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New Polymer Syntheses. 78. Star-Shaped and Hyperbranched Polyesters by Polycondensation of Trimethylsilyl 3,5-Diacetoxybenzoate

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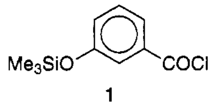
ABSTRACT: 3,5-Diacetoxybenzoic acid and its trimethylsilyl ester were polycondensed in bulk at various temperatures to optimize the reaction conditions. Whereas polycondensations of the free acid above 250 °C resulted in partial cross-linking, the silylated monomer yielded perfectly soluble hyperbranched polyesters even at 280 °C. Addition of Ti(OPr)$_4$ as a transesterification catalyst gave lower molecular weights. ^{1}H NMR spectroscopy indicates a degree of branching around 0.5 regardless of the reaction conditions. GPC measurements revealed M_w/M_n ratios > 5 and weight-average molecular weights (M_w) up to 700 × 10^3. Copolycondensations with acetylated Bisphenol-P yielded star-shaped hyperbranched polyesters. Their molecular weight can be varied by the feed ratios of monomer and comonomer. ^{1}H NMR spectroscopy allowed the determination of their average degrees of polymerization. Further star-shaped polyesters with dendritic star arms were prepared by polycondensations of silylated 3,5-diacetoxybenzoic acid with acetylated tetraphenols.

Introduction

Polycondensations of trifunctional monomers having two different functional groups may in principle yield branched, tree-shaped polycondensates without cross-linking as demonstrated by nature with the enzymatic synthesis of glycogen. The success of a synthetic approach following the principles of nature depends on the presence or absence of side reactions that may cause cross-linking, and thus, insoluble gels. In a previous part of this series[1] the syntheses of soluble, branched poly(3-hydroxybenzoate)s were described based on the cocondensation of 3-(trimethylsiloxy)benzoy]chloride (**1**)- and 3,5-bis(trimethylsiloxy)benzoyl chloride (**2**). More recently, another research group[2] used this approach for the synthesis of a soluble dendritic polyester by the polycondensation of neat **2**. In contrast, several cocondensations of 3-acetoxybenzoic acid (3-ABA, **3a**) and 3,5-diacetoxybenzoic acid (3,5-BABA, **4a**) catalyzed with MgO yielded insoluble, apparently cross-linked products.[1] However, at lower temperatures and without catalyst, a polycondensation of monomer **4a** yielding a soluble dendritic homopolyester was successful.[3] Quite recently, a new, relatively clean condensation reaction was elaborated, the condensation of silylated carboxylic acids with acetylated phenol groups.[4,5] This condensation avoids acidic protons and, thus, reduces the risk of acid-catalyzed side reactions such as the Fries rearrangement.[6] Therefore, it was the purpose of this work to study polycondensations of the silylated monomer **4b**. Cocondensations of **3b** and **4b** will be described in a future part of this series.



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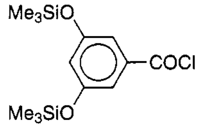

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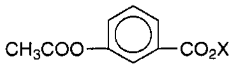
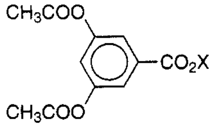


3a, X = H
b, X = Si(CH$_3$)$_3$



4a, X = H
b, X = Si(CH$_3$)$_3$

Experimental Section

Materials. 3,5-Dihydroxybenzoic acid, tetrachlorophthalic acid, *tert*-butylamine, potassium *tert*-butoxide, and 4-mercaptophenol were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without purification. 3,5-Dihydroxybenzoic acid was acetylated with acetic anhydride and a catalytic amount of pyridine in refluxing toluene, yielding 3,5-diacetoxybenzoic acid with a melting point of 155–156 °C (mp 157–159 °C in ref 3).

Trimethylsilyl 3,5-Diacetoxybenzoate (4b). 3,5-Diacetoxybenzoic acid (0.5 mol) and chlorotrimethylsilane (0.6 mol) were dissolved in dry toluene (1 L), and triethylamine (0.6 mol) was added dropwise with stirring and heating. The reaction mixture was refluxed for 2 h, cooled with ice, and filtered under exclusion of moisture. The product was isolated from the filtrate by distillation in vacuo over a short-path apparatus. Yield 79%; mp 40–42 °C. Anal. Calcd for $C_{14}H_{18}O_6Si$ (310.4): C, 54.18; H, 7.10. Found: C, 53.91; H, 7.08. ^{1}H NMR ($CDCl_3$/TMS): δ 0.42 (s, 9H), 2.31 (s, 6H), 7.10 (t, 1H), 7.70 (d, 2H).

Acetylated Bisphenol-P (6). Bisphenol-P (0.1 mol), acetic anhydride (0.4 mol), and pyridine (1 mL) were refluxed in dry toluene for 4 h. The reaction mixture was then concentrated in vacuo, and the residue was diluted with toluene and concentrated. Finally, the crystallization of the product was completed by portionwise addition of ligroin and cooling. Yield 94%; mp 151–153 °C. Anal. Calcd for $C_{28}H_{30}O_4$ (346.5): C, 78.11; H, 7.02. Found: C, 77.82; H, 7.17. ^{1}H NMR ($CDCl_3$/TMS): δ 16.5 (2, 12H), 2.28 (s, 6H), 7.11 (m, 12H).

***N,N'*-Bis(3,5-diacetoxybenzoyl)-Bisaniline-P (7).** Triethylamine (0.2 mol) was added dropwise with stirring to a warm solution of Bisaniline-P (50 mmol) and chlorotrimethylsilane (0.2 mol) in dry toluene (200 mL). The reaction mixture was then refluxed for 4 h, cooled with ice, diluted with ligroin (200 mL), and filtered under exclusion of moisture. The filtrate was concentrated in vacuo, and the residue was dissolved in dry chloroform (100 mL). A solution of 3,5-diacetoxybenzoyl chloride (40 mmol) in chloroform (100 mL) was added with stirring, and the reaction mixture was stored at 20 °C for 20 h. The crystallized product was isolated by filtration and recrystallized from dioxane with addition of a

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Table 1. Polycondensations of 3,5-Diacetoxybenzoic Acid (4a) and Its Trimethylsilyl Ester 4b in Bulk

expt no.	monomer [cat.]	reacn conditions	solubility	yield (%)	η_{inh}[a] (dL/g)	T_g (°C)	elem anal[b]		DB[c]
							% C	% H	
1	**4a**	15 min/180 °C 90 min/220 °C 50 min/240 °C + 10 min vacuum	perfect in THF	81	0.35	163	59.94	3.26	0.47
2	**4a** [Ti(OPr)$_4$]	1 h/230 °C 3 h/250 °C + 0.5 h vacuum	perfect in THF	62	0.22	164	60.31	3.54	0.48
3	**4a**	1 h/230 °C	partially cross-linked	91		158	60.85	4.39	
4	**4a** [Ti(OPr)$_4$]	3 h/280 °C + 0.5 h vacuum	cross-linked	82		162	59.60	4.35	
5	**4b**	1 h/230 °C	perfect in THF	75	0.34	159	60.24	3.78	0.43
	[Ti(OPr)$_4$]	3 h/280 °C + 0.5 h vacuum		77	0.36	162	60.26	3.60	0.49
6	**4b**	0.4 h/230 °C 0.6 h/250 °C 3.0 h/280 °C + 0.5 h vacuum	perfect in THF						
7	**4b**	5 h/200−300 °C 0.5 h/310 °C, vacuum	perfect in THF	83	0.42	177	60.41	3.77	0.50

[a] Measured at 20 °C with $c = 2$ g/L in 4:1 CH_2Cl_2/TFA. [b] Calcd. for $C_9H_6O_4$ (178.14): C, 60.68; H, 3.40. [c] Degree of branching calculated according to eq 1.

small amount of water: yield 65%; mp 233−235 °C. Anal. Calcd. for $C_{46}H_{44}N_2O_{10}$ (784.8): C, 70.40; H, 5.65; N, 3.57. Found: C, 70.09; H, 5.74; N, 3.93. ^{1}H NMR (DMSO-d_6): δ 1.61 (s, 12H), 2.30 (s, 12H), 7.11−7.69 (m, 18H), 10.28 (2NH).

***N-tert*-Butyltetrachlorophthalimide (9).** A solution of *tert*-butylamine (0.35 mol) in dry DMF (100 mL) was added dropwise with stirring to a warm (50−60 °C) suspension of tetrachlorophthalic anhydride in dry DMF (400 mL). The reaction mixture was stirred at 20 °C for 24 h, acetic anhydride (0.4 mol) was then added, and heating at 100 °C was continued for 6 h. The cold reaction mixture was poured into water, and the precipitated product was isolated by filtration and dried at 115 °C in vacuo. Because IR and ^{1}H NMR spectra proved that the cyclization was incomplete, the crude product was heated to 200 °C for 3 h in vacuo and recrystallized from chloroform/ligroin. Yield 68%; mp 260−262 °C. Anal. Calcd for $C_{12}H_9Cl_4NO_2$ (341.0): C, 42.26; H, 2.66; Cl, 41.58; N, 4.11. Found: C, 41.76; H, 2.76; Cl, 41.84; N, 4.05. ^{1}H NMR ($CDCl_3$/TMS): δ 1.70 (s, 9H).

Tetraphenol 8a. Potassium *tert*-butoxide (200 mmol) was added portionwise to a solution of 4-mercaptophenol (200 mmol) in dry DMF (200 mL) with stirring under nitrogen. A solution of *N-tert*-butyltetrachlorophthalimide (40 mmol) in dry DMF (50 mL) was then added dropwise, and the reaction mixture was stirred at 25 °C for 60 h and 80 °C for 4 h. The reaction mixture was finally poured into water, and the precipitated product was isolated by filtration, dissolved in warm dioxane, and crystallized by dropwise addition of water. Yield 67%; mp 249−251 °C. Anal. Calcd for $C_{36}H_{29}NO_4S_4$ (699.9): C, 61.78; H, 4.18; N, 2.00; S, 18.32. Found: C, 60.98; H, 4.16; N, 1.84; S, 17.95. ^{1}H NMR (DMSO-d_6/TMS): δ 1.39 (s, 9H), 6.54−6.89 (16H), 9.57 (s, 4OH).

Acetylation of Tetraphenol 8a. Tetraphenol (20 mmol), acetic anhydride (100 mmol), and pyridine (1 mL) were refluxed in dry toluene (200 mL) for 6 h. The resulting solution was concentrated to 50% of its former volume, and the product was crystallized by portionwise addition of ligroin. The acetate **8b** was recrystallized from toluene/ligroin. Yield 83%; mp 176−178 °C. Anal. Calcd for $C_{44}H_{37}NO_{10}S_4$ (868.0): C, 60.88; H, 4.30; N, 1.61; S, 14.77. Found: C, 61.30; H, 4.39; N, 1.63, S, 14.73. ^{1}H NMR ($CDCl_3$/TMS): δ 1.51 (s, 9H), 2.27 (s, 12H), 6.89−7.26 (16H).

Polycondensations of Silylated Monomers (Table 1). (A) Homopolycondensation. Trimethylsilyl 3,5-diacetoxybenzoate (50 mmol) (with or without addition of Ti(O-*i*-Pr)$_4$ (0.05 mmol), in toluene) was weighed into a cylindrical reactor equipped with a glass stirrer and gas inlet and outlet tubes. The reaction vessel was placed into a metal bath preheated to 200 °C. The temperature was raised in 20 °C steps over a period of 1 h and finally maintained at 280 °C for 4.0 h. Vacuum was then applied for an additional 0.5 h. Finally, the cold reaction product was powdered, dissolved in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1), and precipitated into cold methanol. All other polycondensations of Table 1 were conducted analogously.

(B) Cocondensations with "Star Centers". Trimethylsilyl 3,5-diacetoxybenzoate (**4b**, 40 mmol) and acetylated Bisphenol-P (**6**, 1 mmol) were weighed (under dry nitrogen) into a cylindrical glass reactor equipped with a glass stirrer and gas inlet and outlet tubes. The monomers were successively heated to 230 (45 min), 240 (45 min), 250 (45 min), and 260 °C (30 min without vacuum and 10 min with vacuum). The cold product was dissolved in $CHCl_3$ and precipitated into methanol.

Measurements. The inherent and intrinsic viscosities were measured with an automated Ubbelohde viscometer thermostated at 20 °C. The DSC measurements were conducted with a Perkin-Elmer DSC-4 at a heating rate of 20 °C/min in aluminum pans under nitrogen.

The ^{13}C NMR spectra were recorded with a Bruker MSL 300 FT NMR spectrometer in 10 mm o.d. sample tubes. Solutions of 300 mg of polyester in 3 mL of $CDCl_3$/trifluoroacetic acid (volume ratio 4:1) were used with TMS as an internal shift reference.

The 100 MHz ^{1}H NMR spectra were recorded on a Bruker AC-100 in 5 mm o.d. sample tubes. For 300 MHz ^{1}H NMR spectra, a Bruker MSL-300 FT NMR spectrometer was used.

The GPC measurements were conducted with a Kontron equipped with a Waters Md differential refractometer using a combination of four Ultrastyragel columns.

Results and Discussion

Homopolymerization of 4a and 4b. 3,5-Diacetoxybenzoic acid (3,5-BABA) and 3-acetoxybenzoic acid (3-ABA) were silylated with chlorotrimethylsilane and triethylamine in refluxing toluene. In contrast to the acid chlorides **1** and **2**, no polycondensations compete with distillation when the silylated monomers **3** and **4** are purified by distillation in vacuo, and yields around 80% were easily obtained.

First, the polycondensation of the free acid **4a** was studied at 240 and 280 °C (Table 1). The polyester obtained at the maximum reaction temperature of 280 °C (no. 3) was found to be partially cross-linked, in contrast to the completely soluble polyester prepared at 240 °C (no. 1). A further polycondensation of **4a** was conducted at a maximum temperature of 250 °C in the presence of Ti(OPr)$_4$ as a transesterification catalyst (no. 2, Table 1). Again a soluble material was isolated, but surprisingly its molecular weight was considerably lower than that of the polyester prepared without catalyst (no. 1). When the final reaction temperature

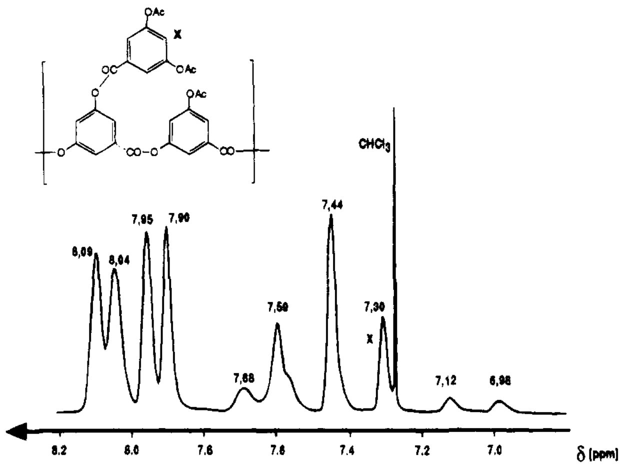


Figure 1. 300 MHz ^{1}H NMR spectrum of polyester **5** prepared from the silylated monomer **4b** at 280 °C (no. 6, Table 1).

was raised to 280 °C in the presence of $Ti(OPr)_4$, again a partially cross-linked product was obtained (no. 4). Taken together, these results indicate that successful polycondensations of **4a** are limited to a maximum reaction temperature around 250 °C, in agreement with recent literature data.[3]

With the silylated monomer **4b**, two polycondensations were conducted at temperatures up to 280 °C (nos. 5 and 6, Table 1). Regardless of whether $Ti(OPr)_4$ was added or not, soluble polyesters were isolated from both experiments and their viscosities were similar. Three polycondensations with two different batches of **4b** were then conducted at a final reaction temperature of 310 °C. Two of the three polyesters turned out to be cross-linked, but the third polyester was perfectly soluble in THF (no. 7, Table 1). This sample possessed the highest viscosity value, indicating that the higher temperature is in principle favorable for a higher conversion. The high molecular weight of no. 7 (Table 1) corresponds to the highest glass transition temperature (T_g) reported so far (177 °C).

Characterization of Homopolyesters 5. The two structural parameters which are of particular interest for the characterization of the polyesters **5** are the average degree of branching (DB) and the molecular weights along with the molecular weight distribution. For the discussion of the DB it is useful to label the three building blocks which make up the homopolyester **5** "L" (linear), "B" (branching point), and "T" (terminal). A DB may be calculated according to eq 1, provided that the number of end groups can be determined by a spectroscopic method. (In eq 1, I_T, I_B, and I_L are the ^{1}H NMR signal intensities of the terminal, branched, and linear building blocks.) NMR spectroscopic studies of model compounds such as 3,5-bis(benzoyloxy)benzoic acid (for "B") and 3,5-diacetoxybenzoic acid or its methyl ester (for "T") revealed in agreement with the literature[3] that the para proton of the "T" units (X in Figure 1) gives a ^{1}H NMR signal upfield of all other signals. The best resolution of the aromatic signals was found in $CDCl_3$/trifluoroacetic acid mixtures (Figure 1), with poorer resolution in tetrahydrofuran (THF) or dimethyl sulfoxide (DMSO). Surprisingly, even high-resolution (90.4 MHz) ^{13}C NMR spectra provide little sequence information. Both the CH_3 and CO carbons of the acetate groups give sharp singlet signals regardless of their neighborhood. Again sharp singlets were observed for the aromatic CO groups and the ether (O–C) carbon (Figure 2).

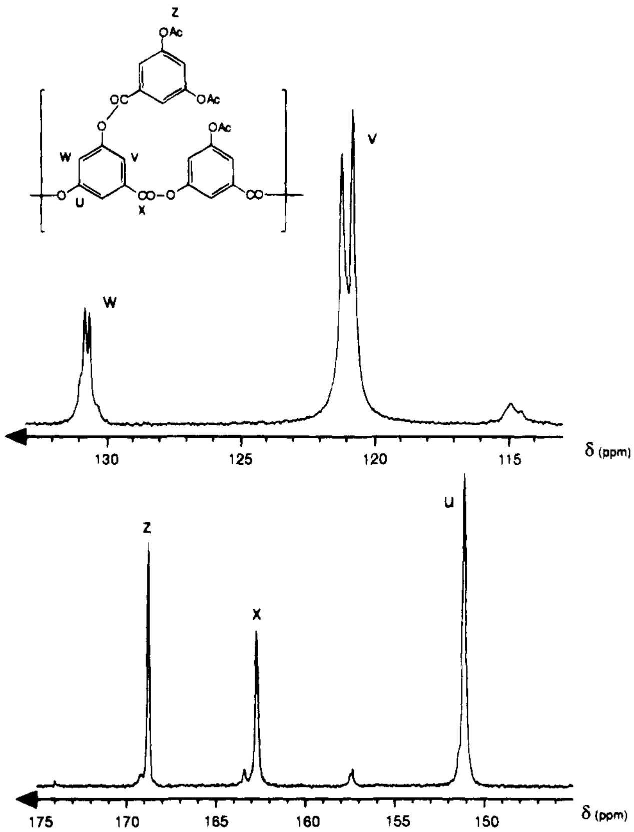
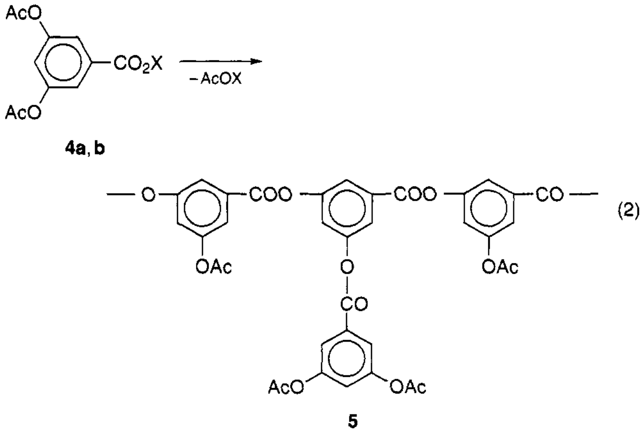


Figure 2. 75.4 MHz ^{13}C NMR spectrum of polyester **5** prepared from the silylated monomer **4b** at 280 °C (no. 6, Table 1).

$$\mathrm{DB} = \frac{I_T + I_B}{I_T + I_B + I_L} = \frac{2I_T}{I_T + I_B + I_L} \qquad (1)$$

Therefore, the DB values listed in Table 1 were all calculated according to eq (1) on the basis of ^{1}H NMR spectra. Taking into account that all samples with structure **5** (eq 2)possess DB's around 0.48 (±0.2), the present results indicate that the DB varies little with the reaction conditions. Because transesterification should be faster in the presence of acidic protons (polycondensation of **4a**), the DB seems to be a thermodynamically controlled property of all samples.



4a,b

(2)

5

The weight-average molecular weights (M_w) were determined in two ways, based on intrinsic viscosity measurements in tetrahydrofuran (Table 2). Pairs of

Table 2. Viscosity and Molecular Weight Measurements

sample no.	η_{inh}[a] (dL/g)	$[\eta]$[b]	M_w[c] (ref 3)	M_w[d] (GPC)	M_w^d/M_n^d
1, Table 1	0.35	0.20	330 000		
2, Table 1	0.22	0.18	280 000	190 000	
5, Table 1	0.34	0.20	300 000		
6, Table 1	0.36	0.22	440 000	270 000	10
7, Table 1	0.42	0.27	700 000		
1, Table 3	0.18	0.14	150 000	90 000	6
2, Table 3	0.24	0.20	330 000	180 000	8
3, Table 3	0.27	0.21	450 000	230 000	10
4, Table 3	0.37	0.24	530 000	280 000	10

[a] See footnote *a* of Table 1. [b] Measured at 25 °C in neat tetrahydrofuran. [c] Calculated from the $[\eta]/M_w$ correlation in ref 3. [d] GPC measurements in tetrahydrofuran, calibrated with commercial polystyrene standards.

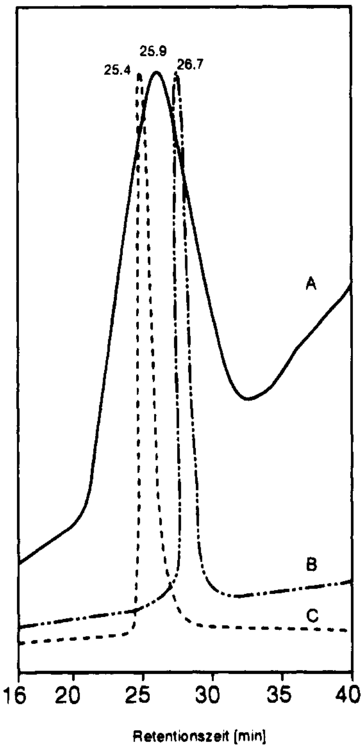


Figure 3. GPC elution curves of (A) polyester **5** prepared from **4b** at 280 °C (no. 6, Table 1), (B) polystyrene (M_w ~ 70 000, M_n ~ 66 000), and (c) polystyrene (M_w ~ 133 000, M_n ~ 120 000).

intrinsic viscosities and M_w values were published by Turner et al.[3] These values form a straight line in a double-logarithmic plot and served for the calculation of M_w values from the intrinsic viscosities measured in this work. A second series of molecular weights were determined from GPC measurements using Ultrastyragel columns and commercial polystyrene standards. The molecular weights were calculated from the maximum of the elution curves on the basis of the universal calibration method. Such molecular weights may somewhat underestimate the true M_w's in cases of broad molecular weight distributions, but the molecular weights obtained in this way are considerably lower than those obtained via the literature data.[3] This discrepancy illustrates the difficulty of measuring correct molecular weights of dendritic polymers. A basic problem is the use of linear polymers as standards.

Therefore, it was of particular interest to determine number-average molecular weights (M_n) by ^{1}H NMR "end group" analyses of polyesters containing suitable end groups or "star centers".

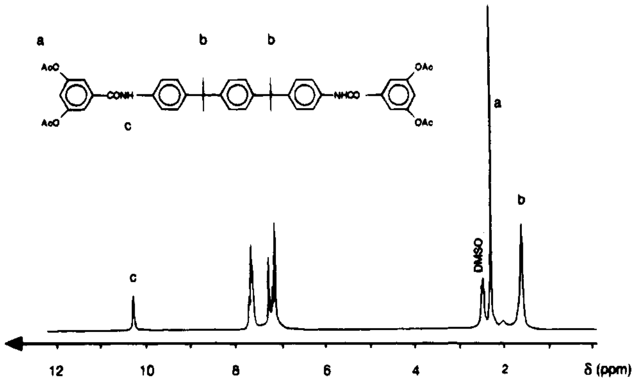


Figure 4. 100 MHz ^{1}H NMR spectrum of *N,N'*-bis(3,5-diacetoxybenzoyl)-Bisaniline-P (**7**).

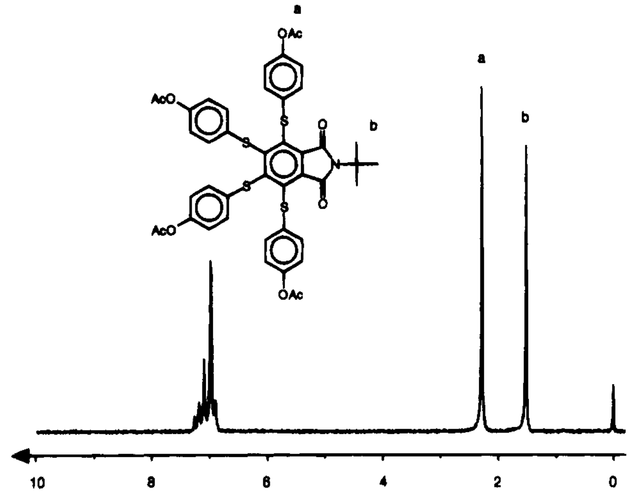


Figure 5. 100 MHz ^{1}H NMR spectrum of comonomer **8b**.

Synthesis of "Star Centers". Polycondensations of monomers **4a** or **4b** with acetylated diphenols or multifunctional phenols should result in the formation of star-shaped polyesters with hyperbranched star arms. In principle, numerous diphenols and a few tri- or tetraphenols are commercially available. However, the comonomers used in this work should meet a special requirement. They should possess at least one (better several) isolated CH_3 group which yields a singlet signal in the ^{1}H NMR spectra of the resulting polyester. If acetylated phenols free of carboxyl groups or other reactive functional groups are used, each polyester should possess only one star center, and the quantification of the ^{1}H NMR signals should allow the calculation of average degrees of polymerizations (DP's). In other words, the multifunctional phenols play the role of a "star center" and initiator. Therefore, the variation of the monomer/initiator ratio should allow a systematic variation and control of the DP and number-average molecular weight (M_n). In this connection, it should be mentioned that the synthesis of star-shaped polycondensates by polycondensation of A–B or A_2B monomers with a B_4 monomer (star center) has been reported for poly(ether sulfone)s in a previous part of this series[7] and for aliphatic polyesters by Hult and co-workers.[8] However, the star centers used in those previous studies do not meet the analytical requirements discussed above.

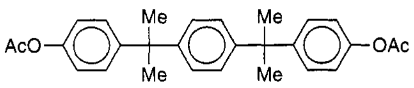
The diphenol selected for the purpose of this work is the commercial Bisphenol-P in its acetylated form **6**. An acetylated tetraphenol (**7**) was prepared by acylation of *N,N'*-bis(trimethylsilyl)-"Bisaniline-P" with 3,5-diacetoxybenzoyl chloride. Furthermore, the acetylated tetraphenol **8b** was synthesized starting from *tert*-buty-

Table 3. Copolycondensations[a] of Trimethylsilyl 3,5-Diacetoxybenzoate (4b) with Acetylated Bisphenol-P (6)

expt no.	monomer/init[b]	yield (%)	η_{inh}[c] (dL/g)	T_g (°C)	DP[d]	M_n	elem anal.	% C	% H
1	20	63	0.18	144	45 ± 5	$\sim 8 \times 10^3$	calcd	62.56	3.74
							found	60.25	3.48
2	40	72	0.24	149	65 ± 5	$\sim 12 \times 10^3$	calcd	61.67	3.60
							found	59.66	3.53
3	80	75	0.27	150	100 ± 10	$\sim 18 \times 10^3$	calcd	61.19	3.50
							found	60.00	3.57
4	150	75	0.37	152	180 ± 20	$\sim 32 \times 10^3$	calcd	60.96	3.45
							found	60.12	3.50
5	250	76	0.38	154		$(\sim 40 \times 10^3)$	calcd	60.85	3.43
							found	60.24	3.60

[a] 1 h/200 °C + 3 h/280 °C + 0.5 h/280 °C with vacuum. [b] Molar feed ratio of **4b** and **6**. [c] Measured at 20 °C with c = 2 g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1). [d] Average degree of polymerization as determined from the ratio of Bisphenol-P and acetate groups.

lamine and tetrachlorophthalic anhydride. The *N-tert*-butyltetrachlorophthalimide **9** was then reacted with 4-mercaptophenol and potassium *tert*-butoxide in DMF (eq 3). Because the mercapto group is more acidic than the hydroxy group and the sulfide anion is more nucleophilic than the phenoxide ion, the substitution of **9** (eq 3) is highly regioselective with regard to the mercaptophenol and almost quantitative with regard to imide **9**. Finally, the resulting tetraphenol **8a** was acetylated. In addition to elemental analyses, the ^{1}H NMR spectra of Figures 4 and 5 prove the structure of the comonomers **7** and **8b**.



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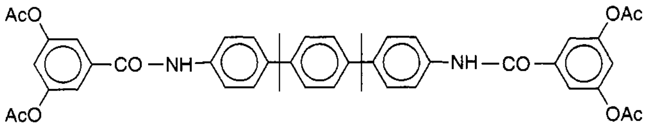

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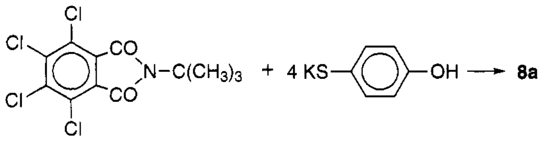

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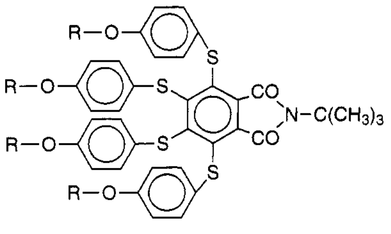


8a, R = H
b, R = Ac

Star-Shaped Branched Polyesters. Polycondensations of the silylated monomer **4b** with the difunctional "star center" (or initiator) **6** were conducted at a maximum reaction temperature of 280 °C. The monomer/initiator ratio was varied between 20 and 250, and soluble polyesters were obtained in all cases. As illustrated by the data compiled in Table 3, the inherent viscosities increase with higher monomer/comonomer ratios up to a ratio of 150, whereas the increase is poor up to 250. Furthermore, it is worth noting that the T_g increases in the same direction. These results clearly indicate an incorporation of the comonomer **6** parallel to the feed ratio. The ^{1}H NMR spectra (Figure 6) provide a more quantitative confirmation of this conclusion. The CH_3 signal of the "star center" is clearly detectable (signal X), and its quantification and comparison with the acetate signal (Z) or with the aromatic protons yields the DP.

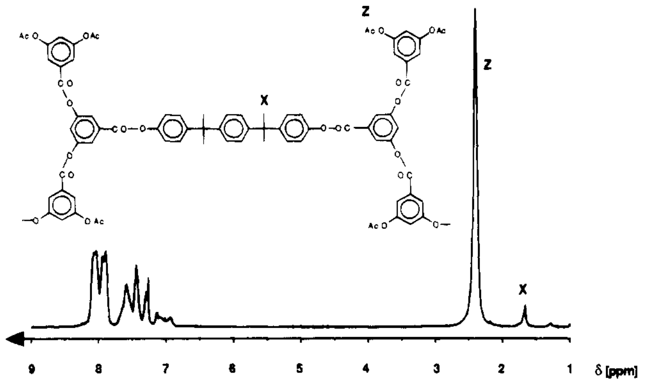


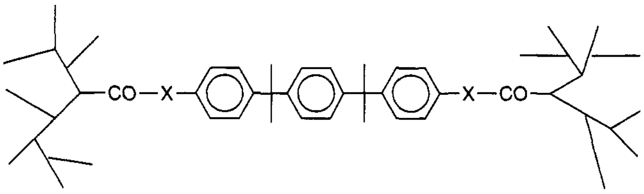
Figure 6. 100 MHz ^{1}H NMR spectrum of the star-shaped hyperbranched polyester **10a** (no. 1, Table 3).

The DP values listed in Table 3 are higher than the monomer/initiator ratios. This difference is a consequence of the fractionation resulting from the precipitation into methanol. In all cases the methanol filtrate contained a low molecular weight fraction of polyesters rich in Bisphenol-P units. This result is reasonable because the molecular weight distribution is broad as discussed above.

The number-average molecular weights (M_n's) calculated via the ^{1}H NMR spectroscopic DP values (Table 3) are certainly an upper limit, because it may happen that all polyester chains are attacked to the star centers. However, the maximum M_n values of 32×10^3 or 40×10^3 calculated for the polyesters nos 4 and 5 seem to represent a reasonable order of magnitude, if the viscosity data and GPC measurements are taken into account (Table 2). Considering M_w/M_n ratios on the order of 10, the M_n of sample no. 4 (Table 3) corresponds to a M_w of 320 000, which agrees well with the M_w value obtained from direct GPC measurements. In the case of sample nos 1–3 (Table 1), the M_n values even seem to be too low when compared to the M_w data from by GPC.

The M_w values calculated via the calibration reported in ref 3 are obviously too high when compared to the NMR spectroscopic M_n values. In this connection, it should be emphasized that the accuracy and reliability of both light scattering and GPC measurements may be affected by aggregation of hyperbranched polymers via their numerous polar end groups. Even a slight aggregation may easily double or triple the apparent M_w values. ^{1}H NMR spectroscopic end group analyses are insensitive to aggregation and, thus, are obviously more reliable from this point of view.

When the silylated monomer **4b** was polycondensed with the acetylated tetraphenols **7** at 280 °C partial cross-linking was observed in ca. 50% of all experiments. Reduction of the reaction temperature to 260 °C yielded soluble polyester in all cases (nos. 1–4, Table 4). Despite the lower reaction temperature, the viscosities are comparable with those of polyesters prepared at 280 °C using star center **6** as comonomer (Table 3). The ^{1}H NMR spectra of polyesters **10b** are almost identical with those of **5** and do not need separate discussion. However, the DP values calculated from the CH_3 signal of the star center are in this case probably higher than the true DP's due to incomplete conversion.



10a, X = O
b, X = NH

The polycondensations of **4b** with **8b** were feasible at 280 °C without significant cross-linking. Again, both viscosities and T_g increase with the monomer/initiator ratio and, thus, prove the incorporation of **8b**. Unfortunately, the CH_3 signal of the *tert*-butyl groups was extremely weak in all cases (approximately 10% of the expected intensities). Obviously, most *tert*-butyl groups were split off in the form of isobutylene. This conclusion was confirmed by heating *N*-*tert*-butyltetrachlorophthalimide for 3 h to 280 °C.

Table 4. Polycondensations of Monomer 4b with the Acetylated Tetraphenol Initiator 7 or 8b

expt no.	init	monomer init[a]	yield (%)	η_{inh}[b] (dL/g)	DP[c]	T_g[d] (°C)
1[e]	**7**	20	78	0.18	38	151
2[e]	**7**	40	79	0.24	80	153
3[e]	**7**	80	74	0.34	170	154
4[e]	**7**	150	76	0.36	320	154
5[f]	**8b**	20	83	0.13		147
6[f]	**8b**	40	84	0.18		150
7[f]	**8b**	80	88	0.25		153
8[f]	**8b**	150	83	0.31		154

[a] Feed ratio of **4b**/**7** or **4b**/**8b**. [b] Measured at 25 °C with $c = 2$ g/L in tetrahydrofuran. [c] Apparent DP is determined by ^{1}H NMR spectroscopy. [d] DSC measurements with a heating rate of 20 °C/min. [e] Maximum reaction temperature: 260 °C. [f] Maximum reaction temperature: 280 °C.

Finally, it should be mentioned that ^{1}H NMR spectroscopy end group analyses revealed a degree of branching in the range of 0.55 for all polyesters listed in Tables 3 and 4.

References and Notes

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