

# New polymer syntheses 85. Telechelic, star-shaped and hyperbranched polyesters of $\beta$ -(4-hydroxyphenyl) propionic acid

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The trimethylsilylester of  $\beta$ -(4-acetoxyphenyl) propionic acid (APPA), which is easier to isolate than the free acid, was used as monomer for all polycondensations. Copolycondensations with small amounts of 4-tert-butylbenzoic acid or 4-tert-butylphenol acetate yielded oligo- and polyesters with two different endgroups. All oligoesters show a reversible first order phase transition between 240 and 265°C yielding a solid mesophase upon heating. The formation of an isotropic melt occurs between 340 and 380°C depending on the degree of polymerization (DP). The glasstransition temperatures increased from 48–50°C to values around 63–65°C with increasing molecular weight. Copolycondensations with acetylated bisphenol-P yielded telechelic oligoesters with two identical endgroups. Four-armed star-shaped polyesters were prepared by copolycondensation of a tetraacetoxyspirobisindan. Since the bisphenol-P and the spirobisindane units are unfavourable for the crystallization, the crystallinity depends on the DP, and the solubility depends in turn on the crystallinity. Hyperbranched copolyesters were synthesized by copolycondensation of silylated APPA with silylated or free 3,5-bisacetoxybenzoic acid with variation of the molar ratio. The hyperbranched character of these copolyesters was demonstrated by their reluctance to crystallize and by  $^{13}\text{C}$  n.m.r. spectroscopic sequence analyses. The  $T_g$ s of these hyperbranched copolyesters follow almost exactly the Fox equation. G.p.c. measurements revealed number average molecular weights ( $M_n$ ) up to 31 000  $\text{g mol}^{-1}$  (for the 1/1 copolyester) and  $M_w/M_n$  ratios in the range of 3.5–6.5. © 1997 Elsevier Science Ltd.

**(Keywords: phloretic acid; telechelics; star-shaped polyesters; hyperbranched polyesters; copolycondensation; chainstopper)**

## INTRODUCTION

The present work is part of a broader study of syntheses and properties of polyesters derived from hydroxycarboxylic acids (A–B type monomers)<sup>1–5</sup> and syntheses of star-shaped or hyperbranched polycondensates<sup>6–13</sup>.

$\beta$ -(4-Hydroxyphenyl) propionic acid (HPPA, phloretic acid) was selected as monomer for two reasons. Firstly, its polyesters (particularly, the copolyesters) may be considered to be biodegradable materials<sup>14–16</sup>, because the aliphatic CO-group is significantly more sensitive to hydrolysis than the CO-groups of hydroxybenzoic acid, and because HPPA is a non-toxic degradation product which occurs in the metabolism of several plants. Secondly, copolyesters containing 4-hydroxybenzoic acid are thermotropic forming a nematic melt<sup>17,18</sup>.

Unfortunately, the homopolyester of HPPA<sup>19</sup> is a highly crystalline material which is insoluble in all common inert solvents, and thus, difficult to characterize. Therefore, this work was aimed at studying syntheses and properties of telechelic, star-shaped and hyperbranched polyHPPA to find out how these structural variations influence the properties of this polyester particularly its solubility.

## EXPERIMENTAL

### Materials

$\beta$ -(4-Hydroxyphenyl) propionic acid (phloretic acid) was purchased from Lancaster Synth. (Mülheim, Main, Germany). 4-Methylbenzoic acid, 4-*t*-butylbenzoic acid, *t*-butylphenol, 3,5-dihydroxybenzoic acid and 5,5',6,6'-tetrahydroxy-3,3',3',3'-tetramethylspirobisindan were purchased from Aldrich Co. (Milwaukee, Wisconsin, USA). Bisphenol-P was purchased from Kennedy and Klim (Little Silver, N.J., USA).

### Trimethylsilyl $\beta$ -(4-acetoxyphenyl)propionate

$\beta$ -(4-Hydroxyphenyl) propionic acid (0.5 mol) was refluxed in acetic anhydride (150 ml) for 1 h. After cooling dry toluene (300 ml) was added, and the turbidity resulting from a precipitation of oligomers was removed by filtration. The filtrate was concentrated *in vacuo* and the syrupy residue was dried at 100°C and a pressure of 0.1 mbar for 8 h. Afterwards the residue was again dissolved in hot toluene (700 ml), chlorotrimethylsilane (0.6 mol) was added and triethylamine (0.6 mol) was added dropwise with stirring. After 2 h of reflux the reaction mixture was cooled with ice, filtered under exclusion of moisture, and the product was isolated by distillation *in vacuo* (0.01 mbar) over a short-path apparatus. Yield 62%,  $n_D^{20}$  1.4859. Analyses calcd. for  $\text{C}_{14}\text{H}_{20}\text{O}_4\text{Si}$  (280.4): C 59.97, H 7.19, found: C 59.97, H 7.22%.

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<sup>1</sup>H n.m.r. (CDCl<sub>3</sub>/TMS), δ = 0.26(*s*, 9H), 2.28 (*s*, 3H), 2.59–2.94 (*m*, 4H), 6.99 (*d*, 2H), 7.21 (*d*, 2H) ppm.

#### Silylation of 4-methyl- and 4-*t*-butylbenzoic acid

A substituted benzoic acid (0.4 mol) and chlorotrimethylsilane (0.45 mol) were dissolved in hot, dry toluene (500 ml) and triethylamine (0.45 mol) was added dropwise with stirring. The reaction mixture was refluxed for 3 h, cooled with ice and filtered under exclusion of moisture. The product was isolated from the filtrate by distillation *in vacuo* (0.1 mbar) at a bath temperature of 130 or 150°C.

Trimethylsilyl-4-methylbenzoate: Yield 77%,  $\eta_D^{20}$  1.4928. Analyses calcd. for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>Si (208.3): C 63.42, H 7.74, found: C 63.19, H 7.68%.

<sup>1</sup>H n.m.r. (CDCl<sub>3</sub>/TMS): δ = 0.38 (*s*, 9H), 2.39 (*s*, 3H), 7.21 (*d*, 2H), 7.92 (*d*, 2H) ppm. Trimethylsilyl-4-*t*-butylbenzoate: Yield 90%,  $\eta_D^{20}$  1.4899.

Analyses calcd. for C<sub>14</sub>H<sub>22</sub>O<sub>2</sub>Si (250.4): C 67.15, H 8.86, found: C 67.07, H 8.78%.

<sup>1</sup>H n.m.r. (CDCl<sub>3</sub>/TMS): δ = 0.39 (*s*, 9H), 1.34 (*s*, 9H), 7.46 (*d*, 2H), 7.97 (*d*, 2H) ppm.

#### Acetylation of 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethylspirobisindan

The spirobisindan (0.1 mol), acetic anhydride (0.5 mol) and pyridine (0.5 ml) were refluxed in dry toluene (200 ml) for 6 h. Afterwards the reaction mixture was concentrated *in vacuo*, the residue diluted with toluene and concentrated again. The product was recrystallized from a mixture of toluene and ligroin (volume ratio 2/1). Yield 78%, m.p. 174–176°C.

Analyses calcd. for C<sub>29</sub>H<sub>32</sub>O<sub>8</sub> (508.6): C 68.49, H 6.34; found: C 68.54, H 6.27%.

<sup>1</sup>H-n.m.r. (CDCl<sub>3</sub>/TMS): δ = 1.32–1.36 (2\**s*, 12H), 2.20–2.35 (*m*, 16H), 6.63 (*s*, 2H), 6.94 (*s*, 2H) ppm.

Bisphenol-P acetate (yield: 88%, m.p. 157–159°C)<sup>9</sup> and acetylated *t*-butylphenol (yield: 92%,  $\eta_D^{20}$  1.4988)<sup>20</sup> were prepared analogously.

#### Model compound

5,5',6,6' - Tetraacetoxy - 3,3,3',3' - tetramethylspirobisindan (SBI, 10 mmol) and silylated 4-methylbenzoic acid (45 mmol) were weighted into a cylindrical glass-reactor equipped with stirrer, gas-inlet and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 150°C. The temperature was rapidly raised to 200°C, maintained for 3 h and finally kept at 250°C for 3 h. Afterwards vacuum was applied at 250°C for 15 min. The cold product was dissolved in ethyl acetate (250 ml) and rapidly stirred for 2 h with 1 N HCl (100 ml). The phases were then separated, the aqueous phase was extracted with ethyl acetate (150 ml) and the combined ethyl acetate solutions were extracted three times with cold KHCO<sub>3</sub> solutions (5% by weight). The organic phase was extracted with neutral water, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo*. The crude product was dissolved in hot toluene, ligroin was added until a turbidity appeared, and the product was then allowed to crystallize in the refrigerator. Yield 74%, m.p. 179–181°C.

Analyses calcd. for C<sub>53</sub>H<sub>48</sub>O<sub>8</sub> (813.0): C 78.30, H 5.95; found C 78.05, H 6.09%.

<sup>1</sup>H n.m.r. (CDCl<sub>3</sub>/TMS): δ = 1.42 (*s*, 12H), 2.32–2.45 (*m*, 16H), 6.90 (*s*, 2H), 7.09–7.23 (*m*, 10H), 7.86–7.97 (*m*, 8H) ppm.

#### Polycondensations

*Telechelic and star-shaped polyesters.* Silylated β-(4-acetoxyphenyl) propionic acid, (APPA-Si, 20 mmol) and a chain stopper (or 'star centre') were weighed into a cylindrical glass reactor equipped with stirrer, gas-inlet and gas-outlet tubes. The reactor was placed into an oil bath preheated to 150°C and the temperature was raised to 270°C in approx. 0.5 h. This temperature was maintained for 4 or 8 h. The liberated trimethylsilylacetate was removed with a slow stream of nitrogen. Finally vacuum was applied for 30 min. The cold product was dissolved in a mixture of CH<sub>2</sub>Cl<sub>2</sub> and trifluoroacetic acid (volume ratio 4/1), precipitated into methanol and dried at 100°C *in vacuo*.

*Hyperbranched copolyesters.* Silylated APPA and silylated 3,5-bisacetoxybenzoic acid were weighed into a cylindrical glass reactor and polycondensed for 5 h as described above. Polycondensations with the free 3,5-bisacetoxybenzoic acid were carried out analogously but with a maximum temperature at 240°C instead of 270°C.

#### Measurements

The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20°C.

The WAXD powder patterns were recorded with a Siemens D-500 diffractometer using Ni-filtered CuK<sub>α</sub>-radiation.

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

The 100 MHz <sup>1</sup>H n.m.r. spectra were recorded on a Bruker AC-100 FT n.m.r. spectrometer in 5 mm o.d. sample tubes.

The 25.2 MHz <sup>13</sup>C n.m.r. spectra were recorded with the same n.m.r. spectrometer using 10 mm o.d. sample tubes.

The s.e.c. measurements were performed at 25°C on a Hewlett–Packard HP 1090M combined with a viscometer VISCOTEK 200. Five Styragel<sup>®</sup>, HR columns, HR-1, HR 2+, HR 3, HR 4 and HR 5 were used with THF as eluent. The elution curves were evaluated with the TRISEC 270 software in combination with commercial polystyrene standards.

## RESULTS AND DISCUSSION

### Telechelic oligoesters

Most polyesters of aromatic hydroxy carboxylic acids including the copolyesters of HPPA<sup>16</sup> were prepared by thermal polycondensation of their O-acetyl derivatives. Unfortunately the normal acetylation procedure using an excess of acetic anhydride either in an inert solvent such as toluene or dioxane or as neat reagent involves the formation of smaller or larger amounts of oligomers when applied to HPPA. An explanation of this phenomenon has been discussed previously<sup>18</sup>. Furthermore β-(4-acetoxyphenyl) propionic acid (HPPA) (1) does not crystallize well from the crude reaction mixture (in this regard we disagree with a comment in ref. 21). Therefore, the reaction mixture obtained by refluxing HPPA in neat acetic anhydride was silylated and the silylated APPA (1b) was isolated by distillation. This procedure allows a perfect separation from the

oligoesters. The silylated HPPA can easily be hydrolysed by water to yield a pure APPA or it can itself be used as a monomer. It was recently demonstrated<sup>8-10,22</sup> that silylated carboxyl groups undergo a noncatalysed transesterification with acetylated phenol groups. This condensation method has the advantage that acidic protons and proton catalysed side reactions are avoided. Therefore, this method is particularly useful for the synthesis of hyperbranched polyesters<sup>8-10</sup>. A shortcoming of this new condensation method is the lower reactivity of the silylated carboxyl group relative to the free CO<sub>2</sub>H group, so that higher reaction temperatures ( $\geq 250^\circ\text{C}$ ) are required. Anyway, the silylated monomer **2** was used for all polycondensations in this work.

In a first series of polycondensations silylated 4-t-butylbenzoic acid was used as reaction partner and chain stopper of monomer **1b** [equation (1)]. The molar ratio was varied from 10 over 20 and 40 to 80 (*Table 1*). Regardless of whether a reaction time of 4 or 8 h was used, all resulting oligoesters of structure **2** were insoluble in common inert solvents. Therefore, no characterization was feasible in solution. For a second series of polycondensations 4-t-butylphenol acetate was used as chain stopper in molar ratios of 10, 20 and 40 (*Table 2*). After a reaction time of 4 h the oligoesters were still partially soluble in CDCl<sub>3</sub>/trifluoroacetic acid, but the <sup>1</sup>H n.m.r. spectra indicated incomplete conversions by the presence of CO<sub>2</sub>SiMe<sub>3</sub> endgroups. When the reaction time was extended to 8 h all resulting oligoesters turned completely insoluble. The WAXS

**Table 1** Yields and properties of oligo- and polyesters **2a-d** and **3a-c** prepared in bulk at 270°C/8.5 h

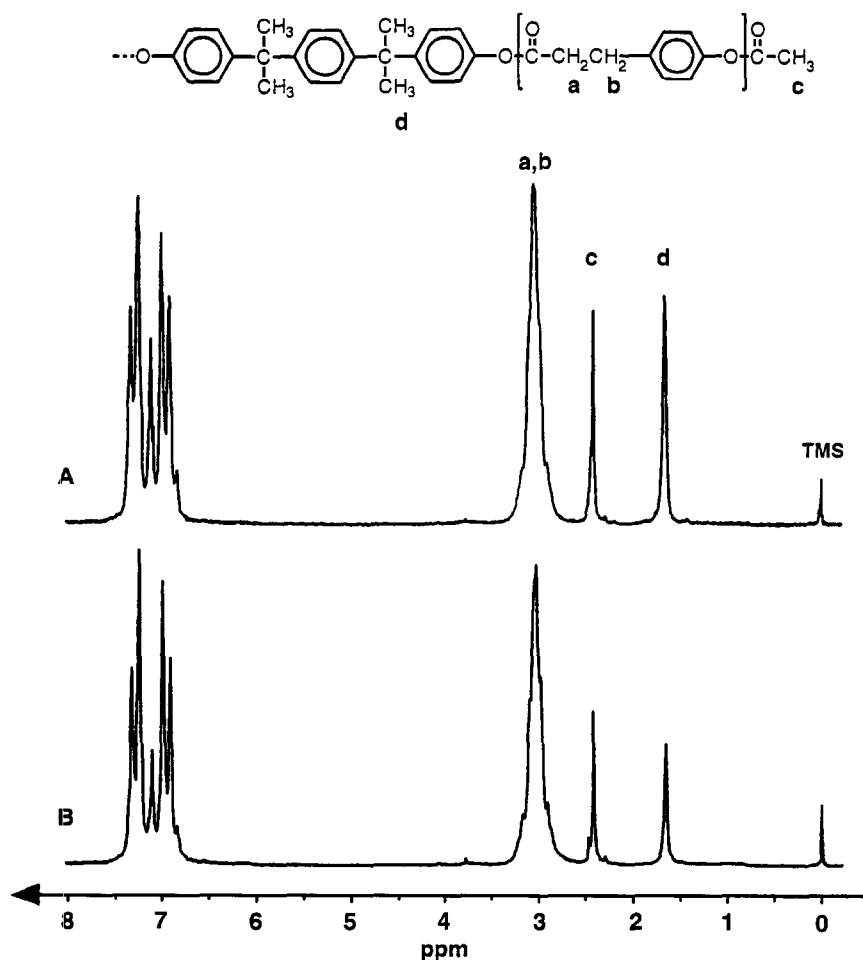
Formula no.	APPA (1b)		$T_g^a$ (°C)	$T_m^a$ (°C)	1st heat	$T_m^a$ (°C)	1st heat
	Comon.						
<b>2a</b>	10/1		56	250	(268)	(248)	265
<b>2b</b>	20/1		57	245	(264)	(238)	266
<b>2c</b>	40/1		58	248	(260)	244	—
<b>2d</b>	80/1		60	(235)	266	(236)	263
<b>3a</b>	10/1		50	234	—	240	(268)
<b>3b</b>	20/1		52	246	(266)	238	268
<b>3c</b>	40/1		54	235	(270)	240	(267)

<sup>a</sup> From d.s.c. measurements with a heating rate of 20°C min<sup>-1</sup>: 1st heating (weak endotherms in parentheses)

<sup>b</sup> From d.s.c. measurements: 2nd heating after cooling with -20°C min<sup>-1</sup> (weak endotherms in parentheses)

powder patterns indicated a high degree of crystallinity (comparable to that of polyester **8e** in *Figure 6B*).

When the silylated APPA was polycondensed with acetylated bisphenol-P (**4**), oligo- and polyesters with two identical endgroups were obtained (**5a-e**, *Table 2*). Another interesting consequence is the localization of the 'chain stopper' more or less in the middle of the chain. Since bisphenol-P does not fit into the crystal lattice of polyHPPA, this structure is unfavourable for the crystallization of the oligoesters. Therefore, the samples with relatively low DPs were soluble in mixture of CH<sub>2</sub>Cl<sub>2</sub> (or CHCl<sub>3</sub>) and trifluoroacetic acid (TFA), so that inherent viscosities could be measured. These viscosity measurements clearly indicate that the DP increases with higher



**Figure 1** 100 MHz <sup>1</sup>H n.m.r. spectrum of (A) oligoester **5a** and (B) oligoester **5b**

**Table 2** Yields and properties of telechelic polyesters prepared from acetylated bisphenol-P in bulk at 270°C

Formula no.	APPA <sup>a</sup> Bis-P	Time (h)	Yield (%)	$\eta_{inh}^b$ (dl g <sup>-1</sup> )	$T_g^c$ (°C)	$T_m^{c,d}$ (°C)	1st heat	$T_m^{c,d}$ (°C)	2nd heat	Solubility		
										CHCl <sub>3</sub> TFA 4/1	4/1 <sup>e</sup>	2/1 <sup>e</sup>
5a	10/1	4.5	95	0.10	48	232	—	237	(268)	+	+	+
5b	20/1	4.5	96	0.14	52	234	(268)	238	261	+	+	+
5c	40/1	4.5	96	0.22	58	232	265	(245)	259	—	+	+
5d	80/1	4.5	94	0.26	63	(240)	257	(243)	257	—	—	+
5e	160/1	4.5	93	Insol.	63	230	268	(240)	257		Insoluble	
5a'	80/1	8.5	91	Insol.	63	—	254	—	254		Insoluble	
5b'	160/1	8.5	95	Insol.	64	—	256	—	254		Insoluble	

<sup>a</sup> Molar ratio of silylated APPA and acetylated bisphenol-P

<sup>b</sup> Measured 20°C with  $c = 2 \text{ g l}^{-1}$  in CH<sub>2</sub>Cl<sub>2</sub>/trifluoroacetic acid (volume 4/1)

<sup>c</sup> From d.s.c. measurements with a heating rate of 20°C min<sup>-1</sup>

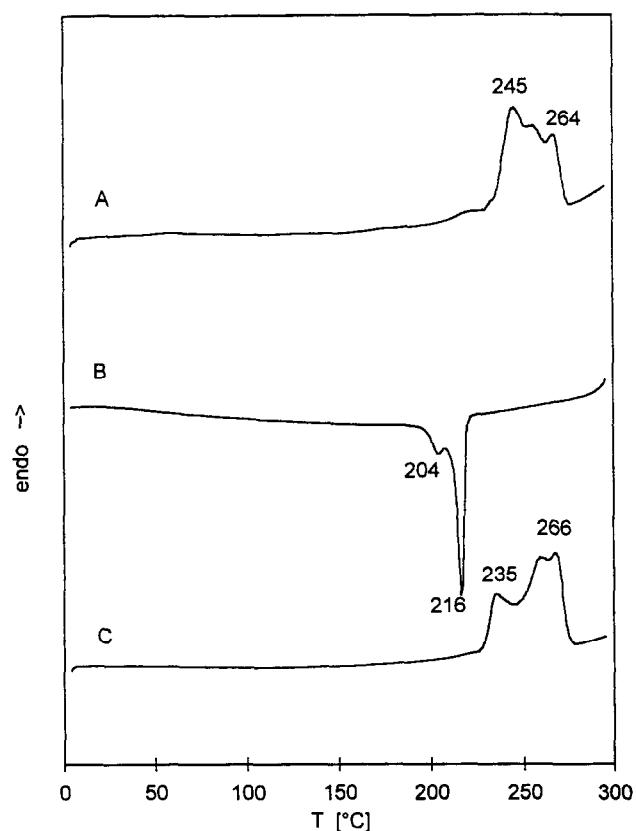
<sup>d</sup> Values in parentheses are weak endotherms or shoulders

<sup>e</sup> Volume ratio of CH<sub>2</sub>Cl<sub>2</sub>/trifluoroacetic acid

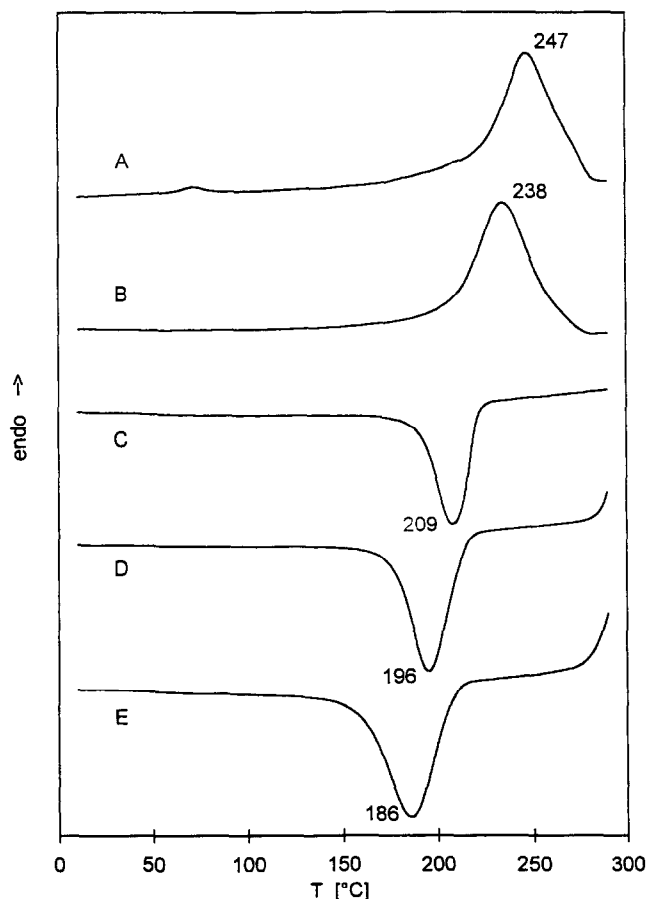
monomer/chain stopper (4) ratios. Furthermore, <sup>1</sup>H n.m.r. spectra prove the incorporation of the bisphenol-P unit, due to the CH<sub>3</sub>-signal at  $\delta = 1.65 \text{ ppm}$  (in CDCl<sub>3</sub>/TFA 4/1) (Figure 1). The quantification of the signal intensities confirms that the composition agrees with the feed ratio (Table 2) within the limits of  $\pm 5\%$ .

D.s.c. measurements of the oligoesters 2a–d, 3a–c and 5a–e gave the following interesting results. The glass transition temperatures increase with higher monomer/chain stopper ratio and all fall below the value of the high molecular weight sample 10f ( $T_g = 65^\circ\text{C}$  in Table 4). These findings are in reasonable agreement with the assumption that the molecular weights of 2a–d and 3a–c were controlled by the chain stopper. In addition to the

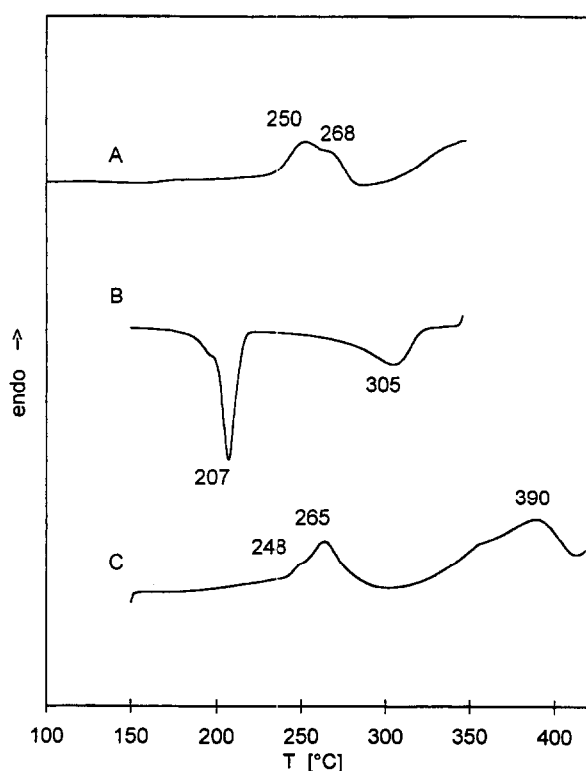
glass-transition step the d.s.c. curves of all oligoesters exhibited two endotherms, one in the range 235–248°C and a second one in the range 260–270°C (Table 1 and Figure 2). The relative intensities of both endotherms depend on the individual sample and vary with the thermal history. Annealing favours the high-temperature endotherm at the expense of the lower one. This finding and microscopic observations show clearly that the existence of two endotherms does not indicate the formation of a liquid-crystalline phase. Furthermore



**Figure 2** D.s.c. measurements of polyester 2b (heating and cooling rate 20°C min<sup>-1</sup>): (A) first heating, (B) first cooling, (C) 2nd heating



**Figure 3** D.s.c. measurements of polyester 10f: (A) first heating (+20°C min<sup>-1</sup>), (B) 2nd heating (+20°C min<sup>-1</sup>), (C) first cooling with -10°C min<sup>-1</sup>, (D) 2nd cooling with -40°C min<sup>-1</sup>, (E) 3rd cooling with -80°C min<sup>-1</sup>



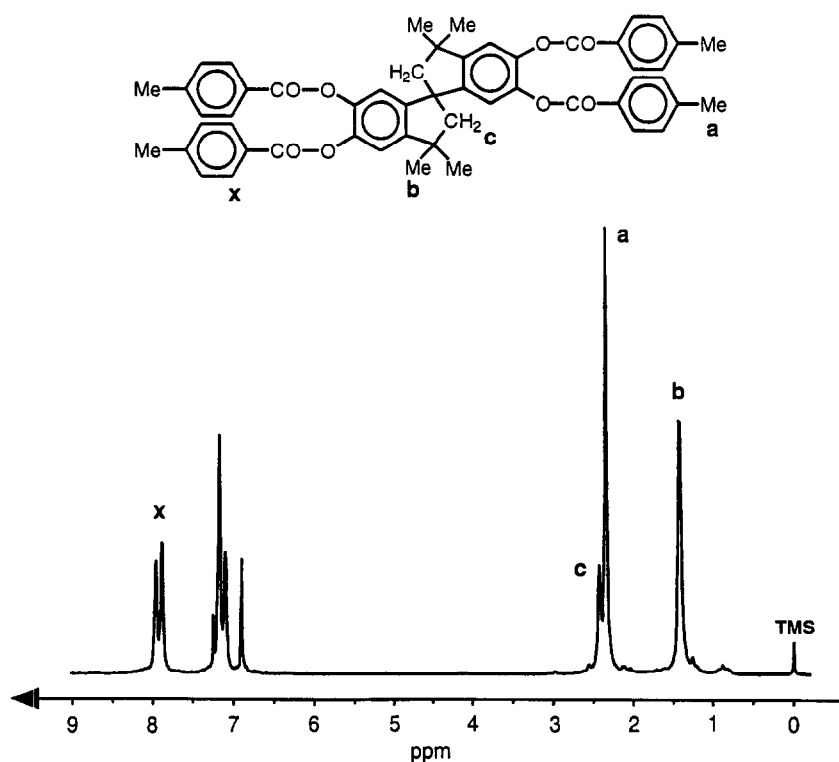
**Figure 4** D.s.c. measurements of polyester **2a** (heating and cooling rate  $20^{\circ}\text{C min}^{-1}$ ), (A) first heating, (B) first cooling after annealing at  $350^{\circ}\text{C}$  (15 min), (C) second heating

only one endotherm is detectable in the heating trace of the polyester **10f**. Interestingly this endotherm appears below  $250^{\circ}\text{C}$ , and no additional endotherms appear at higher temperatures upon annealing at  $250^{\circ}\text{C}$ . Another sample of polyHPPA prepared at  $270^{\circ}\text{C}$  without chain

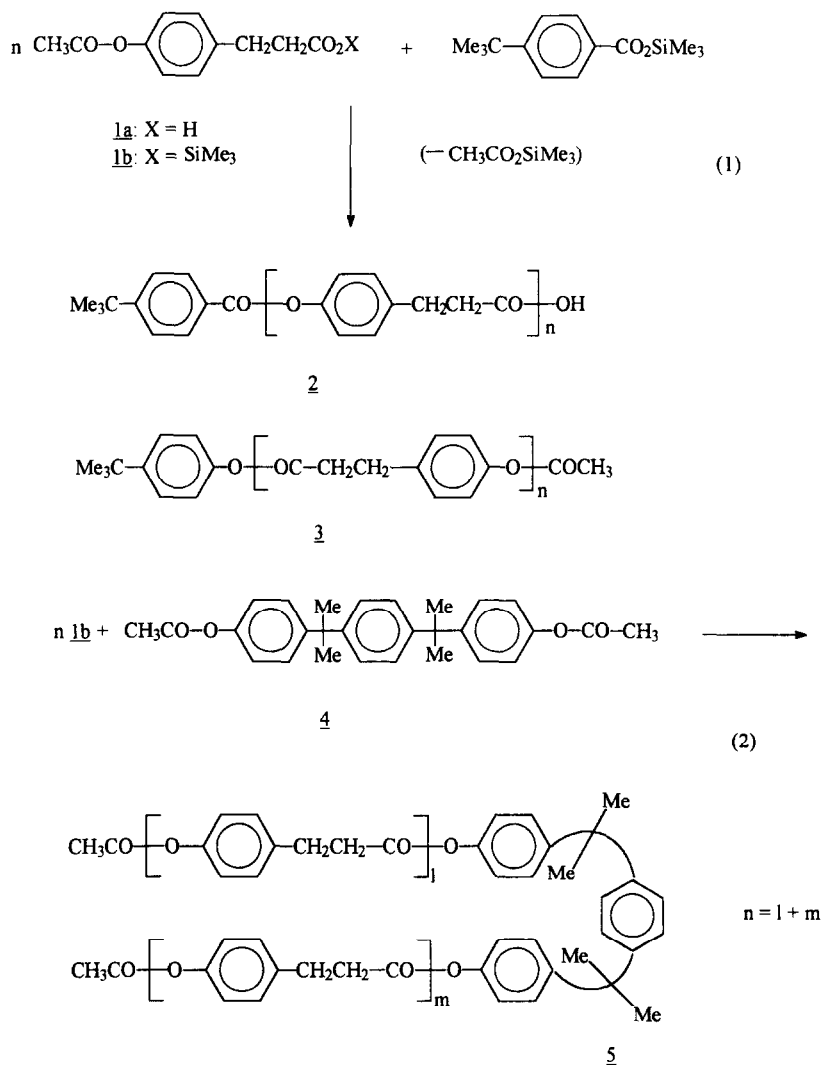
stopper but with catalytic amounts of  $\text{Ti}(\text{OiPr})_4$  showed one endotherm at  $240^{\circ}\text{C}$  in the first heating curve and one endotherm at  $235^{\circ}\text{C}$  in the second heating trace. These endotherms agree well with the low-temperature endotherms of the oligoesters. However, the oligoesters can form crystallites with a higher stability either due to a higher perfection or due to a slightly different modification. A detailed study of this aspect was not intended in this preparative work. However, it should be mentioned that similar observations were recently reported for poly(ether-ketone)s<sup>23</sup>. The oligomers were capable of forming crystallites with higher melting temperatures ( $T_m$ s) and perfection.

At this point it should be emphasized that the endotherms (and exotherms) in the temperature range  $230\text{--}260^{\circ}\text{C}$  indicate a reversible first-order solid  $\rightarrow$  solid transition and not a true melting process. The rather high rate of this transition is illustrated by the poor supercooling effect in the case of **10f** in Figure 3. Both the oligoesters and the polyester **10f** are solid and birefringent up to temperatures in the range  $340\text{--}380^{\circ}\text{C}$ . In the case of **10f** the formation of an isotropic melt occurs above  $380^{\circ}\text{C}$  and is accompanied by rapid degradation, which prevents the reversibility of the thermal phase transition. The melting temperature of the oligoesters is more or less reduced depending on the DP. In the case of **2a** and **2b** melting and solidification occurred at temperatures  $\geq 340^{\circ}\text{C}$ , so that the reversibility of this process could be documented by d.s.c. measurements (Figure 4). The existence of solid mesophase up to temperatures above  $350^{\circ}\text{C}$  has already been reported for a low molecular weight polyHPPA<sup>17</sup>. A detailed study of the chain packing and of the solid–solid transition ( $T_{m1}$ ) is in progress and will be published separately.

Finally a comparison of polyHPPA and poly(ethy-



**Figure 5** 100 MHz  $^1\text{H}$  n.m.r. spectra (measured in  $\text{CDCl}_3$ ) of model compound **7**



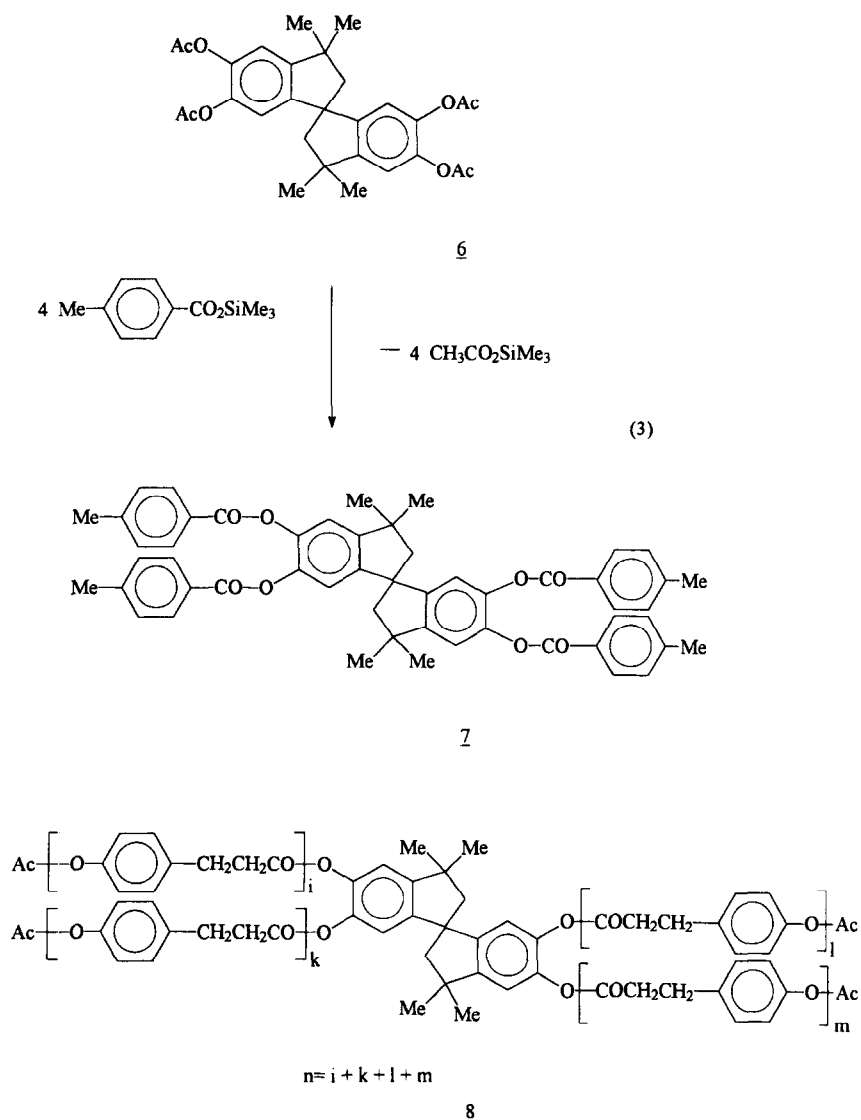
leneterephthalate) (PET) is worth mentioning. The structure of PET differs from that of polyHPPA by an additional polar ester group. Hence, both  $T_g$  and  $T_m$  of polyHPPA should be lower. This is true for the  $T_g$  of 65°C which is approx. 20°C lower than that of PET. It is also true for  $T_{m1}$  which again is approx. 20°C below that of PET. Thus the  $T_g/T_{m1}$  ratio of polyHPPA is around 0.64 quite analogous to PET and many other polymers. This consideration points toward  $T_{m1}$  as a kind of melting of true crystallites and the formation of a (solid) mesophase at higher temperatures. Taken together, the thermal properties of polyHPPA and its oligomers resemble more those of poly(4-hydroxybenzoate) or poly(4'-hydroxybiphenyl-4-carboxylate) than those of PET or PBT.

#### Star-shaped oligo- and polyesters

In order to prepare star-shaped oligo- and polyesters of HPPA, 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethylspirobisindan was selected as 'chainstopper' playing the role of a star-centre. This compound was selected for the following reasons. Firstly, it is a commercial product with four OH-groups of similar reactivity. Secondly, it possesses four CH<sub>3</sub> groups which give one singlet signal in the <sup>1</sup>H n.m.r. spectra. Thirdly, its stereochemistry is of

particular interest with regard to rheological and mechanical properties of LC-copolyesters of HPPA which will be described in a future publication.

Because it was not *a priori* clear that the four acetate groups of **6** react quantitatively with silylated carboxyl groups under the given reaction conditions, a model reaction with silylated 4-methylbenzoic acid was conducted [equation (3)]. The desired model compound **7** was isolated in a yield of 74% after recrystallization suggesting a satisfactory reactivity of **6**. The structure of **7** is evidenced by the <sup>1</sup>H n.m.r. spectrum of *Figure 5* (along with the elemental analyses). The polycondensation of **1b** and **6** were conducted with the same variation of the monomer/'comonomer' ratio as before (*Table 3*). However, at a reaction time of 4.5 h (analogous to the syntheses of **5a–5e**) only low inherent viscosities (0.12 ± 0.2 dl g<sup>-1</sup>) were obtained for all products. Therefore, the reaction time was doubled, and this time soluble oligo- and polyesters were obtained up to monomer/'chainstopper' ratio of 80/1. Furthermore, the viscosities showed a continuous increase with this ratio. The solubilities compared in three different solvents demonstrate the influence of the lengths of the star arms. A star-centre like the spirobisindane unit in the polyesters **8a–e** (*Table 2*) is highly unfavourable for the crystallization. Therefore, longer star-arms favour a higher degree of


**Table 3** Yields and properties of telechelic polyesters prepared from acetylated SBI in bulk at 270°C

Formula no.	APPA <sup>a</sup> SBI	Yield (%)	$\eta_{\text{inh}}^b$ (dl g <sup>-1</sup> )	Solubility			$T_g^d$ (°C)	$T_m^d$ (°C)
				CHCl <sub>3</sub> / TFA 4/1	4/1 <sup>c</sup>	2/1 <sup>c</sup>		
<b>8a</b>	10/1	94	0.10	+	+	+	53	231
<b>8b</b>	20/1	93	0.14	+	+	+	55	233
<b>8c</b>	40/1	96	0.20	-	+	+	57	243
<b>8d</b>	80/1	91	0.36	-	-	+	62	242
<b>8e</b>	160/1	96	—		Insoluble		64	242

<sup>a</sup> Molar ratio of silylated APPA and acetylated SBI

<sup>b</sup> Measured 20°C with  $c = 2 \text{ g l}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ /trifluoroacetic acid (volume 4/1)

<sup>c</sup> Volume ratio of  $\text{CH}_2\text{Cl}_2$ /TFA

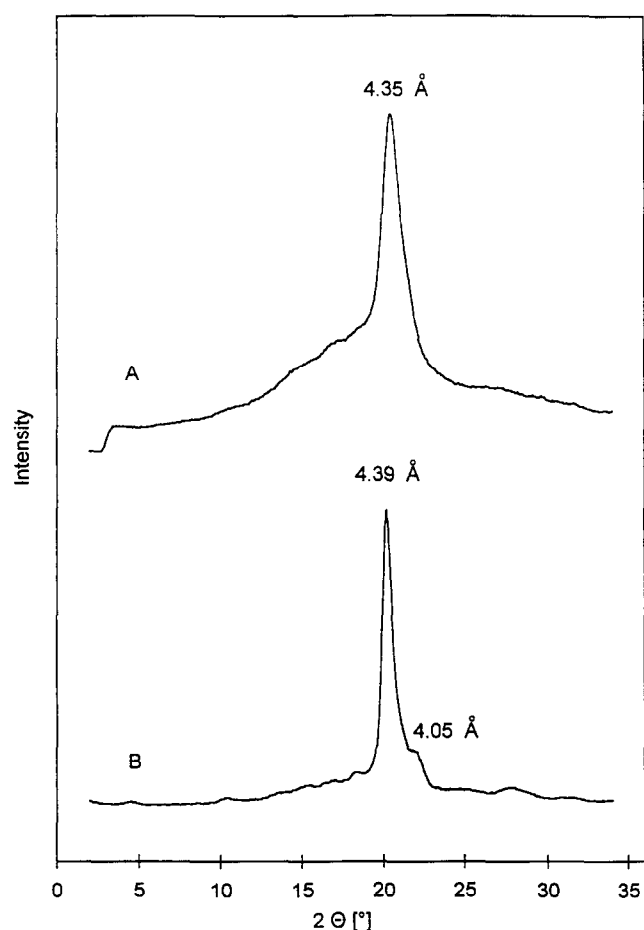
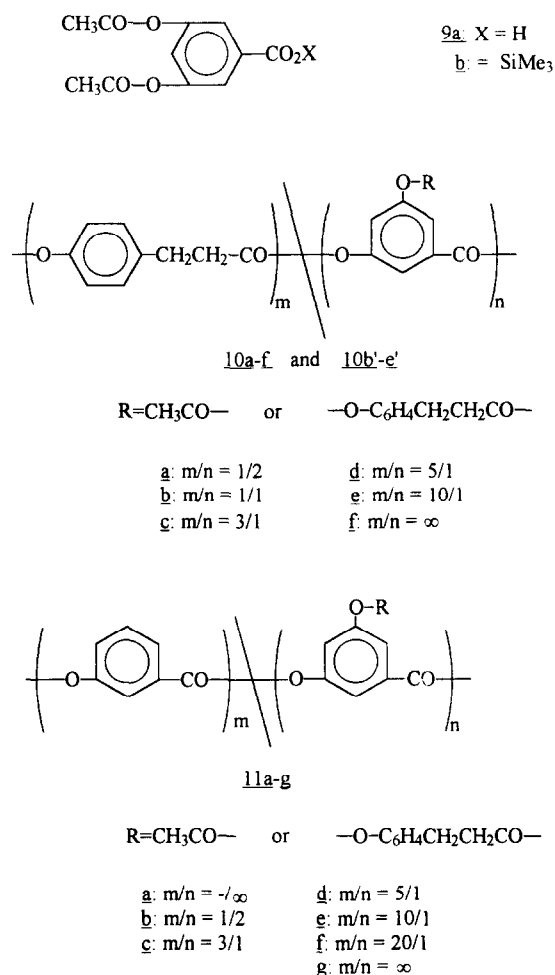
<sup>d</sup> From d.s.c. measurements with a heating rate of  $20^\circ\text{C min}^{-1}$

crystallinity and a greater perfection of crystallites. This trend is documented by the WAXD powder patterns of *Figure 6*. This trend in turn reduces the solubility. This means the solubility is under the chosen reaction conditions dependent on the crystallinity and not on covalent crosslinks resulting from side reactions. This conclusion is supported by the following observations. Firstly, the telechelic polyesters **5a–e** show the same trend. The crystallinity increases and the solubility decreases with higher molecular weights. Secondly,

annealing of **5d** and **8d** at 120°C reduced the solubility, a consequence typical for an improved crystallinity. Thirdly, the telechelic polyesters **2** and **3** which do not contain a sterically unfavourable 'star-centre' are all highly crystalline and insoluble.

#### Hyperbranched copolyesters

The first hyperbranched copolyesters were prepared from activated derivatives of 3-hydroxybenzoic acid and 3,5-dihydroxybenzoic acid<sup>6</sup>. In the present work again


 Figure 6 WAXS powder patterns of: (A) oligoester **8a**, (B) polyester **8e**


3,5-bisacetoxymethylbenzoic acid **9a** or its trimethylsilylester **9b** were used as comonomers of **1b** and copolyesters with the simplified structure **10** were isolated. The yields and properties of the copolyesters prepared from **1b** and silylated 3,5-bisacetoxymethylbenzoic acid (**9b**) are summarized in Table 4.

The success of this copolycondensation is documented by the fact that high yields were obtained after precipitation into methanol, and that all copolyesters

(**10a–10c**) were soluble. The solubility shows the expected trend with the molar composition. Whereas **10a** and **10b** were completely soluble in tetrahydrofuran (THF) **10c** and **10d** were partially insoluble in this solvent, but soluble in neat CHCl<sub>3</sub> (or CH<sub>2</sub>Cl<sub>2</sub>), whereas **10e** required the addition of trifluoroacetic acid for complete dissolution (Table 4). A molar composition close to the feed ratio is indicated by the high yields and

 Table 4 Yields and properties of hyperbranched polyesters prepared from **1b** and silylated 3,5-bisacetoxymethylbenzoic acid in bulk at 270°C

Formula no.	APPA <sup>a</sup> SBI	Yield (%)	$\eta_{\text{inh}}^b$ (dl g <sup>-1</sup> )	Solubilities <sup>c</sup> in			$T_g^d$ (°C)	$T_m^d$ (°C)	Elemental analyses		
				THF	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub> /TFA			C	H	
<b>10a</b>	1/2	93	0.34	+	+	+	107	—	Calcd.	64.29	4.00
									Found	64.12	4.05
<b>10b</b>	1/1	95	0.24	+	+	+	94	—	Calcd.	66.26	4.32
									Found	66.42	4.39
<b>10c</b>	3/1	98	0.28	—	+	+	75	—	Calcd.	69.45	4.86
									Found	69.09	4.95
<b>10d</b>	5/1	95	0.26	—	+	+	73	—	Calcd.	70.58	5.05
									Found	70.22	5.12
<b>10e</b>	10/1	91	0.22	—	—	+	69	231	Calcd.	71.64	5.22
									Found	71.67	5.30
<b>10f</b>	∞	92	(0.45) <sup>e</sup>	—	—	—	65	247 <sup>f</sup>	Calcd.	72.96	5.44
									Found	72.96	5.52

<sup>a</sup> Molar ratio of silylated APPA (**1b**) and silylated 3,5-bisacetoxymethylbenzoic acid

<sup>b</sup> Measured at 20°C with  $c = 2 \text{ g l}^{-1}$  in CH<sub>2</sub>Cl<sub>2</sub>/trifluoroacetic acid (volume ratio 4/1)

<sup>c</sup> Measured at 20°C with  $c = 6 \text{ g l}^{-1}$

<sup>d</sup> From d.s.c. measurements with a heating rate of 20°C min<sup>-1</sup>

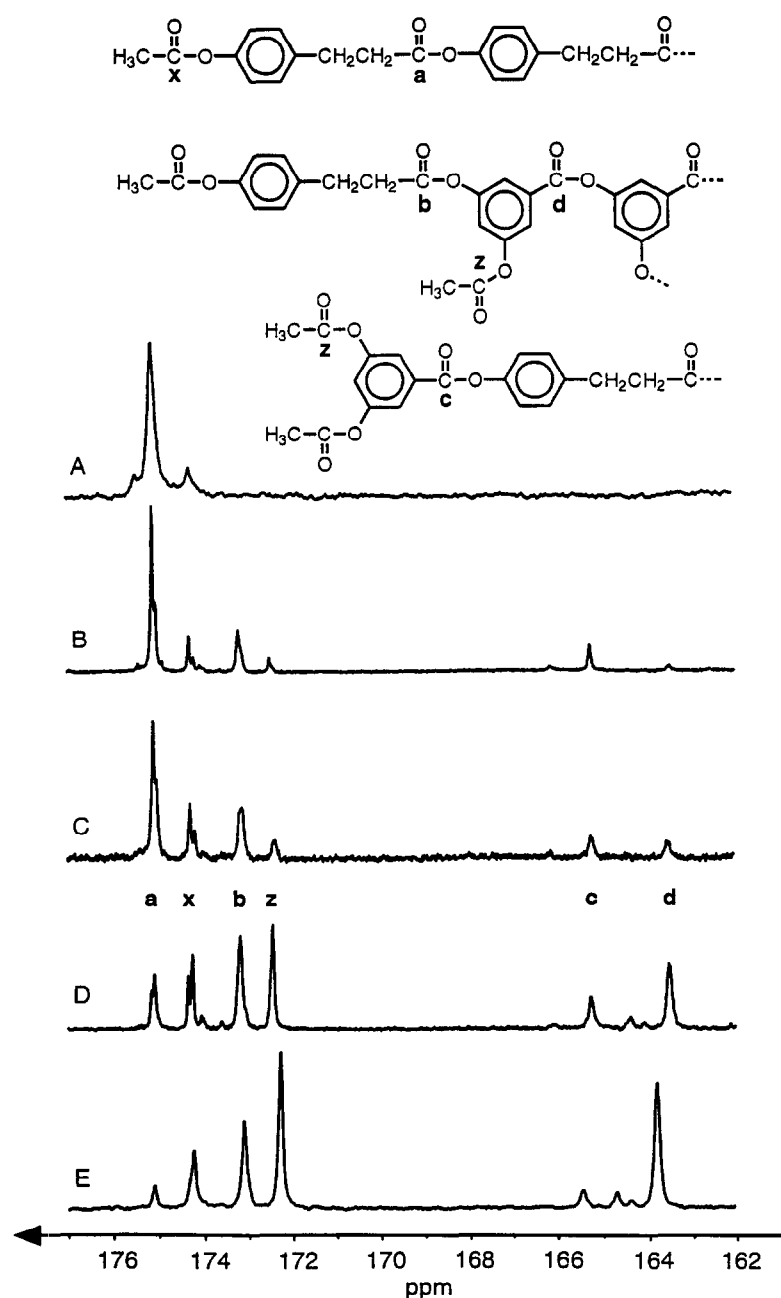
<sup>e</sup> Fraction extracted with CH<sub>2</sub>Cl<sub>2</sub>/TFA (volume ratio 2/1)

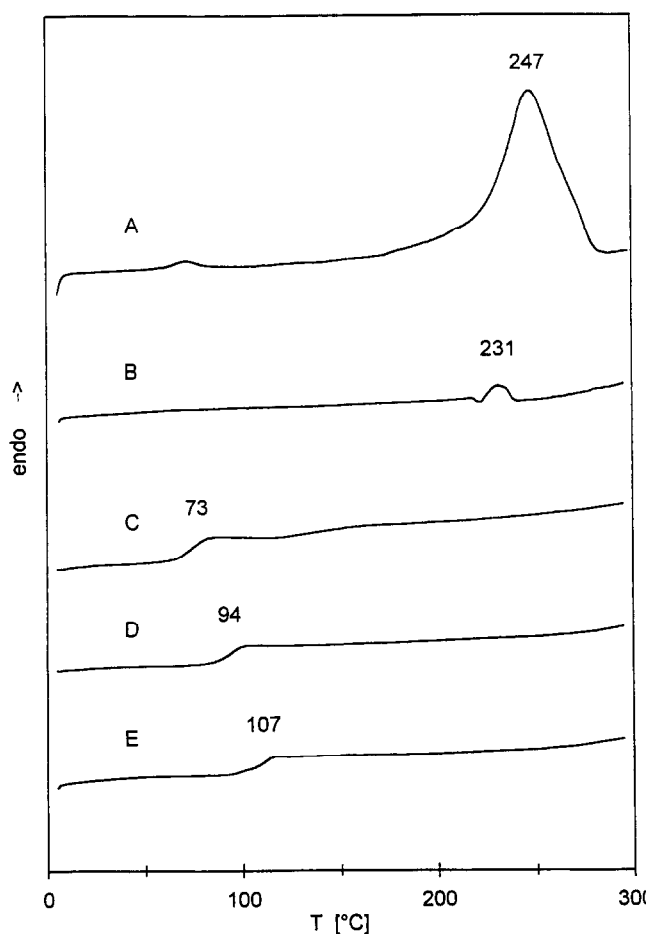
<sup>f</sup>  $T_m = 238^\circ\text{C}$  in the second heating trace, after annealing at 250°C/1 h a  $T_m$  at 232°C in the third heating trace



**Table 5** Yields and properties hyperbranched prepared from **1b** and 3,5-bisacetoxybenzoic acid in bulk at 240°C

Formula no.	APPA <sup>a</sup>		Yield (%)	$\eta_{inh}^b$ (dl g <sup>-1</sup> )	Solubilities <sup>c</sup> in			$T_g^d$ (°C)
	3,5-BABA				THF	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub> /TFA	
<b>10b'</b>	1/1		92	0.50	+	+	+	99
<b>10c'</b>	3/1		95	0.32	-	+	+	75
<b>10d'</b>	5/1		96	0.26	-	+	+	72
<b>10e'</b>	10/1		93	0.22	-	-	+	69 <sup>e</sup>

<sup>a</sup> Molar ratio of silylated APPA (**1b**) and silylated 3,5-bisacetoxybenzoic acid<sup>b</sup> Measured at 20°C with  $c = 2 \text{ g l}^{-1}$  in CH<sub>2</sub>Cl<sub>2</sub>/trifluoroacetic acid (volume ratio 4/1)<sup>c</sup> Measured at 20°C with  $c = 6 \text{ g l}^{-1}$ <sup>d</sup> From d.s.c. measurements with (1 heat) with a rate of 20°C min<sup>-1</sup><sup>e</sup>  $T_m = 230^\circ\text{C}$ , weak endotherms**Figure 7** 25.2 MHz <sup>13</sup>C n.m.r. spectra recorded in CDCl<sub>3</sub>/TFA (volume ratio 1/1): (A) oligoester **3a**, (B) copolyester **10d**, (C) copolyester **10c**, (D) copolyester **10b**, (E) copolyester **10a**



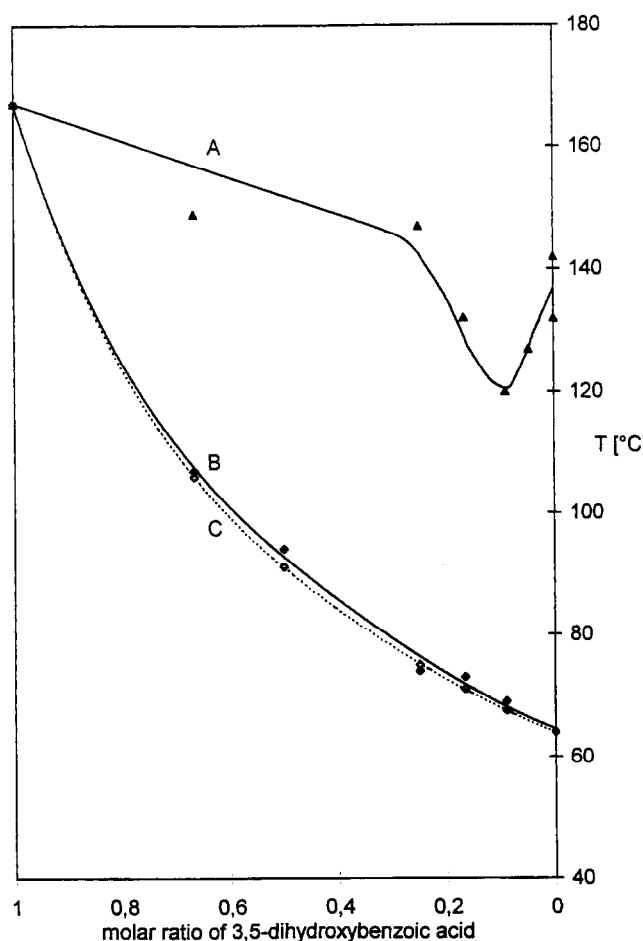
**Figure 8** D.s.c. measurements (first heating, rate  $20^{\circ}\text{C min}^{-1}$ ) of: (A) copolyester **10f**, (B) copolyester **10e**, (C) copolyester **10d**, (D) copolyester **10b**, (E) copolyester **10a**

by the elemental analyses. The  $^1\text{H}$  n.m.r. spectroscopy is less suited for an accurate determination of the composition in this particular case, because the aromatic proton of both comonomers overlap in all solvents studied (in  $\text{CDCl}_3$  or mixtures of this solvent the signal of  $\text{CHCl}_3$  is an additional problem for a quantitative evaluation).

The success of all copolycondensations was also evident from the  $^{13}\text{C}$  n.m.r. spectra (Figure 6). The signal assignments were obtained in two ways: firstly, by comparison with the corresponding homopolyesters (e.g. spectrum A in Figure 7), and secondly from the correlation of the signal intensities and the molar composition. The  $^{13}\text{C}$  n.m.r. spectra indicate in all cases that nearly random cocondensations took place. This also means that at higher APPA/3,5-DHBA ratios almost all 3,5-DHBA units form branching points.

The syntheses of the copolyesters **10b–10e** were repeated in such a way that the silylated monomer **1b** was polycondensed with free 3,5-bisacetoxybenzoic acid **9a**. The presence of the acidic protons should catalyse ester interchange reactions. The yields and properties of the resulting copolyester **10b'–10e'** are compiled in Table 5. Higher molecular weights were found for **10b'** and **10c'** but identical viscosities for **10d'** and **d'** or **10e** and **e'**. Also the  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra were almost identical. These results also mean that the small amounts of acidic protons of **9a** did not cause crosslinking.

The good solubility of most hyperbranched copolyesters allowed molecular weight measurements by means of s.e.c. in THF. A combination of s.e.c. and viscosity



**Figure 9** Plot of measured glass transition temperatures of the copolyesters **11a–g** (A), of the copolyesters **10a–10f** (B) and of the Fox equation calculated for the copolyesters **10a–10f** (C)

measurements was used along with commercial polystyrene standards. On the basis of the universal calibration method the following results were obtained for the samples with the highest inherent viscosities (**10a**, Table 4 and **10b'**, Table 5):

**10a**,  $M_n = 19 \times 10^3$ ,  $M_w = 160\,000$ , polydispersity 8.5.

**10b'**,  $M_n = 24 \times 10^3$ ,  $M_w = 180\,000$ , polydispersity 7.5.

Similarly broad molecular weight distribution (MWD) have been reported for other hyperbranched copolyesters<sup>9,21</sup>. These broad MWDs are a normal consequence of the polycondensation statistics of tri- or multifunctional monomers. In the case of difunctional (e.g. A–B-type) monomers all species of a reaction mixture possess the same number of functional groups and nearly identical reactivities, so that the probability of a condensation step is identical for all combinations of monomeric, oligomeric or polymeric species. In the case of trifunctional ( $A_2B$ -type) monomers the number of functional groups increases with the molecular weight, and thus, the probability of condensation steps. The theory of so-called cascade reactions has been discussed by Flory<sup>24</sup>.

The d.s.c. measurements revealed that all hyperbranched copolyesters were amorphous (Figure 8). The  $T_g$ s display a sharp but continuous decrease from the high value of the hyperbranched homopolyester of 3,5-dihydroxybenzoic acid **11g** ( $260\text{–}270^{\circ}\text{C}$ ) down to the low

value of polyHPPA ( $65 \pm 1^\circ\text{C}$ ) (Figure 9B). When the  $T_g$ s were compared with the values calculated from the Fox equation (Figure 9C) an almost identical curve was obtained. This result is worth noting, because in the case of the hyperbranched copolyesters **11a–f** the  $T_g$ s show a minimum at a branching ratio of 10/1 (**11e**) as illustrated in Figure 9A<sup>10</sup>. A straightforward explanation for these different thermal properties of **10a–f** and **11a–g** cannot be offered at this time. However, it is worth noting that the thermal properties of poly(3-oxybenzoate) are somewhat unusual in many respects. For instance, the  $T_g/T_m$  ratios of most polymers are on the order of 0.6–0.7 (measured in Kelvin) and the value of polyHPPA ( $0.64 \pm 0.01$ ) is almost exactly in the middle of this range. In contrast, the  $T_g/T_m$  ratio of **11g** amounts to  $0.94 \pm 0.01$ . Furthermore, the dependence of the  $T_g$  on the molecular weight is rather weak for polyHPPA ( $\Delta T \sim 15^\circ\text{C}$ ) as evidenced by the data listed in Tables 1 and 2. When samples of **10g** with  $\eta_{inh}$  in the range of 0.09 and  $0.55 \text{ dl g}^{-1}$  (in  $\text{CHCl}_3$ ) were compared, the  $T_g$ s varied between 100 and  $145^\circ\text{C}$ . Thus, it is obvious, that the properties of homo- and copolyesters of 3-hydroxybenzoic acid are somewhat unusual.

Finally the shape of the d.s.c. curves of **10c**, **10d** need a discussion. At first glance these d.s.c. curves look as if the main glass-transition step is followed by a second flat glass transition in the range  $110\text{--}150^\circ\text{C}$ . Two  $T_g$ s may be explained by a bimodal distribution of branching points in these samples, so that a large fraction contains few branching units and another large fraction many branching units. Such a bimodal distribution might originate from different reactivities of the monomers **1b** and **9b** in combination with a low degree of transesterification. However, two strong arguments contradict this hypothesis. Firstly, the  $^{13}\text{C}$  n.m.r. spectra prove a random or nearly random sequence of both kinds of monomeric units. Secondly, the d.s.c. curves of the second series of copolyesters (**10b'–e'**) were almost identical with those of **10b–e**. Therefore, all d.s.c. curves were interpreted in terms of one single glass-transition.

## CONCLUSIONS

Silylated  $\beta$ -(4-acetoxyphenyl)propionic acid proved to be an easy to isolate useful monomer for the syntheses of telechelic oligoester star-shaped oligo- and polyesters or hyperbranched copolyesters. Linear oligo- and polyesters crystallize rapidly, and thereby lose the solubility in common organic solvents. The melting temperatures of linear oligoesters may be higher than that of high molecular weight polyesters. The hyperbranched copolyesters containing 3,5-dihydroxybenzoic acid are amorphous when the molar fraction of this branching unit is  $\geq 10\text{ mol}\%$ . The  $T_g$ s vary with the molar composition according to the Fox equation. The

solubility of these copolyesters increases with the degree of branching and the 1/1 copolyester is even soluble in THF. G.p.c. measurements suggest that  $M_n$ s up to  $31\,000 \text{ g mol}^{-1}$  were obtained along with extremely broad molecular weight distribution ( $M_w$  up to 190 000).

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