18 h (no. 3, Table 1), significant increase of the DP was found. No end-group signal was detectable in the ^{13}C NMR CP/MAS spectrum (Figure 3C). Considering the signal-to-noise ratio, the DP certainly exceeds 10. In agreement with this observation no "acetate band" was found in the IR spectrum of sample no. 3 (Figure 2C), but when compared with a true polyester (Figure 2D), a broad shoulder of the carboxyl end groups is detectable around 1680–1700 cm^{-1}. Of particular interest is the fibrous morphology of sample no. 3 (Figure 4), which is another indirect proof for the higher DP of this oligoester. Examination of several parts of this sample by SEM suggests that 60–80% of the sample possesses a fibrous morphology. However, the WAXD patterns discussed below indicate that the crystal structure of oligoester no. 3 is rather imperfect. A more detailed study of polycondensations in bulk will be presented in a future part of this series.

Poly(4′-HBCA). The results obtained from polycondensations at 235 or 270 °C suggest that such low temperatures are not suited for the synthesis of high molecular weight poly(4′-HBCA). This suggestion agrees well with our previous studies on the polycondensation

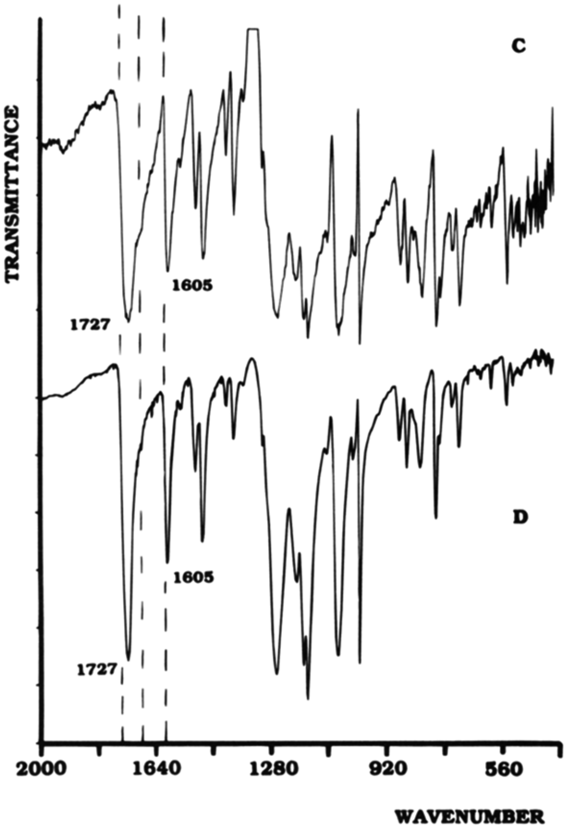


Figure 2. IR spectra (KBr pellets) of (C) oligo(4′-HBCA) prepared in bulk, 18 h/270 °C (no. 3), and (D) poly(4′-HBCA) no. 5 prepared at 400 °C/4 h.

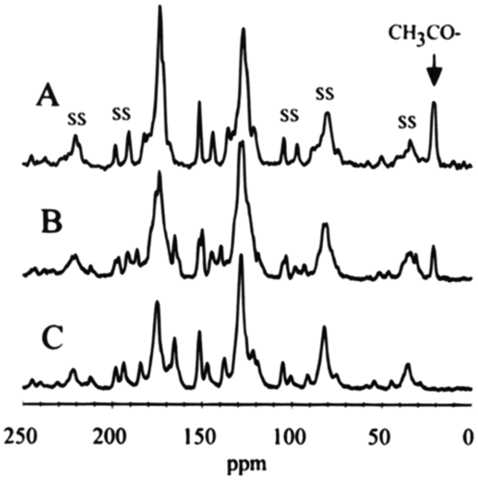


Figure 3. 75.4 MHz ^{13}C NMR CP/MAS spectra of (A) 4′-acetoxybiphenyl-4-carboxylic acid, (B) oligo(4′-HBCA) prepared in chloronaphthalene (no. 1), and (C) oligo(4′-HBCA) prepared in bulk, 18 h/270 °C (no. 3).

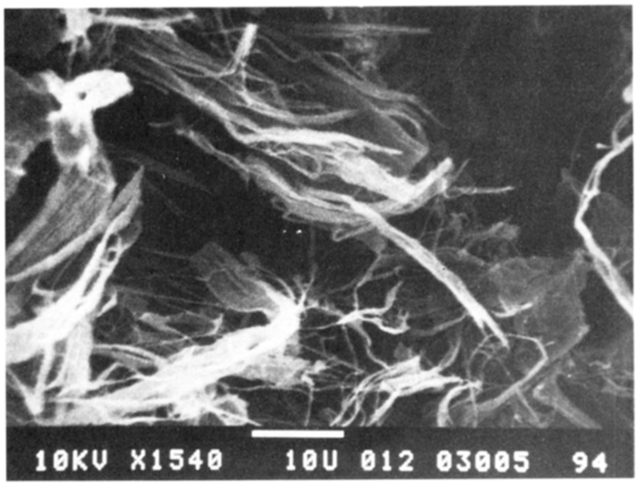


Figure 4. SEM micrograph of the oligo(4′-HBCA) prepared in bulk, 18 h/270 °C (no. 3).

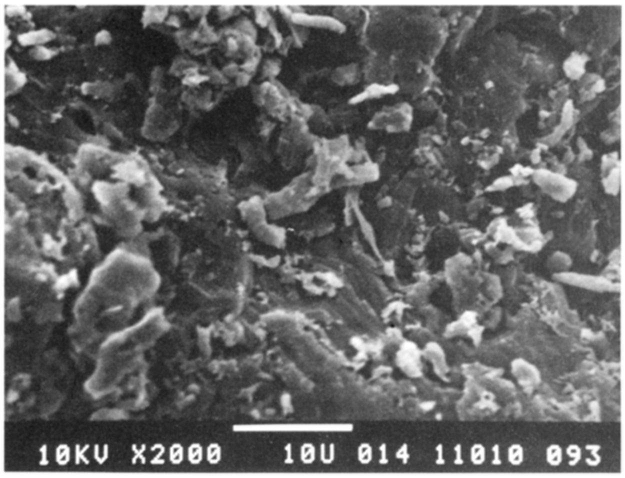


Figure 5. SEM micrograph of the poly(4′-HBCA) prepared in Marlotherm-S, 16 h/320 °C (no. 4).

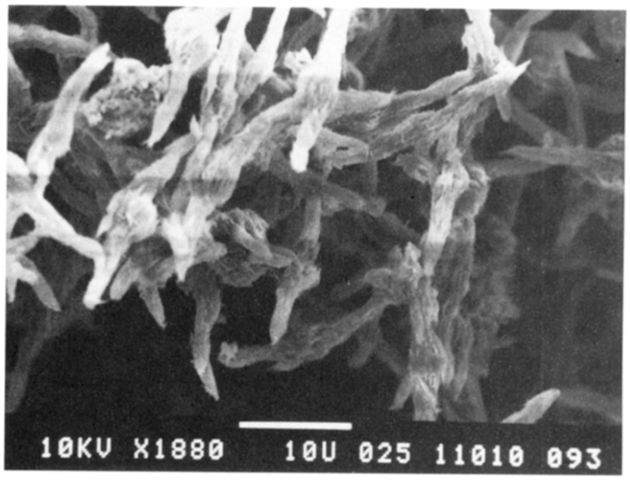


Figure 6. SEM micrograph of the poly(4′-HBCA) prepared in Marlotherm-S, 4 h/400 °C (no. 5).

of 4-acetoxybenzoic acid.[20] Since poly(4′-HBCA) was previously prepared by polycondensations of 4′-ABCA in Marlotherm-S at temperatures of 320, 350, or 400 °C,[13,14] similar reaction conditions were used again in this work. One sample (no. 4, Table 1) was prepared by polycondensation of a recrystallized 4′-ABCA in high concentration (0.3 mol/L) at 320 °C in Marlotherm-S. This experiment, designed for preparative purposes (high yields), reproduces exactly a previous polycondensation.[14] A batch of the monomer was sublimed after recrystallization, and this sublimed monomer polycondensed at 400 °C in Marlotherm-S at a concentration of 0.1 or 0.05 mol/L (nos. 5 and 6, Table 1).

All three polyesters (nos. 4–6) have in common that no end-group signals were detectable in their IR or ^{13}C NMR CP/MAS spectra (Figures 2D and 15A). However, their morphologies (Figures 5–8), WAXD patterns, and DSC traces (see below) were different. The SEM micrograph of sample no. 4 (Figure 5) displays a mass of material which does not allow any detection of individual crystals. The SEM micrograph of poly(4′-HBCA) no. 5 (Figure 6) shows a more defined morphology, which, after further magnification, looks like plaits of tiny whiskers. These whiskers have lengths around 1–2 μm. Whisker-like crystals with lengths up to 10 μm were clearly obtained from the polycondensation at

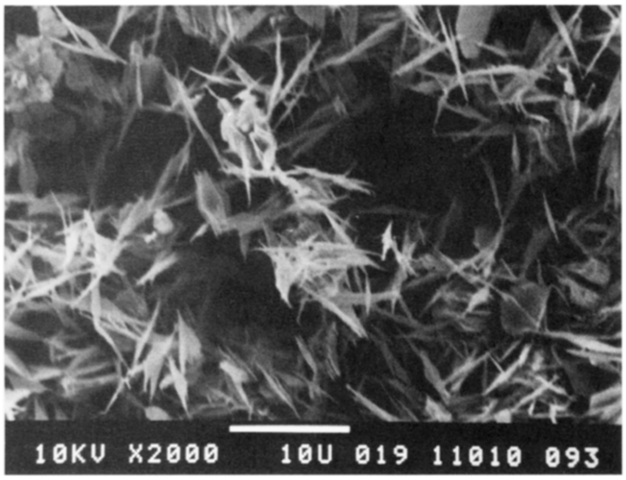


Figure 7. SEM micrograph of the poly(4′-HBCA) prepared in Marlotherm-S, 16 h/400 °C (no. 6).

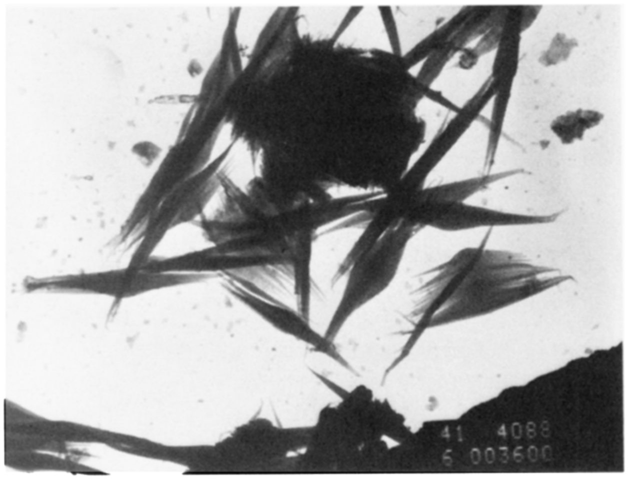


Figure 8. TEM micrograph of the whiskers no. 6.

lower concentration and longer reaction time (no. 6, Figures 7 and 8). The TEM micrograph suggests that these whiskers are single crystals or aggregates made up by extended chain crystals. Almost identical single crystals are known from poly(4-HBA).[1,20] These findings indicate that a successful synthesis of whiskers of poly(4′-HBCA) is favored by (a) a high purity of the monomer, (b) high reaction temperatures, and (c) low monomer concentrations. Exactly the same correlation between reaction conditions and morphology was found for polycondensation of 4-acetoxybenzoic acid[12] and 6-acetoxy-2-naphthoic acid.[21]

Chain Packing and Phase Transitions. All oligo- and poly(4′-HCBA) samples were characterized by WAXD powder patterns. When the WAXD patterns of the oligomers (Figures 9B,C) are compared to those of the monomer (Figure 9A) and of the polyesters (Figure 10A,B), it is evident that even the shortest oligoesters adopt an orthorhombic crystal lattice which differs largely from that of the monomer but resembles that of the whiskers (Figure 10B).

Not unexpectedly, the crystals of the oligomers slowly crystallized from 1-chloronaphthalene are considerably more perfect than those obtained by polycondensation in bulk. Nonetheless, it is surprising that the complete transformation of the crystal lattice and the formation of DP's > 10 are possible in bulk at the relatively low temperature of 270 °C. This result suggests that the segmental mobility of the oligoester chains is relatively high at this temperature. The phase transitions and DSC measurements discussed below indeed indicate that the segmental mobility of poly(4′-HBCA) is higher than that of poly(4-HBA) at temperatures below 320 °C. The WAXD powder patterns of the whiskers nos. 5 and 6 are almost identical (Figure 10B). The reflections were satisfactorily indexed according to the orthorhombic modification I of poly(4-HBA)[22] (Table 2). Taking into account that the repeating unit of 4′-HBCA has a length of 10.90 Å and that of 4-HBA a length of 6.45 Å, it is trivial that all reflections involving the *c*-axis (defined to parallel the chain axis), such as the 001 and 211 reflections, have different ϑ values. The measurements with synchrotron radiation at 50 °C gave the same values (Figures 11, 12, and Table 3). The WAXD patterns of the poly(4′-HBCA) samples nos. 5 and 6 also exhibit a weak reflection at $2\vartheta = 11.3°$ (Figure 10B), which does not fit in with the orthorhombic modification discussed above. The same reflection was observed together with a reflection at $2\vartheta = 25.3$ Å for an oligoester by Geil and co-workers.[15] These reflections were interpreted as the 200 and 110 reflections of a second orthorhombic modification. The X-ray data obtained in this work do not allow a final decision. However, it is interesting to note that poly(4-HBA) also forms in low "concentration" a second orthorhombic modification at room temperature.[22]

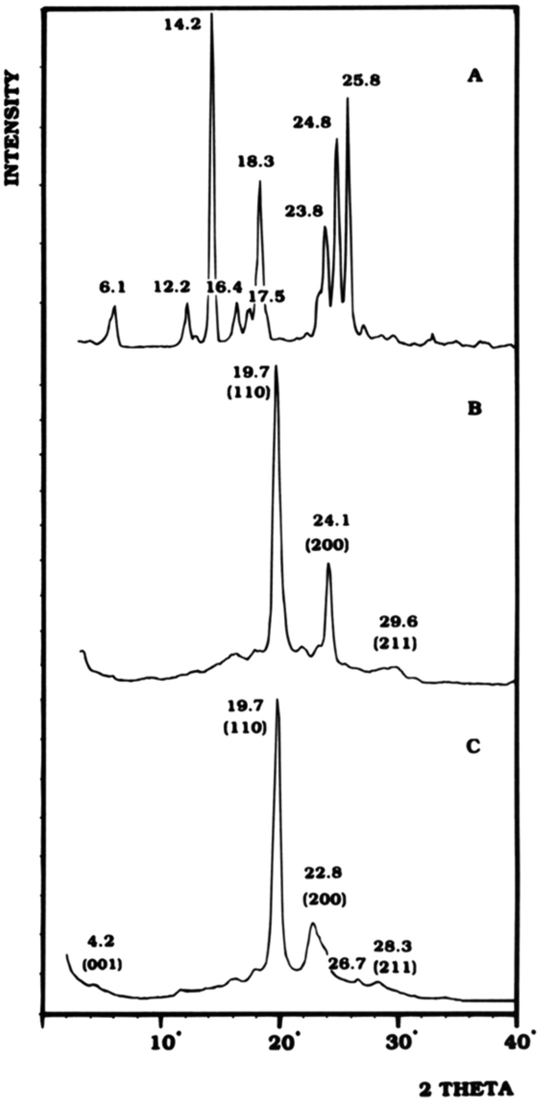


Figure 9. WAXD powder patterns of (A) acetoxybiphenyl-4-carboxylic acid, (B) oligo(4′-HBCA) prepared in 1-chloronaphthalene (no. 1), and (C) oligo(4′-HBCA) prepared in bulk, 18 h/270 °C (no. 3).

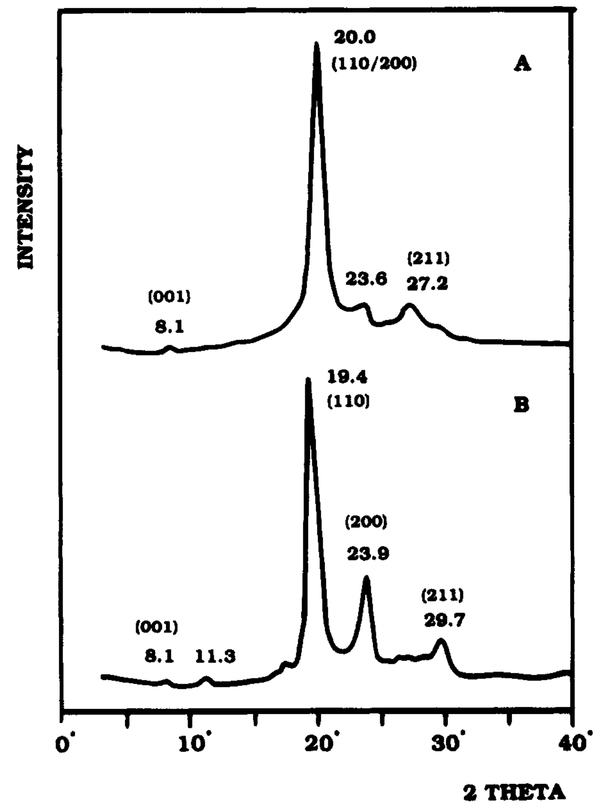


Figure 10. WAXD powder patterns of poly(4′-HBCA) prepared in Marlotherm-S: (A) 16 h/320 °C (no. 4); (B) 16 h/400 °C (no. 6, whiskers).

Table 2. X-ray Reflections (and Their Evaluation) As Determined by Cu Kα Radiation at 25 °C

Whiskers Sample No. 6

2ϑ (deg)	d (Å)	*hkl*
8.1	10.90	001
19.4	4.57	110
23.9	3.72	200
29.7	3.00	211

$a = 7.44$ Å, $b = 5.79$ Å, $c = 10.90$ Å

$a \times b = 43.1$ Å^2, $a \times b \times c = 470$ Å^3

Sample No. 4

2ϑ	d (Å)	*hkl*
8.1	10.9	001
20.0	4.43	110 200
27.8	3.2	211

$a = 8.86$ Å, $b = 5.12$ Å, $c = 10.90$ Å

$a \times b = 45.4$ Å^2, $a \times b \times c = 495$ Å^3

The whiskers no. 6 were also subjected to synchrotron radiation measurements at temperatures up to 410 °C, which were repeated up to 430 °C. The stacked plot and the contour map of Figures 11 and 12 are based on a heating rate of 10 °C/min. Two phase transition become clearly detectable. The first transition occurs at 240–250 °C and yields another orthorhombic crystal lattice (phase II) with larger lateral dimensions. The basal plane of the elementary cell calculated at 280 °C amounts to 48.7 Å^2 compared to 43.1 Å^2 of modification I at room temperature.

The second phase transition at 400–410 °C results in the formation of a hexagonal chain packing. This transition is characterized by the disappearance of the 211 reflection in the WAXD patterns (Figure 11). Quite analogous phase transitions and modifications were reported for poly(4-HBA). For poly(4-HBA) the high-temperature orthorhombic modification was labeled the smectic E phase[23] and the hexagonal phase the smectic B phase.[5] This labeling makes sense, because the 001 reflection is observable even in the hexagonal phase (up to 500 °C[24] and because the smectic E and B phases are solid mesophases in the case of liquid crystalline main chain polymers in contrast to liquid crystalline side chain polymers. Also in the case of poly(4′-HBCA) whiskers the 001 reflection was observable in the hexagonal phase (measured up to 430 °C). This means the polar ester groups register in a layer plane as illustrated by Figure 13A. Thus a columnar mesophase with hexagonal chain packing but without registration of identical groups (Figure 13B) is excluded.

Table 3. X-ray Reflections (and Their Evaluation) As Determined by Synchrotron Radiation

Whiskers No. 6, at 50 °C

2ϑ (deg)	d (Å)	*hkl*
8.1	10.90	001
19.4	4.57	110
23.9	3.72	200
–	–	211

$a = 7.44$ Å, $b = 5.79$ Å, $c = 10.90$ Å

$a \times b = 43.1$ Å^2, $a \times b \times c = 470$ Å^3

Whiskers No. 6, at 280 °C

2ϑ (deg)	d (Å)	*hkl*
8.1	10.90	001
19.3	4.59	−110 200
26.9	3.31	211

$a = 9.18$ Å, $b = 5.30$ Å, $c = 10.90$ Å

$a \times b = 48.7$ Å^2, $a \times b \times c = 535$ Å^3

The driving force for the phase transitions observed for both poly(4-HBA) and poly(4′-HBCA) is the thermal energy which intensifies or unfreezes rotational or vibrational motions of all monomer units. It was shown in the case of poly(4-HBA) that the first phase transition (330–350 °C) mainly results from 180° flip motions of the phenylene rings,[25] which require more space in the lateral dimensions (increase of the a–b plane). The transition to the hexagonal phase is obviously the result of full rotations of the phenylene rings and flip motions of the ester groups.[5,26] These motions render the entire polyester chain a columnar shape, which in turn favors a hexagonal chain packing. Similar changes of the molecular motion are certainly responsible for the phase transitions of poly(4′-HBCA). The lower temperature of its phase transitions indicates a higher group mobility when compared to poly(4-HBA) at identical temperatures. This conclusion agrees well with good progress of the polycondensation in bulk at 270 °C. At this temperature the oligomers exist in the more mobile (smectic E) phase II. The polycondensation of oligo(4-HBA) at temperatures below 300 °C is slower, because it must proceed in the less mobile phase I.

As indicated by DSC measurements, a third phase transition occurs around 585 °C (Figure 14). As reported previously,[3] the temperature of this phase transition depends on the perfection of the crystallites and may be lower for less perfect materials such as sample no. 4. This third phase transition represents a simultaneous melting and degradation process. When whiskers (no. 6, Table 1) were heated under nitrogen to 590 °C at a rate of 20 °C/min and quenched to room temperature, their chemical structure had completely changed, albeit it had been exposed to temperatures

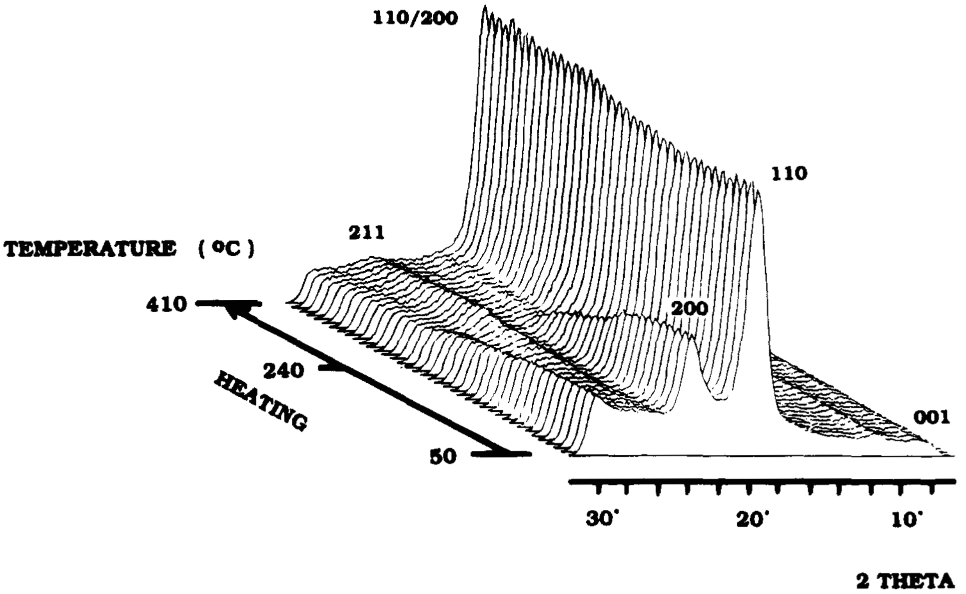


Figure 11. WAXD powder patterns of whiskers (no. 6) measured with synchrotron radiation at a heating rate of 10 °C/min.

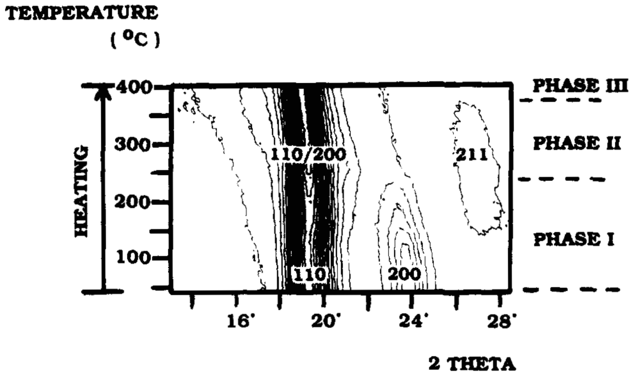
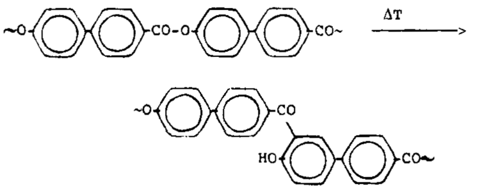


Figure 12. Contour map of the synchrotron radiation measurements of sample no. 6.

above 580 °C for only 30 s. The IR spectrum of the degraded "whiskers" (Figure 15B) display three interesting features. First, the "CO band" of the ester groups has almost completely disappeared. Second, a new "CO band" shows up at 1663 cm^{-1}. Third, a broad "OH band" appears between 3000 and 3500 cm^{-1}. All these spectroscopic features may be explained by the Fries rearrangement outlined in eq 2. This Fries rearrangement requires space and a high mobility of the chain segments, and thus, it is clearly the high order and tense packing of the solid smectic B phase (when compared to a liquid crystalline melt), which prevents this rearrangement from occurring at lower temperature.



(2)

Suprisingly, the second transition (smectic E → smectic B) is not detectable in the DSC heating curves of the whiskers no. 6. Obviously, its enthalpy change is extremely low. This finding parallels the thermal properties of poly(4-HBA). The DSC curve of poly(4-HBA) shows only a very weak endotherm for the second transition.[24,27,28]

Interestingly, the endotherm of the second phase transition shows up in the DSC curve of poly(4′-HBCA) No. 4 (Figure 14B), whereas the first transition is not

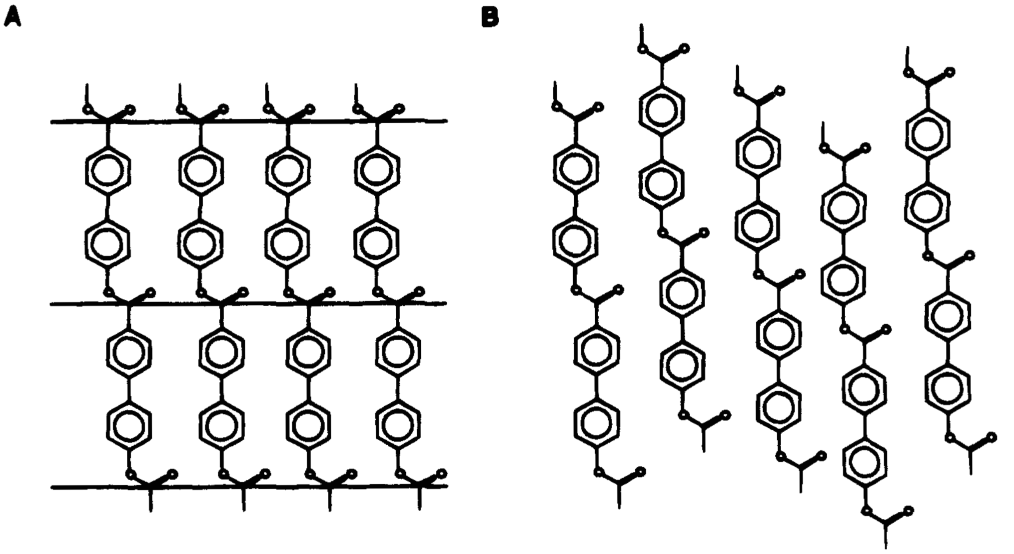


Figure 13. Schematic chain packing of poly(4′-HBCA) (A) with and (B) without registration of the ester groups.

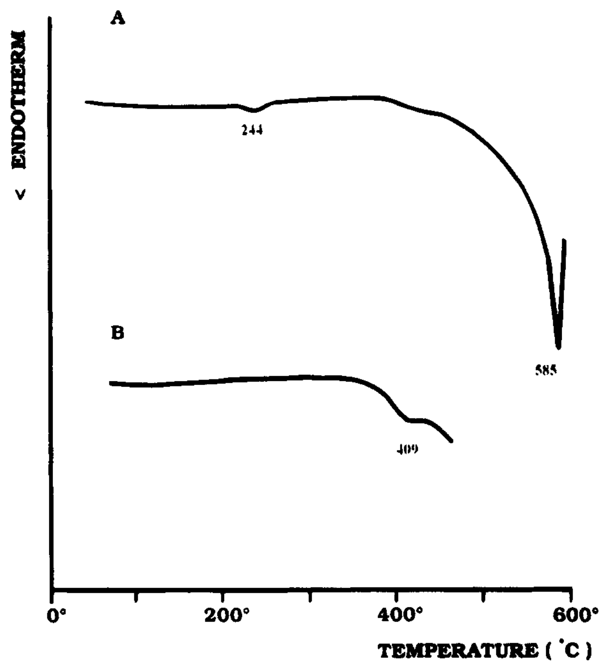


Figure 14. DSC measurements (heating rate 20 °C/min) of (A) whiskers no. 6 and (B) poly(4'-HBCA) no. 4 prepared at 320 °C in Marlotherm-S.

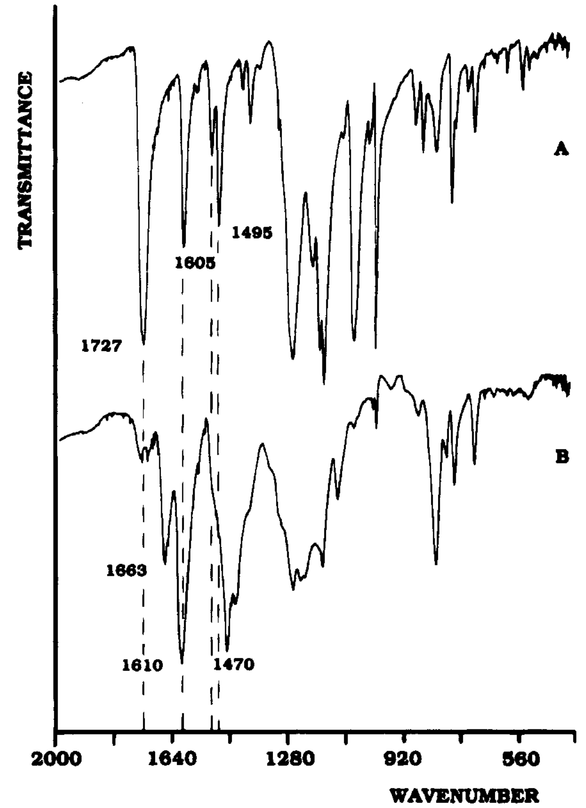


Figure 15. IR spectra (KBr pellets) of (A) whiskers no. 6 as polymerized and (B) the same sample after heating to 590 °C at a rate of 20 °C/min.

detectable. The WAXD powder pattern provides an explanation because it indicates that the chain packing of this sample is closer to that of phase II than to phase I. Thus, a phase I → phase II transition cannot take place, whereas the transition to phase III is more pronounced. In the case of sample no. 5 the DSC trace exhibits a first phase transition at 305 °C, whereas the second transition is barely detectable. A more detailed study of this and further samples of poly(4'-HBCA) will be reported in a future part of this series. Nonetheless, the results discussed above demonstrate that chain packing and phase transitions of poly(4'-HBCA) are extremely sensitive to the reaction conditions used for its synthesis.

Conclusion

The results presented above allow the conclusion that polycondensations of 4'-ABCA at temperatures ≤ 270 °C yield oligoesters but not high molecular weight poly(4'-HBCA). The formation of whiskers of poly(4'-HBCA) is favored by high reaction temperatures, high purity, and low concentration of the monomer, in perfect agreement with syntheses of whiskers from 4-acetoxybenzoic acid or 6-acetoxynaphthoic acid. Again in close analog with poly(4-HBA) or poly(6-HNA), whiskers of poly(4'-HBA) adopt three orthorhombic phases and one hexagonal phase. Whereas both transitions between these three phases are reversible, the third phase transition around 580 °C involves an extremely rapid Fries rearrangement and is, thus, irreversible.

References and Notes

(1) Yamashita, Y.; Kato, Y.; Endo, S.; Kimura, K. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 687.
(2) Endo, S.; Kimura, K.; Ohta, T.; Kato, Y.; U.S. Pat. 4673724, 1987 (to Toyobo Co.); *Chem. Abstr.* **1987**, *105*, 227578e.
(3) Kricheldorf, H. R.; Schwarz, G.; Ruhser, F. *Macromolecules* **1991**, *24*, 3485.
(4) Taesler, C.; Petermann, J.; Kricheldorf, H. R.; Schwarz, G. *Makromol. Chem.* **1991**, *192*, 2255.
(5) Schwarz, G.; Kricheldorf, H. R. *Macromolecules* **1991**, *24*, 2829.
(6) Kimura, K.; Endo, S.; Kato, Y.; Yamashita, Y. *Polymer* **1993**, *34*, 1054.
(7) Kricheldorf, H. R.; Schwarz, G.; Adebahr, T. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34* (1), 768.
(8) Kricheldorf, H. R.; Schwarz, G.; Adebahr, T.; Wilson, D. J. *Macromolecules* **1993**, *26*, 6622.
(9) Kricheldorf, H. R.; Thomsen, S. A. *Macromolecules* **1993**, *26*, 6628.
(10) Kricheldorf, H. R.; Thomsen, S. A. *Makromol. Chem.* **1993**, *194*, 2063.
(11) Kricheldorf, H. R.; Adebahr, T. *J. Polym. Sci. Part A: Polym. Chem.*, in press; **1994**, 32, 159.
(12) Kricheldorf, H. R.; Ruhser, F.; Schwarz, G.; Adebahr, T. *Makromol. Chem.* **1991**, *192*, 2371.
(13) Schwarz, G.; Kricheldorf, H. R. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 717.
(14) Kricheldorf, H. R.; Ruhser, F.; Schwarz, G. *Macromolecules* **1991**, *24*, 4990.
(15) Liu, J.; Rybnikar, F.; East, A. J.; Geil, P. H. *J. Polym. Sci., Part B: Polym. Phys.* **1993**, *31*, 1923.
(16) Gray, G. W.; Hartley, G. B.; Jones, B. *J. Chem. Soc.* **1955**, 1412.
(17) Lieser, G.; Schwarz, G.; Kricheldorf, H. R. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1599.
(18) Economy, J.; Storm, R. S.; Matkovich, V. I.; Cottis, S. G.; Nowak, B. E. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2207.
(19) Liu, J.; Geil, P. *Polymer* **1993**, *34*, 1366.
(20) Taesler, C.; Petermann, J.; Kricheldorf, H. R.; Schwarz, G. *Makromol. Chem.* **1991**, *192*, 2255.
(21) Kricheldorf, H. R.; Adebahr, T. *High Perform. Polym.* in press.
(22) Lieser, G. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1611.
(23) Yoon, D. Y.; Masciocchi, N.; Depero, L. E.; Viweg, C.; Parresh, W. *Macromolecules* **1990**, *23*, 1793.
(24) Kricheldorf, H. R.; Schwarz, G. *Polymer* **1990**, *31*, 481.
(25) Thomsen, T.; Zachmann, H. G.; Kricheldorf, H. R. *J. Macromol. Sci., Phys.*
(26) Kalika, D. S.; Yoon, D. Y. *Macromolecules* **1991**, *24*, 3404.
(27) Economy, J.; Volksen, W.; Viney, C.; Geiss, R.; Siemens, R.; Karis, T. *Macromolecules* **1988**, *21*, 2777.
(28) Yoon, D. Y.; Masciocchi, N.; Depero, L. E.; Viney, Ch.; Parrish, W. *Macromolecules* **1990**, *23*, 1793.

MA946132S