

New polymer syntheses:

10. Syntheses of high molecular weight poly(4-hydroxybenzoate)s by bulk condensations of 4-hydroxybenzoic acids

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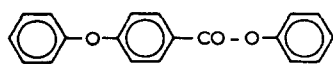
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The condensation of 4-hydroxybenzoic acid by means of various carboxylic acid anhydrides, acid chlorides and diphenylcarbonate has been investigated. All condensations were conducted in 'one-pot procedures'. The average degrees of polymerization (\overline{DP}) were determined by means of ^1H nuclear magnetic resonance (n.m.r.) spectroscopic end-group analyses. The bulk condensation of 4-hydroxybenzoic acid by means of acetic anhydride at temperatures between 320° and 350°C was found to be the simplest and least expensive procedure. Yields between 97 and 99% and \overline{DP} up to 300 were obtained in this way. Bulk condensations of purified acetoxybenzoic acid or condensations of 4-hydroxybenzoic acid with acetic anhydride in an inert solvent gave similar yields and \overline{DP} . Also, the bulk condensations of 3,5-dimethyl-4-hydroxybenzoic acid, 3-methoxy-4-hydroxybenzoic acid, 3-chloro-4-hydroxybenzoic acid, 3,5-dichloro-4-hydroxybenzoic acid and 3,5-dibromo-4-hydroxybenzoic acid by means of acetic anhydride gave yields above 90%. However, the \overline{DP} 's varied greatly with the nature of the substituents. 'One-pot procedures' using a variety of phosphorus derivatives as condensing reagents did not yield pure polyesters. The differential scanning calorimetry (d.s.c.) curves of the substituted poly(4-hydroxybenzoate)s do not show any endotherm, although X-ray diffraction measurements indicate a high degree of crystallinity. The thermogravimetric analyses demonstrate that the thermal stability depends largely on the synthetic procedure.

Keywords Polycondensation; nuclear magnetic resonance end-group analysis; crystallinity; thermal stability; poly(4-hydroxybenzoate); poly(chloro-4-hydroxybenzoate)s

INTRODUCTION

Since the work of Economy¹⁻⁵, poly(*p*-hydroxybenzoate) ((4-Hybe)_n) and copolyesters containing large amounts of 4-hydroxybenzoic acid⁵ have been the subject of much scientific and industrial interest. Although (4-Hybe)_n is difficult to process, it may be useful as a starting material for transesterification with other polyesters and as reinforcing filler for other polymers. Whatever its final application, an inexpensive procedure for its synthesis is desirable. One of the oldest methods reported in the literature for the preparation of (4-Hybe)_n is the thermal condensation of 4-acetoxybenzoic acid⁶⁻⁸. However, Economy was able to demonstrate that this method leads to partial decarboxylation and etherification, and the side product (I) was isolated. Because of these side reactions the condensation of acetoxybenzoic acid, and in particular the bulk condensation, was not considered to be a useful preparative method, and the condensation of 4-hydroxybenzoic acid phenyl ester in a liquid reaction medium at 300°-320°C was patented and used for technical applications¹⁻⁵.



(I)

Since this condensation method requires synthesis and purification of a monomer along with heating and purification of a suitable reaction medium, it is certainly not an attractive procedure for the inexpensive preparation of large quantities of (4-Hybe)_n. In our previously published study⁹ on the synthesis of (4-Hybe)_n from a variety of monomers we have found that the reaction mechanism is quite different from that proposed by Economy *et al.*¹. The conversion of the monomers leads to crystalline oligomers of \overline{DP} 's 6-10 and further chain growth takes place mainly in the solid state, involving the surfaces of the oligomer lamellae. Such chain growth is rather independent of the nature of the monomer but requires reaction temperatures >260°C. This finding prompted us to reinvestigate the thermal condensation — and in particular the bulk condensation — of 4-acetoxybenzoic acid. Furthermore, we intended to reinvestigate several 'one-pot procedures' described in the literature¹⁰⁻¹⁴ and to compare the results.

EXPERIMENTAL

Materials

4-Hydroxybenzoic acid was a gift from Bayer AG

(Leverkusen, FRG) and 3,5-dimethyl-4-hydroxybenzoic acid a gift from Dynamit Nobel AG (Troisdorf, FRG). They were both used without further purification. 4-Hydroxy-3-methoxybenzoic acid was purchased from EGA Chemie (Stinheim, FRG). Chloro-4-hydroxybenzoic acid was prepared¹⁵ by chlorination of 4-hydroxybenzoic acid by means of HCl/H₂O₂, whereas 3,5-dichloro- and 3,5-dibromo-4-hydroxybenzoic acid were prepared by halogenation with chlorine or bromine in acetic acid. These monomers were recrystallized two or three times until relatively sharp melting points were obtained. Marlotherm-S, a mixture of isomeric dibenzyl benzenes, was a gift from BASF AG (Ludwigshafen, FRG).

4-Acyloxybenzoic acids. 4-Hydroxybenzoic acid was heated with ~20% molar excess of acetic anhydride, propionic or hexanoic acid anhydride in boiling toluene for 2 h. The resulting acyloxybenzoic acids were crystallized from the concentrated reaction mixture by portionwise addition of ligroin. They were recrystallized twice.

Polycondensations

4-Acyloxybenzoic acids (Table 1). 0.1 mol of a 4-acyloxybenzoic acid was heated in a glass flask under a slow stream of nitrogen to 260°C whereby the monomers began to reflux. In the course of 30 min the reaction mixture began to solidify. The reaction temperature was then maintained for 15 h or raised to 320°C (350°C). After cooling the polymer was powdered, refluxed with acetone for 30 min, filtered off and dried at 80°C/12 mbar.

4-Hydroxybenzoic acid with various anhydrides and acid chlorides (Table 2). (0.2 mol of 4-hydroxybenzoic acid and 0.24 mol acetic anhydride (or another acid anhydride and acid chloride respectively) were heated to 180°C. This temperature was maintained for 30 min, and most of the acetic acid was removed with a slow stream of nitrogen. Then the reaction temperature was raised to its final value. At temperatures >260°C the reaction mixture solidified within 30 min, whereas several hours were required at 220°C. In the case of high-boiling reaction products, such as hexanoic acid or phenol, a vacuum of 12

Table 1 Bulk condensation of various 4-acyloxybenzoic acids

No.	Monomer	Temp. (°C)	Time (h)	Yield ^a (%)	\overline{DP}	\overline{M}_n	Elemental analyses ^b	
							C	H
1	4-Acetoxybenzoic acid, recryst.	260	16	80.5	90	10 800	Found 70.41	3.68
2	recryst.	260/320	0.5/15.0	87.9	260	31 200	Found 70.27	3.59
3	recryst.	260/350	0.5/15.0	89.9	500	60 000	Found 70.19	3.30
4	4-Propyloxybenzoic acid, recryst.	260	16	100.0	27	3200	Found 69.12	3.54
5	4-Hexanolyoxybenzoic acid, recryst.	260	16	67.9	17.0	2030	Found 69.79	3.74

^a After washing with boiling acetone

^b Calculated: C, 70.00; H, 3.36

Table 2 Reaction conditions and results of bulk condensations of 4-hydroxybenzoic acid by means of various anhydrides and acid chlorides

No.	Condensing reagent (20% molar excess)	Temp. (°C)	Time (h)	Yield ^a (%)	\overline{DP}	\overline{M}_n
1	Acetic anhydride	180/200	1.5/16	0	—	—
2	Acetic anhydride ^b	180/200	1.5/16	99	10	1200
3	Acetic anhydride	180/220	1.5/16	84	6.7	800
4	Acetic anhydride ^b	180/220	1.5/16	101	16.5	2000
5	Acetic anhydride	180/260	1.5/16	101	17.0	2000
6	Acetic anhydride	180/320	1.5/3	99	31.0	3750
7	Acetic anhydride ^c	180/320	1.5/3	100	39.0	4650
8	Acetic anhydride ^b	180/320	1.5/16	97	250	30 000
9	Acetic anhydride	180/320	1.5/16	93	87	10 500
10	Acetic anhydride	180/350	1.5/16	98	300	36 000
11	Propionic acid anhydride	190/320	1.5/3	97	55	6700
12	Propionic acid anhydride	190/320	1.5/16	97	87	10 500
13	Butyric acid anhydride	190/320	1.5/16	93	40	4800
14	Butyric acid chloride	190/320	1.5/16	93	45	5400
15	Hexanoic acid anhydride	250/320	1.5/16	94	40	4800
16	Hexanoic acid chloride	180/250/320	2/1/16	89	62	7500
17	Lauric acid chloride	180/250/320	1/1/16	91	50	6000
18	Diphenylcarbonate	200/250/320	1/1/16	91	—	—
19	Di(<i>m</i> -cresyl)carbonate	200/250/320	1/1/16	60	45	5400
20	Phenylchloroformate	180/250/320	1/1/16	84	—	—

^a After washing with refluxing acetone; calculated for the monomer unit C₇H₄O₂

^b 1% *p*-toluolsulphonic acid was added

^c 100% molar excess

mbar was applied after solidification. After cooling the resulting (4-Hybe)_n was worked up as described above.

Substituted 4-hydroxybenzoic acids with acetic anhydride (Table 3). The same procedure as described for Table 2 was used.

4-Hydroxybenzoic acids with acetic anhydride in Marlotherm-S (Table 4). 0.1 mol of a 4-hydroxybenzoic acid was heated with a 10% molar excess of acetic anhydride in 150 ml Marlotherm to 200°C. In the course of 30 min most acetic acid was removed under stirring in a slow stream of nitrogen. Afterwards the reaction temperature was raised to 320°C for 16 h. After cooling the reaction mixture was diluted with methylene chloride, the precipitated polyesters were isolated by filtration, washed with refluxing diethyl ether and dried at 80°C/12 mbar.

'One-pot condensations' with phosphorus reagents (Table 5). The condensations and the purification of the polymers were conducted exactly according to the procedures given in the corresponding references.

Oligomerization by means of acetyl chloride

In method (A), 0.2 mol 4-hydroxybenzoic acid and 0.25 mol acetyl chloride were refluxed for 24 h in 150 ml dry

toluene (or 1,2-dichlorobenzene). Then the reaction mixture was cooled to ~70°–80°C and stirred into ~1 litre ligroin. After cooling to 0°C the crystalline precipitate was isolated by filtration and dried at 80°C/12 mmHg. The yields were in the range 96–99%, when the acetyl end-groups and the experimentally found \overline{DP} were taken into account. The \overline{DP} , determined by means of ¹H n.m.r. spectroscopic end-group analyses, were around 1.5 for toluene as reaction medium and 1.8 for 1,2-dichlorobenzene. Extractions with hot organic solvents, such as ethyl acetate, acetone or dioxane, removed residual monomer, dimer and partially trimer. Depending on the nature of the solvent and on the member extracted, the \overline{DP} may increase to 6–8 and the yield may decrease to ~10%.

In method (B), 0.2 mol 4-hydroxybenzoic acid, 0.2 mol acetic anhydride and 0.05 mol acetyl chloride was refluxed in 150 ml dry toluene for 24 h and worked up as described above. Yield (96%) and \overline{DP} (=1.4) were similar to those obtained with pure acetyl chloride, whereas in the absence of acetyl chloride exclusively 4-acetoxybenzoic acid was obtained.

Acid-catalysed reactions of phenol acetate

0.5 mol phenol acetate and 0.005 mol *p*-toluene sulphonic acid were refluxed under nitrogen at a bath

Table 3 Reaction conditions and results of bulk condensations of substituted 4-hydroxybenzoic acids by means of acetic anhydride

No.	Monomer	Temp. (°C)	Time (h)	Yield ^a (%)	\overline{DP}	\overline{M}_n	Elemental analyses		
							C	H	Cl
1	3-Methoxy-4-hydroxybenzoic acid ^b	190/320	1.5/16	98	37	5500	Calcd 64.00 Found 63.12	4.03 4.29	—
2	3-Methoxy-4-hydroxybenzoic acid ^c	190/320	1.5/16	97	44	6600	Found 63.23	4.02	—
3	3,5-Dimethyl-4-hydroxybenzoic acid ^b	190/320	1.5/16	103	17	2530	Calcd 72.96 Found 69.67	5.44 5.32	—
4	3-Chloro-4-hydroxybenzoic acid ^c	190/320	1.5/16	91	450	70 000	Calcd 54.40 Found 55.54	1.96 1.97	22.94 22.50
5	3,5-Dichloro-4-hydroxybenzoic acid ^c	190/320	1.5/16	91	410	78 000	Calcd 44.48 Found 44.45	1.07 1.07	37.52 37.37
6	3,5-Dibromo-4-hydroxybenzoic acid ^c	190/320	1.5/16	101	16	4000	Calcd 30.25 Found 30.69	0.73 0.84	57.51 54.58

^a Referred to the monomer unit

^b Monomer of technical purity (96–97%)

^c Recrystallized monomer

Table 4 Condensations of various 4-hydroxybenzoic acids by means of acetic anhydride in Marlotherm-S^a

No.	Monomer	Temp. (°C)	Time (h)	Yield (%)	\overline{DP}	\overline{M}_n
1	4-Hydroxybenzoic acid ^b	200/260	0.5/16	84		22 000
2	4-Hydroxybenzoic acid ^b	200/320	0.5/16	77	190	60 000
3	4-Hydroxybenzoic acid ^b	200/350	0.5/16	82	500	8800
4	3,5-Dimethyl-4-hydroxybenzoic acid ^b	200/320	0.5/16	77	60	12 000
5	3-Methoxy-4-hydroxybenzoic acid ^c	200/320	0.5/16	99	80	62 000
6	3-Chloro-4-hydroxybenzoic acid ^c	200/320	0.5/16	61	400	2700
7	3,5-Dichloro-4-hydroxybenzoic acid ^c	200/220	0.5/16	86	14	12 500
8	3,5-Dichloro-4-hydroxybenzoic acid ^c	200/260	0.5/16	88	65	50 000
9	3,5-Dichloro-4-hydroxybenzoic acid ^c	200/320	0.5/16	83	300	8500
10	3,5-Dibromo-4-hydroxybenzoic acid ^c	200/260	0.5/16	85	30	

^a Mixture of isomeric dibenzyl benzenes

^b Technical purity

^c Twice or three times recrystallized

Table 5 Reaction conditions and results of 'one-pot condensations' of 4-hydroxybenzoic acid by means of various phosphorus reagents

No.	Condensing reagent	Solvent	Temp. (°C)	Time (h)	Yield (%)	Elemental analyses			
						C	H	N	
1	Hexachlorocyclotriphosphazene	Pyridine (+LiCl)	115–120	4	115.4 ^a	Calcd	70.00	3.36	0
						Found	57.71	3.39	2.50
2	Hexachlorocyclotriphosphazene	Pyridine (+LiCl)	115–120	4	103.6 ^b	Found	64.06	3.27	1.06
							64.07	3.22	1.04
3	Phenyldichlorophosphane	Pyridine (+LiCl)	115–120	4	90.8 ^c	Found	66.44	3.43	0.41
							66.16	3.40	0.34
4	Diphenyl phosphite	Pyridine (+LiCl)	115–120	4	28.5	Found	65.95	3.53	—
							65.65		
5	Triphenyl phosphite	<i>N</i> -Methylpyrrolidone + pyridine (1 : 1)	135–140	4	49.1 ^d	Found	67.09	3.67	1.79
6	Triphenylphosphine + carbon tetrachloride	Dimethylformamide	100	3	83.3 ^e	Found	67.44	3.58	1.92
							67.09	3.62	1.89
7	Poly(ethyl phosphate) imidazole	+Imidazole <i>N</i> -methylpyrrolidone-2	100	4	22.8 ^f	Found	64.81	3.62	1.01
							65.01	3.58	1.01

^a see refs. 11 and 13^b in contrast to refs. 11 and 13^c see refs. 10 and 12^d see refs. 10 and 12^e see ref. 14a^f see ref. 14b

temperature of 220°C for 16 h. The reaction mixture was diluted with 400 ml ethanol and 300 ml 4 N sodium hydroxide and refluxed for 30 min. The ethanol was removed *in vacuo*, the residue extracted with 500 ml diethyl ether, and the ester layer was twice extracted with 4 N sodium hydroxide. The residue obtained after evaporation of the ether solution was stirred with 200 ml 5 N sodium hydroxide and extracted with 200 ml diethyl ether. This second extract was dried over sodium sulphate and concentrated *in vacuo* whereby ~2 ml of a dark, viscous residue was obtained. This residue was subjected to gas chromatography and the peak of diphenyl ether was identified by addition of the pure compound and repeated measurements. The area of the original diphenyl ether peak amounted to ~0.5% of the sum of all peaks.

End-group analyses

The average degrees of polymerization (\overline{DP} 's) were determined by means of ¹H n.m.r. spectra as described previously⁸. Since all polyesters of this work are insoluble in all common solvents, 100 mg of a polyester was hydrolysed in a mixture of 0.5 ml 40% (by weight) NaOD and 1.0 ml CD₃OD. TMS was added as internal standard and 80 MHz ¹H n.m.r. spectra were measured on a Bruker WP-80 in 5 mm o.d. sample tubes. Depending on the \overline{DP} up to 10 000 transients were accumulated, and the intensities of end-group and monomer signals were determined by the 'cut and weigh method'. In the case of propionyl, butyryl, hexanoyl and lauryl residues the triplet of the CH₂ protons attached to the CO group (~2.6 ppm) were evaluated. In the case of cresyl carbonate (No. 19; Table 2) the CH₃ protons were analysed.

The differential scanning calorimetry (d.s.c.) was conducted on a Du Pont 990 Thermal Analyzer in aluminium probes at a heating rate of 50°C min⁻¹.

The thermogravimetric analyses (t.g.a.) were obtained on a Perkin-Elmer TGS-2 at a heating rate of 8°C min⁻¹ in air.

The X-ray diffraction patterns of Figures 1 and 2 were measured with a pinhole camera (Anton Paar KG, Graz, Austria) at a distance of 70 mm using the CuK α radiation.

RESULTS AND DISCUSSION

Bulk condensations

In a first series of experiments the bulk condensation of 4-acetoxy-, 4-propionyloxy- and 4-hexanoyloxybenzoic acid was studied (Table 4). The highest reaction temperature applicable in the initial stage of the condensation of 4-acetoxy- and propionyloxybenzoic acid is 260°C because both monomers strongly reflux above 250°C. When this reaction temperature was maintained over the whole course of the condensation,

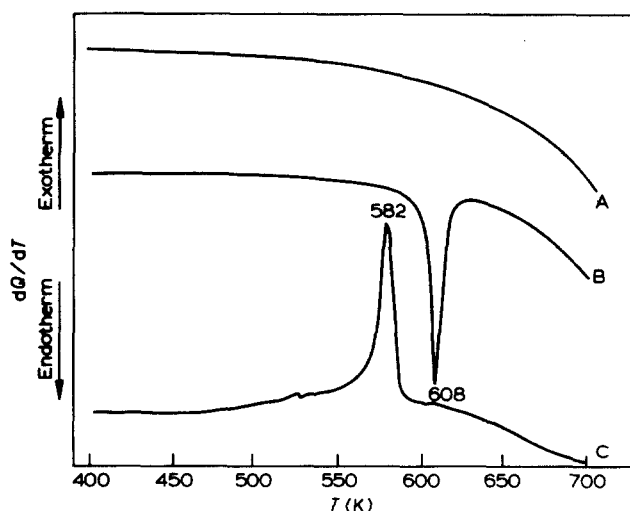


Figure 1 D.s.c. curves measured at a heating rate of 40K min⁻¹: curve A, poly(3,5-dichloro-4-hydroxybenzoate) No. 9 in Table 4; curve B, poly(4-hydroxybenzoate) No. 9 in Table 2; curve C cooling curve of B

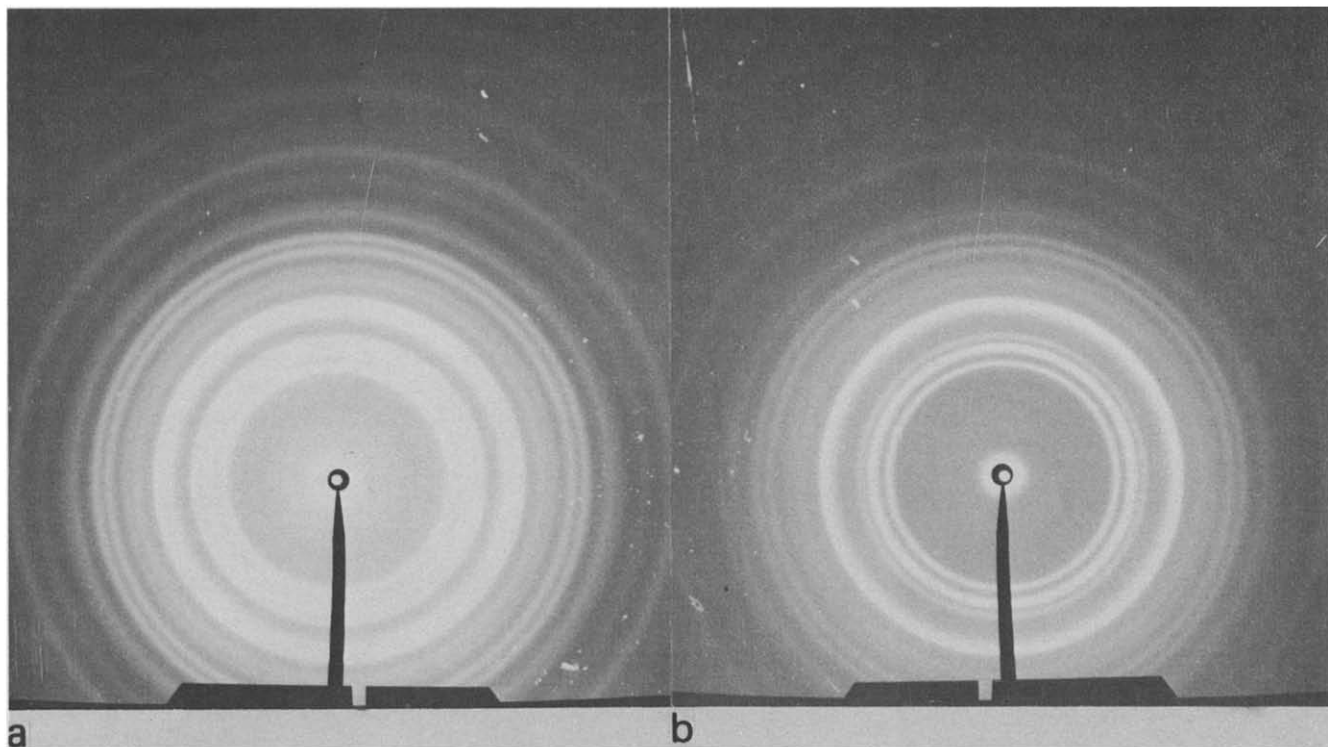


Figure 2 X-ray powder patterns of (a) poly(3-methoxy-4-hydroxybenzoate), No. 2 in Table 3; (b) poly(3-chloro-4-hydroxybenzoate), No. 4 in Table 3

number average molecular weights (\overline{M}_n) up to $\sim 10\,000$ were obtained (Nos. 1, 4, 6; Table 1). The molecular weights decrease with increasing chain length of the acyl residue, indicating that the steric and electronic properties of these substituents considerably affect the reactivity of the system. These results agree well with our previous observations⁹ that 4-pivaloyloxybenzoic acid only yields (4-Hybe)_n with \overline{M}_n 's < 8000 when condensed in a liquid reaction medium at 320°C. The data of Table 1, furthermore, demonstrate that \overline{M}_n 's up to 40000 are accessible when the reaction temperature is increased to 320° or 350°C after the initially formed oligomers have solidified (Nos. 2, 3; Table 1). The reaction product obtained in this way was not an intractable mass, but a brittle, porous material which was easily powdered and removed from the glassy reaction vessel. Hence, we may conclude that the bulk condensation of 4-acetoxybenzoic acid is an effective method for the preparation of high molecular weight (4-Hybe)_n despite the formation of small amounts of subliming side products.

In order to simplify the synthesis of (4-Hybe)_n, further we have investigated the conversion of 4-hydroxybenzoic acid with various anhydrides and acid chlorides at high temperatures (Table 2). Heating of 4-hydroxybenzoic acid with excess acetic-anhydride to 180°C yields initially two liquid phases which turn homogeneous within 15 min under evolution of acetic acid. Further heating to higher temperatures results in solidification of the reaction mixture. The comparison of condensations Nos. 1, 2, 5, 7, 9 and 10 (Table 2) indicates that reaction temperatures above 300°C are required to attain \overline{M}_n 's > 10000 .

The comparison of Nos. 3 or 4 with No. 6 (Table 2) demonstrates that even after solidification of the reaction mixture the reaction time strongly influences the molecular weight. These results agree well with our

previously published reaction mechanism⁹. The conversion of monomers to oligomers proceeds in solution or in the melt, whereas further chain growth takes place mainly in the solid state. The two mechanisms depicted in Figure 3 can account for the solid-state chain growth. Mechanism (a) represents an 'intercrystalline' condensation involving two or more surfaces of oligomer lamellae. This mechanism is supported by electron microscopy, electron diffraction and X-ray diffraction measurements^{17,18}. Mechanism (b) is an 'intracrystalline' process which might be operative when crystal surfaces do not come into close contact. Since both mechanisms are compatible with one another, they eventually contribute simultaneously to the observed chain growth.

When propionic, butyric and hexanoic anhydrides are used as condensing reagents, a decrease of the \overline{M}_n 's is

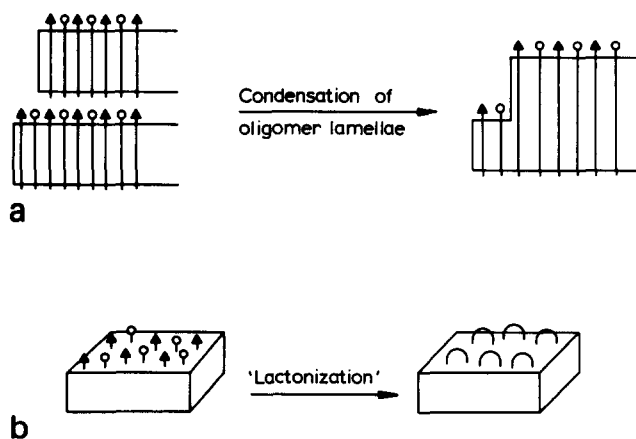


Figure 3 Hypothetical chain growth of crystalline oligo(4-hydroxybenzoate): (a) 'intercrystalline' condensation of stacked oligomer lamellae; (b) 'intracrystalline' formation of ester loops

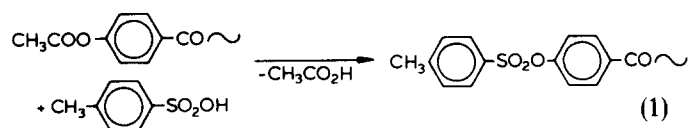
observable (Nos. 12, 13, 15; Table 2) in analogy with the results of Table 1. Also, butyryl chloride, hexanoyl chloride and lauroyl chloride (Nos. 14, 16, 17; Table 2) yielded polyesters with lower \overline{DP} than acetic anhydride (No. 9). Certainly the electrophilicity of the acyloxy groups decreases with increasing length of the aliphatic chain. Yet this slight reduction in reactivity would not be effective at the high reaction temperatures of our experiments. It is more likely that the increasing steric requirements of the longer acyl residues affect the efficiency of mechanism (a) (Figure 3). The strong temperature dependence of the \overline{M}_n 's (Nos. 1, 3, 5, 9, 10; Table 2) also suggests that mechanism (a) is predominantly (if not exclusively) operating in the solid-state condensation. The condensations (Nos. 1, 3, 5; Table 2) demonstrates that the end-groups are reactive enough for transesterifications even at temperatures $\leq 260^\circ\text{C}$. Thus, also mechanism (b) (Figure 3) should be operating at such low temperatures. However, the formation of polymer crystals by condensation of several oligomer crystals (mechanism (a)) requires a relatively high segmental mobility of the chains because diffusion of the eliminated carboxylic acids and 'heating of crystal defects' is necessary (discussed in ref. 9). As demonstrated by Economy *et al.*¹, (4-Hybe)_n undergoes a reversible phase transition between 300° and 350°C. Although, we do not agree with Economy's interpretation of this phenomenon^{9,17,19}, it is uncontested that the high-temperature modification of (4-Hybe)_n is a less densely packed crystalline phase. It is the initial formation of this less densely packed modification at temperatures $> 260^\circ\text{C}$ which allows the polyester chains to participate in transesterification and propagation reactions. Thus, variation of the reaction temperature alone suffices for either the synthesis of oligomers with \overline{DP} 's < 10 (No. 3; Table 2) or for the synthesis of high polymer with \overline{DP} 's around 300 (No. 10; Table 2).

In addition to 4-hydroxybenzoic acid, various substituted 4-hydroxybenzoic acids were subjected to bulk condensations in the presence of acetic anhydride (Table 3). The most conspicuous result is the huge difference of the molecular weights of mono- and dichloro-4-hydroxybenzoic acid on the one hand, and methoxy-, dimethyl- and dibromo-4-hydroxybenzoic acid on the other. In the case of the dibromo derivative the low \overline{M}_n 's are understandable because the reaction temperature must be lowered to avoid decomposition of the monomer and because the two bromines cause considerable steric hindrance of the transesterification reactions. However, these explanations do not hold for the other two monomers. When the condensation of 3-methoxy-4-hydroxybenzoic acid was repeated with a twice recrystallized monomer (No. 2; Table 3) a slightly higher \overline{DP} was found. However, this purification effect does not explain the difference from the chlorinated polyester (Nos. 4, 5; Table 3). Perhaps different rates of decarboxylation or different segmental mobilities of the polyester chains are responsible for largely differing \overline{DP} 's. At the current state of affairs, we have no satisfactory explanation.

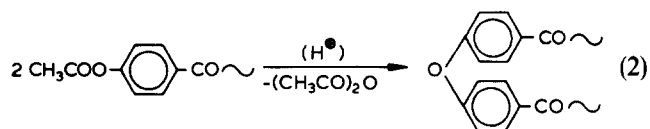
Influence of acidic catalysts

An interesting aspect of the bulk condensations is the catalytic effect of 4-toluene sulphonic acid (Nos. 2, 4, 8;

Table 2). In order to find out whether the \overline{DP} derived from acetoxy end-groups are correct, we have investigated two potential side reactions. First, we looked for the incorporation of tosyloxy end-groups (equation (1)):



Because the CH_3 protons of tosyl residues absorb ~ 0.5 ppm downfield of acetyl groups, they are easily detectable in ^1H n.m.r. spectra. Yet, we could not find tosyl groups in our samples Nos. 2, 4 and 8 (Table 2). An alternative side reaction leading to the elimination of acetyl groups is the etherification reaction (equation (2)):



We have studied a model reaction by refluxing phenylacetate and 1 mol% toluolsulphonic acid for 16 h at 220°C . The resulting reaction mixture was extracted several times with sodium hydroxide and finally analysed by means of gas chromatography. Although diphenyl ether was detected, its concentration was only of the order of 10 ppm. Hence, it is unlikely that this side reaction is responsible for the elimination of acetyl end-groups at temperatures of $200^\circ\text{--}220^\circ\text{C}$. In other words, 4-toluene sulphonic acid or the sulphuric acid resulting from its thermal decomposition seem to have a true catalytic effect on the condensation of 4-acetoxybenzoic acid. This conclusion also agrees with the observation of Aclony and Renfrew¹⁶ that the oligomerization of 4-acetoxybenzoic acid in refluxing tetrahydronaphthalene is catalysed by 4-toluene sulphonic acid.

In contrast to this finding, no catalytic effect of HCl was detectable, because the use of acid chlorides (Nos. 14, 16, 17; Table 2) does not result in molecular weights $> 10\,000$. This lack of catalytic activity is probably due to its volatility. When 4-hydroxybenzoic acid was refluxed with excess acetyl chloride in inert solvents, such as toluene or 1,2-dichlorobenzene, we found that the acetylation of 4-hydroxybenzoic acid is accompanied by oligomerization (see above). Since the conversion of 4-hydroxybenzoic acid with pure acetic anhydride exclusively yields 4-acetoxybenzoic acid, it is obvious that the oligomerization with acetyl chloride is due to a catalytic effect of HCl. Thus, these one-pot procedures and those of Table 2 (Nos. 3 and 4) can be used for the preparation of oligo(4-hydroxybenzoate)s.

In this connection it is noteworthy that the (4-Hybe)_n obtained at 320°C in the presence of 4-toluene sulphonic acid had a dark colour. Obviously, the thermal decomposition of 4-toluene sulphonic acid is responsible for the colour, because the oligomers obtained at lower temperature were white (Nos. 2, 4; Table 2). Furthermore, it is to be mentioned that the (4-Hybe)_n prepared with acetic anhydride at temperatures $\geq 260^\circ\text{C}$ has a brownish colour, whereas those samples obtained by means of other aliphatic anhydrides were only slightly tan. When the nitrogen normally used in our experiments was replaced by a purer one or by argon, the colour did not change. Hence, oxidation cannot be its origin. Furthermore, we

could observe that the addition of a small amount of *p*-toluene sulphonic acid (No. 8; Table 2) deepens the colour. Moreover, pure acetic anhydride turned black within a few minutes when it was distilled with a few drops of concentrated sulphuric acid or phosphorus pentoxide. Thus, we suppose that the brownish colour results from acid-catalysed Aldol condensations of acetic anhydride.

Condensations in solution

For comparisons of yield, \overline{DP} and crystallinity we want to conduct several condensations in a liquid reaction medium. Because solution condensations of purified monomers, such as 4-acetoxybenzoic acid, 4-pivaloyloxybenzoic acid, 4-hydroxybenzoic acid, 4-hydroxybenzoic acid phenyl ester or 4-trimethylsiloxybenzoyl chloride, were described in our previous paper⁹, only 'one-pot procedures', i.e. direct condensations of 4-hydroxybenzoic acid, were investigated in this work. Two series of 'one-pot procedures' were conducted, the first based on acetic anhydride as condensing reagent and Marlotherm-S as reaction medium⁹ (Table 4), and the second a reinvestigation of condensations conducted by Higashi *et al.*¹⁰⁻¹⁴ by means of various phosphorus derivatives (Table 5).

The results obtained with acetic anhydride/Marlotherm-S (Table 4) allow some informative comparisons with the bulk condensations of Tables 2 and 3. In most cases the yields of the solution condensations are lower than those of the bulk condensations and also lower than those obtained from purified monomers⁷. Yet, they are still acceptable for preparative purposes. The \overline{DP} 's are comparable with those of Tables 2 and 3. Again the reaction temperature has a predominant influence on the \overline{DP} (Nos. 1-3 and 7-9; Table 4). Interestingly, a comparison of the substituted polyesters reveals a tendency already observed and discussed for the bulk condensations (Table 3). The 3,5-dimethyl-, the 3-methoxy- and 3,5-dibromo-4-hydroxybenzoic acids give polyesters of considerably lower \overline{DP} than 4-hydroxybenzoic acid (No. 2; Table 4) and its chloro derivatives (Nos. 6, 9; Table 4). However, it is noteworthy that the \overline{DP} obtained by condensation of 3,5-dimethyl-4-hydroxybenzoic acid in solution (No. 4; Table 4) is remarkably higher than that resulting from bulk condensation (No. 3; Table 3). In individual cases, also, the crystallinity of the polyesters condensed in solution may be higher (see below).

The second series of condensations was conducted exactly according to the procedures given in the literature¹⁰⁻¹⁴. According to the literature, the best yields, namely 100%, are attainable with hexachlorotriphosphazene. Our experiments with this reagent (Nos. 1, 2; Table 5) gave yields above 100% and the elemental analyses indicate that the polyesters are heavily contaminated with derivatives of the elements N, O and P. Higashi *et al.*^{11,12} have presented correct C and H analyses in two papers, dealing with different synthetic procedures. Surprisingly the analytic data were exactly identical, although we were never able to obtain identical analyses even if the same sample was repeatedly analysed (Table 5). Also all other reaction products of the 'phosphorus series' gave C elemental analyses which were several per cent below the calculated values (Table 5). In the optimum case with respect to the C analysis (No. 6) ~2% nitrogen was found. These poor results are

paralleled by those of (3-Hybe)_n, which was prepared from 3-hydroxybenzoic acid by means of various phosphorus reagents²⁰. In the case of (3-Hybe)_n we were able to determine the \overline{M}_n 's by vapour pressure osmometry (v.p.o.). \overline{M}_n 's above 3000 were never found when phosphorus reagents were used. The relatively low reaction temperatures in Table 5 and the heterogeneous course of the condensation suggest that the \overline{M}_n 's of the (4-Hybe)_n samples of Table 5 are not higher. A further argument against high molecular weights results from the thermogravimetric analyses discussed below. In this connection it is noteworthy that Aclony and Renfrew¹⁶, who were the first to condense 4-hydroxybenzoic acid by means of a phosphorus reagent (e.g. triphenylphosphite), obtained a large amount of oligomers with \overline{DP} in the range of 10-13.

Crystallinity and thermostability

Economy's investigation of synthesis and properties of (4-Hybe)_n have shown¹⁻⁴ that (4-Hybe)_n produced at high temperatures is a highly crystalline material which exhibits a sharp endotherm between 320° and 350°C when differential scanning calorimetry measurements are conducted. This endotherm is reproducible upon repeated heating and cooling and indicates a reversible phase transition but not a melting/crystallization process. Originally this phase transition was interpreted as an unwinding of a double-stranded helix. In a recent paper¹⁸ Lieser could demonstrate by means of X-ray measurements that 3₁-helices do not exist, so that the endotherm must represent a transition between two crystalline modifications. When (4-Hybe)_n was prepared from 4-trimethylsiloxybenzoyl chloride even two reversible phase transitions were found⁹, indicating that (4-Hybe)_n may exist in up to four different solid phases.

When d.s.c. measurements of the polyesters listed in Tables 2 and 3 were conducted the (4-Hybe)_n samples showed the expected endotherm (Figure 1, curve B) and the powder patterns obtained by X-ray diffraction confirmed the high degree of crystallinity. Hence, our results obtained in this work agree well with those published previously and they also agree with those reported by Economy *et al.*¹ We wish to emphasize this point because Wunderlich *et al.*²¹ have recently reported that a (4-Hybe)_n sample of the Carborundem Inc. showed a glass transition at ~340°C after quenching. We were not able to detect a glass transition in the d.s.c. curves of our (4-Hybe)_n samples. When the polyesters built up of substituted 4-hydroxybenzoic acids were measured (Figure 1, curve B), the resulting d.s.c. curves were bare of any endotherm or glass transition. A similar result was reported by Higashi *et al.*¹⁴ for poly(3,5-dichloro-4-hydroxybenzoate). The finding that all substituted poly(4-hydroxybenzoate)s show plain d.s.c. curves indicates that the thermal behaviour of (4-Hybe)_n is an exception. However, it can be rationalized assuming that the densely packed low-temperature modification cannot be formed if the monomer units are substituted.

In this connection we would like to emphasize that the plain d.s.c. curves of substituted poly(4-hydroxybenzoate)s do not mean these polymers are not crystalline. The X-ray powder patterns (Figures 2a, b and 4b) clearly demonstrate that most samples possess a high degree of crystallinity. However, in the case of poly(3,5-dichloro-4-hydroxybenzoate) the condensation method

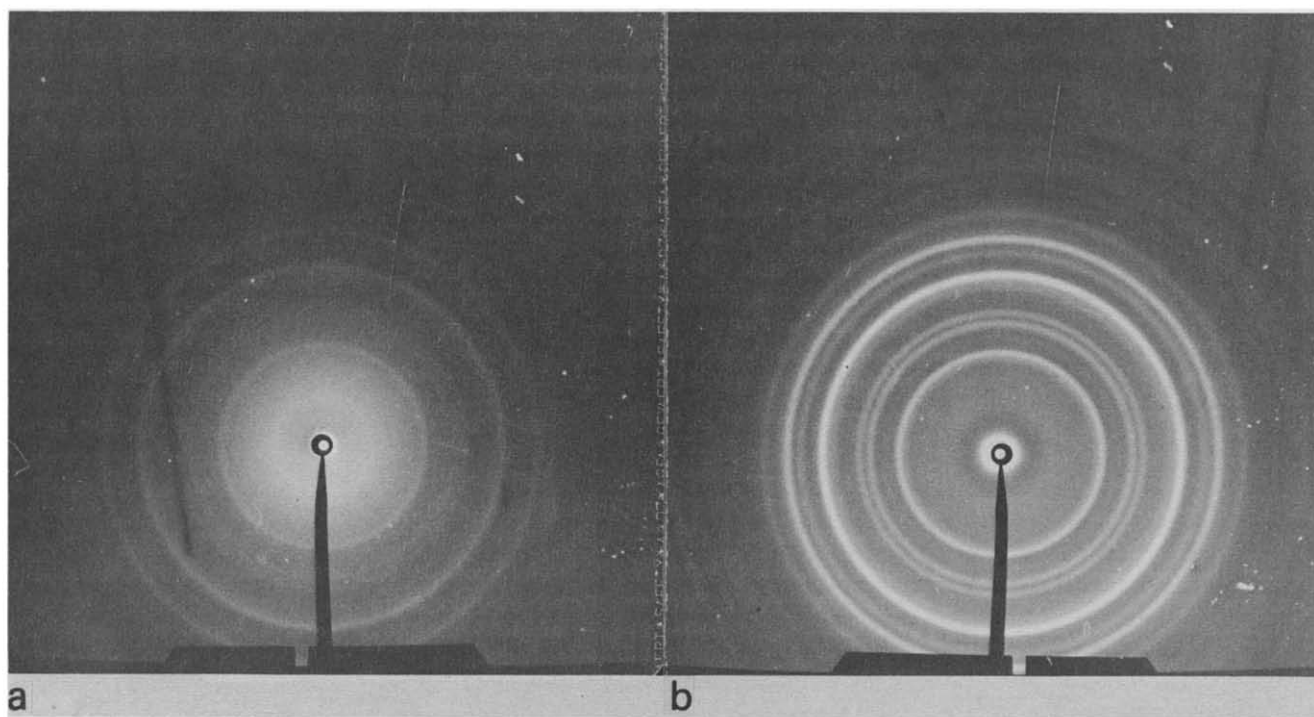


Figure 4 X-ray powder patterns of poly(3,5-dichloro-4-hydroxybenzoate): (a) No. 5 in Table 3; (b) No. 9 in Table 4

has a considerable influence on the degree of crystallinity. The bulk condensation of 3,5-dichloro-4-hydroxybenzoic acid (No. 5, Table 3) results in a significantly lower crystallinity (Figure 4a) than the condensation in Marlotherm-S (No. 9, Table 4b). Also in the case of (4-Hybe)_n, both d.s.c. and X-ray pattern suggest that the products obtained by bulk condensations (Nos. 9, 12, 16, Table 2) are slightly less crystalline than the samples prepared in Marlotherm-S (Nos. 2, 3, Table 4 and ref. 9). However, this difference is barely detectable and in the case of 3-chloro-4-hydroxybenzoic acid or 3-methoxy-4-hydroxybenzoic acid no influence of the condensation procedure was observed.

Thermogravimetric analyses were conducted in air at a heating rate of 8K min⁻¹. The results summarized in Table 6 show that the thermostability depends on the nature of the substituents. In the case of poly(3,5-dibromo-4-hydroxybenzoate) the thermal dissociation of the Br-C bond causes the decomposition. In the case of methyl and methoxy substituents it is presumably attack by oxygen which initiates the degradation. The chlorinated poly(hydroxybenzoate)s exhibit a thermostability which is comparable with that of (4-Hybe)_n. The thermogravimetric analyses also demonstrate that the synthetic procedures have a strong influence on the thermostability of poly(4-hydroxybenzoates). When the three versions of the 'acetoxy method'—(a) the condensation of 4-acetoxybenzoic acid in solution (in Marlotherm-S⁹), (b) the condensation of 4-hydroxybenzoic by means of acetic anhydride in solution (No. 2, Table 4) and (c) the bulk condensation of 4-hydroxybenzoic acid (No. 9, Table 2) — are compared we find a decreasing thermostability of the resulting (4-Hybe)_n in this order (Table 2 and Figure 5, curves A, B). Obviously, the thermostability parallels the degree of crystallinity and the perfection of the crystallites, when polyesters of similar molecular weight are compared. However, the differences of thermostability of the 'acetoxy polyesters' are small, when compared with those found for

the polyesters prepared via phosphorus reagents. When the temperature of 1% loss of weight is taken as a measure, we find that the (4-Hybe)_n samples of Table 5 begin to degrade 150°–250°C below the decomposition temperatures of the 'acetoxy polyesters' (Table 5 and Figure 5). Furthermore, their t.g.a. curves exhibit a step pattern (curves C and D, Figure 5). A similar step pattern was observed for oligomeric (4-Hybe)_n prepared from 4-acetoxybenzoic acid or 4-trimethylsiloxybenzoyl chloride⁹. It was explained⁹ by post-condensation of the oligo esters in the solid state, when heated above 250°C. Hence, we believe that also the step pattern of the t.g.a. curves C and D in Figure 5 indicate that the (4-Hybe)_n samples of Table 5 possess only low molecular weights. Anyway, owing to their low thermal stability, they are useless for any technical application.

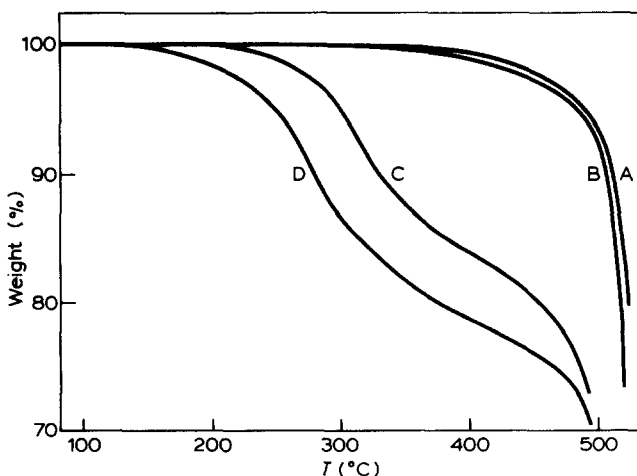


Figure 5 Thermogravimetric analyses of poly(4-hydroxybenzoate)s measured at a heating rate of 8K min⁻¹ in air: curve A, No. 3 in Table 4; curve B, No. 9 in Table 2; curve C, No. 2 in Table 5; curve D, No. 6 in Table 5

Table 6 Thermogravimetric analyses of various poly(4-hydroxybenzoate)s measured at a heating rate of 8K min⁻¹ in air

Polyester	Cross-reference	Temperature (°C) at which the following weight losses occur			
		1%	5%	10%	20%
Poly(4-hydroxybenzoate)	see ref. 9	417	485	513	523
		418	487	512	525
Poly(4-hydroxybenzoate)	No. 2 in Table 1	404	506	525	534
		406	507	525	534
Poly(4-hydroxybenzoate)	No. 9 in Table 2	396	487	504	520
		397	488	505	520
Poly(4-hydroxybenzoate)	No. 2 in Table 5	246	300	356	456
		250	302	358	454
Poly(4-hydroxybenzoate)	No. 3 in Table 5	196	316	380	465
		200	318	382	466
Poly(4-hydroxybenzoate)	No. 6 in Table 5	177	249	285	379
		180	250	288	381
Poly(4-hydroxybenzoate)	No. 7 in Table 5	209	269	306	402
		212	268	304	399
Poly(3-methoxy-4-hydroxybenzoate)	No. 1 in Table 3	340	372	382	392
		342	374	386	395
Poly(3,5-dimethyl-4-hydroxybenzoate)	No. 3 in Table 4	325	369	380	390
		326	371	381	391
Poly(3-chloro-4-hydroxybenzoate)	No. 4 in Table 3	390	459	484	501
		386	455	479	499
Poly(3,5-dichloro-4-hydroxybenzoate)	No. 5 in Table 3	390	490	526	542
		389	490	523	541
Poly(3,5-dibromo-4-hydroxybenzoate)	No. 6 in Table 3	314	356	382	479
		316	358	385	483

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