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All-Aromatic Hyperbranched Polyesters with Phenol and Acetate End Groups: Synthesis and Characterization

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ABSTRACT: This report describes the synthesis of all-aromatic hyperbranched polyesters with phenol and acetate end groups. The synthesis was based on the melt condensation of the A_2B monomers 3,5-bis(trimethylsiloxy)benzoyl chloride (**2**) and 3,5-diacetoxybenzoic acid (**3**). The trimethylsilyl groups of the polyesters from monomer **2** are hydrolyzed during workup, resulting in polymers with phenol terminal groups. Although the acetate groups of polymers prepared from **3** are quite stable and remain in the polymer, conditions were found where they could be hydrolyzed to give a phenolic polymer similar to that obtained from **2**. The special structure of the monomers results in highly branched (hyperbranched) materials with a high number of terminal groups. Comparison of Mark-Houwink plots of linear polystyrene and a hyperbranched polyester sample and Mark-Houwink "a" values of less than 0.5 for numerous samples were consistent with highly branched structures. These polyesters are noncrystalline and are thermally stable to at least 350 °C. As predicted for such step-growth polymerizations, the molecular weight distributions broadened significantly at high conversions.

Introduction

Branched polymers based on the step-growth reaction of A_xB monomers were first described by Flory in 1952.[1] However, it has only been in the last few years that these materials have received much attention. Interest in the A_xB polymer synthesis was stimulated by the synthesis of "perfect" dendritic polymers by Tomalia,[2] Newkome,[3] and Fréchet.[4] In these synthetic schemes, dendrimers are built up by step-by-step sequences, requiring isolation and purification after each step. These processes yield highly regular dendritic polymers whose unique structure, shape, and high terminal functionality have suggested a number of potential applications.[2]

The current synthetic schemes do not lend themselves easily to the preparation of scaled-up quantities of dendritic polymers to fully study and develop the potential of these novel materials. Several efforts have been reported on one-step syntheses of highly branched polymers, which have been termed hyperbranched polymers,[5] whose properties could mimic those of the perfect dendrimers. Unlike dendritic polymers, which are characterized by a very controlled defect-free branching and step-by-step or generation growth, the hyperbranched polymers are synthesized in a one-step reaction, using a high functionality monomer of the type A_xB. Control of the degree of branching is difficult and is mainly dependent on statistics, steric effects, and the reactivity of the functional groups. This results in a highly branched, irregular structure. The theory for condensation kinetics and the molecular weight growth and distribution of A_xB-type polycondensations was developed by Flory in 1952,[1] but without good examples. Recently, Kim and Webster[5] have reported a one-step A_2B synthesis of hyperbranched polyarylenes, and the syntheses of hyperbranched aromatic polyesters and polyethers have been reported by Fréchet.[6,7] Other A_2B polycondensations have been reported by Percec on thermotropic liquid crystalline structures,[8] Kim[9] on lyotropic liquid crystalline polyaramides, and Mathias[10] on polysiloxanes. This report describes the synthesis of all-aromatic hyperbranched polyesters by melt condensation of 3,5-diacetoxybenzoic acid in a conventional acidolysis polymerization under various conditions and a description of some of the basic polymer properties of this structure. For comparison, we also prepared and condensed the 3,5-bis(trimethylsiloxy)benzoyl chloride, as reported by Fréchet.[6]

Experimental Section

The synthesis of monomer 2 and the polymerizations were performed under a nitrogen or argon atmosphere. Benzene was freshly distilled from sodium prior to use. Other starting materials and reagents were used as obtained from the suppliers (Aldrich, Eastman Kodak Co.).

Monomer Synthesis. Trimethylsilyl 3,5-bis(trimethylsiloxy)benzoate (**1**) and 3,5-bis(trimethylsiloxy)benzoyl chloride (**2**) were prepared according to the published procedure of Fréchet.[6]

3,5-Diacetoxybenzoic Acid (3).[11] 3,5-Dihydroxybenzoic acid (0.5 mol, 77 g) and 200 mL of acetic anhydride (Ac_2O) were mixed in a 500-mL round-bottomed flask that was fitted with a reflux condenser. As the mixture was refluxed, the dihydroxy acid went into solution. The reaction mixture was refluxed for 5 h. A brown solution was obtained with a small amount of insoluble material. The excess Ac_2O was removed in vacuo, and the remaining solid was dried in vacuo at 40 °C. The solid was dissolved in about 200 mL of refluxing chloroform ($CHCl_3$), filtered hot, and then diluted with 70 mL of petroleum ether (bp 60-80 °C). The compound crystallized overnight and was isolated by filtration and washed with a 1:1 mixture of petroleum ether and $CHCl_3$. The compound was then recrystallized a second time using the same procedure. Yield: 59 g (50%), white crystals. Mp: 157-159 °C. ^1H NMR (DMSO-d_6): δ 2.1 (s, 6H), 7.23 (1H), 7.55 (2H), 13.3 (b, 1H). IR (KBr): ν 3400-2400, 1775 (COOR), 1695 (COOH), 1605 cm^{-1}.

3-Acetoxybenzoic Acid (4). A mixture of 27.4 g (0.2 mol) of 3-hydroxybenzoic acid and 40.8 g (0.4 mol) of acetic acid anhydride was refluxed for 3 h. The reaction mixture was poured into water and stirred for 3 h at 25 °C. The product precipitated, was collected by filtration, and was recrystallized from $CHCl_3$. Yield: 21 g (58%), white crystals. Mp: 128-129.5 °C. ^1H NMR (DMSO-d_6): δ 2.24 (s, 3H), 7.35, 7.55, 7.65, 7.8 (m, 4H), 13.2 (b, 1H). IR (KBr): ν 3500-2300, 1765 (COOR), 1680 (COOH), 1585 cm^{-1}.

Polymerization. Polymerization of 3,5-Bis(trimethylsiloxy)benzoyl Chloride (2) to P1-TMS and P1. The polym-

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erization procedure developed by Fréchet[6] was used to prepare **P1** and **P1-TMS**. The polymers were dissolved in a mixture of tetrahydrofuran (THF), methanol, and a small amount of water by refluxing overnight. For high molecular weight polymers it was necessary to add a small amount of *N*,*N*-dimethylformamide (DMF) to obtain solubility. The polymer solution was filtered, precipitated into water, collected, and dried in vacuo at 50 °C. At this reaction stage the product showed only phenol end groups (**P1**). The polymer also could be analyzed before dissolution and precipitation. In this case the trimethylsilyl groups (TMS) remained as end groups (**P1-TMS**). The yield varied between 70 and 94%. ^{1}H NMR (DMSO-d_6) of **P1**: δ 6.5, 7.0, 7.45, 7.7–8.2 (aromatic protons), 9.78 and 10.4 (OH, phenol). IR (KBr): ν 3600–2500, 1740 (COOR), 1585 cm^{-1}. ^{1}H NMR (THF-d_8) of **P1-TMS**: δ 0.25 (9H, TMS protons), 6.6, 7.1–7.3, 7.45–7.8, 7.95–8.23.

Polymerization of 3,5-Diacetoxybenzoic Acid (3) to P2. 3,5-Diacetoxybenzoic acid (10–20 g) was placed in a dry reaction flask under argon. The reaction vessel consists of a 100-mL round-bottomed flask with a long neck, a mechanical stirrer (glass stirring rod with Teflon blade), a nitrogen inlet with a long glass tube going to the bottom of the flask, and a 24/40 ground joint for connection to a vacuum pump. In the first stages of the polycondensation the reaction vessel was also connected with a condenser and a receiver to distill acetic acid. The reaction vessel, containing the monomer, was evacuated and flushed with argon twice and then placed in a salt bath at the desired reaction temperature. In some cases a small amount of catalyst was added (Mg, TsOH, 0.6–2 mol %). The monomer usually melted within 5 min. A slow inert gas (nitrogen) stream was applied during the first stage of the reaction until viscosity was built up (after about 0.5–5 h, depending on the temperature). Then vacuum was applied (about 10^{-2} Torr) to drive the reaction to high conversion (0.5–3 h). At the end of the reaction, stirring with the mechanical glass stirrer was no longer possible due to the high viscosity of the polymer. The polymer was elastic and almost colorless at the polymerization temperature of 185 °C. The polymerization flask was flushed with argon and cooled to room temperature. At room temperature the polymer was very brittle and could be easily broken into small pieces. The polymer was dissolved in THF overnight, filtered, and precipitated into methanol to yield a white powder. The yield was 80–90%. ^{1}H NMR (DMSO-d_6): δ 2.25 (s, 3H), 4 broad signals between 7.25 and 8.18 (3H), no OH protons. IR (KBr): ν 3045, 2940, 1765 (br, COOR), 1600 cm^{-1}.

Hydrolysis of the Acetate Groups (Hydrolyzed Polyester P2H). In order to obtain free phenol groups as end groups for the polymer **P2**, it was necessary to hydrolyze the acetate groups carefully without degrading the polyester backbone. The polyester **P2** (0.5 g) was dissolved in 100 mL of THF, 15 mL of methanol, and 10 mL of water (more water or methanol leads to precipitation). Hydrochloric acid (concentrated; 0.5 mL) was added (pH = 2–3), and the solution was refluxed for 16 h. After the hydrolysis, the solvent was removed under vacuum and the polymer was dissolved in pure THF and precipitated in water. After collecting and drying, 0.35 g of the product was obtained as a white powder. The hydrolysis degree was calculated to be 85–89% by NMR. ^{1}H NMR (DMSO-d_6): similar to that from **P1** except for remaining acetate protons at 2.25 ppm. The degree of branching was calculated to be 48–50% from NMR.

Polymerization of 3,5-Diacetoxybenzoic Acid in Diphenyl Ether (P3). 3,5-Diacetoxybenzoic acid (10 g) and 10 g of diphenyl ether were placed in the condensation flask. The mixture was evacuated at 25 °C for 20 min and flushed with argon. The flask was then placed in the salt bath that was preheated to 210 °C. The temperature was maintained for 20 min and then raised to 225 °C. After 45 min the temperature was reduced to 180 °C and the reaction was completed by pulling vacuum for 2 h. The resulting polymer was dissolved in THF overnight at 25 °C, filtered, precipitated in methanol, collected, and dried. The yield was 6.7 g (89%). ^{1}H NMR (DMSO-d_6): δ identical to **P2**; no residual diphenyl ether.

P3 (2 g) has been hydrolyzed under the conditions described for **P2H**, resulting in polymer **P3H**. Hydrolysis of 80% of the acetate groups could be achieved. NMR data and the branching degree (50%) are identical to the data obtained for **P2H**.

Copolymerization of 3-Acetoxybenzoic Acid and 3,5-Diacetoxybenzoic Acid (P4). 3-Acetoxybenzoic acid (1.8 g, 0.01 mol) and 3,5-diacetoxybenzoic acid (2.4 g, 0.01 mol) were placed in the condensation flask. The flask was evacuated and flushed with argon twice and then placed in the salt bath at 180–185 °C. The monomers melted within 5 min. A slow nitrogen stream was applied during the first stage of the reaction for 3.5 h until the viscosity increased appreciably. Then vacuum was applied (10^{-2} Torr) for 1 h to remove all of the acetic acid. The reaction was stopped, and the polymer was dissolved in THF, filtered, and precipitated in methanol. The isolated yield of polymer was 2 g (67%). ^{1}H NMR (DMSO-d_6): δ 2.21, 7.2–8.2 (br). The composition of the copolyester calculated from the integration is found to be 55:45 (3,5-diacetoxybenzoic acid/3-acetoxybenzoic acid).

Copolymerization of 3,5-Diacetoxybenzoic Acid and 4-Methoxybenzoic Acid (P5). The condensation was carried out with 5.0 g of **3** (0.021 mol) and 3.2 g of 4-methoxybenzoic acid (0.021 mol), as described for **P2**, at a reaction temperature of 180–185 °C without catalyst. The monomer mixture was kept at the reaction temperature under a slow nitrogen stream for 4.5 h, and then vacuum was applied for 1.5 h. The resulting polymer was dissolved in THF, and the solution was filtered and precipitated into methanol. The yield of polymer was 4.1 g (60%). ^{1}H NMR (DMSO-d_6): δ 2.2 (br, acetate), 3.78 (br, methoxy), 7.0 (br), 7.2–8.15 (br). Ratio acetate/methoxy/aromatic protons = 3.2/2.9/10.3, mol % acetate end groups in the polymer = 52, mol % of 4-methoxy end groups = 48.

Characterization. The NMR studies were done on a QE 300 General Electric instrument and the IR analysis on a Perkin-Elmer 1430. Thermal analysis data were obtained from a Du Pont-TA-Instrument 912 and Perkin-Elmer DCS 7 and TGA 7. Molecular weight distributions were obtained by size-exclusion chromatography (SEC) in THF using three PL gel mixed-bed 7.5 mm i.d. × 300 mm, 10-μM particle diameter columns (Polymer Laboratories, Amherst, MA). The system consisting of coupled differential viscometry (DV), low-angle laser light scattering (LALLS), and differential refractive index (DRI) detection has been described previously.[12] Absolute molecular weights were obtained by universal calibration using the DV or directly from LALLS. Samples with free phenol groups were protected with a silylating agent [*N*-methyl-(*tert*-butyldimethylsilyl)trifluoroacetamide = MTBSTFA] to prevent adsorption to the SEC columns. Capillary viscosity measurements were made with Ubbelohde viscometers. Gas chromatography/mass spectrometry (GC/MS) measurements on the volatiles were done on an Environchem thermal desorption unit coupled with Hewlett-Packard 5890 GC and 5970 MSD.

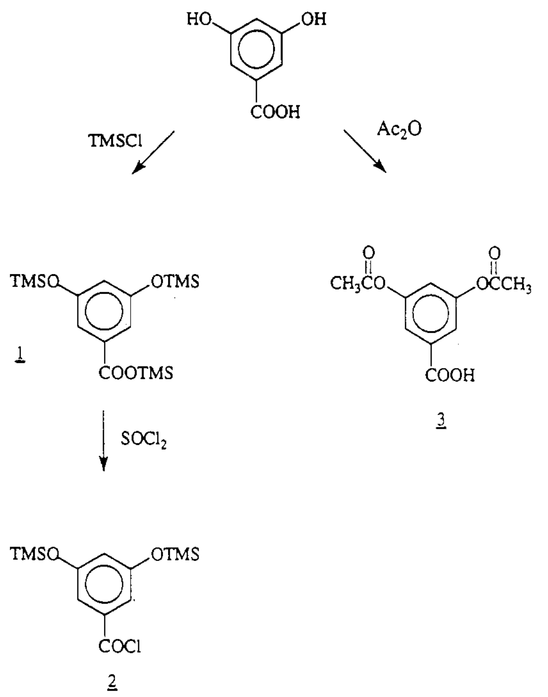
Results and Discussion

Monomer Synthesis. 3,5-Diacetoxybenzoic acid (**3**), prepared from 3,5-dihydroxybenzoic acid and acetic anhydride as shown in Scheme I, is neither air nor moisture sensitive and is readily purified by recrystallization. On the other hand, 3,5-bis(trimethylsiloxy)benzoyl chloride (**2**), which was prepared by the method of Fréchet,[6] was found to be extremely sensitive to ambient moisture and had to be carefully handled and purified using dry conditions under an inert atmosphere.

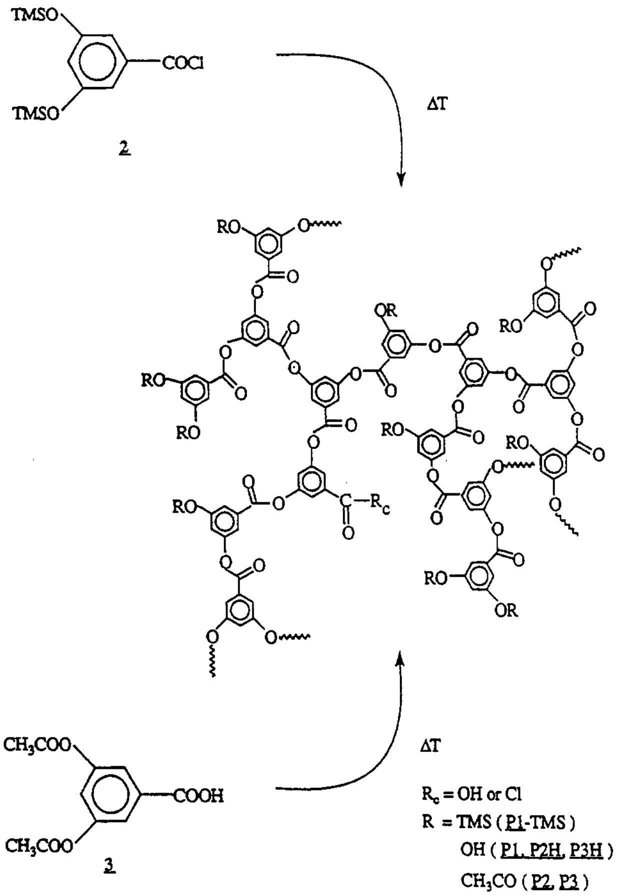
Polymerization. Monomers **2** and **3** were polymerized thermally in bulk (Scheme II). Some of the polymerization conditions examined and the properties of the resulting polymers are summarized in Table I.

The condensation of monomer **2** proceeded as reported by Fréchet.[6] The polymerizations were sensitive to the temperature of polymerization; e.g., polymerizations carried out at temperatures above 180 °C often resulted in only partly soluble very dark products. Reducing the polymerization temperature to below 160 °C slows the reaction considerably but leads to soluble and colorless polymers. Although temperature is important, the quality and duration of the vacuum, which is applied toward the end of the reaction to remove trimethylsilyl chloride, has

Scheme I



Scheme II



the greatest effect on the molecular weight. Even at a low temperature (155 °C) a $\bar{M}_w$ of over 800 000 (MTBSTFA protected) could be obtained. At this temperature, the last stage of the polymerization is actually a solid-state polymerization and stirring of the reaction mixture is no longer possible. The dependence of the degree of polycondensation on the applied vacuum makes it very difficult to control the molecular weight. $\bar{M}_w$ ranged from 5000 to 800 000 (polymers protected by MTBSTFA for SEC analysis), depending on temperature, time, and vacuum.

The polymerization of monomer **3** (**P2**) shows similar characteristics as described above for **P1**. The reaction temperature used for this type of acidolysis polycondensation, which is quite commonly used to prepare aromatic polyesters, was usually higher than the one used for the acid chloride monomer. The condensation reaction is very slow below 170 °C. No polymerizations were attempted at temperatures above 250 °C, since at that temperature the reaction was already very fast. The product obtained at 250 °C remained totally soluble, with $\bar{M}_w > 1\,000\,000$ (Table I, **P2**-149). The color and solubility of the resulting polymer is much less sensitive to the purity of the starting material and to air and moisture impurities than for the synthesis of **P1**. Several condensation catalysts have been tested (Mg, *p*-TsOH), but it was found that a catalyst does not significantly improve the reaction and therefore most of the polymers were synthesized without any catalyst. The extent of the condensation of **3** is also more or less determined by the quality and duration of the applied vacuum at the end of the polymerization reaction. Again, this makes it difficult to control the molecular weight. However, the lower glass transition temperature (T_g) of the acetate polymer **P2** ($T_g \sim 155$ °C) compared to **P1** allows better stirring and better control of the polymerization melt, even at high conversion.

The progression of molecular weight with time for **P2** was followed by immersing a monomer-charged polymerization flask into a preheated salt bath at 195 °C and taking periodic samples for molecular weight determination by SEC. Figure 1 shows the increase of molecular weight versus reaction time. The kinetics appear to be typical for a polycondensation. The molecular weight increases very slowly in the beginning and increases rapidly at high conversion. However, at high conversions there is an increasing gap in the growth of $\bar{M}_n$ and $\bar{M}_w$ that leads to very broad molecular weight distributions. This observation agrees with Flory's theoretical predictions[1] on the molecular weight distribution behavior for highly branched systems. He reported an almost regular growth of $\bar{M}_n$ with conversion but a rapid increase of $\bar{M}_w$, resulting in an infinitely broad distribution for a conversion close to 100%.

In an additional experiment, which resulted in **P3**, an inert diluent was added to the acetate monomer in order to make the polymer melt more processible at high conversion and to allow stirring until the end of the reaction. A 1:1 mixture of 3,5-diacetoxybenzoic acid and diphenyl ether was used. It was found that the viscosity of the melt can be lowered considerably even though the reaction temperature in the second stage of the condensation must be lowered to avoid the distillation of diphenyl ether from the reaction mixture when vacuum was applied. The resulting characteristics of the polymer were comparable to earlier results on **P2** polymers, and $\bar{M}_w = 127\,000$ was obtained (see Table I, polymer **P3**-53). The acetate groups of the polymer could be hydrolyzed, and the degree of branching calculated from the phenol-terminated sample was also comparable to the results obtained with **P2**. Thus, it is possible to synthesize very high molecular weight, soluble, all-aromatic polyesters with high terminal group functionality from either monomer **2** or **3**. In comparison, the linear equivalent, poly(*m*-hydroxybenzoate), using a similar synthetic approach only gave low molecular weight polymer with solubility limited to highly polar solvents.[13]

Molecular Weight. Some recent results from these laboratories[14] have shown that characterization of dendritic macromolecules is best accomplished by multidetector

Table I. Polymerization Conditions and Polymer Characterization Results, with Phenol-Terminated Samples Protected Prior to Analysis (Marked with "p")

	T(polym)/°C	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	remarks	T_g/°C	T_{dec}/°C
P1-TMS-69	145–150	43 000	6.0	soluble, not hydrolyzed	185	411
P1-43	140–155	27 000p	2.2	soluble	199	403
P1-153	155	50 000p	5.8	soluble after hydr	209	404 (N_2), 408 (air)
P1-112	155, high vacuum	360 000p	7.7	soluble after hydr	226	
P1-27	155, high vacuum	801 000p	65.7	soluble after hydr	219	
P2-65	175–200	30 000	6.3	soluble	147	
P2-63[a]	200–230	62 000	12.0	soluble	149	355 (N_2), 352 (air)
P2-167	190	498 000	30.2	soluble	155	392
P2-149	250	>1 000 000[b]	broad	soluble, almost colorless	156	367
P2H-110		39 600p	4.8	89% hydrolyzed from P2-63	197	
P2H-24		166 000p	12.6	84% hydrolyzed from P2-167	200	386
P3-53	225–180	127 000	3.9	polymn in phenyl ether	158	399
P3H-57		97 000p	3.3	80% hydrolyzed from P3-53	197	
P4-164	190	77 900	5.6	copolyester, 50% 3-acetoxybenzoic acid	126	
P5-86	180–185	98 000	14.0	copolyester, 50% 4-methoxybenzoic acid	152	393

[a] TsOH used as catalyst. [b] Polymer elutes at the SEC column exclusion limit. An accurate distribution cannot be obtained.

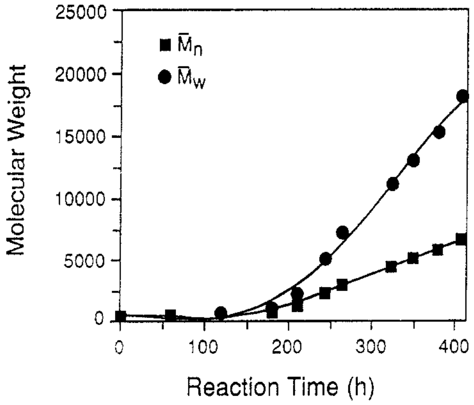


Figure 1. Reaction time/molecular weight plot for the condensation reaction of monomer 3 at 195 °C.

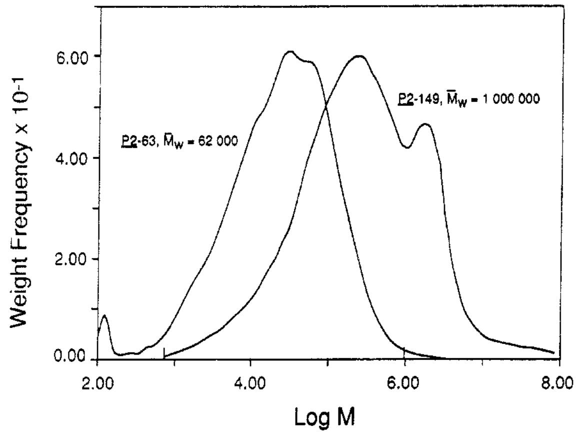


Figure 2. SEC traces of P2-63 and P2-149 in THF using column sets and an instrument described in the Experimental Section.

SEC. In this case dn/dc was determined from the DRI and $\bar{M}_w$ was measured by LALLS. In addition, molecular weight distributions were calculated from the DV using universal calibration. The molecular weights obtained from LALLS and DV were in excellent agreement, and because of the better sensitivity of DV across broad distributions, we relied mainly on the DV results.

The acetate polymers could be directly injected onto the SEC column after they had been dissolved in THF. However, the polymers **P1** and **P2H**, which had a high number of terminal phenol groups, absorbed to the column, resulting in incomplete elution and poor reproducibility. Reacting the phenol groups with *N*-methyl-(*tert*-butyldimethylsilyl)trifluoroacetamide (MTBSTFA) prevented the adsorption. Unfortunately this silyl protecting group increases the molecular weight considerably and also changes the character and the polarity of the polymer. The molecular weights obtained for **P1** are therefore not identical with the actual molecular weights, and caution is necessary for any discussion of the data (in the tables such data are marked with a "p"). Protection of the polymers also means that the viscosity data and Mark–Houwink constants that have been obtained from the SEC measuments can only be used to compare polymers of the same structure and cannot be taken as absolute values. However, by protecting the OH groups it was possible to obtain reproducible data on molecular weights for **P1**.

As seen in Table I, samples with a broad range of molecular weights were prepared. For high molecular weight hyperbranched polyesters the distribution became very broad (Figure 2). Some samples contain high molecular weight fractions that elute at the column exclusion limit and thus are outside the range of the column. It should also be noted that by working up the polymers (dissolving, filtering, precipitating), especially for **P1**, it is possible that some of the low molecular weight polymer stays in solution in the nonsolvent used for precipitation (water in the case of **P1**). This can influence the molecular weight distribution considerably. Evidence for this is given in the behavior of **P1-TMS**-69. This polymer was analyzed by SEC directly without reprecipitation and shows a broader distribution than **P1**-153, a sample with a slightly higher molecular weight.

By comparison to polystyrene standards of known hydrodynamic size, it was possible to estimate a range of hydrodynamic radii of approximately 2.5 nm for polymers in the 20 000 $\bar{M}_w$ range to around 9.0 nm for polymers in the 1 000 000 $\bar{M}_w$ range.

Viscosities. Hyperbranched acetate-terminated and OH-terminated polymers are soluble in several organic solvents including THF and DMF. THF is a "better" solvent for the OH-terminated polymers than DMF. THF was found to be the best solvent for solution characterization studies. A linear dependence between reduced viscosity and concentration was observed for the hyperbranched polyesters when measured at 25 °C in THF using an Ubbelohde capillary tube viscometer (Figure 3); e.g., for the sample P-149 ($\bar{M}_w$ = 1 010 000) $[\eta]$ = 0.34 dL/g was obtained.

Previously, we showed the advantages of measuring the polymer $\bar{M}_w$ and $[\eta]$ for dendrimers from SEC by integration of the LALLS and DV responses. This method circumvents some of the problems with applying SEC and universal calibration for highly compact polymer structures.[14] These results are summarized in Table II.

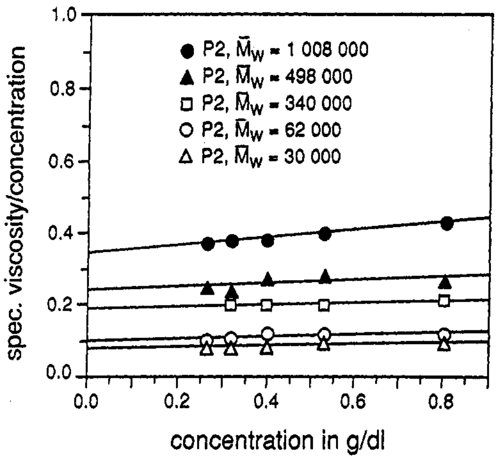


Figure 3. Concentration/viscosity plot for several **P2** polymers, THF, 25 °C, using an Ubbelohde viscometer.

Table II. Viscosity Data of the Hyperbranched Polyesters, Intrinsic Viscosities Obtained from SEC and Ubbelohde Viscometer (VISC) [T = 25 °C, Solvent = THF, a_{MH} Calculated from SEC, Phenol-Terminated Samples Protected (with MTBSTFA) Prior to Analysis (Marked with "p")]

			[η]/(dL/g)	
	$\bar{M}_w$	a_{MH}[a]	SEC	VISC
P2-149	1 008 000	0.38	0.341	0.34
P2-167	498 000	0.24	0.240	
P2-123	340 000	0.34	0.198	0.187
P2-63	62 000	0.28	0.120	0.095
P2-65	30 000	0.29	0.104	0.0735
P2H-24	166 000p 90 000[b]	0.42	0.292	
P2H-110	39 600	0.39	0.181	
P3-53	127 000	0.35	0.183	
P3H-57	97 600	0.44	0.241	
P1-TMS-69	43 000	0.40	0.119	
P1-27	801 000p 434 000	0.39	0.482p	
P1-112	361 000p 195 000	0.42	0.412p	0.358
P1-153	50 700p 27 400	0.39	0.200p	0.158
P1-43	27 700p 15 900	0.22	0.138p	0.158
P1-20	7 200	0.26	0.077p	
P4-164	77 900	0.30	0.134	
P5-86	98 000	0.21	0.12	

[a] Mark–Houwink constant. [b] The molecular weight for the unprotected polymer is calculated from the molecular weight obtained from the protected polymer under the assumption that all functional groups have reacted and by using $\bar{M}_w$ as base.

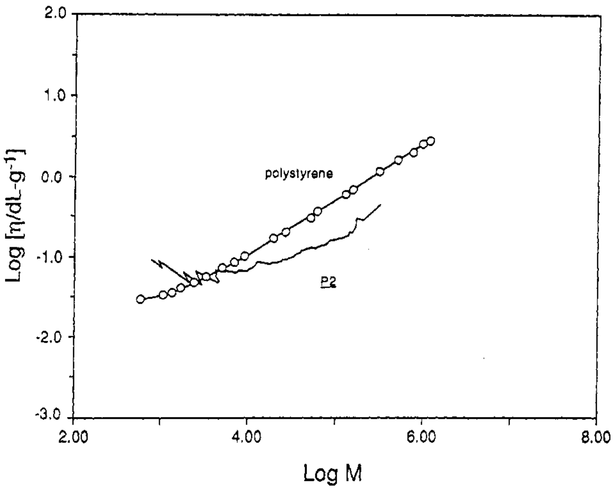


Figure 4. Plot of log [η] vs log [M] for polystyrene and **P2** as obtained from SEC.

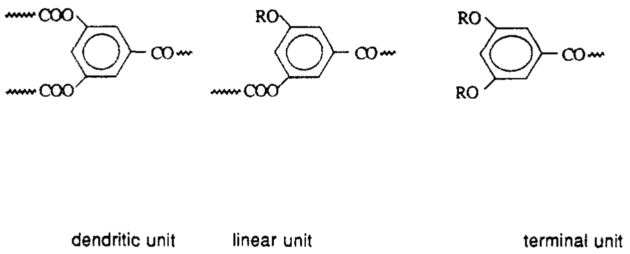
Generally the polymer intrinsic viscosities increase with increasing $\bar{M}_w$.

The relationship between [η] and molecular weight is obtained across the molecular weight distribution with the SEC experiment. This relationship is often described by the empirical Mark–Houwink equation $[\eta] = KM^a$. In some instances the degree of branching can be inferred from comparison of logarithmic plots of [η]–MW data (Mark–Houwink plot) for the branched polymer to data for a linear polymer of the same structure. Unfortunately the closest linear analog, poly(*m*-hydroxybenzoate), is semicrystalline and insoluble in THF.[13] However, a comparison of log [η]–log MW plots of hyperbranched polyesters to linear polystyrene (Figure 4) does provide some indication that these materials are highly branched; the slope of the polyester data is considerably less than that for linear polystyrene. The exponent *a* is the slope of the data in Figure 4, which, for the case of the whole polymer, is an average obtained by weighted least-squares fitting of the data. Results are given in Table II. The value of *a* normally approaches 0.5 at Θ conditions and is commonly between 0.65 and 0.75 for a flexible, linear random-coil polymer in a good solvent. Values of *a* are commonly below 0.5 for branched polymers. Such values are obtained for all these polyester samples, indicating a highly branched compact structure.

The data shown in Figure 4 are unlike those for convergent growth polyether dendrimers.[14] The "ideal" polyether dendritic structures do not shown a monotonic relationship between viscosity and molecular weight. The Mark–Houwink plots actually pass through a maximum. This was shown to be a direct consequence of the ratio of mass to volume for each successive dendrimer generation. The hyperbranched structures obtained from this one-step synthesis share some common properties with perfect dendritic structures, i.e., a large number of terminal groups and a compact structure. It is apparent from the viscosity–molecular weight relationship, however, that the radial density distribution of hyperbranched structures is distinctly different from perfect dendrimers.

Structure. The polymerization described in this paper is based on common polyesterification reactions. The degree of polymerization is determined by the conversion and therefore by temperature and the applied vacuum. However, the A_2B type monomer is unique in that there is double the amount of A functionality compared to the B functionality in the polymerization mixture. Despite this stoichiometric imbalance, high molecular weight polymer is achieved because both functionalities are located on the same molecule and, for each B functionality reacted, a new B functionality is connected to the polymer chain. In an ideal case both A functionalities would react with a B functionality and therefore lead to branching in each condensation step until the condensation reaction is stopped or high conversion is reached. In reality, because of steric effects and statistical effects and since the second A functionality does not have a greater reactivity than the first, there are nonbranched (linear) units in the polymer structure. A nonideal hyperbranched polyester, as is described here, has three different structures: linear, terminal, and branched units.

There will be exactly one unreacted acid or acid chloride in each polymer molecule, assuming that there are no side reactions. No matter what the degree of branching is, the number of terminal groups is given by the number of units in the polymer: *n* polymer units result in *n* + 1 terminal functionalities (can be located on a terminal or a linear



R = Me_3Si (P1-TMS)
OH (P1, P2H)
$COCH_3$ (P2, P3)

unit). The terminal groups of **P1** are trimethylsilyl groups or, after hydrolysis, phenol groups. **P2** polyesters are terminated with acetate groups.

The degree of branching for OH-terminated polyesters, measured by proton NMR using the method described by Fréchet[6] for **P1** is approximately 57% and was found to be independent of molecular weight. This indicates that *branching does not change as a function of conversion.* This NMR method was unsuccessful for the acetate-terminated polyesters because of overlapping resonances. Instead, acetate groups of **P2** were hydrolyzed with dilute HCl in THF/MeOH/water at elevated temperatures. Minor degradation of the polymer occurred under these conditions (Table I; **P2H**-110 from hydrolysis of **P2**-63), although it is considerably less than that observed for basic hydrolysis. With up to 89% of the acetate groups hydrolyzed, a degree of branching of approximately 50% was measured for **P2H**-24 (P2-167 hydrolyzed). Previous studies[13] lead to the prediction that the less reactive monomer **3** would branch less effectively than **2**.[13] The similar degrees of branching in the two materials indicate that the branching efficacies of **3** and **2** are actually quite comparable in these polymerizations.

Thermal Properties. In contrast to linear poly(*m*-hydroxybenzoate) which is semicrystalline with a T_g of 145 °C and a T_m of 183 °C,[13] the hyperbranched polyesters are amorphous. No evidence for crystallinity was observed after various annealing and thermal treatments. The T_g's determined by differential scanning calorimetry (DSC) for these polyesters are very much dependent on the terminal groups (Table I). T_g was also observed to modestly increase with molecular weight. The T_g of the TMS-protected **P1-TMS** is approximately 185 °C, the phenol polymer **P1** ranged from 200 to 225 °C, and the T_g of the acetate polymer **P2** ranged from 147 to 160 °C.

The all-aromatic hyperbranched polyesters possess thermal stabilities similar to those of their linear counterpart. Thermal gravimetric analysis (TGA) measurements on the **P1-TMS** polymer gave a decomposition temperature of 411 °C (T_{onset}) versus 410 °C for poly(*m*-hydroxybenzoate). A considerable weight loss of about 12% between 100 and 350 °C was observed. GC/MS studies of the volatiles showed that this is due to the loss of trimethylsilyl derivatives (trimethylsilanol, hexamethyldisiloxane, octamethyldisiloxane) which means that the polymerization reaction can be started again by heating the solid polymer, yielding a higher molecular weight polymer. The same behavior was observed for the phenol polymer **P1**. This polymer also shows a major decomposition temperature of about 408 °C in air and a weight loss of about 7% below this temperature. Here the GC/MS analysis did not show any volatiles other than THF. We assume that part of the weight loss is due to water as a result of the continued condensation reaction that cannot be detected by the GC/MS analysis. The other part (about 4.6% weight loss below 100 °C) was solvent (THF) trapped in the polymer structure. For the analysis of the volatiles, the samples were heated to about 190 °C and kept there, and the evolved volatiles were trapped with liquid nitrogen at the head of a capillary gas chromatographic column and analyzed. The decomposition temperature of **P1** in air (408 °C) and in nitrogen (404 °C) is almost identical.

The acetate polymers **P2** show a major decomposition temperature around 350 °C in nitrogen as well as in air. The weight loss, in the range of 1–2% up to 350 °C, is considerably less than that for **P1**. NMR showed that less solvent is trapped in the polymer structure, and GC/MS identified the major volatile component as acetic acid. The T_g's of hydrolyzed acetate polyesters were compared to the T_g of the phenol-terminated polyesters **P1**. The hydrolysis reaction was usually not complete, and 10-20% of acetate groups still remained in the polymer structure. However, conversion of the acetate groups to phenol groups caused the T_g to increase from 155 to 200 °C (Table I; **P2H**-24, hydrolyzed from **P2**-167). This is similar to the T_g's for **P1** structures of similar molecular weight.

Copolymers. A copolyester, **P4**, was prepared by condensation of monomer **3** and 3-acetoxybenzoic acid. The condensation was carried out under conditions similar to those of the melt homopolymerizations. The presence of a nonbranching monomer should lead to an increased number of linear units in the copolymer. Although there were significant changes in the ^{1}H NMR, it was not possible to calculate the degree of branching from either the acetate-terminated or hydrolyzed polymers due to overlap of the proton resonances.

The copolymer has characteristics similar to the homopolymers: broad molecular weight distribution, low $[\eta]$, and a consistent with a branched structure. One major difference was a surprisingly low T_g 126 °C, or 25 °C lower than the **P2** homopolymers and even lower than the T_g of the poly(*m*-hydroxybenzoate).

The other copolyester **P5** was made as a model to explore the possibility of introducing different functionalities into the structure in the condensation step and not in an additional second reaction step. For this, monomer **2** was copolymerized in a 1:1 mixture with *p*-methoxybenzoic acid. This compound was chosen because its melting point was high enough so that it did not sublime out of the reaction and change the composition of the monomers. NMR analysis of the copolymer showed that almost half of the terminal groups were methoxy groups; the other half were acetate groups. This indicates that addition of a monofunctional B unit can be used to control the terminal functionality of these hyperbranched structures. The T_g for **P5** was found to be 152 °C, close to what was found for the homopolymer. In this case, the change of the terminal groups had no effect on the T_g. The SEC analysis of the sample showed a high molecular weight ($\bar{M}_w$ = 98 000), a very low viscosity, and an extremely low Mark–Houwink constant (Table II). Unfortunately the NMR resonances did not allow determination if the branching degree was affected.

Conclusions

The melt polymerization of 3,5-diacetoxybenzoic acid was found to yield a hyperbranched all-aromatic polyester with acetate terminal groups. Mild acid hydrolysis of the acetate groups resulted in a phenolic-terminated hyperbranched polymer with a branched structure very similar (ca. 50% branching) to that previously reported for melt polymerization of 3,5-bis(trimethylsiloxy)benzoyl chloride. The acetate polymerization offers a much simpler and less expensive route to these novel structures. The polymerization was followed by SEC, and extensive molecular weight distribution broadening, as predicted by Flory, was observed as conversion increased. The acetate hyperbranched polyesters are colorless and soluble in a number of common organic solvents. Even at high molecular weights of ca. 1 × 10^6, they exhibit very low intrinsic viscosities. They have excellent thermal stability as measured by TGA. The T_g was found to be dependent on molecular weight and terminal group functionality. Copolymerization with an AB monomer was found to proceed as expected. Condensation with a monofunctional B monomer was found to offer a facile method to modify the terminal groups of these hyperbranched structures.

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References and Notes

(1) Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 2718.

(2) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138 and references therein.

(3) Newkome, G. R.; Moorefield, C. N.; Baker, G. R. *Aldrichimica Acta* **1992**, *25*, 31 and references therein.

(4) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.

(5) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592; *Macromolecules* **1992**, *25*, 5561.

(6) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583. Wooley, K. J.; Fréchet, J. M. J., unpublished results.

(7) Uhrich, K. E.; Hawker, C. J.; Fréchet, J. M. J.; Turner, S. R. *Macromolecules* **1992**, *25*, 4583.

(8) Percec, V.; Kawasumi, M. *Macromolecules* **1992**, *25*, 3843.

(9) Kim, Y. H. *J. Am. Chem. Soc.* **1992**, *114*, 4947.

(10) Mathias, L.; Carothers, T. *J. Am. Chem. Soc.* **1991**, *113*, 4043.

(11) Huls, R.; Hubert, A. *Bull. Soc. Chim. Belg.* **1956**, *65*, 596.

(12) Mourey, T. H.; Miller, S. M.; Balke, S. T. *J. Liq. Chromatogr.* **1990**, *13*, 435.

(13) Kricheldorf, H. R.; Zeng, Q.-Z.; Schwarz, G. *Polymer* **1982**, *23*, 1821.

(14) Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Fréchet, J. M. J.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **1992**, *25*, 2401.