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New Polymer Syntheses. 103. In Situ End Group Modification of Hyperbranched Poly(3,5-dihydroxybenzoate)

Hans R. Kricheldorf,* Oliver Bolender, and Thomas Wollheim

Institut für Technische und Makromolekulare Chemie, Bundesstrasse 45, D-20146 Hamburg, Germany

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ABSTRACT: 3,5-Bis(trimethylsiloxy)benzoyl chloride (BTBC) was polycondensed with *N*,*N*′-bis(trimethylsilyl)bisaniline-P in bulk with variation of the feed ratio. In this way star-shaped hyperbranched polyesters were prepared, and the average degree of polymerization (DP) was controlled by the monomer/comonomer (M/C) ratio. A star-shaped, hyperbranched polyester having a DP of 50 was treated with an excess of an acid chloride in refluxing 1-chloronaphthalene, and the trimethylsiloxy groups were almost quantitatively transformed into ester groups. The following acid chlorides were used: acetyl, chloroacetyl, undecenoyl, stearoyl, 4-methoxycinnamoyl, and perfluorooctanoyl. Due to the low boiling point, the acylation with acetyl chloride required two steps for completion. The solubilities and glass-transition temperatures varied largely with the nature of the end groups. Irradiation with UV light (254 nm) caused rapid cross-linking of films cast from poly(3,5-dihydroxybenzoate) bearing 4-methoxycinnamoyl end groups.

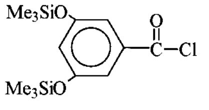
Introduction

In the case of linear polymers the end groups have no influence on the physical properties of the material provided that the term polymer is justified and the number-average molecular weight M_n is above 10^4. The situation is different for hyperbranched polymers because of the large number of end groups, which in the case of a homopolymer derived from a AB_2 monomer equals the number of repeating units. A typical example is the comparison of the glass-transition temperatures (T_g's) of poly(3,5-dihydroxybenzoate)s, poly(DHB), having acetate or OH end groups and poly(5-hydroxy isophthalate) having CO_2H end groups. Despite similar molecular weights and polymer chains, the T_g's vary between 140 and 260 °C.[1−6] In this case the three different end groups were obtained by polycondensation of three different monomers.

In this connection the present work had the purpose to elaborate a convenient "one-pot procedure" for the synthesis and in situ end groups modification of poly(DHB). This approach is based on the polycondensation of BTBC (**1**) or its copolycondensation with 3-trimethylsiloxybenzoyl chloride (**2**)[1,3] followed by an acylation of the trimethylsiloxy end groups of the resulting hyperbranched (co)polyesters **3**. A reliable comparison of the influence the end groups have on the physical properties such as T_g or solubilities requires samples having similar molecular weights. Therefore, the present work had the second purpose to study the copolycondensation of the monomer **1** with silylated bisaniline-P (**4**). Provided that the reaction of BTBC with **4** is faster than the polycondensation of BTBC, the C_2 comonomer **4** should play the role of a star center and chain terminator, so that star-shaped, hyperbranched polyesters of tailor-made M_n's should be obtained. A few examples of this synthetic strategy have recently been reported.[7−10]

Experimental Section

Materials. 3-Hydroxybenzoic acid, 3,5-dihydroxybenzoic acid, chlorotrimethylsilane, thionyl chloride, and 1-chloronaphthalene were gifts of Bayer AG (Leverkusen, FRG). The 1-chloronaphthalene was distilled over P_4O_{10} in vacuo prior to use. The trimethylsiloxybenzoyl chlorides **1** and **2** were prepared as described previously[5,6] and purified by distillation over a short-path apparatus. Acetyl chloride, stearoyl chloride, undecenoyl chloride, perfluorooctanoyl chloride, and 4-methoxycinnamic acid were purchased from Aldrich Co. (Milwaukee, WI) and used as received. The acid chloride of 4-methoxycinnamic acid (mp 50 °C in ref 11) was prepared in a refluxing mixture of $SOCl_2$ and chloroform (volume ratio 1:4) with addition of a catalytic amount of dimethylformamide.



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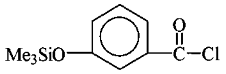

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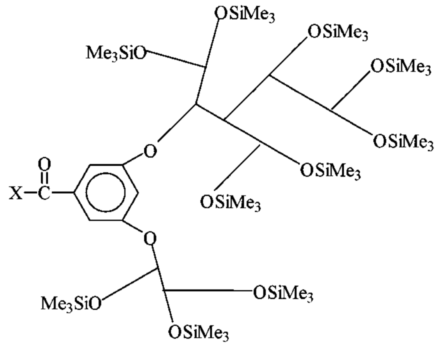

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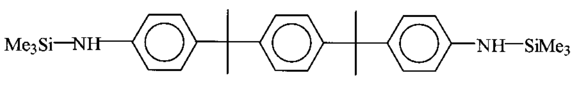

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N,*N*′*-Bis(trimethlysilyl)bisaniline-P.* Bisaniline-P (0.15 mol) and chlorotrimethylsilane (0.32 mol) were dissolved in dry toluene (500 mL) at 60 °C, and triethylamine (0.32 mol) was added dropwise with stirring. The reaction mixture was refluxed for 6 h, cooled, and filtered with exclusion of moisture. The filtrate was concentrated in vacuo, and the product was distilled over a short-path apparatus at a bath temperature of 230−240 °C and 10^{-3} mbar.Yield: 85%, mp 134 °C. ^{1}H NMR ($CDCl_3$), δ: 0.22 (s, 18 H), 1.58 (s, 12 H), 3.32 (s, 2 H), 6.49 (d, 4 H), 6.96 (d, 4 H), 7.09 (d, 4 H) ppm.

N,*N*′*-Bis(3,5-dihydroxybenzoyl)bisaniline-P.* *N*,*N*′-Bis(trimethylsilyl)bisaniline-P (10 mmol) was dissolved in dry diox-

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Table 1. Yields and Properties of Star-Shaped Hyperbranched Poly(3,5-dihydroxybenzoate)s

3,5-BTBC/bisaniline-P[a]	DP[b] (^{1}H NMR)	yield (%)	η_{inh}[c] (dL/g)	M_n[d] (GPC)	M_w/M_n[d]	T_g[e] (°C)
50:1	55:1	67	0.12	16 000	1.7	132
100:1	170:1	65	0.16	21 000	1.9	143
150:1	230:1	63	0.18	24 000	2.0	152
200:1	400:1	63	0.21	27 000	2.0	165

[a] Molar feed ratio of the monomers **1** and **4**. [b] After precipitation into methanol. [c] Measured at 25 °C with $c = 2$ g/L in THF. [d] GPC measurements in THF calibrated with polystyrene. [e] DSC measurements with a heating rate of 20 °C/min (second heating).

ane (50 mL), and 3,5-bis(trimethylsiloxy)benzoyl chloride (20 mmol) was added. The reaction mixture was refluxed for 1 h and after cooling mixed with 2 N hydrochloric acid (100 mL) with rapid stirring. After 30 min, the precipitated product was filtered off, washed intensively with water, and dried at 80 °C in vacuo. Yield: 51%, mp 353 °C (by DSC). Anal. calcd for $C_{38}H_{36}N_2O_4$ (616.7): C, 74.01; H, 5.88; N, 4.54. Found: C, 73.36; H, 5.94; N, 4.29%. ^{1}H NMR (DMSO/TMS): $\delta = 1.59$ (s, 12 H), 6.39 (t, 2 H), 6.74 (d, 4 H), 7.20 (s, 4 H), 7.24 (d, 4 H), 7.62 (d, 4 H), 9.54 (s, 4 H), 10.1 (s, 2 H) ppm.

Polycondensations. 3,5-Bis(trimethylsiloxy)benzoyl chloride (50 mmol), *N*,*N*′-bis(trimethylsilyl)bisaniline-P, and benzyltriethylammonium chloride (10 mg) were weighed (under an atmosphere of dry nitrogen) into a cylindrical glass reactor equipped with stirrer, gas-inlet tubes, and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 150 °C, and the temperature was rapidly raised to 245−250 °C. This temperature was maintained for 3 h, and finally vaccum was applied for 10 min. The cold product was dissolved in tetrahydrofuran (THF), precipitated into cold methanol, and dried at 100 °C in vacuo.

Modification of the End Groups. The crude polyester prepared from **1** (50 mmol) and **4** (1 mmol) was cooled to 170 °C and dissolved in dry 1-chloronaphthalene (50 mL), and an acid chloride (55 mmol) and benzyltriethylammonium chloride (10 mg) were added. This solution was heated to 190 °C for 3 h and refluxed for 0.5 h. After cooling the reaction mixture was poured into cold methanol, isolated by filtration, and dried at 65 °C in vacuo. In the case of the perfluorooctanoyl end groups dry diethyl ether was used for the precipitaion.

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 25 °C.

The DSC measurements were conducted with a Perkin-Elmer DSC-7 in aluminum pans under nitrogen at a heating rate of 20 °C/min.

The 100 MHz ^{1}H NMR spectra were recorded with a Bruker AC-100 FT NMR spectrometer in 5 mm o.d. sample tubes using $CDCl_3$/TMS or DMSO-d_6/TMS as solvents and shift reference.

The samples used for UV radiation were prepared by casting a solution of a polyester having 4-methoxycinnamoyl end groups in tetrahydrofuran (5 mL) on six glass plates (size 15 × 50 mm). The radiation was performed with a 60 W low-pressure mercury lamp (Heraeus AG, Germany) at a wavelength of 254 nm. The distance between samples and lamp was 5 cm, and the irradiation times were 1, 3, 5, 10, 20, and 60 min.

Results and Discussion

Syntheses of Star-Shaped Poly(DHB). *N*,*N*′-Bissilylated bisaniline-P was used as the star center for the following reasons. First, it contains four identical CH_3 groups which yield one intensive singlet signal in the ^{1}H NMR spectra, allowing for an easy detection (and quantification) of the star center even in high molecular weight poly(DHB). The silylation of the amino groups enables purification by distillation and enhances their nucleophilicity, so that an acylation is feasible below 100 °C, in contrast to the polycondensation via the trimethylsiloxy groups. To check the reactivity of **4**, it was heated with a double molar amount of 3,5-bis(trimethylsiloxy)benzoyl chloride (**1**) in dioxane. After acidic hydrolysis of the trimethylsiloxy groups the bis(3,5-dihydroxybenzoyl)bisaniline-P (**6**) was isolated. The result indicates that the silylated precursor molecule **5** is the initial reaction product, when the monomer **1** is polycondensed with the comonomer **4**.

The polycondensations were conducted in bulk at a reaction temperature of 245−250 °C. At higher temperatures all samples were partially cross-linked, and even at this temperature cross-linking was observed in two experiments which were repeated until conpletely soluble samples were obtained.

The highest possible reaction temperature was of interest to achieve the highest possible conversion. A real polycondensation never reaches 100% conversion of the functional groups unless cyclization takes place. Regardless, whether incomplete conversion or cyclization take place, the consequence for the system under investigation is an incomplete binding of oligomeric and polymeric chains to the star center molecule. Nevertheless, the viscosity data listed in Table 1 together with the GPC measurements clearly indicate that the average molecular weight increases with the feed ratio of both reactants. The silylated bisaniline-P plays the expected role of a chain terminator. Since no analytical method exists that allows an accurate determination of number-average molecular weights (M_n's) of polycondensates having broad molecular weight distribution, we were not able to determine whether the M_n's exactly parallel the feed ratios of **1** and **4** or not. However, in addition to the viscosity and GPC measurements, also the glass-transition temperatures (T_g's, Table 1) prove that at least a crude relationship between the molecular weights and feed ratios exists.

The ^{1}H NMR spectra of the polyesters isolated from the precipitation in methanol proved the incorporation of the bisaniline-P (Figure 1). The average degrees of polymerization (DPs) were higher than expected from the feed ratios of the reactants due to fractionation. The low molar mass fraction recovered from the filtrate proved to contain the missing amount of bisaniline-P. Yet, even when both fractions were taken into account, the ^{1}H NMR spectra do not reliably indicate that all oligo- and polyester chains were attached to the bisaniline-P moiety. Despite a potential imperfection of these polycondensations, the results of this study demonstrate that **4** plays the hoped-for role of a star center and chain terminator, allowing for a control of the molecular weight.

Modification of End Groups. All experiments designed for the modification of the trimethylsiloxy end groups were conducted with a star-shaped poly(DHB) prepared with a feed ratio of 50:1. The hot melt of the poly(DHB) was cooled to 170 °C and diluted with 1-chloronaphthalene, so that a homogeneous easily stirrable concentrated solution was obtained. An acid chloride (slight excess) and chloride ions (as catalysts) were added, and the heating was continued with variation of the temperature according to the properties of

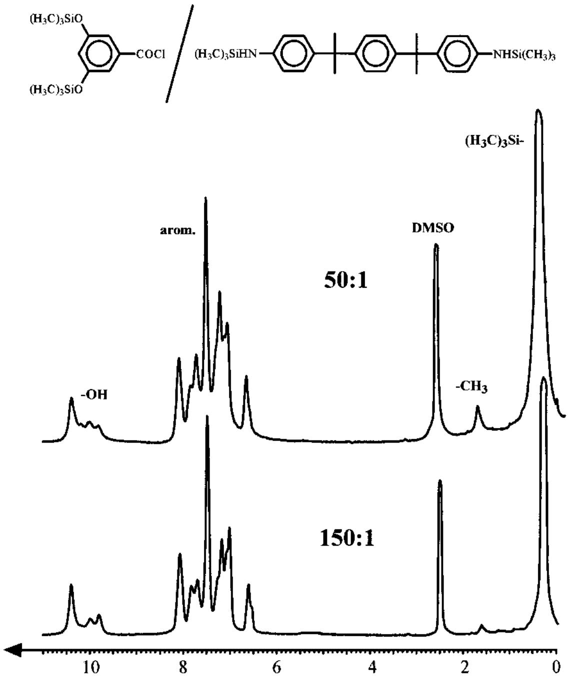
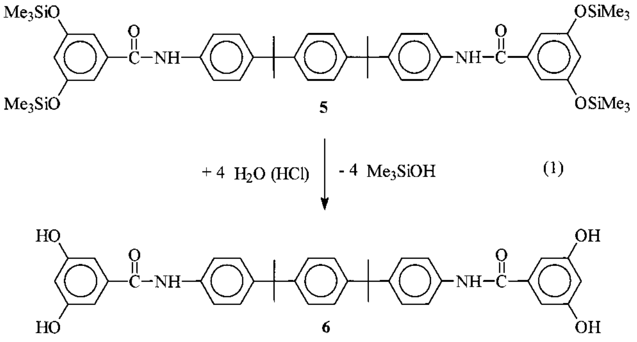


Figure 1. The 100 MHz ^{1}H NMR spectra of star-shaped, hyperbranched poly(DHB) prepared with two different monomer/star center ratios (recorded in $CDCl_3$ after precipitation in methanol).



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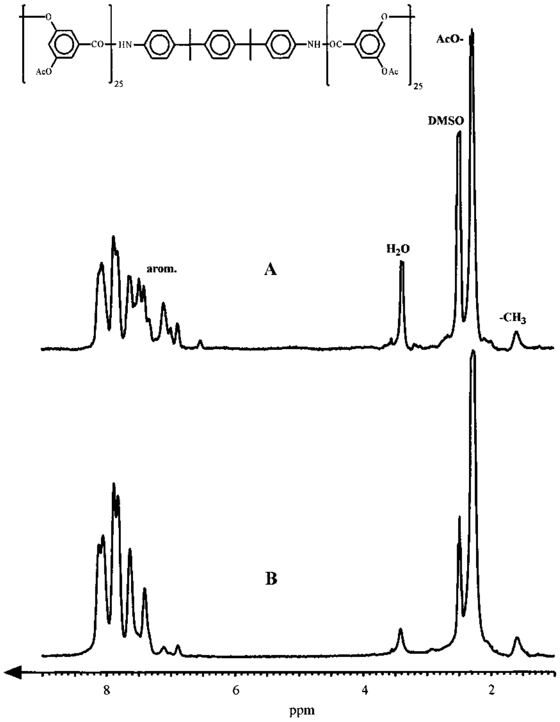


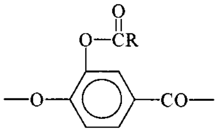
Figure 2. The 100 MHz ^{1}H NMR spectra of acetylated, hyperbranched poly(DHB): (A) one-step acetylation conducted at 120 °C with an 10% excess of acetyl chloride and (B) product of the two-step acetylation.

the acylation agent (see Table 2). The first acylation experiments were conducted with acetyl chloride. Due to its low boiling point, the reaction temperature was limited to 120 °C in this case. For the product isolated after the standard time of 3 h only a conversion around 60% was found. This incomplete conversion not only was evident from the intensity of the CH_3 signal in the ^{1}H NMR spectrum but also was reflected in the signal pattern of the aromatic protons (Figure 2A). In the second experiment most of the unreacted acetyl chloride and of the liberated chlorotrimethylsilane were distilled off, and after cooling to 120 °C fresh acetyl chloride was added. With this second acylation nearly 100% conversion was achieved, and the ^{1}H NMR of the isolated product was identical with the spectrum of a polyester prepared from 3,5-bis(acetoxy)benzoic acid (Figure 2B).

Table 2. Yields and Properties of Poly(3,5-dihydroxybenzoate)s[a] Having Acylated End Groups

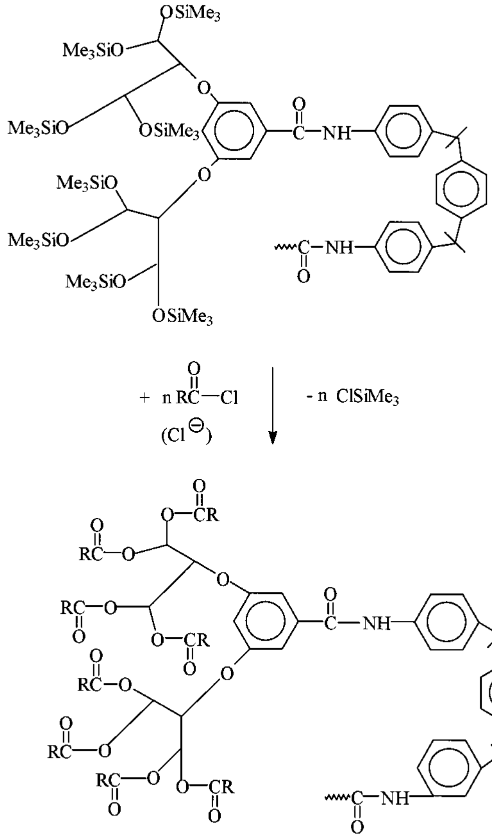
end groups	yield (%)	% acylation	T_g[b] (°C)	elem formula[c] (form weight)	elem analysis	C	H
acetyl	65	97–100[d]	161	$C_9H_6O_4$	calcd	60.68	3.39
				(178.1)	found	60.15	3.29
chloroacetyl	63	97–100	171	$C_9H_{25}O_4Cl$	calcd	50.95	2.37
				(212.6)	found	52.05	2.54
undecenoyl	60	97–100	107	$C_{18}H_{22}O_4$	calcd	71.49	7.34
				(302.2)	found	71.78	7.11
stearoyl	60	88–92	94	$C_{25}H_{38}O_4$	calcd	74.58	9.52
				(402.3)	found	74.75	9.46
perfluoroocatanoyl	60	96–100	189	$C_{15}H_3O_3F$	calcd	34.90	0.59
				(516.0)	found	32.65	1.53
4-methoxycinnamoyl	66	97–100	154	$C_{17}H_{12}O_5$	calcd	68.90	4.08
				(296.1)	found	68.42	4.17

[a] Prepared with a **1**/**4** feed ratio of 50/1. [b] From DSC measurements with a heating rate of 20 °C/min (second heating). [c] Calculated for a linear repeating unit:



[d] After two-step acetylation.

A third acetylation experiment was again conducted in one step using a 50% excess of acetyl chloride (instead of the usual 10%), and the time was extended to 20 h. In this way a conversion around 90% was achieved in a "one-step experiment".



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The higher boiling point of chloroacetyl chloride allowed a higher reaction temperature of 150 °C. Using again an excess of 50% in combination with a time of 20 h gave a conversion near 100% in one step. In the case of undecenoyl chloride, stearoyl chloride, 4-methoxycinnamoyl chloride, and perfluorooctanoyl chloride an initial reaction temperature of 170 °C was used and then continued at 190 °C. With a 10% excess of acylating agent an almost complete conversion was obtained in three cases (Table 2), and only for 4-methoxycinnamoyl chloride was a somewhat lower conversion found.

In all these experiments the conversion was checked in two ways. At first, ^{1}H NMR spectra of the crude reaction products were recorded (after distillation of the liberated chlorotrimethylsilane) to detect the presence of unreacted trimethylsiloxy groups. Second, the ^{1}H NMR spectra of the isolated polyesters were recorded, and the signal intensities of the aliphatic and aromatic protons were compared (Figure 3). For this purpose 4-methoxycinnamoyl chloride was used instead of cinnamoyl chloride. In the case of the perfluorooctanoyl end groups the NMR sepectroscopic characterization was, of course, useless, but here the elemental analyses were more informative. They agreed with a conversion in the range 90−100%.

The T_g's of all modified poly(DHB)s were determined by DSC measurements at a heating rate of 20 °C/min. The data listed in Table 2 show that the lowest T_g's were found for the undecendeconyl and stearoyl end groups, because these end groups play the role of plasticizers. Interestingly, no endotherm was detectable which might indicate a crystallization of the stearoyl end groups. The highest T_g was surprisingly observed for the polyester having perfluorooctanoyl end groups. Its T_g's was 95 °C higher than that of the stearoyl product, proving the strong influence of the end groups.

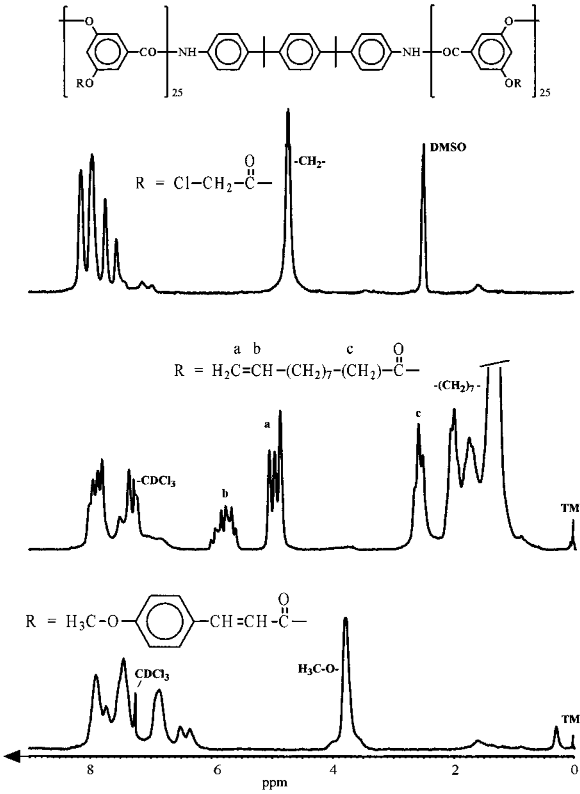

Figure 3. The 100 MHz ^{1}H NMR spectra of poly(DHB): (A) acylated with chloroacetyl chloride at 150 °C, (B) acylated with undecenoyl chloride at 170/190 °C, and (C) acylated with 4-methoxycinnamoyl chloride at 170/190 °C.

The solubilities were determined in seven solvents or solvent mixtures, preferentially in solvents that are useful for GPC and NMR measurements (Table 3). The following characteristic results were obtained. Those polyesters bearing the least polar end groups, namely undecenoyl or stearoyl groups, were insoluble in DMSO. This is also true for the 4-methoxycinnamoyl group, which surprisingly was also insoluble in dioxane (in contrast to THF). Only the poly(DHB)s containing undecenoyl or stearoyl groups were soluble in toluene. The poly(DHB) having perfluorooctanoyl groups was insoluble in all chlorinated solvents. These results altogether clearly demonstrate the significant influence different end groups may have on the physical properties of hyperbranched polyesters.

A particularly interesting example of the influence of photosensitive end groups was found in the case of the 4-methoxycinnamoyl groups. When films cast on glass plates were irradiated with a wavelength of 254 nm, the beginning of cross-linking was observed after 3 min and an almost complete cross-linking after 5 min. This result is noteworthy for two reasons. First, it demonstrates that the end groups of neighboring polyester molecules can penetrate and have sufficient mobility for efficient photo-cross-linking. This point is worth noting because hyperbranched polymers, having a high branching density like dendrimers, are known to be not capable of a deep mutual penetration and not capable of forming entanglements. Second, this approach may be useful to

Table 3. Solubilities[a] of Acylated Poly(3,5-dihydroxybenzoate)s

end group	THF	dioxane	DMSO	$CHCl_3$	CH_2Cl_2	CH_2Cl_2 + TFA	toluene
acetyl	+	+	+	−	+	+	−
chloroacetyl	+	+	+	+	−	+	−
undecenoyl	+	+	−	+	+	+	−
stearoyl	+	+	−	+	+	+	+
perfluoroocatanoyl	+	+	+	−	−	−	−
4-methoxycinnamoyl	+	−	−	+	+	+	−

[a] Determined with 50 mg of polyester in 1 mL of solvent at 25−50 °C.

produce tough coatings with high mechanical properties. In this connection it should be noted that this approach can be extended to copolyesters of BTBC and 3-trimethylsiloxybenzoyl chloride (**2**), so that a systematic variation of the branching density and number of end groups is feasible.[1] In combination with photosensitive or thermolabile end groups, interesting photosetting or thermosetting materials can be prepared in this way as will be published in a future part of this series.

Conclusion

The results of the present study indicate that copolycondensations of BTBC with a silylated aromatic diamine allow the syntheses of star-shaped hyperbranched poly(DHB)s combined with a control of the average DP. Furthermore, it is demonstrated that an in situ modification of the end groups by chloride ion catalyzed acylation of the trimethylsiloxy groups is feasible. Conversions in the range 97−100% were found in most cases. The variation of the end groups allows in turn a broad variation of the chemical and physical properties without any variation of the polymer backbone or of the molecular weight. The differences of the solubilities suggest that also a significant variation of the compatibility with other polymers may be achieved. This is an interesting aspect for the preparation of polymer blends. Furthermore, the incorporation of photosensitive end groups allows the preparation of tough films and coating by cross-linking. Taken into account the copolycondensation of BTBC with difunctional monomers such as **2**, this new approach allows an extremely broad variation of both chemical and physical properties and opens new ways for potential applications.

References and Notes

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