New polymer syntheses: 6*. Linear and branched poly(3-hydroxy-benzoates)

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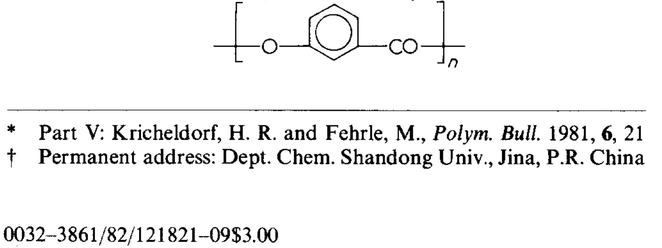
Synthesis of poly(3-hydroxybenzoate) were conducted in three ways: (a) condensation of the novel monomer, 3-(trimethylsiloxy)benzoyl chloride in bulk and in solution, (b) bulk condensation of 3-acetoxybenzoic acid, (c) condensation of 3-hydroxybenzoic acid by means of phosphorus reagents in solution. The bulk condensation of 3(trimethylsiloxy)benzoyl chloride gave the best results with respect to both yields (89–99%) and molecular weights ($Mn = 10\,000$–$14\,000$). Because amorphous poly(3-hydroxybenzoate) is soluble in various solvents the molar weights could be determined by both vapour pressure osmometry and ^{1}H n.m.r. endgroup analyses. Crystalline poly(3-hydroxybenzoate) was only obtainable by solvent induced crystallization; yet not by annealing. Glass transition ($Tg = 145°C$) and melting point ($Tm = 181°$–$185°C$) were determined by means of differential scanning calorimetry and torsion pendulum. Branched poly(3-hydroxybenzoate) was prepared by condensation of 3-(trimethylsiloxy) benzoyl chloride and 3,5-(bistrimethylsiloxy) benzoyl chloride. Thus, for the first time a branched polycondensate was obtained which did not crosslink regardless of the conversion.

Keywords Polymer synthesis; condensation; bulk condensation; poly(3-hydroxy-benzoates); differential scanning calorimetry

INTRODUCTION

The first synthesis of oligo(3-hydroxybenzoates) was described by Schiff in the year 1882[1], i.e. four decades before the existence of polyesters had been generally accepted. In 1959 Gilkey and Caldwell[2] presented a detailed report on synthesis and properties of poly(*m*-hydroxybenzoate) (3-Hybe)$_n$. Because 3-hydroxybenzoic acid decarboxylates upon heating above 200°C, these authors used 3-acetoxybenzoic acid (**1**) as monomer for their bulk condensations at 200°–300°C. Depending on the reaction conditions, they obtained amorphous or partially crystalline polyesters with alleged molecular weights (*Mn*'s) in the range 12000–25000. The condensation polymerization of 3-hydroxybenzoic acid in pyridine or imadazole by means of various phosphorous derivatives was recently reported by Higashi and coworkers[3–6]. However, neither *Mn*'s nor any other property of the resulting (3-Hybe)$_n$ were investigated.

In a previous short communication we have shown[7] that (3-Hybe)$_n$ with *Mn*'s in the range 10000–13000 is obtainable by bulk condensation of 3-(trimethylsiloxy)-benzoyl chloride (**2**). Synthesis, purification and properties of this novel monomer were described in a recent paper[8]. This work was aimed to describe syntheses and properties of linear and branched homo- or copolyester of 3-hydroxybenzoic acid in more detail.



EXPERIMENTAL

Materials

3-Hydrobenzoic acid was a gift of Bayer AG and was used without purification. Marlotherm-S, a product of the Chemische Werke Hüls AG (Marl-Hüls, FRG), is a mixture of isomeric di- and tribenzyl benzenes. It was heated to ~300°C under a slow stream of nitrogen to remove traces of water and oxygen. 3-(Trimethylsiloxy)-benzoyl chloride **2** was prepared and distilled as described in Ref. 8. Pyridine and other amines were refluxed and distilled over freshly powdered calcium hydride, dioxane and other ethers were dried over sodium wire, aromatic solvents and chloroform were refluxed and distilled over P_4O_{10}.

Condensations of 3-(Trimethylsiloxy)benzoyl chloride

(a) Condensations in solution (*Table 1*). 11.5 g (50 mmol) 3-(Trimethylsiloxy)benzoyl chloride was heated for 15 or 20 h in 80 ml of a boiling solvent. Then, the polyester was precipitated from ~600 ml cold methanol, dried at $80°C/10^{-1}$ mbar and subjected to vapour pressure osmometry measurements.

(b) Bulk condensations (No. 2, *Table 2*). 11.5 g (50 mmol) 3-(Trimethylsiloxy)benzoyl chloride were heated in a 50 ml two necked flask (pretreated with dimethyl dichlorosilane) under a slow stream of nitrogen to the final reaction temperature (normally 250°C). Initially a rapid evolution of trimethylchlorosilane occurred; finally a yellowish, viscous melt of the polyester was obtained. The crude reaction product was cooled with liquid nitrogen, powdered and dissolved at ~50°C in a mixture of 50 ml dry pyridine and 50 ml dry benzene. Immediately after a clear solution was obtained—prolonged stirring leads to crystallization—the polyester was precipitated from 700 ml cold methanol or dry diethylether and dried at 80°C/1 mbar. Analyses: Calcd. for $C_7H_4O_2$ (120.1): C 70.00, H 3.36; Found C 69.77, H 3.21.

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Table 1 Condensation polymerization of 3(trimethylsiloxy)benzoyl chloride in solution

No.	Solvent (refluxing)	Catalyst	Time (h)	Yield[a] (%)	$\frac{\eta_{sp}}{c}$[b] ($cm^3\ g^{-1}$)	$\bar{M}_n$[c]
1	Pyridine + benzene (1 :1, by volume)	Pyridine	20	50	4.6	1400
2	2,4,6-Trichlorobenzene	—	15	80	7.6	2300
3	"	Pyridine	15	82	7.2	2200
4	"	$AlCl_3$	15	85	6.9	2100
5	"	$FeCl_3$	15	63	6.2	1800

[a] After precipitation from methanol
[b] $c = 2.3\ g\ l^{-1}$ in phenol/tetrachloro ethane (3:2, by weight) at 30°C
[c] Vapour pressure osmometry in $CHCl_3$

The synthesis of branched poly(3-hydroxybenzoate) was conducted analogously; only the desired quantity of 3,5-bistrimethylsiloxybenzoylchloride was added. The elemental analyses found after precipitation from pyridine + benzene/methanol agreed with the calculated values within the limits of ±0.3%.

Condensation of 3-acetoxybenzoic acid (No. 3, Table 3)

9.0 g (50 mmol) recrystallized 3-acetoxybenzoic acid and 90 mg magnesium were heated at 220°C for 2 h under a slow stream of nitrogen. Then a vacuum (~0.1 mbar) was applied for 1 h and finally heating under nitrogen was continued for 2 h at 300°C. The reaction product was worked up as described above. Analyses: Found C 69.68, H 3.12.

Condensations of 3-hydrobenzoic acid by means of hexachlorocyclo triphosphazene (Table 4)

(1) A solution of 1.7 g (40 mmol) lithium chloride, 5.5 g (40 mmol) 3-hydroxybenzoic acid and 4.9 g (14 mmol) hexachlorocyclo triphosphazene in 100 ml dry pyridine was refluxed for 4 h. The resulting polyester was precipitated from 800 ml cold methanol and dried at ~70°C/10^{-1} mbar; yield 8.8 g (183%). This crude material was refluxed in 200 ml methanol for 2 h; stirred with 1 N HCl at 25°C for 0.5 h, then filtered and dried; yield: 5.35 g (111.5%). Then, the crude polyester was refluxed in 1 N HCl for 10 min, washed with neutral water and dried; yield: 4.76 g (99%). The polyester was now soluble in chloroform and in a 1:1 mixture (by volume) of pyridine and benzene.

Table 2 Bulk condensation of 3-trimethylsiloxy benzoyl chloride under various conditions

No.	Time (h)	Temp. (°C)	Yield[a] (%)	$\frac{\eta_{sp}}{c}$ ($cm^3 g^{-1}$)[b]	$\frac{\eta_{sp}}{c}$ ($cm^3 g^{-1}$)[c]	$[\eta]_{inh}$ ($dl\ g^{-1}$)[c]	Mn[d]	Mn[e]	Mn[f]
1	3	200	88	17.2	14.1	0.14	4 000	4 250	4 150
2	3	250	99	75.4	—	—	13 300	—	—
3	3	250	97	60.5	—	—	10 600	11 300	11 450
4	3	250	96	60.5	80.1	0.74	10 300	—	—
5[g]	3	250	95	58.5	—	—	10 000	—	—
6	10	250	89	62.5	—	—	11 800	—	—
7	3	300	98	72.3	—	—	12 500	13 200	13 400
8	3	350	93	61.7	—	—	11 800	—	—

[a] After reprecipitation from pyridine + benzene/methanol
[b] $c = 2\ g\ l^{-1}$ in chloroform at 20°C
[c] $c = 2.3\ g\ l^{-1}$ in phenol/tetrachloro ethane (3:2, by weight) at 30°C
[d] Vapour pressure osmometry in chloroform
[e] ^1H n.m.r. endgroup analyses after reprecipitation from methanol (s.a.)
[f] ^1H n.m.r. endgroup analyses after reprecipitation from dry diethylether
[g] Crude monomer

Table 3 Bulk condensation of 3-acetoxybenzoic acid with magnesium as catalyst

No.	Time (h)	Temp. (°C)	Yield[a] (%)	$\frac{\eta_{sp}}{c}$ ($cm^3 g^{-1}$)[b]	$\frac{\eta_{sp}}{c}$ ($cm^3 g^{-1}$)[c]	$[\eta]_{inh}$ ($dl\ g^{-1}$)[c]	$\bar{M}_n$[d]	$\bar{M}_n$[e]	$\bar{M}_n$[f]
1	3.0 + 0.25	220 + 300	89	16.2	12.8	0.13	3800 ± 100	4000	4050
2	18.0 + 0.25	220 + 300	90	15.9	12.1	0.13	3700 ± 100	3800	3900
3	3.0 + 2.0	220 + 300	87	19.6	22.0	0.21	4600 ± 100	4900	5000
4	ref. 2	=	—	—	—	0.33	11400		—
5	ref. 2	=	—	—	—	0.59	25000		—

[a] After reprecipitation from pyridine + benzene/methanol
[b] $c = 2\ g\ l^{-1}$ in chloroform at 20°C
[c] $c = 2.3\ g\ l^{-1}$ in phenol/tetrachloroethane (3:2, by weight) at 30°C
[d] Vapour pressure osmometry in chloroform
[e] ^1H n.m.r. endgroup analyses after reprecipitation from methanol
[f] ^1H n.m.r. endgroup analyses after reprecipitation from dry diethyl ether

Table 4 Condensation polymerization of 3-hydroxybenzoic acid by means of various phosphorus reagent

No.	Condensing reagents	Solvent	Time (h)	Temp. (°C)	Yield[a] (%)	Yield[b] (%)	El. Analyses C 70.00	H 3.36[c]
1	Hexachloro cyclotriphosphazene	Pyridine + LiCl	4	120	183	94	62.08[b]	3.70
2	"	Pyridine + LiCl	4	120	185	99	65.47[b]	3.77
3	"	Pyridine	4	120	182	–	–	–
4	"	Pyridine + LiCl	8	120	183	75	57.81[b]	3.75
5	Polyethylphosphate	Pyridine + LiCl	4	120	33	–	64.42[a]	3.88
6	Polyethylphosphate	*N*-Methylmorpholine + Imidazole	4	120	3	–	–	–
7	Triphenylphosphine + CCl_4	DMF + Imidazole	4	120	73	–	68.54[a]	3.56
8	Ethyl dichlorophosphoridate	Pyridine + LiCl	4	120	25	–	64.72[a]	3.66
9	Dichlorophenylphosphine	Pyridine + LiCl	4	120	45	25	65.37[b]	3.40
10	Dichlorophenylphosphine	Pyridine	4	120	25	19	66.01[b]	3.76
11	1-Diethoxy-phosphine 1,3,4-triazole	Pyridine + LiCl	4	120	19	–	67.44[a]	3.51
12	4,5-Benzo-2-chloro-1,3 dioxaphospholan	Pyridine + LiCl	4	120	0	–	–	–

[a] After precipitation from methanol without further purification
[b] After several purification steps (Exp. Part)
[c] Calculated values

Analysis calculated for $C_7H_4O_2$: C 70.00, H 3.36; Found: C 62.08, H 3.70. After reprecipitation from pyridine + benzene/methanol the $\bar{M}n$ determined by v.p.o. in $CHCl_3$ was in the range of 2600–2700 Daltons.

(2) The reaction mixture of a parallel experiment was also precipitated from methanol and the crude polyester dried *in vacuo*; yield: 8.9 g (185%). Then, the crude product was refluxed for 1 h in methanol, for 1 h in 1 N HCl, washed with water and dried *in vacuo*; yield: 5.0 g (104%); v.p.o. measurements in chloroform gave $\bar{M}n = 2400$. The crude polyester was then again refluxed for 1 h with 1 N HCl and dried *in vacuo*; yield: 4.5 g (93.8%); $Mn = 1740$; Analyses, Found: C 65.47, H 3.36.

(3) The reaction mixture was refluxed for 8 h and precipitated from methanol. The crude polyester (yield: 183%) was divided into two parts. One part was stirred with 2 N ammonia solution for 2.5 h, washed with water and dried; yield: 75%. The purified polyester was insoluble in chloroform and the carbon analysis did not agree with the calculated value (Found: C 57.81; H 3.75). The second part was refluxed for 12 h with 1 N HCl, washed with water and dried *in vacuo*; yield 94%. Analyses: Found: C 64.03; H 3.41.

Various condensations of 3-hydroxybenzoic acid (Table 4)

In all other experiments of *Table 4* the reaction mixture was also precipitated from methanol, and the crude polyester was dried *in vacuo*. In the case of Nos. 9 and 10 the crude polyester was refluxed in methanol for 1 h and washed with water as recommended in Ref. 6. However, the elemental analyses did not agree with the calculated ones (*Table 4*).

Crystallization of linear poly(*3-hydroxybenzoate*)

(1) Preparative procedure: 5 g poly(3-hydroxybenzoate) were dissolved under stirring in a warm mixture of 50 ml dry pyridine and 50 ml dry benzene. The clear solution was stored at 25°C for 2 days, after which the precipitated material was filtered off and washed with chloroform or methylene chloride.

(2) Analytical procedure: 200 mg reprecipitated poly(3-hydroxybenzoate) was shaken or stirred in 4 ml of a distilled solvent at 40°–50°C. The resulting solution or suspension was stored in a stoppered probe-tube for up to four weeks. Class I solvents (*Table 5*) gave solutions that remained clear after storage for four weeks at ~25°C. Class II solvents (*Table 5*) gave clear solutions which the polyester crystallized from more or less rapidly. The precipitated material was filtered off and dried after one week. Class III solvents (*Table 5*) are best characterized by describing two extreme cases. For example, the suspension of the amorphous polyester in acetone does

Table 5 Classification of solvents and nonsolvents with respect to their interaction with amorphous $(3\text{-Hybe})_n$

Solvents forming kinetically stable solutions Class I	Solvents causing spontaneous crystallization Class II	Nonsolvents inducing crystallization Class III	Nonsolvents without influence on $(3\text{-Hybe})_n$ Class IV	δ_1 $(cal/cm^3)^{1/2}$
Chloroform	Nitrobenzene	Acetone	Hexamethyl disiloxane ca.	5.0
Methylenechloride	γ-Picoline	Acetonitrile		
1,1,2,2-Tetrachloroethane	Pyridine	Ethylacetate	Diisopropyl ether	6.9
1,4-Dioxane	Quinoline	*N*,*N*-Dimethylaniline	n-Hexane	7.4
m-Cresol	Tetrahydrofurane	Diethyl-Phthalate	Diethyl ether	
Hexamethyl phosphorus triamide	Dimethylformamide	2,6-Lutidine		7.4
Dichloroacetic acid	Pyridine + Benzene (1:1)	Pyridine + Xylene (1:1)	Ethanol	12.7
	Pyridine + DMSO (1:1)	Pyridine + Phenol (1:1)	Methanol	14.5
		Pyridine + Acetonitrile (1:1)	Formamide	19.2
		Pyridine + Nitromethane (1:1)	Water	23.4
		Pyridine + Acetic acid (1:1)		
		Pyridine + Carbontetrachloride (1:1)		

not exhibit any change to the naked eye. However, when the polyester is filtered off after a storage of one week, the d.s.c. curve shows a melting endotherm (*Figure 3*). When a mixture of pyridine and chloroform is used, the polyester begins to dissolve; yet the precipitation of crystallizing material is so fast that never a clear solution was obtained.

Measurements

The viscosities were measured in an Ostwaldt viscosimeter thermostatically controlled at 20°C. The number molecular weights were obtained with a 'Hitachi-Perkin-Elmer (Mod. 115)' vapour-pressure osmometer in chloroform.

The g.p.c. measurements were carried out on a 'Waters GPC-200' chromatograph on Toyo Soda columns: G 6000 S, G 5000 S, G 4000 S and G 3000 S. The solvent was chloroform, the sample volume 1 ml and the permeation rate 1.2 ml min^{-1}.

The d.s.c. curves were measured with a 'Perkin-Elmer DSC-2' at heating rates varying from 2.5 to 80 K min^{-1}.

The X-ray diffraction patterns were measured with Ni-filtered CuKα radiation at a distance of 50 mm.

The thermogravimetric analyses were run on a 'Mettler thermoanalyser TA-1' in air in open aluminium probes. The sample size was 20–30 mg and the heating rate 8 K min^{-1}.

The 22.63 MHz ^{13}C n.m.r. spectra were measured on a Bruker WH-90 *FT* spectrometer at ~30°C. Samples of 400 mg were dissolved in a 2 ml mixture of trifluoroacetic acid (TFA) and deuterated chloroform (volume ration 1:3). The measurements were run in 10 mm od. sample tubes with a coaxial 4 mm od. tube containing a mixture of dioxane-d$_8$ and TMS (1:1 by volume). The following acquisition parameters were used: pulse width 5 μs (~40°); 18 K data points/5000 Hz spectral width zero-filled to 16 K before Fourier-transform; exponential line-broadening 0.8 Hz; ~20 000 transients. The 90 MHz ^{1}H n.m.r. spectra were obtained on the same Bruker WH-90 *FT* spectrometer in 5 mm od. sample tubes. Solutions of 60 mg polyester in 0.6 ml $CDCl_3$ were measured with internal TMS as standard using the following parameters: pulse width 2 μs (~60°); 4 K data points/1000 Hz spectral width, 1000 transients.

RESULTS AND DISCUSSION

Syntheses of poly(3-hydroxybenzoate)

Since (trimethylsiloxy)benzoyl chlorides are reactive monomers at first condensations of 3-(trimethylsiloxy)benzoyl chloride (**2**) in solution were investigated (*Table 1*). A pyridine/benzene mixture was used as reaction medium, because such mixtures are good solvents for the (3-Hybe)$_n$ and because pyridine activates acid chlorides by intermediate formation of acylium ions. Due to the poor yield and the low *Mn* attained in this first experiment the following condensations were run in a higher boiling solvent (Nos. 2–5). Although yields and *Mn*'s increased, the results were not satisfactory in as much as potential catalysts such as pyridine and Lewis acids turned out to be ineffective; yields up to 99% and *Mn*'s up to 13 000 (degree of polymerization ≈120) were obtained when bulk condensations were conducted (*Table 2*). Optimum results were found for reaction temperatures in the range of 250°–300°C and a reaction time of 3 h (Nos. 2–5 and 7, *Table 2*). While the condensations Nos. 1, 2 and 6–8 were conducted with monomer of one batch condensations Nos. 2–5 were run with monomer of another badge to test the reproducibility. Whereas both yields and *Mn*'s of condensations Nos. 2–4 agree well with each other, the *Mn*'s are ~20% lower than those of experiments Nos. 2 and 7. This difference is probably the result of different contaminations with triethylamine hydrochloride, which was found to be an effective condensation catalyst for various siloxy benzoyl chlorides (published elsewhere). Triethylamine hydrochloride is formed as a byproduct of the synthesis of monomer **2**[8], and it is difficult to remove, because it can sublime and accompany the monomer upon distillation. The condensation of non distilled monomer of the second badge (No. 5, *Table 2*) demonstrates, that the distillation of the monomer does not have a significant influence on yield and $\bar{M}n$.

The glassy (3-Hybe)$_n$ resulting from the bulk condensations was dissolved in a 1:1 mixture (by volume) of pyridine and benzene and precipitated from cold methanol. In this way, the 3-Hybe)$_n$ was obtained in the form of an amorphous powder which showed a good solubility in a variety of organic solvents. This property allowed us to determine the $\bar{M}n$'s by vapour pressure osmometry (v.p.o.) and by ^{1}H n.m.r. spectroscopic end-group analysis in chloroform or $CDCl_3$ respectively. To ensure that the trimethylsiloxy end-groups quantitatively evaluated by means of ^{1}H n.m.r. spectra (*Figure 1b*) were not hydrolysed upon precipitation from methanol; several polyester solutions were divided into two parts and one part was precipitated from dry diethylether (last column of *Table 2*) whereas the end-group analyses agree well with each other, the *Mn*'s obtained by v.p.o. are ~10% lower. This difference may be considered the margin or error of both methods because any contamination with small molecules (e.g. solvent) reduces the v.p.o. values while any loss of siloxy end-groups increases the ^{1}H n.m.r. values.

We had a strong interest in reliable *Mn*'s because Gilkey and Caldwell[2] reported a maximum value of 25 000 for a polyester obtained by bulk condensation of 3-acetoxybenzoic acid. This value was surprising because the viscosities of our best products (Nos. 3 and 4, *Table 2*)

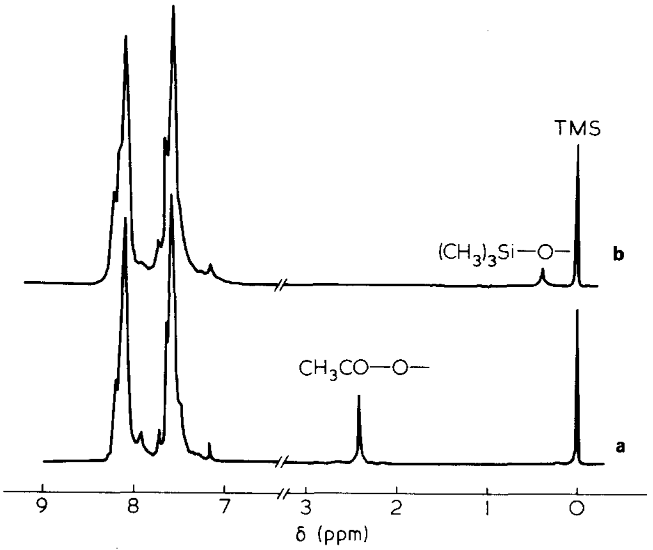


Figure 1 90 MHz ^{1}H-n.m.r. spectra of (3-Hybe)$_n$ solution in $CDCl_3$. (a) Prepared from 3-acetoxybenzoic acid; (b) prepared from 3-trimethylsiloxy benzoyl chloride

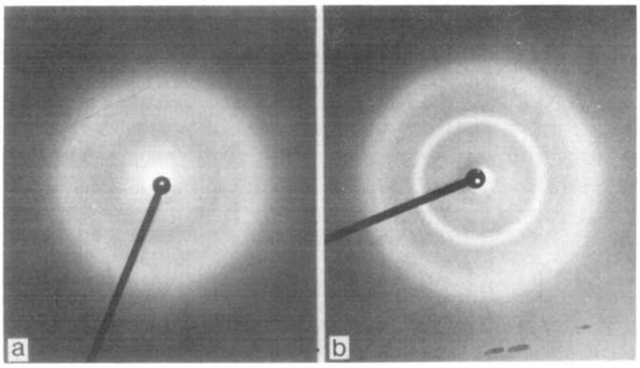


Figure 2 X-ray diffraction pattern of (3-Hybe)$_n$. (a) Reprecipitated from pyridine + benzene/methanol; (b) crystallized from pyridine + benzene (1 : 1) at 25°C

were higher than those of Gilkey and Caldwell, although our *Mn*'s were significantly lower. Hence, we have reinvestigated the bulk condensation of 3-acetoxybenzoic acid, with slight variations of the reaction conditions given in Ref. 2 (Nos. 1–3, *Table 3*). The *Mn*'s of the resulting (3-Hybe)$_n$ were determined by both v.p.o. and ^{1}H n.m.r. spectroscopy, using the acetoxy end-groups (*Figure 1b*). The good agreement between these two different analytical methods and between the results of experiments Nos. 1–3 of *Table 3* let us conclude that our measurements are correct. However, this means that the above authors have overestimated their $\bar{M}n$'s. Since their *Mn*'s were determined by end-group titration, correct values were only obtained if all polyester chains really possessed carboxyl end-groups. However, acetoxy benzoic acids undergo decarboxylation at temperatures of 250°C, and thus, the formation of chains without carboxyl end-groups is highly probable.

The third method reported for the synthesis of (3-Hybe)$_n$, namely the condensation of 3-hydroxybenzoic acid by means of the reactive phosphorous reagents[3–6] seems to be the simplest procedure because no derivative of 3-hydroxybenzoic acid needs to be prepared. However, the (3-Hybe)$_n$ samples isolated by Higashi *et al.*[3–6] from various experiments are not well characterized. The *Tg* (325°C) reported in Ref. 4 is far from being correct and neither purity nor *Mn*'s were determined. This situation prompted us to investigate the condensation of 3-hydroxybenzoic acid by means of tri- and pentavalent phosphorous derivatives. Most condensations (Nos. 1–4, *Table 4*) were conducted with hexachlorocyclotriphosphazene, because Higashi *et al.* obtained the highest yields with this reagent. The yields of the crude polyesters precipitated from methanol were amazing (180–185%) and several purification steps were required to bring the yields below 100%. However, even then the C-analyses were unsatisfactory and the *Mn*'s determined by v.p.o. in chloroform in all cases were below 2500. Repeated treatment with diluted HCl (a reagent recommended in Refs. 3–6) leads to a higher purity but reduces the $\bar{M}n$'s owing to hydrolysis. Treatment with 2 N ammonia, a reagent used successfully for the purification of polypeptides from phosphoric acid derivatives[9], yielded a polyester which was insoluble in chloroform (No. 3, *Table 4*). The results of all the other condensations of *Table 4* were likewise disappointing. Trivalent phosphorus derivatives including the 1-phosphino triazole (DPT) we have successfully used for the synthesis of several polypeptides[9], gave extremely poor yields and in no case were satisfactory C-analyses obtained. Thus, the 'phosphorus-method' is certainly inferior to the 'acetoxy- or siloxy-method'.

Finally, we investigated whether the structure of (3-Hybe)$_n$ prepared from 3-acetoxybenzoic acid or 3-trimethylsiloxybenzoyl chloride is modified by Fries rearrangements. The Fries rearrangement normally occurs when a phenol ester is heated in the presence of a Friedel–Craft catalyst to temperatures between 50° and 150°C. Although our condensations were run without addition of acidic catalysts, Fries rearrangements might occur due to the high reaction temperatures. Since the Fries rearrangement yields aromatic keto groups, it is easily detectable by means of ^{13}C n.m.r. spectroscopy. Aromatic keto groups absorb between 190 and 200 ppm, a shift range which does not overlap any other signals of (3-Hybe)$_n$. Using concentrated solutions of (3-Hybe)$_n$ in $CDCl_3$ we have accumulated 60 000–80 000 FIDs, so that signal intensity ratios of 1:100 were easily measurable. However, aromatic keto groups were never detected. This means that at best, one out of 200 monomer units might have undergone a Fries rearrangement. If so, this low concentration of keto groups is unlikely to influence the properties of (3-Hybe)$_n$.

*Crystallization of poly(*m*-hydroxybenzoate)*

For all investigations on the properties of (3-Hybe)$_n$ the amorphous polyester obtained after reprecipitation from pyridine + benzene/methanol was used as starting material ($\bar{M}n = 10\,000–13\,000$). This amorphous (3-Hybe)$_n$ shows a glass transition at 155°C when d.s.c.

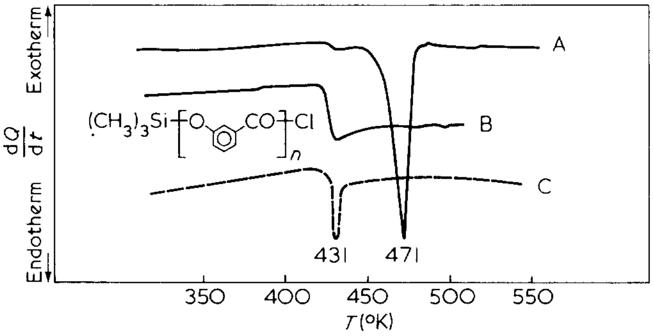


Figure 3 D.s.c. curves (heating rate 40 K min^{-1}) of (A) amorphous, freshly reprecipitated (3-Hybe)$_n$; (B) (3-Hybe)$_n$ crystallized from pyridine + benzene at 25°C; (C) reheating of quickly cooled sample B

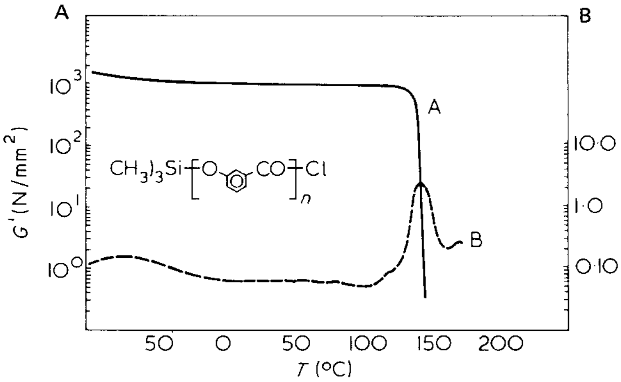


Figure 4 Torsion pendulum measurement of amorphous (*m*-Hybe)$_n$ at 0.1–1.0 Hz, heating rate 1 K min^{-1}

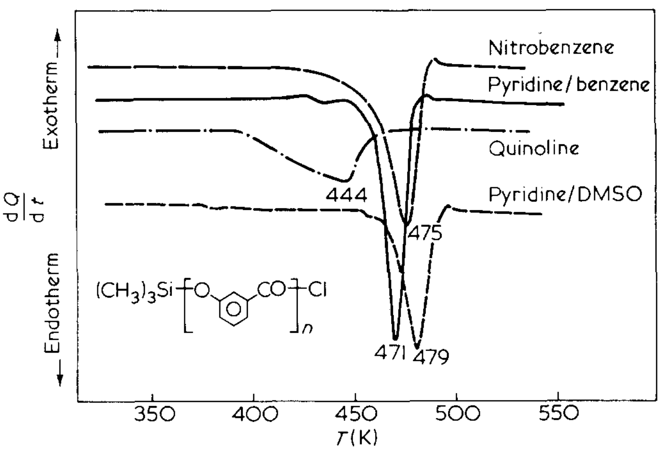


Figure 5 D.s.c. curves of $(3\text{-Hybe})_n$ crystallized from various solvents (heating rate 40 K min^{-1})

measurements are conducted at a heating rate of 40 K min^{-1} (*Figure 3a*). Torsion pendulum measurements (0.1–1 Hz) show the glass transition at 145°C due to the slower heating rate (1 K min^{-1}, *Figure 4*). Hence, 145°C must be the true *Tg*. *Figure 4* also reveals that above the glass transition any elasticity is lost as expected for a completely amorphous non crosslinked material. Furthermore, another second order transition is observable in the range of −70° to −50°C. This transition may result from unfreezing of rotations of the benzene rings around the CO–O bonds. The energy of activation required for rotations around ester bonds is in the order of 40–50 K J mol^{-1}, and thus, fits well into this picture.

We have attempted to crystallize $(3\text{-Hybe})_n$ by annealing amorphous samples at various temperatures above the glass transition. Although the reaction time was extended to 8 days, we were not able to detect any crystallinity. This result contrasts sharply with the finding that $(3\text{-Hybe})_n$ crystallizes rapidly at room temperature if it comes into contact with a suitable solvent or nonsolvent. We have investigated the influence of about thirty common organic solvents or solvent mixtures on the crystallization of $3\text{-Hybe})_n$. The results allow us to subdivide the solvents into four classes (*Table 5*). In class I solvents kinetically stable solutions of amorphous $(3\text{-Hybe})_n$ were obtained, i.e. these solutions remained clear at 20°–25°C over a period of 4–5 weeks, although crystalline $(3\text{-Hybe})_n$ is insoluble. The class IV nonsolvents do not induce crystallization and thus, are useful for the precipitation of entirely amorphous $(3\text{-Hybe})_n$.

Most solvents which effect isothermal crystallization of $(3\text{-Hybe})_n$ from solution (class II) and those which induce crystallization when added to chloroform solutions of $(3\text{-Hybe})_n$ are aromats. This observation suggests that the aromatic solvents favour a special conformation of the dissolved $(3\text{-Hybe})_n$, which in turn favours the nucleation step. Such a conformation could be a coplanar orientation of several 3-Hybe units resulting from a solvation shell which may be described as a weak CT-complex or a rather stable collision complex between aromatic solvent and coplanar 3-Hybe units. Yet, neither u.v. nor ^{13}C n.m.r. measurements gave any confirmation of this hypothesis. Furthermore, we have looked at the solubility parameters δ_1. All class I, II and III solvents have δ_1 values in the order of 9.1–12.1 (cal $cm^{-3})^{\frac{1}{2}}$, while the nonsolvents of class IV possess δ_1-values < 7.5 or > 12.5 (*Table 5*). This observation suggests that δ_2 of $(3\text{-Hybe})_n$ is in the range of 10.0–11.0 (cal $cm^{-3})^{\frac{1}{2}}$ in agreement with the δ_2-value (10.7) of poly(ethylene terephthalate)[10,11].

We have compared the crystallinity of numerous $(3\text{-Hybe})_n$ samples crystallized at 25°C from various solvents or nonsolvents. The X-ray diffraction patterns confirm the formation of crystalline regions (*Figures 2a* and *b*). The d.s.c. curves reveal that crystalline $(3\text{-Hybe})_n$ of different origin may vary with respect to both shape of the melting endotherm and temperature of its maximum (*Figure 5*). The temperature which varies by 8 degrees, if only sharp endotherms are compared, reflects mainly the perfectness of the crystalline regions, while the shape of the endotherms reflects the distribution of the crystallite sizes. The sharpest melting peak was obtained with pyridine + benzene (1:1) and the highest *Tm* with pyridine + dimethylsulphoxide (1:1). A similar variation of shape and maximum of the melting endotherms was observed for samples crystallized in contact with nonsolvents (*Figure 6*). However, all maxima appeared at lower temperatures than those found for solution crystallized $(3\text{-Hybe})_n$ suggesting that crystallization induced by nonsolvents leads to less perfect crystallites. In a couple of cases, the melting endotherm appears at such a low temperature (165°–170°C), that it overlaps with the glass transition. Sharp endotherms (e.g. in the case of pyridine + benzene) allow a separate observation of the glass transition, indicating that even under the optimum conditions only partially crystalline $(3\text{-Hybe})_n$ was

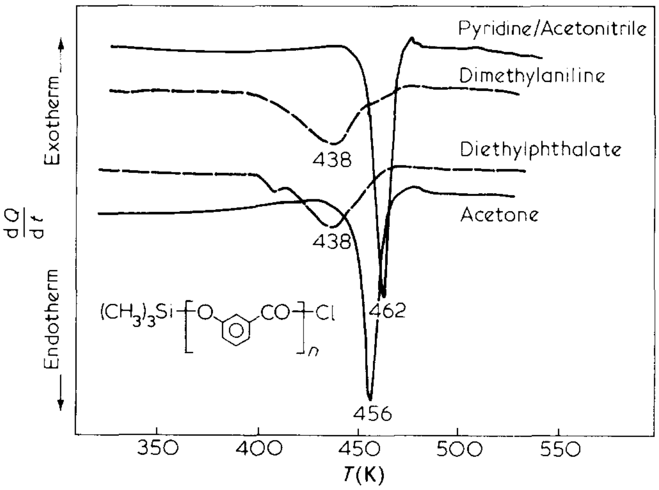


Figure 6 D.s.c. curves of $(3\text{-Hybe})_n$ crystallized in contact with various nonsolvents

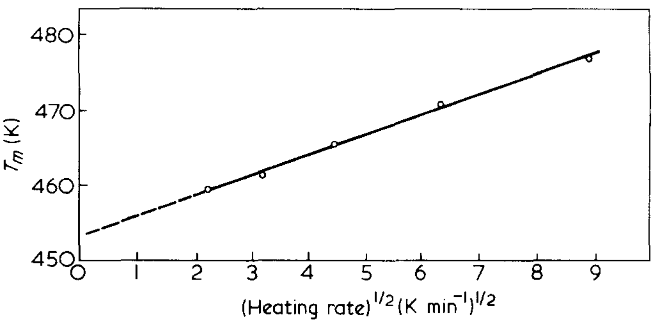


Figure 7 Plot of d.s.c. maxima of $(3\text{-Hybe})_n$ crystallized from pyridine + benzene (1 : 1) *versus* the square root of the heating rate

Table 6 Partially crystalline (3-Hybe)$_n$: dependence of *Tm* and relative crystallinity on the nature of the solvent

Solvent (class II)	*Tm* (K)	Relative crystallinity	Solvent (class III)	*Tm* (K)	Relative crystallinity
Pyridine/Benzene[a]	471[a]	1.00[a]	*N,N*-Dimethylaniline	438	1.11
γ-Picoline	467	0.99	2,6-Lutidine	469	0.74
Pyridine	469	1.04	Phthalic acid diethyl ester	438	1.09
Chinoline	444	1.11			
Dimethylformamide	470	1.31	Acetone	456	0.85
Nitrobenzene	475	1.25	Pyridine/*p*-Xylene	466	1.21
Pyridine/Nitrobenzene	475	1.08	Pyridine/Phenol	418	2.10
Pyridine/Dimethyl Sulphoxide	479	0.87	Pyridine/Chloroform	464	0.93
Pyridine/Tetrahydrofuran	471	1.10	Pyridine/Carbontetrachloride	467	0.94
			Pyridine/Nitromethane	468	0.87
			Pyridine/acetic Acid	461	0.77
			N,N-Dimethylaniline/Benzene	458	0.97

[a] Standard

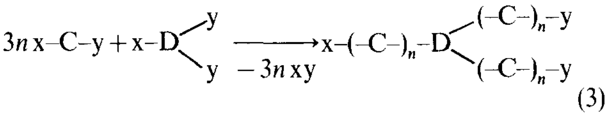
obtained (*Figures 3* and *5*). In order to get an idea as to what extent the degreee of crystallinity can vary with the nature of solvent or nonsolvent, we have compared the peak areas of the d.s.c. endotherms (*Table 6*). Finally, it is to be noted that we have measured a sample crystallized from pyridine + benzene at various heating rates. The extrapolation presented in *Figure 7* demonstrates that the true *Tm* equals 181°C but may be slightly higher (184°–185°C) if a mixture of pyridine and dimethylsulphoxide is used for the crystallization (*Figure 5*).

Branched poly(3-hydroxybenzoate)

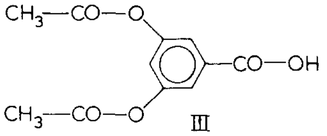
Textbooks often mention that addition of trifunctional monomers to condensation polymerizations yields crosslinked polycondensates, provided that the conversion is sufficiently high. This is correct if two different kinds of monomers, each one with two identical functional groups, are involved (equation 1). However, the condensation of monomers with two different functional groups (equation 2) leads to branched polymers if a trifunctional monomer is added (equation 3). Provided that side reactions of y groups are excluded, crosslinking cannot take place regardless of the conversion. Flory[12] and Burchard[13,14] have published theoretical treatments of structure and light scattering behaviour of such branched polycondensates in solution. Highly branched, but not crosslinked polycondensates of this type are the 'invention' of those living cells, which have first realized syntheses of amylopectin and glycogen. However, to our knowledge, a fully synthetic system has not yet been reported.

$$n\,x\text{–}A\text{–}x + n\,y\text{–}B\text{–}y \xrightarrow[-(2n-1)xy]{} x\text{–}(\text{–}A\text{–}B\text{–})_n y \qquad (1)$$

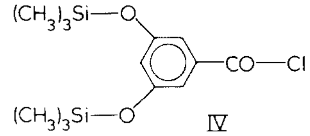
$$n\,x\text{–}C\text{–}y \xrightarrow[-(n-1)xy]{} x\text{–}(\text{–}C\text{–})_n\text{–}y$$



$$3n\,x\text{–}C\text{–}y + x\text{–}D\begin{matrix}\text{y}\\ \text{y}\end{matrix} \xrightarrow[-3n\,xy]{} x\text{–}(\text{–}C\text{–})_n\text{–}D\begin{matrix}(\text{–}C\text{–})_n\text{–}y\\ (\text{–}C\text{–})_n\text{–}y\end{matrix} \qquad (3)$$



III



IV

We have attempted to synthesize branched (3-Hybe)$_n$ by bulk condensation of either 3-acetoxy benzoic acid (I) and 3,5-(bisacetoxy)benzoic acid III or (3-(trimethylsiloxy)benzoyl chloride II and 3,5-(bistrimethylsiloxy)benzoyl chloride IV. The results summarized in *Table 7* demonstrate that the cocondensation of I and III fails to yield branched (3-Hybe)$_n$ because the expected increase of the molecular weight is not detectable. We suppose that the second acetoxy group of 3 after incorporation of the trifunctional comonomer into the linear chain is not reactive enough to initiate the branching step. The cocondensation of the acid chlorides II and IV under the optimum conditions

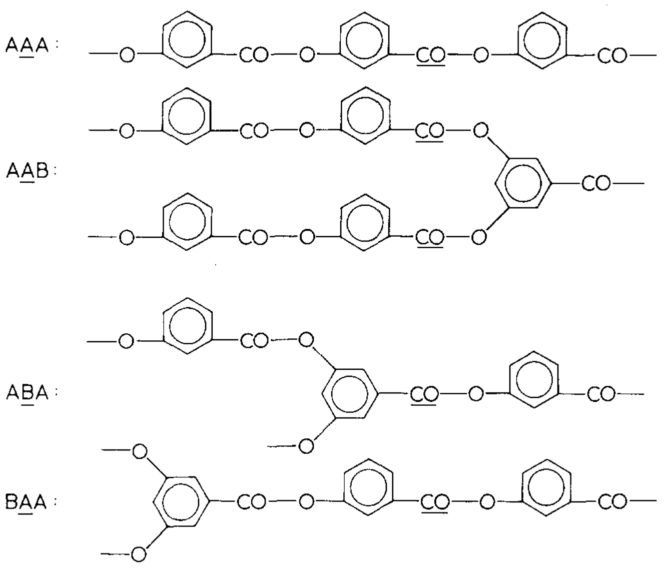
Table 7 Syntheses of branched poly(*m*-hydroxybenzoate) from 3-trimethylsiloxy benzoyl chloride or 3-acetoxybenzoic acid

No.	Monomer	Branching comonomer	Monomer[a]/comonomer	Time (h)	Temp. (°C)	Yield[c] (%)	$\bar{M}_n$[d]
1	3-Trimethylbenzoyl chloride	3.5-Bistrimethylsiloxybenzoyl chloride	160:1	3	250	96.0	10 000
2	"	"	80:1	3	250	96.2	12 500
3	"	"	40:1	3	250	96.5	25 000
4	"	"	20:1	3	250	96.5	28 900
5	"	"	10:1	3	250	97.5	–[e]
6	"	"	5:1	3	250	99.5	–[e]
7	3-Acetoxybenzoic acid	3.5-Bisacetoxybenzoic acid	40:1	3.0 + 0.25[b]	220 + 300	86.0	3 700
8	"	"	20:1	3.0 + 0.25[b]	220 + 300	80.0	3 300

[a] Mole ratios
[b] 2 h without and 1 h with vacuum
[c] After reprecipitation from pyridine + benzene/methanol
[d] Vapour pressure osmometry in chloroform
[e] Not completely soluble in chloroform (but soluble in DMF)

Table 8 Intensities of the CO-signals of branched $(3\text{-Hybe})_n$ calculated from the probabilities of the four triads $A\underline{A}A$, $A\underline{A}B$, $A\underline{B}A$ and $B\underline{A}A$ (Scheme I)

	Mole ratios of A and B units			
Triad	5:1	10:1	20:1	40:1
$A\underline{A}A$	5	10	20	40
$A\underline{A}B$	2	2	2	2
$A\underline{B}A$	1	1	1	1
$B\underline{A}A$	1	1	1	1



Scheme I: Formulas and symbols of the four most probable triads of branched poly(3-hydroxybenzoate)

worked out for the condensation of II (No. 2, *Table 2*) was far more successful. Increasing concentrations of the branching monomer to increasing molecular weights (Nos. 1–4, *Table 10*). Because the yields of reprecipitated polyesters were in the range of 96–99% we may assume that the conversion was nearly complete. Thus, we may calculate the number of branching points from the mole ratios of the monomers II and IV. Unfortunately, those branched polyesters with the highest degree of branching were not completely soluble in chloroform (Nos. 5, 6, *Table 10*), so that their molecular weights could not be determined by v.p.o. However, these highly branched $(3\text{-Hybe})_n$ samples were completely soluble in polar solvents, such as dimethylformamide or pyridine + benzene (1 + 1), so that the absence of crosslinking is clearly established. The change of solubility with increasing mole ratio IV/II may be considered as further evidence for the increasing number of branches. It should be noted that a high purity of both monomers II and IV is required to avoid crosslinking. If crude monomers are used, a part of the branched $(3\text{-Hybe})_n$ is insoluble in pyridine + benzene and remains in the form of gel particles on the filter. Presumably, traces of thionylchloride, which is required for the syntheses of II and IV react with the triethylsiloxy groups forming sulphite or, after elimination of SO_2, ether linkages.

In order to obtain direct spectroscopic evidence for the formation of branching points from condensations of monomer IV, we have measured ^{13}C-n.m.r. spectra of the polyesters of condensations Nos. 3–6, *Table 7*. On the basis of ^{13}C n.m.r. spectroscopic sequence analyses of various copolyesters[15,16], we have expected that the carbon signals are sensitive to sequence effects. For random cocondensations of monomers II and IV, one can calculate the probabilities of all possible triads. However, for mole ratios of II and IV > 5:1 the probabilities of triads containing two or three branching units are so low that they are not detectable by ^{13}C n.m.r. spectroscopy. Thus, it is sufficient to calculate the probabilities and signal intensities respectively for the four most probable triads (Scheme I). The signal intensities (*Table 8*) deviate from the triad probabilities, because the triad $A\underline{A}B$ contains two identical central units, so that its CO-signal must have the double intensity. Our measurements in chloroform confirm that the experimental intensities agree well with the calculated ones (*Figure 8* and *Table 8*).

Since isothermal crystallization from pyridine + benzene (1:1) is a characteristic property of linear $(3\text{-Hybe})_n$ and because the yield of crystallized polyester depends on the $\bar{M}n$ we have expected that the degree of branching also has a strong influence on the yield of crystallizable material. *Figure 9* demonstrates a linear relationship between the yield of crystallized $(3\text{-Hybe})_n$ and the number of branching points found

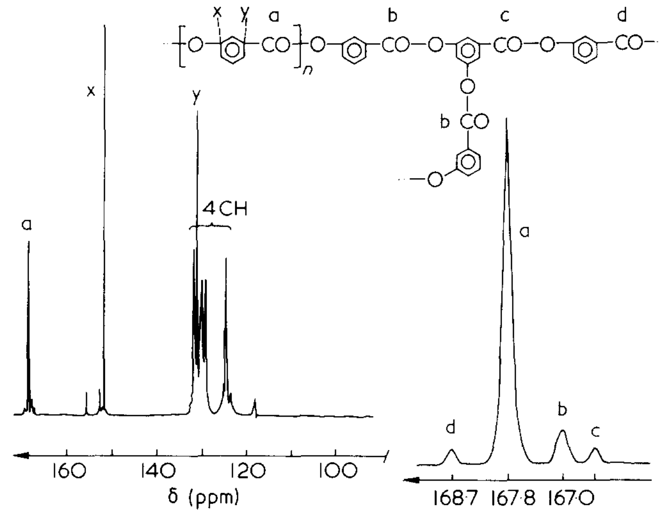


Figure 8 22.63 MHz ^{13}C n.m.r. spectrum of branched $(3\text{-Hybe})_n$ with 5 mol% branching monomer dissolved in trifluoroacetic acid (for simplification the solvent signals are eliminated)

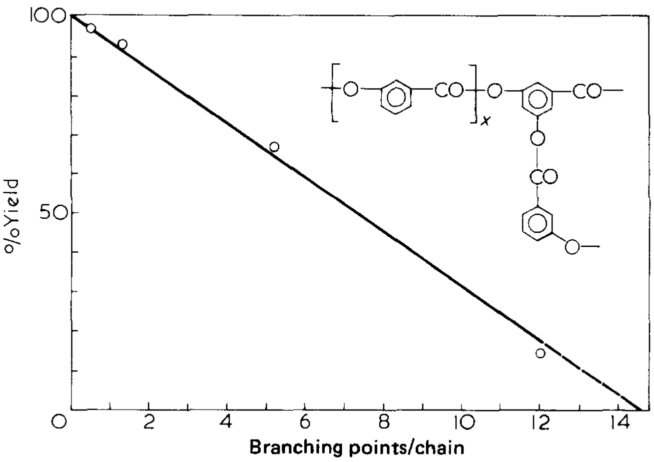


Figure 9 Yields of branched $(3\text{-Hybe})_n$ crystallized from pyridine + benzene (1 : 1) at 25°C plotted *versus* the concentration of branching points per chain

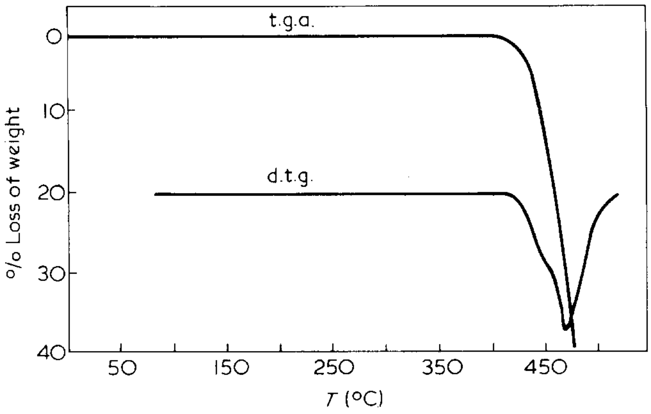


Figure 10 Thermogravimetrical analyses of linear and branched (3-Hybe)$_n$ ($\bar{M}_n \geqslant 10\,000$) in air, measured at a heating rate of 8 K min

experimentally. This may be rationalized considering that not the absolute *Mn* of the sample but the average lengths of polymer segments are responsible for the crystallization. Of course, the linear standard polyester must have a value of *Mn* which allows more than 95% crystallization and the *Mn*'s of the branched samples may not be lower (Nos. 1–4, *Table 7*). If these requirements are met, the crystallization is governed by the lengths of the linear chain segments, since crystallization requires parallel or antiparallel alignment of the polyester chains. This also means that the thermodynamically controlled crystallization we have conducted should lead to a fractionation of the branched (3-Hybe)$_n$ according to its chemical heterogeneity of the first order. This deserves further investigation. Branching not only influenced the yield of crystalline (3-Hybe)$_n$, but also the rate of crystallization. When pyridine+benzene solutions of linear (3-Hybe)$_n$ with $\bar{M}n \geqslant 10\,000$ is stored at room temperature 90–94% of crystalline material has precipitated after 24 h. A second fraction of 1–5% can be isolated after an additional 24 h. In the case of branched (3-Hybe)$_n$ 3–6 days are required until the crystallization equilibrium is reached. When filtered after 7 days, the filtrates of all samples remained clear.

Furthermore, it is to be noted that the molecular weight distribution of sample Nos. 1, 2 and 4 (*Table 7*) were compared by g.p.c. in chloroform. The main result of these measurements was that the shapes of the three curves were nearly identical. Of course, V_E was shifted to slightly lower values with increasing *Mn*. As expected, this effect was poor, since branched polymers have a smaller hydrodynamic volume than linear polymers of identical *Mn*. However, neither did we find a bimodal weight distribution nor a small peak at low V_E which might indicate the presence of microgels. Thus, the g.p.c. measurements support our conclusion that the branched (3-Hybe)$_n$ prepared from monomers II and IV is the result of an almost complete and random cocondensation.

Finally, we have compared the thermal stability of branched and linear (3-Hybe)$_n$ in air. Any degradation involving the phenol endgroups must result in a low stability of the branched samples. However, measurements of two samples containing 10 and 40 mol% branching monomer showed that branching does not significantly affect the thermal stability. Thus, the degradation of linear and branched samples can be described by one t.g.a. curve (*Figure 10*) which indicates 1% loss of weight at 410° ± 6°C and 5% at 440° ± 5°C. Furthermore, measurements of the energy flow indicated that the degradation above 400°C is exothermic. All observations suggest that the thermal degradation is the result of a nonspecific oxidation rather than cyclyzation or elimination processes involving the chain ends.

CONCLUSION

Comparisons of various condensation methods have shown that the thermal condensation of 3-(trimethylsiloxy)benzoyl chloride in bulk at temperatures between 250° and 300°C gives the best yields and highest molecular weights of (3-Hybe)$_n$. Poly(3-hydroxybenzoate) may be useful for coating more oxidation sensitive materials, such as aliphatic plastics, fibres or metal surfaces. In the amorphous state (3-Hybe)$_n$ may be processed in solution yet insolubility can be brought about quickly by solvent induced crystallization. Cocondensation of 3-(trimethylsiloxy)benzoyl chloride and 3,5-(bistrimethylsiloxy)benzoyl chloride allows the synthesis of branched soluble (3-Hybe)$_n$ without the risk of crosslinking. Branching may have several advantages. The molecular weight increases, the crystallinity which can cause brittleness and shrinking is reduced, the number of hydroxy endgroups which improve the adhesion on polar surfaces is enhanced and irreversible crosslinking can be achieved by reaction with difunctional reagents, such as diisocyanates or epichlorohydrin. In other words, the properties of poly(3-hydroxybenzoates) are more interesting than the first report of Gilkey and Caldwell[2] has suggested.

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