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Whiskers: 13. Polyesters based on 4,4′-biphenyldiol and biphenyl-4,4′-dicarboxylic acid

Hans R. Kricheldorf*, Oliver Struve and Gert Schwarz
Institüt für Technische und Makromolekulare Chemie der Universität Hamburg, Bundesstrasse 45, D-20146 Hamburg, Germany
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Acetylated 4,4′-biphenydiol (ABD) and biphenyl-4,4′-dicarboxylic acid (BDCA) were polycondensed in inert aromatic reaction media at various temperatures and monomer concentrations. At temperatures ≤300°C oligoesters were obtained, which according to infra-red and ^{13}C nuclear magnetic resonance cross-polarization/magic-angle spinning spectroscopic characterization preferentially possess two carboxyl end-groups. Furthermore, polycondensations were conducted at 400°C whereby high-molecular-weight polyesters were obtained. Electron microscopy revealed the formation of lengthy crystallites, but true needle-like whiskers were never formed. Analogous polycondensations were conducted with acetylated hydroquinone and BDCA or with ABD in combination with terephthalic acid. Furthermore, all three polyesters were prepared by polycondensation of the free diphenols with terephthaloyl chloride or biphenyl-4,4′-dicarboxylic acid dichloride in Marlotherm-S at 400°C. Highly crystalline polyesters were obtained whenever the polycondensations were conducted at 400°C in Marlotherm-S, but in all cases the morphology was that of irregular particles. Wide-angle X-ray diffraction powder patterns measured with synchrotron radiation up to 440°C revealed that all three polyesters undergo a gradual transition from an orthorhombic crystal lattice to pseudo-hexagonal and finally to hexagonal chain packing with increasing temperature. These transitions cover a temperature range of more than 400°C. Only in the case of the polyester derived from hydroquinone and BDCA was a reversible first-order phase transition observed around 506°C. Copyright © 1996 Elservier Science Ltd.

(Keywords: polyesters; biphenyldiol; biphenyldicarboxylic acid; whiskers; phase transitions)

INTRODUCTION

Previous work of a Japanese research group[1-3] and of the present authors[4-10] has shown that a selected number of aromatic hydroxycarboxylic acids are capable of yielding polyesters in the form of whisker-like crystals. Whisker-like is here defined as a long crystal with length/diameter ratio above 10. In the ideal case such whiskers have a needle-like appearance and are single crystals. Although the whisker-forming hydroxycarboxylic acids can be polycondensed under a broad variety of reaction conditions, the crystal growth of whiskers requires carefully selected and optimized reaction conditions. Despite such optimized reaction conditions and selected chemical structures, we have not been able to prepare whiskers from diphenols and dicarboxylic acids (e.g. hydroquinone and terephthalic acid), as briefly reported in a previous paper[5]. Quite recently also the Japanese group have reported[11] on the synthesis and morphology of poly(hydroquinone terephthalate). Yet, despite favourable reaction conditions, whisker-like crystals were never obtained although the isomeric poly(4-hydroxybenzoate), poly(4-Hybe), yields whiskers[1,4,10].

The present work was aimed at studying the synthesis and morphology of polyesters derived from biphenyl-4,4′-dicarboxylic acid and 4,4′-biphenyldiol (structures **1**–**3**). The polyester **1** is an isomer of the polyester **4**, which has recently been demonstrated to form whiskers[8]. A question should be answered: Is the failure of poly(hydroquinone terephthalate) to yield whiskers a single case? The alternative hypothesis is the assumption that polyesters derived from A–A/B–B type monomers cannot form whiskers, in contrast to the isomeric polyesters derived from A–B type monomers.

EXPERIMENTAL

Materials

Biphenyl-4,4′-dicarboxylic acid and 4,4′-biphenyldiol were purchased from Aldrich Co. (Milwaukee, WI, USA) and used without additional purification. Hydroquinone and terephthalic acid were gifts of Bayer AG (Leverkusen, Germany). The diphenols were acetylated with an excess of acetic anhydride and a catalytic amount of pyridine in refluxing toluene and recrystallized from toluene/ligroin. Diphenyl ether was a gift of Bayer AG and purified by distillation. Marlotherm-S, a commercial solvent of Hüls AG (Marl, Germany), was used without additional purification.

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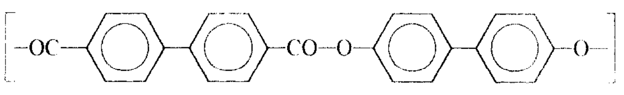
* To whom correspondence should be addressed



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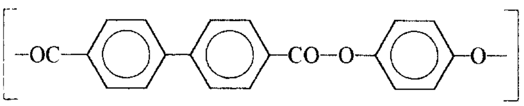

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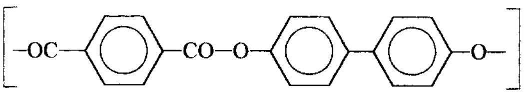

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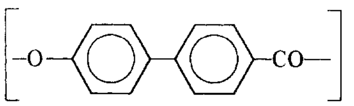

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Table 1 Polycondensations of acetylated 4,4′-biphenyldiol with biphenyl-4,4′-dicarboxylic acid or from biphenyldiol with biphenyl-4,4′-dicarbonyl dichloride in Marlotherm-S

Exp. No.	Method[a]	Conc. (mol l^{-1})	Temp. (°C)	Time (h)	Yield (%)	CO_2H end-groups[b] (i.r.)
1	A	0.01	350	10	43	+
2	A	0.01	400	8	30	−
3	A	0.02	400	8	51	−
4	A	0.05	400	8	58	+
5	A	0.10	400	8	72	+
6	B	0.01	400	8	90	−
7	C	0.01	400	8	50	−
8	C	0.05	400	8	90	−

[a] (A) Polycondensations of BDCA and ABD; (B) post-condensation of the oligoester obtain in experiment No. 5; (C) polycondensation of biphenyl-4,4′-dicarbonyl chloride and biphenyldiol

[b] The + means weak CO band at 1682 ± 2 cm^{-1}

The diphenols were acetylated with an excess of acetic anhydride and a catalytic amount of pyridine in refluxing toluene. For bis-1,4-bisacetoxybenzene a m.p. of 124–126°C was found (123–124°C in ref. 12), and for 4,4′-bisacetoxybiphenyl a m.p. of 158–160°C (159–160°C in ref. 13).

Polycondensations

(A) 'Acetate method' oligomerization. Biphenyl-4,4′-dicarboxylic acid (25 mmol) and acetylated 4,4′-biphenyldiol (25 mmol) were weighed into a 250 ml three-necked flask containing 100 ml of diphenyl ether or Marlotherm-S. The reaction vessel was placed into a preheated metal bath. The reaction mixture was rapidly heated (with stirring) to 260 or 300°C. The final temperature was then maintained for 2 or 6 h. After cooling, the reaction mixture was diluted with toluene, isolated by filtration, washed with toluene and acetone, and dried at 120°C *in vacuo.*

(B) 'Acetate method' polycondensations. Biphenyl-4,4′-dicarboxylic acid (1.25 mmol, or a larger amount) and acetylated 4,4′-biphenyldiol (1.25 mmol, or a larger amount) were weighed into a 500 ml three-necked round-bottomed flask containing Marlotherm-S (250 ml). The reaction vessel was placed into a metal bath preheated to 150°C. The reaction temperature was rapidly raised to 350 or 400°C. Stirring was stopped as soon as the monomers had dissolved. The final temperature was maintained for 8 h and the liberated acetic acid was removed by a slow stream of nitrogen. After cooling, the precipitated polyesters were worked up as described above.

(C) 'HCl method'. Hydroquinone (12.5 mmol) and biphenyl-4,4′-dicarbonyl dichloride (12.5 mmol) were weighed into a 500 ml three-necked flask containing Marlotherm-S (250 ml) and polycondensed as described above. In further polycondensations the concentrations of both monomers were lowered (see *Table 4*). The polyesters **1** and **3** were prepared analogously (see *Tables 1* and *5*).

Measurements

The i.r. spectra were recorded from KBr pellets with a Nicolet-SXB-20 *FT*-n.m.r. spectrometer.

The 75.4 MHz ^{13}C n.m.r. cross-polarization/magic-angle spinning (CP/MAS) spectra were recorded on a Bruker MSL-300 *FT* spectrometer using double-bearing ZrO_2 rotors. A contact time of 1 ms, a repetition time of 4 s and a spinning rate of 4 kHz were used in all cases.

The d.s.c. measurements were conducted with a Perkin Elmer DSC-4 in aluminium pans under nitrogen.

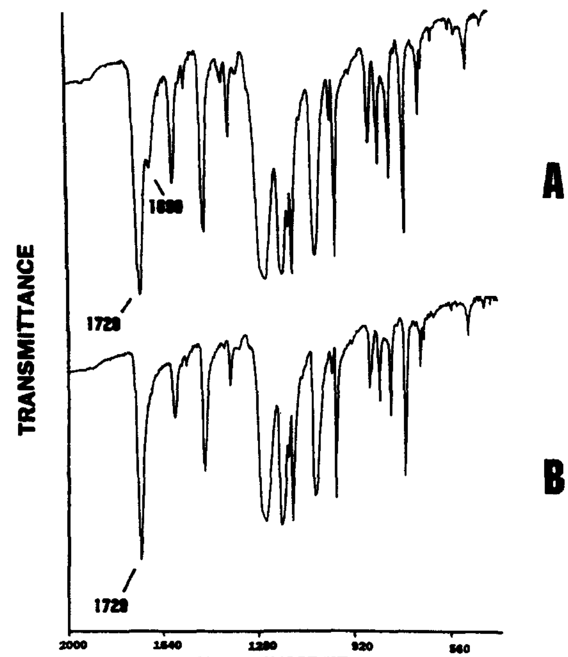


Figure 1 I.r. spectra (KBr pellets) of: (A) polyester **1** prepared at 400°C with a 0.1 M monomer solution (No. 5, *Table 1*); (B) **1** prepared at 400°C with a 0.01 M monomer solution

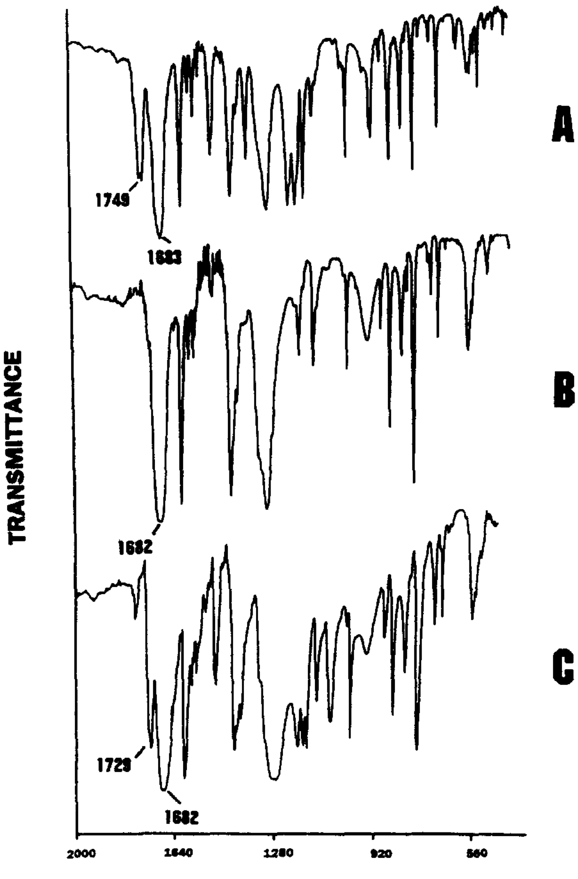


Figure 2 I.r. spectra (KBr pellets) of: (A) 1 : 1 mixture of the monomers ABD and BDCA; (B) product isolated after 6 h at 260°C (No. 1, *Table 2*); (C) this product heated for 4 h to 400°C (No. 3, *Table 2*)

The X-ray measurements were conducted with synchrotron radiation at $\lambda = 1.54\,\text{Å}$ at HASYLAB, DESY (Hamburg). A vacuum oven with a heating rate of 10°C min^{-1} and a position-sensitive one-dimensional detector were used.

RESULTS AND DISCUSSION

Syntheses and morphology of polyester 1

Most samples of oligo- and polyester **1** were prepared by polycondensation of acetylated 4,4′-biphenyldiol (ABD) and biphenyl-4,4′-dicarboxylic acid (BDCA) in an inert aromatic reaction medium. Polycondensations in bulk were not conducted, because the melting temperatures of polyester **1** (and also **2** and **3**) is too high (>500°C), and because previous studies of other aromatic polyesters have demonstrated that polycondensations in inert organic reaction media at low monomer concentrations offer the best chance to obtain whiskers.

A first series of polycondensations was conducted in such a way that a 1 : 1 (molar) mixture of both monomers was dissolved in hot Marlotherm-S and rapidly heated to the final temperature of 350 or 400°C, which was maintained for 8 or 10 h (*Table 1*). The highly crystalline polyester precipitated from the reaction mixture was isolated by filtration after cooling.

Previous polycondensations of acetylated 4-hydroxybenzoic acid or 4′-hydroxybiphenylcarboxylic acid have demonstrated that low monomer concentrations and high reaction temperatures favour the formation of whiskers[8,14]. Reaction temperatures above 400°C cannot be maintained for several hours with commercial organic solvents. The low concentrations are, of course, unfavourable from the preparative point of view, because both the yields relative to the monomers and the yields relative to the volume of the reaction mixture decrease. Furthermore, low concentrations reduce the reaction rate. Thus, it was not surprising that an attempt to produce polyester **1** at a monomer concentration of 0.002 mol l^{-1} (not listed in *Table 1*) failed. In other words the polycondensations Nos. 2 and 6 of *Table 1* represent the optimum for the synthesis of whisker-like polyester **1**.

Since the polyesters **1**, **2** and **3** are insoluble in all common solvents, only a few methods are available for their characterization. However, *FT*i.r. spectra (*Figures 1–3*) and to a minor extent ^{13}C n.m.r. CP/MAS spectra (*Figure 4*) allowed the detection of carboxyl and acetate end-groups. The 'CO band' of the CO_2H groups appears at 1680–1690 cm^{-1}, and is thus well separated from the 'ester CO band' at 1730 cm^{-1}. Furthermore, the absorption coefficient of the 'CO_2H band' is higher than that of the ester CO band, so that small quantities of CO_2H end-groups are detectable. When the polycondensation was conducted at 350°C (No. 1, *Table 1*) the resulting polyester still contained a small, but detectable, quantity of carboxyl groups. No end-groups were detected when the polycondensations were conducted at 400°C with low monomer concentrations (Nos. 2 and 3), whereas higher concentrations again yielded oligoesters (*Figure 1*). The variation of the concentration also had a strong influence on the morphology. As illustrated by the SEM micrographs of *Figure 5*, the highest concentration (No. 5) and the lower temperature (No. 1) yielded irregular particles.

The lower monomer concentrations favoured at 400°C the formation of lengthy particles and short columns, but needle-like whiskers were never obtained.

Based on a positive experience with polycondensations of 4-acetoxybenzoic acid[14], a second approach was launched to synthesize whiskers of polyester **1**. This approach is characterized by the synthesis of oligoesters at lower reaction temperatures (260 or 300°C, see *Table 2*) followed by a post-condensation of the isolated oligoesters at 350–400°C. However, this approach failed completely, because high-molecular-weight samples and whisker-like morphologies were never obtained.

The i.r. spectra of *Figures 2* and *3* provide a hypothetical explanation. As confirmed by the ^{13}C n.m.r. spectra (*Figure 4*), the i.r. spectra allow an identification of acetate end-groups (1750 cm^{-1}, *Figures 2A* and *3A*), carboxyl end-groups (1680–1685 cm^{-1}) and aromatic ester groups (1730 ± 2 cm^{-1}). The i.r. spectra of *Figures 2* and *3* suggest that the products isolated from the polycondensations at 260 and 300°C mainly consist of oligoesters containing two carboxyl groups and unreacted BDCA. This interpretation is supported by the following consideration. All polycondensations of acetylated diphenols and dicarboxylic acids yield automatically mixtures of oligoesters or polyesters with three

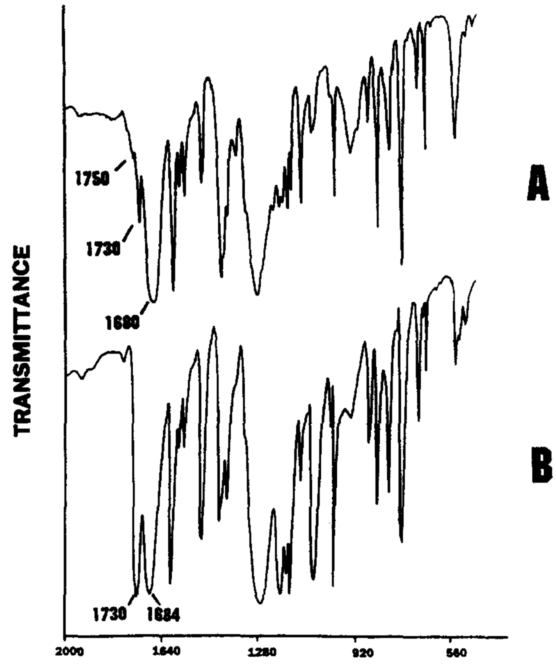


Figure 3 I.r. spectra (KBr pellets) of: (A) oligoesters isolated after 6 h/300°C (No. 2, *Table 2*); (B) polyester obtained from these oligoesters after 4 h/400°C (No. 4, *Table 2*)

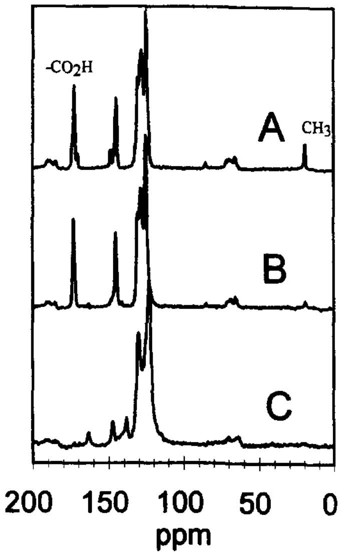


Figure 4 The 75.4 MHz ^{13}C n.m.r. CP/MAS spectra of: (A) 1 : 1 monomer mixture; (B) oligoesters prepared at 300°C (No. 2, *Table 2*); (C) polyester **1** (No. 2, *Table 1*)

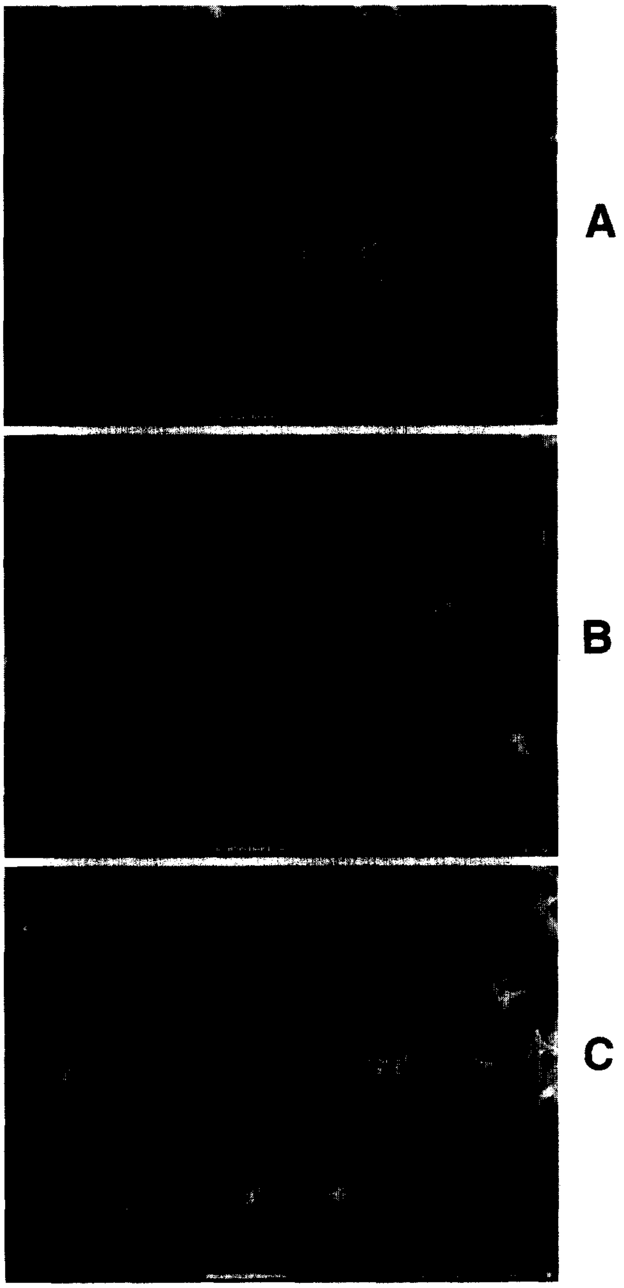


Figure 5 SEM micrographs of polyester **1** prepared from monomers ABD and BDCA at 400°C: (A) conc. 0.1 M; (B) conc. 0.05 M; (C) conc. 0.02 M

Table 2 Syntheses and post-polycondensation of oligoesters from acetylated 4,4′-biphenyldiol and biphenyl-4,4′-dicarboxylic acid

Exp. No.	Method[a]	Conc. ($mol\,l^{-1}$)	Temp. (°C)	Time (h)	Yield (%)	CO_2H end-groups[b] (i.r.)
1	A[c]	0.2	260	2	60	++
2	A	0.2	300	6	58	++
3	B[d]	0.05	400	4	25	+
4	B[e]	0.01	350	8	70	+
5	B[e]	0.05	400	8	38	+

[a] Marlotherm-S served as reaction medium (with exception of experiment No. 1). (A) Direct polycondensation of BDCA and ABD; (B) post-treatment of the oligoesters prepared according to (A)

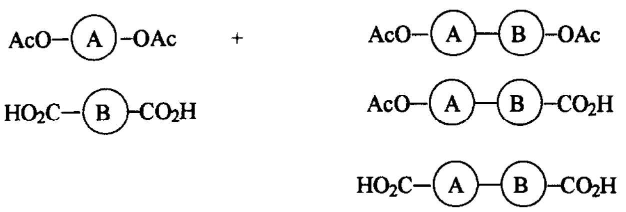
[b] The + or ++ mean weak or strong CO band at 1682 ± 2 cm^{-1}

[c] Diphenyl ether served as reaction medium

[d] The oligoesters of experiment No. 1 served as starting material

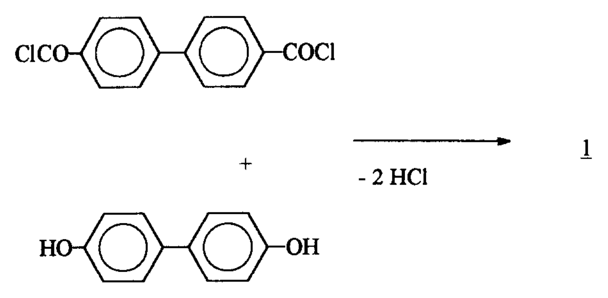
[e] The oligoesters of experiment No. 2 served as starting material

different combinations of end-groups:



It is well known that aromatic dicarboxylic acids are almost insoluble in all inert organic solvents even at higher temperatures. In contrast, acetylated diphenols are soluble in numerous aromatic (and other) solvents. Therefore, oligoesters containing two carboxyl end-groups will preferentially precipitate from any reaction mixture. In consequence the balance of acetate and carboxyl groups is far from unity and the post-condensation at higher temperatures cannot bring much success regardless of the reaction conditions (*Figures 2* and *3*). The situation is completely different in the case of A–B type monomers such as 4-acetoxybenzoic acid, because the oligomers crystallizing from the reaction mixture contain automatically an ideal balance of both end-groups. Thus, the chain growth can continue up to high molecular weights, regardless of whether a liquid reaction medium is present or not[15].

The predominance of carboxyl groups in the precipitated oligoesters not only explains the failure of the two-step approach (*Table 2*), it also explains why it is relatively difficult to obtain high molecular weights by the one-step approach (*Table 1*). Once the precipitation of oligoesters has started, further chain growth can only proceed by the reaction of dissolved diphenol acetates (or acetate-terminated oligoesters) and carboxyl end-groups on the surface of the crystallized oligoesters. In the case of 4-acetoxybenzoic acid and related monomers, chain growth can continue even in the solid state at the interface between crystalline lamellae[15].



Scheme 1

Finally, a third synthetic approach was investigated. This approach consists of the polycondensation of 4,4′-biphenyldiol, with biphenyl-4,4′-dicarbonyl dichloride (HCl method) (*Scheme 1*). Both polycondensations conducted in this way (Nos. 7 and 8, *Table 1*) gave acceptable yields. However, the SEM micrographs revealed particles of irregular shape and no whiskers.

Polyesters 2 and 3

The polycondensations of acetylated hydroquinone and BDCA were conducted like the syntheses of polyester **1** (*Table 3*). Not surprisingly, analogous results were obtained. The *FT*i.r. spectra revealed the presence of CO_2H end-groups in all products. Even under the optimum reaction conditions a polyester with a detectable amount of carboxyl groups was isolated. Nonetheless, the polyesters resulting from monomer concentrations ≤0.05 formed columnar particles (*Figure 6*). However, true whiskers were never observed.

Furthermore, the HCl method was used based on polycondensations of free hydroquinone and the dichloride of BDCA. The reaction conditions and yields of polyester **2** prepared in this way are listed in *Table 4*. From the analytical point of view this approach has the disadvantage that the identification of end-groups by i.r. spectroscopy or ^{13}C n.m.r. CP/MAS spectroscopy is almost impossible. Therefore, only the morphologies of all samples were investigated. Unfortunately particles of irregular shape (quite analogous to those of *Figure 5A*) were found in all cases. In other words the HCl method again proved to be useless for the preparation of whiskers.

The syntheses of polyester **3** were conducted analogously to those of **1** and **2** (*Table 5*). When the acetate method was used, the i.r. spectra revealed high concentrations of carboxyl end-groups for reaction temperatures ≤300°C. However, most polyesters prepared at 400°C did not contain detectable amounts of CO_2H groups, and thus their molecular weights should be higher than those of polyesters **2**. Despite this advantage the morphological studies were disappointing. Irregular particles were found in all cases. Even the columnar

Table 3 Polycondensations of acetylated hydroquinone with biphenyl-4,4′-dicarboxylic acid

Exp. No.	Method[a]	Conc. (mol l^{-1})	Temp. (°C)	Time (h)	Yield (%)	CO$_2$H end-groups[b] (i.r.)
1	A	0.2	260	2	63	++
2	A	0.2	260	6	73	++
3	B	0.05	400	4	30	+
4	C	0.2	300	6	68	++
5	C	0.01	400	8	25	+
6	C	0.02	400	8	56	+
7	C	0.05	400	8	80	−

[a] (A) Polycondensation of BDCA and ABD in diphenyl ether; (B) postcondensation of the oligoesters from experiment No. 2 in Marlotherm-S; (C) polycondensation of the equimolar monomer mixture in Marlotherm-S

[b] The + or ++ mean weak or strong CO band at 1682 ± 2 cm^{-1}

Table 4 Polycondensations of hydroquinone and biphenyl-4,4′-dicarboxylic acid dichloride in Marlotherm-S

Exp. No.	Conc. (mol l^{-1})	Temp. (°C)	Time (h)	Yield (%)
1	0.02	350	8	53
2	0.05	350	8	70
3	0.10	350	8	61
4	0.05	400	7	60
5	0.10	400	7	85

particles typical for the best samples of polyesters **1** and **2** were never observed. Also the HCl method (experiment Nos. 9 and 10, *Table 5*) did not yield whiskers. Thus, all attempts to synthesize needle-like whiskers of polyesters **1**, **2** and **3** were finally without success. In this connection it should be mentioned again that a fourth unsuccessful approach was used by Japanese colleagues for the synthesis of poly(hydroquinone terephthalate)[11]. Considering all these negative results, it seems that polyesters derived from A–A/B–B monomers are unsuited for the formation of whiskers. The unfavourable balance of reactive end-groups is certainly one factor contributing to this negative picture, but this factor is less pronounced in the case of the HCl method, and it was not operating in the experiments of the Japanese group, and thus it cannot be the only reason. In other words, the factors contributing to a successful synthesis of whisker-like polyester crystals are not well understood yet.

Chain packing and phase transitions

For poly(4-Hybe) and polyester **4** the chain packing at room temperature has been reported. When the direction of the chain axis is labelled c as usual, an orthorhombic unit cell with $a = 7.5$ Å and $b = 5.7$ Å was found in both cases. The values in the c direction are, of course, different, with $c = 12.5$ Å for a dimeric repeat unit in the case of poly(4-Hybe) and $c = 10.9$ Å for a monomeric

Figure 6 SEM micrograph of polyester **2** prepared from acetylated hydroquinone and biphenyl-4,4′-dicarboxylic acid (conc. 0.05 M) at 400°C/8 h

Table 5 Syntheses of polyester from acetylated 4,4′-biphenyldiol and terephthalic acid or from biphenyldiol and terephthaloyl chloride

Exp. No.	Method[a]	Conc. (mol l^{-1})	Temp. (°C)	Time (h)	Yield (%)	CO$_2$H end-groups[b] (i.r.)
1	A	0.2	260	2	50	++
2	A	0.2	260	6	81	++
3	B	0.05	400	4	79	+
4	C	0.2	300	6	87	++
5	C	0.01	400	8	0	−
6	C	0.02	400	8	60	−
7	C	0.05	400	8	62	−
8	C	0.10	400	8	78	−
9	D	0.01	400	8	56	−
10	D	0.05	400	8	88	−

[a] (A) Polycondensation of BDCA and ABD in diphenyl ether; (B) postcondensation of the oligoesters from experiment No. 2 in Marlotherm-S; (C) polycondensations of BDCA and ABD in Marlotherm-S; (D) polycondensation of biphenyldiol and terephthaloyl chloride in Marlotherm-S

[b] The + or ++ mean weak or strong CO band at 1682 ± 2 cm^{-1}

repeat unit in the case of **4**. For poly(hydroquinone terephthalate) a similar but slightly monoclinic unit cell has been described with $a = 7.98$ Å, $b = 5.33$ Å, $c = 12.65$ Å and a tilt angle (β) of 98.98° instead of the 90° typical for an orthorhombic cell[16].

On the basis of these known data, the WAXS reflections of polyester **1** (*Figure 7B*) were interpreted in terms of an orthorhombic unit cell with $a = 7.83$ Å, $b = 5.50$ Å and $c = 20.66$ Å (see footnote of *Table 6*). The reflections calculated for this unit cell and the experimental values taken from the powder pattern of *Figure 7B* are listed in *Table 6*. The excellent agreement suggests that the assumption of the mentioned orthorhombic elementary cell is correct. In the same way, an orthorhombic cell with $a = 7.20$ Å and $b = 5.23$ Å was found for polyester **3**. For reasons discussed below, the number of sharp reflections was too small in the case of polyester **2** to allow a calculation of the unit cell.

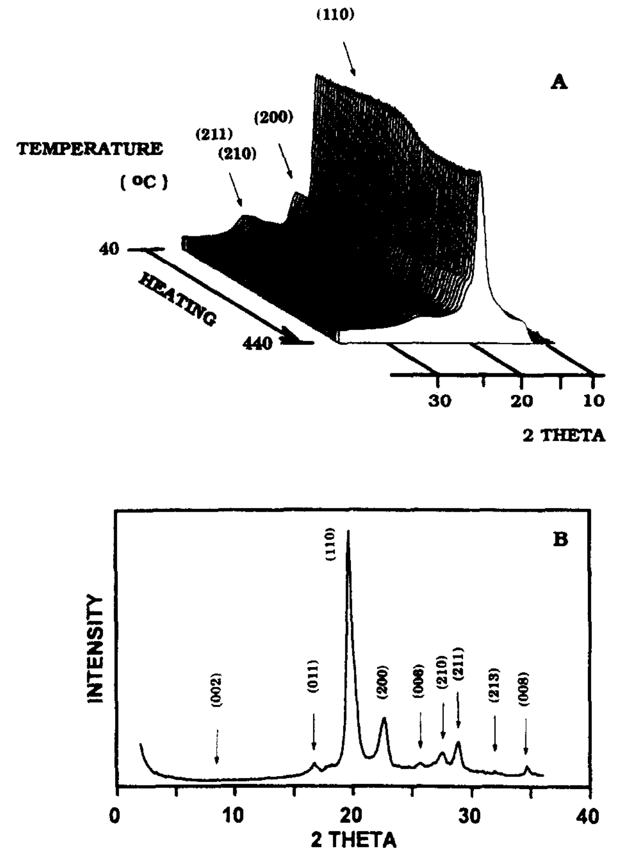


Figure 7 WAXD powder patterns of polyester **1**: (A) recorded with synchrotron radiation at a heating rate of 10°C min^{-1}; (B) recorded at 25°C with Cu Kα radiation

Table 6 Calculated and experimental WAXS reflections of polyester **1** at room temperature[a]

	Calculated		Observed	
Reflection indices	2θ (deg)	d (Å)	2θ (deg)	d (Å)
002	8.55	10.35	8.5	10.39
011	16.68	5.31	16.8	5.27
006	25.87	3.44	25.7	3.46
008	34.73	2.58	34.7	2.58
110	19.70	4.50	19.7	4.50
200	22.72	3.91	22.7	3.91
210	27.94	3.19	27.5	3.24
211	28.30	3.15	28.9	3.09
213	30.90	2.89	31.9	2.80

[a] Assuming an orthorhombic unit cell with $a = 7.83$ Å, $b = 5.50$ Å and $c = 20.66$ Å, $T_{ab} = 43.1$ Å^2 and $V_E = 890$ Å^3

The most interesting aspect of the chain packing of the so-called rigid-rod polyesters is a dependence on thermal energy. In the case of poly(4-Hybe), polyester **4** and poly(6-hydroxynaphthalene-2-carboxylate) two reversible first-order phase transitions occur upon heating and cooling. Depending on the chemical structure and on the perfection of the crystallites, the first phase transition occurs at a temperature of 300–350°C. Above this temperature range another orthorhombic crystal lattice is formed with greater lateral dimensions but identical c distances. This expansion in the ab plane results mainly from the flip motions and librations of the phenylene rings around their *para* axis[17]. The expanded crystal lattice can accommodate motions with a greater amplitude and higher frequency. The second phase transition occurs between 400 and 450°C, and produces a hexagonal chain packing in the case of poly(4-Hybe) and polyester **4**. The lateral distances of poly(2,6-hydroxynaphthoic acid) are disordered and a perfect hexagonal order is not formed, but all three polyesters have in common that a layer structure exists above 400°C. This smectic-B-like chain packing mainly results from full rotations of the phenyl rings and flip motions of the ester groups. When the crystallites are rather perfect, as is typical for most whisker-like single crystals, both phase transitions occur in a narrow temperature range (typically around 10°C). These phase transitions are detectable by endotherms or exotherms in the d.s.c. heating or cooling curves.

The WAXS powder patterns of polyester **3** prove (*Figure 8*) that here in principle the same sort of thermal

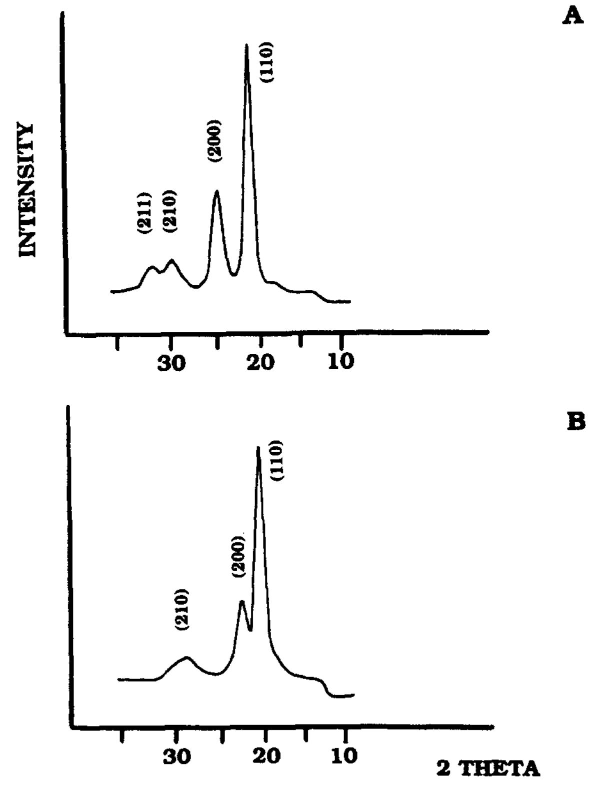


Figure 8 WAXD powder patterns of polyester **3** recorded with synchrotron radiation: (A) 40°C; (B) 440°C

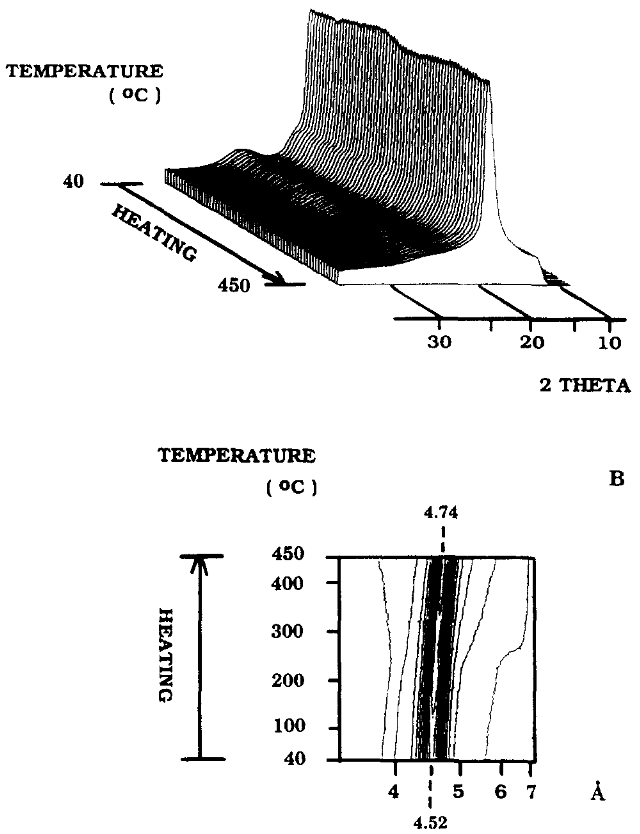


Figure 9 WAXD powder patterns of polyester **2** recorded with synchrotron radiation

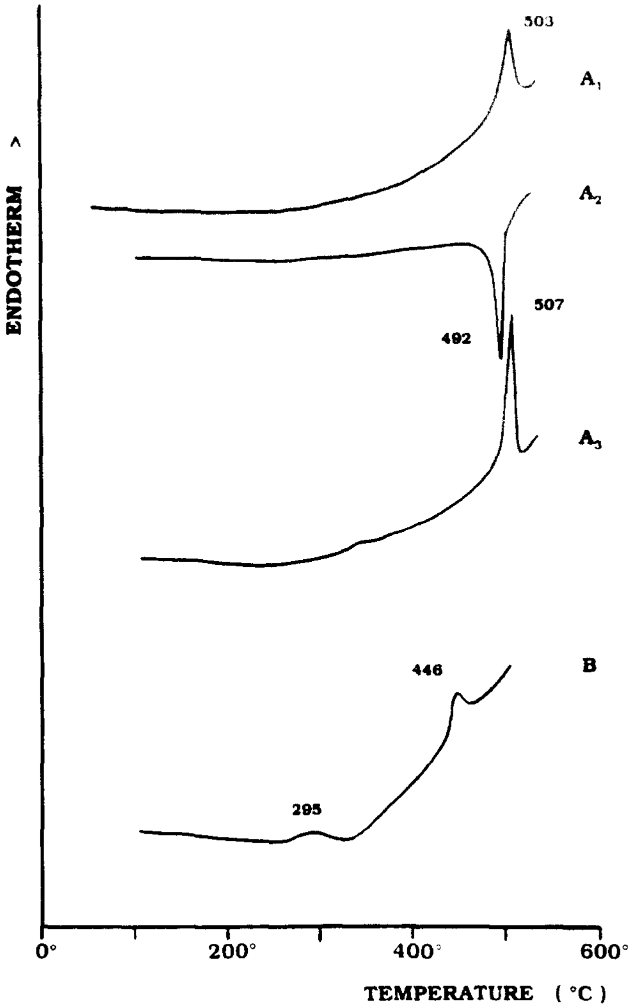


Figure 10 D.s.c. measurements (heating and cooling rate 20°C min^{-1}): (A_1) polyester **3**, first heating; (A_2) polyester **3**, first cooling; (A_3) polyester **3**, second heating; (B) polyester **1** (No. 2, *Table 1*), first heating

phase transition is going on. However, the well defined orthorhombic crystal lattice existing at room temperature is rather stable and its transition to a hexagonal phase is still far from complete at 440°C. All three polyesters (**1**, **2** and **3**) have in common that the thermal change of chain packing takes in principle the same course, which is characterized by volume expansion and by the formation of hexagonal chain packing. The expansion in the *ab* plane is evident from a comparison of the 110 and 200 reflections at 40 and 440°C (*Figure 8*, polyester **3**) and is best illustrated by the contour map of *Figure 9B* for polyester **2**. At this time no explanation can be offered as to why the course of the thermal phase transitions is so different for polyesters **1**, **2** and **3**, on the one hand, and poly(4-Hybe) or polyester **4**, on the other. The thermodynamical background is the same. An unfreezing and intensification of motions require more space. Finally, the full rotation of the phenylene rings gives each polyester chain a columnar shape, which in turn favours a hexagonal chain packing.

At this point it is important to emphasize that those polyester samples prepared by the HCl method at 400°C yielded the same WAXS powder patterns as the samples prepared by the acetate method. This means that the crystal modifications discussed above are independent of the method used for their synthesis. This is a strong indication that the crystal modifications and phase transitions discussed above are thermodynamically controlled properties of the polyesters, in contrast to the morphology.

Finally, the d.s.c. measurements need to be discussed. In the case of polyester **1** samples obtained by the acetate method (e.g. No. 5, *Table 1*), the first heating trace displays two weak endotherms (*Figure 10*, curve B). The first endotherm, which appears around 295°C, is flat and barely detectable without considerable expansion of the amplitude. This endotherm does not appear in the d.s.c. traces of the samples prepared by the HCl method. Since the molecular weights are not high and the end-groups are different, 100% identity of both series of samples cannot be expected. More interesting is the endotherm around 445°C, which shows up in the first heating curves of all samples regardless of the synthetic method. No exotherm appears in the cooling trace and this endotherm is also absent in the second and third heating curves. Unfortunately, the synchrotron radiation measurements needed to be stopped for technical reasons at 440°C, and thus no interpretation of this irreversible event can be given at this time. However, it should be emphasized that heating of polyester **1** up to 500°C in the d.s.c. apparatus does not cause a detectable thermal degradation as evidenced by i.r. spectra recorded before and after the d.s.c. measurements.

In the d.s.c. heating curves of polyester **3** a strong endotherm was observable at around 508°C regardless of the method used for the synthesis of the samples. Furthermore, the corresponding exotherm was detectable in the cooling trace and the endotherm was

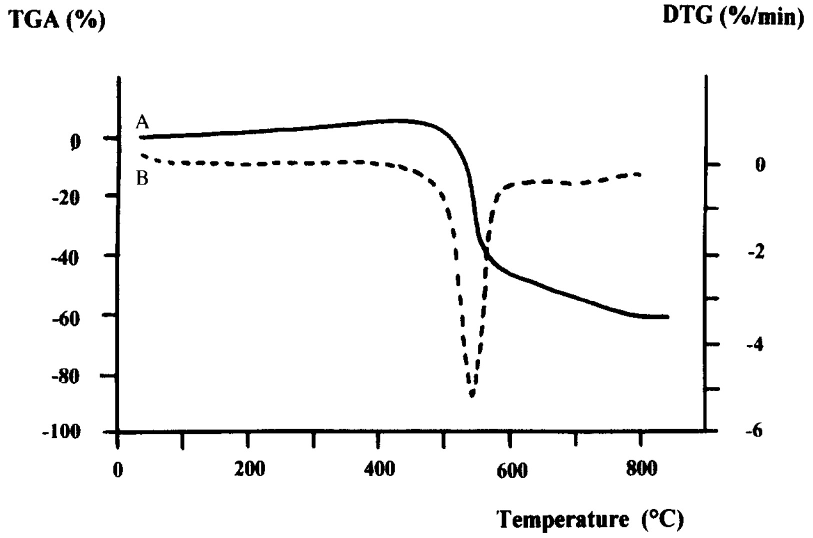


Figure 11 Thermogravimetric analysis (A) and differential thermal analysis (B) of polyester No. 7, *Table 1*, conducted at a heating rate of 10°C min^{-1} under nitrogen

reproducible in the second heating curve (*Figure 10*, curves A_1–A_3). Considering the information extracted from the synchrotron radiation measurement, it is obvious to assume that this polyester undergoes a sharp reversible transition to a hexagonal rotatory phase in analogy to poly(4-hydroxybenzoate)[9] and polyester **4**[8]. No endotherm or exotherm was detectable in the d.s.c. traces of polyester **2** below 550°C in agreement with the synchrotron radiation measurements.

Finally, it should be mentioned that the d.s.c. heating traces of all three polyesters show a strong endotherm between 560 and 600°C, which represents the combined melting and degradation process. In order to obtain more information on the thermostability of the polyesters **1**–**3**, they were subjected to thermogravimetric analyses under nitrogen. As an example representative for all these measurements, the t.g.a. (and d.t.g.) curve of polyester **1** (No. 7, *Table 1*) is displayed in *Figure 11*. The sample prepared by the acetate method under the same reaction conditions (No. 2, *Table 1*) gave an almost identical t.g.a. curve. Characteristic in all cases was the evolution of CO and CO_2 as detected by on-line mass spectroscopy and the formation of a residue with ~ 50% of the original weight. This black residue is not charcoal but an insoluble, presumably crosslinked, material with a well defined i.r. spectrum (*Figure 12*). The i.r. spectra demonstrated that at temperatures above 570°C the ester group disappears in a few minutes, whereas a new type of carbonyl group is formed. The CO band at 1663 cm^{-1} suggests that a Fries rearrangement yielding benzophenone units took place. The same spectroscopic observations were made for the polyesters **2**–**4**[8] and for poly(4-Hybe)[18].

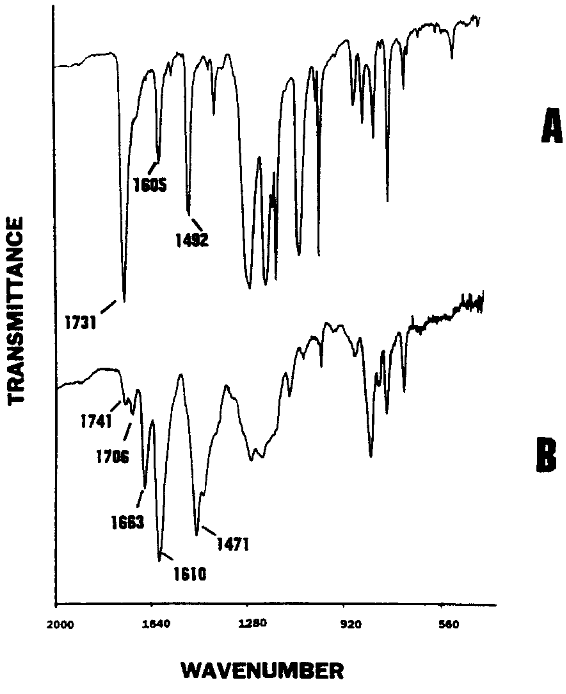


Figure 12 I.r. spectra of polyester **1** (KBr pellets): (A) original sample No. 2, *Table 1*; (B) the same sample after heating to 590°C in aluminium pans under nitrogen at a heating rate of 20°C min^{-1} (followed by quenching)

CONCLUSION

Although three more or less different synthetic methods were used, all attempts to prepare needle-like crystals of polyesters derived from biphenyldiol and biphenyl-4,4′-dicarboxylic acid were unsuccessful. Long particles with an aspect ratio of 5/1 were the optimum result. However, X-ray measurements with synchrotron radiation up to 440°C and d.s.c. measurements gave an interesting (although not perfect) insight into the chain packing and phase transitions of the three polyesters **1**, **2** and **3**. All three polyesters undergo a gradual transition from an orthorhombic crystal lattice in the direction of a smectic-B-like hexagonal chain packing over a temperature range of 500°C. This gradual change of chain packing is particularly slow in the case of polyester **3** and an additional sharp and reversible phase transition occurs at 505–510°C. All three polyesters undergo a rapid change of their chemical structure above 570°C mainly due to a Fries rearrangement.

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