Synthesis, Characterization, and ^{1}H NMR Self-Diffusion Studies of Dendritic Aliphatic Polyesters Based on 2,2-Bis(hydroxymethyl)propionic Acid and 1,1,1-Tris(hydroxyphenyl)ethane

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Abstract: Dendritic aliphatic polyesters of one, two, three, and four generations (M_w: 906, 1856, 3754, and 7549 g/mol) were synthesized in the convergent fashion, using 2,2-bis(hydroxymethyl)propionic acid as building block and 1,1,1-tris(hydroxyphenyl)ethane as core molecule. Dendrons of one to four generations were synthesized from the building block and in a final step coupled to the core molecule. The focal point of the dendrons was protected by a benzyl ester group and deprotected by catalytic hydrogenolysis. The esterifications were performed by conversion of the acid into the corresponding acid chloride and followed by reaction of the acid chloride with the hydroxyl groups in the presence of triethylamine and dimethylaminopyridine. The simplicity of the ^{1}H-NMR and ^{13}C-NMR spectras and elemental analyses suggest that pure and monodisperse dendrimers were obtained. Molecular self-diffusion studies of first, second, third, and fourth generation dendrimers were performed, in chloroform, using pulsed-field spin echo ^{1}H NMR spectroscopy. The self-diffusion coefficients were calculated with the standard form of the Stejskal−Tanner equation. The effective radii of the dendrimers were estimated from the diffusion coefficients by assuming a spherical geometry for all dendrimers. The radii obtained were 7.8, 10.3, 12.6, and 17.1 Å for the first, second, third, and fourth generation dendrimer, respectively.

Introduction

Dendrimers,[1−3] arborols,[4,5] and cascade compounds[6] all represent a new type of polymers which is characterized by a highly branched, well-defined structure with an origin in a central branching point. Hyperbranched polymers[7] resemble dendrimers with the exception that they contain not fully branched AB_x monomers. Properties of dendrimers and hyperbranched polymers have been compared by Frechét *et al.*[8]

Divergent and convergent growth are two different stepwise procedures in the synthesis of well-defined dendritic structures. In the divergent growth, successfully employed by, e.g., Tomalia *et al.*,[1,2] Newkome *et al.*,[4,5] and Meijer *et al.*,[3] the AB_x monomers are added layer by layer, i.e., generation by generation, around the core molecule. In the convergent growth approach, developed by Hawker and Fréchet,[9−11] dendrons are initially synthesized from the AB_x monomer and in a final step coupled to the polyfunctional core molecule to form a dendrimer of a certain generation. The great advantage with the convergent growth approach is that each step in the synthesis of the final dendritic structure can be very well controlled, since fewer functional groups are involved in each reaction. Furthermore the large differences in molecular weight between products and byproducts in the convergent approach makes purification simpler.

From ^{1}H NMR self-diffusion measurements the molecular diffusion coefficients can be calculated. Since the diffusion coefficients depend on the size and geometry of the diffusion molecules, this method may be used as a tool for estimating the molecular size. This method has previously been utilized in a large number of studies of surfactant aggregates in different solvents.[12] However, it has so far only found limited use in the area of dendritic polymers.[13]

This paper deals with the convergent synthesis and characterization of dendritic aliphatic polyesters based on 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) and 1,1,1-tris(hydroxyphenyl)ethane as core molecule. The corresponding hyperbranched system based on bis-MPA with an aliphatic core molecule has been synthesized and well characterized.[14,15] In a future study we hope to compare hyperbranched polymers and dendrimers, based on bis-MPA as a building block. In this work we also present ^{1}H NMR self-diffusion studies that not only yield the diffusion coefficients and estimations of the

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molecular sizes but also indicate that the synthesized dendrimers are monodisperse.

Results and Discussion

Synthesis. Bis-MPA was chosen as the AB_2 monomer in the synthesis of the dendritic aliphatic polyesters **13**, **14**, **15**, and **16**. In the convergent growth approach dendrons of certain generations were initially synthesized. In a final step these dendrons were coupled to the polyfunctional core molecule. To get an acceptable overall yield it is important that all reactions such as coupling, protection, and deprotection are selective and proceed in high yields since a large number of steps are involved in our design of the final dendrimers.

In the synthetic route selected involving bis-MPA (Scheme 1), its hydroxyl groups were protected or deactivated by conversion into the corresponding acetate esters. The diacetate ester of bis-MPA **1** was prepared by reacting bis-MPA with acetyl chloride in the presence of triethylamine (TEA) and dimethylaminopyridine (DMAP) in CH_2Cl_2. Without DMAP significant amounts of monoacetylated bis-MPA and acetic acid were formed. The acid group in bis MPA was protected by a benzyl ester group. The benzyl ester of bis-MPA **2** was prepared by first forming the potassium salt of bis-MPA and in a second step reacting the salt with benzyl bromide. The benzyl ester group could be removed selectively in very high yields by catalytic hydrogenolysis[16] without affecting the ester bonds formed in the convergent growth. Hydrogenolysis was performed at atmospheric pressure using Pd/C (10%) as catalyst. Deprotection was complete in high yields within 30 min. All esterifications were performed by first converting the acid into the corresponding acid chloride. All acid chlorides were prepared using 2 equiv oxalylchloride and a catalytic amount of DMF in CH_2Cl_2. The excess of oxalyl chloride was removed on the rotary evaporator by a stripping procedure with chloroform. The ester bond was then formed by reacting a small excess of the acid chloride with the hydroxyl groups in the presence of TEA and a catalytic amount of DMAP in dry CH_2Cl_2. The use of pyridine instead of TEA resulted in low yields and formation of side products. The use of the same core molecule as in the previously studied hyperbranched system[14] based on bis-MPA 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) resulted in low yields due to restricted steric accessibility to the hydroxyls in the final coupling step of the dendrons. The lack of UV-activity, aromatic structures, or functional groups allowing easy monitoring made the use of thin layer chromatography difficult. These problems were overcome by the use of the less sterically hindered and UV-active 1,1,1-tris(hydroxyphenyl)ethane as core molecule.[9]

In the general procedure for the preparation of acid chlorides **1** was converted into the corresponding acid chloride **3** (Scheme I). Reaction of acid chloride **3** with the protected monomer unit **2**, according to the general esterification procedure gave the second generation dendron **4** in 82% yield after purification by liquid chromatography. Removal of the benzyl ester group by catalytic hydrogenolysis gave the acid **5** in 99% yield. **5** was converted into the acid chloride **6** in 97% yield. The third (**9**) and fourth (**12**) generation dendrons were synthesized in the same manner.

Four generations of tridendron dendrimers (**13**−**16**) were obtained by coupling the respective dendrons (**3**, **6**, **9**, and **12**) with the core molecule 1,1,1-tris(hydroxyphenyl)ethane according to the general esterification procedure (Scheme 2). The final dendrimers were purified by liquid chromatography eluting with a hexane/ethyl acetate gradient. The dendritic aliphatic polyesters of one, two, three, and four generations were obtained in yields of 93, 89, 74, and 30% in the final coupling step. In the synthesis of the fourth generation dendron and in the coupling of the third and fourth generation dendrons to the core molecule yields start to decrease significantly, probably due to restricted steric accessibility of the hydroxyls.

Table 1. SEC- and Diffusion NMR Data of Dendritic Polyesters **13**−**16**

dendrimer	M_w (calcd) (g/mol)	M_w (SEC) (g/mol)	M_n (SEC) (g/mol)	β	$D \times 10^{12}$ (m^2/s)	radius (Å)
13	906	1154	1119	1.00	519	7.8
14	1855	1870	1803	1.00	392	10.3
15	3754	3057	2893	1.00	321	12.6
16	7549	4660	4438	1.00	236	17.1

Characterization of the Dendrimers

General Characterization. The techniques used for the characterization of dendrimers **13**, **14**, **15**, and **16** were ^{1}H NMR, ^{13}C NMR, size exclusion chromatography (SEC), elemental analyses, and pulsed field-gradient spin echo (PGSE) ^{1}H NMR. The simplicity of the ^{1}H NMR and ^{13}C NMR spectra is an indication of the high purity of dendrimers **13**−**16**. Different generations may readily be seen in the ^{1}H NMR spectra of dendrimers **13**−**16** (Figure 1). The resonances from the methyl groups, 1.42, 1.28, 1.22, and 1.19 ppm in dendrimer **16** (A, B, C and D), all result in singlets but of significantly different chemical shifts reflecting the generation number. The resonances from the methylene groups (F, G, and H) are well separated up to the third generation. In the fourth generation dendrimer (**16**), the resonances from the second and third generation methylene groups (G and H) become inseparable. The same pattern can be seen for the quaternary carbons (f, g, h, and i) and the carbonyl carbons (a, b, c, and d) in the ^{13}C NMR spectra (Figure 2). The symmetry of the two doublets emanating from the core molecule at 6.96−7.13 ppm (K and L) indicates a fully substituted core molecule. When only one or two dendrons were coupled to the core molecule, no symmetry was observed.

Since no adequate SEC standards are available linear polystyrene was used as standard. As expected, the molecular weights determined were not in agreement with the theoretical molecular weights as seen in Table 1. This is explained by differences in the hydrodynamic volume of linear polystyrene standards and the synthesized dendritic polyesters. SEC analyses showed polydispersity values (M_w/M_n) below that of the linear polystyrene standards (M_w/M_n: 1.02) for the dendrimers **13**−**16** (Figure 3).

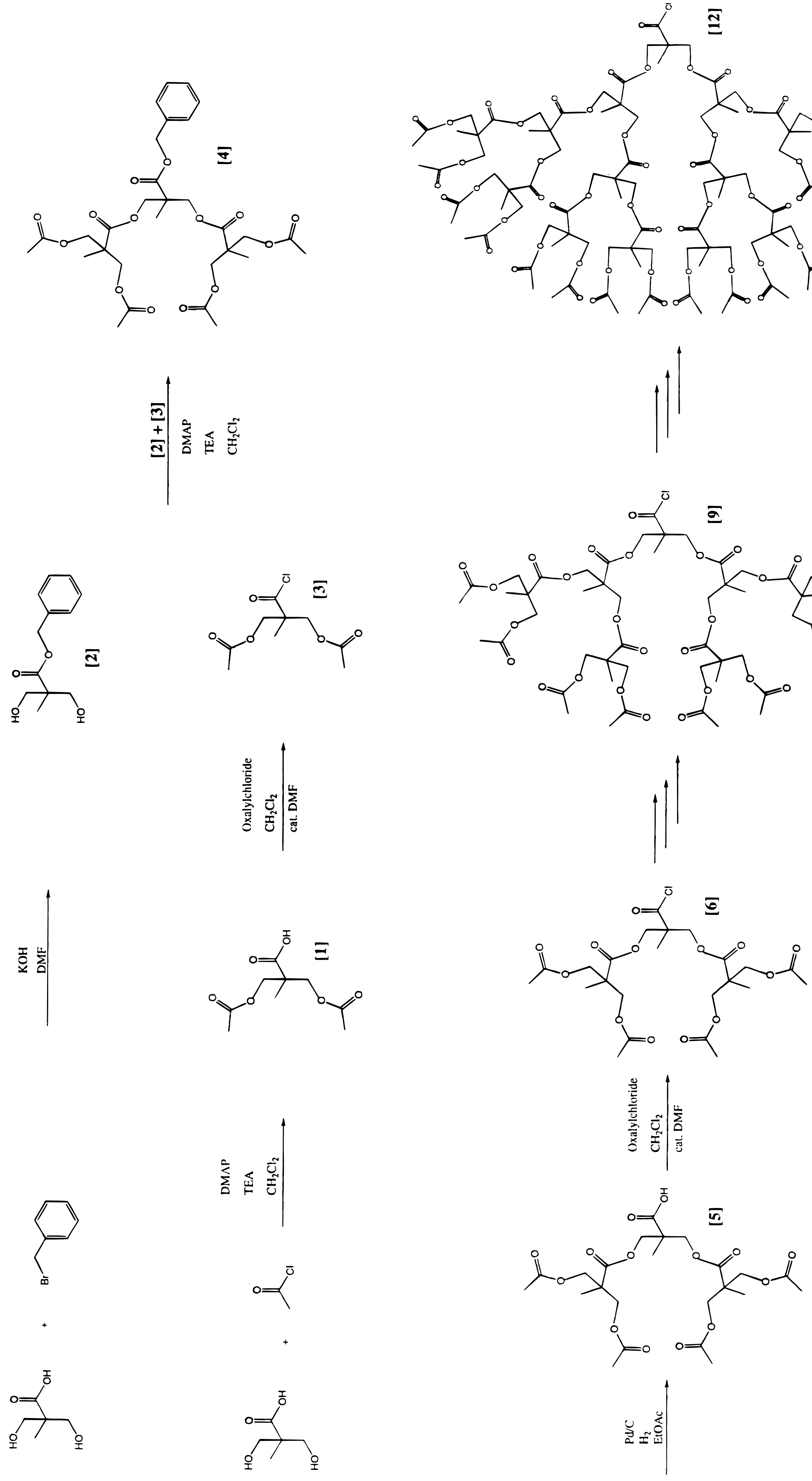
PGSE-^{1}H NMR Experiments

The pulse sequence employed in the PGSE-^{1}H NMR experiments produces a spin echo with an amplitude $I(2\tau)$ (where τ represents the time between the 90° and 180° pulses). For single species undergoing Gaussian diffusion, characterized by the self-diffusion coefficient D, the echo amplitude is described by the Stejskal−Tanner equation

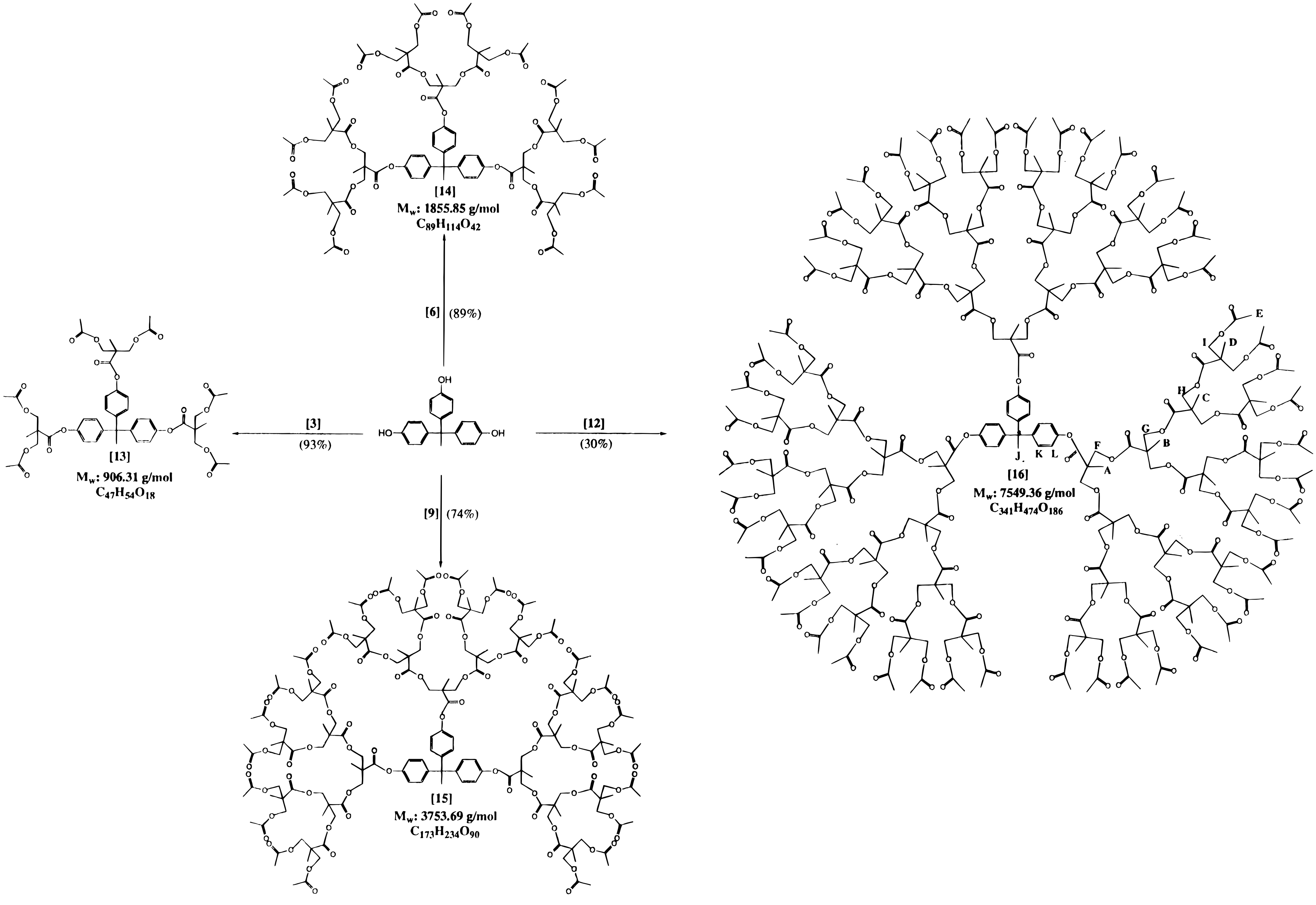
$$I(2\tau) = I(0)e^{-\gamma^2 g^2 \delta^2 (\Delta - \delta/3)D} \qquad (1)$$

In this equation, γ represents the magnetogyric ratio, while δ denotes the duration of the magnetic field gradient pulses separated by a time interval Δ (from leading edge to leading edge), and g their amplitude. It should be noted that eq 1 assumes that the time interval τ between the pulses is kept constant throughout the experiment. This was the case in the present study.

Scheme 1. Synthetic Route for First, Second, Third, and Fourth Generation Dendrons



Scheme 2. Synthetic Route for First, Second, Third, and Fourth Generation Dendrimers



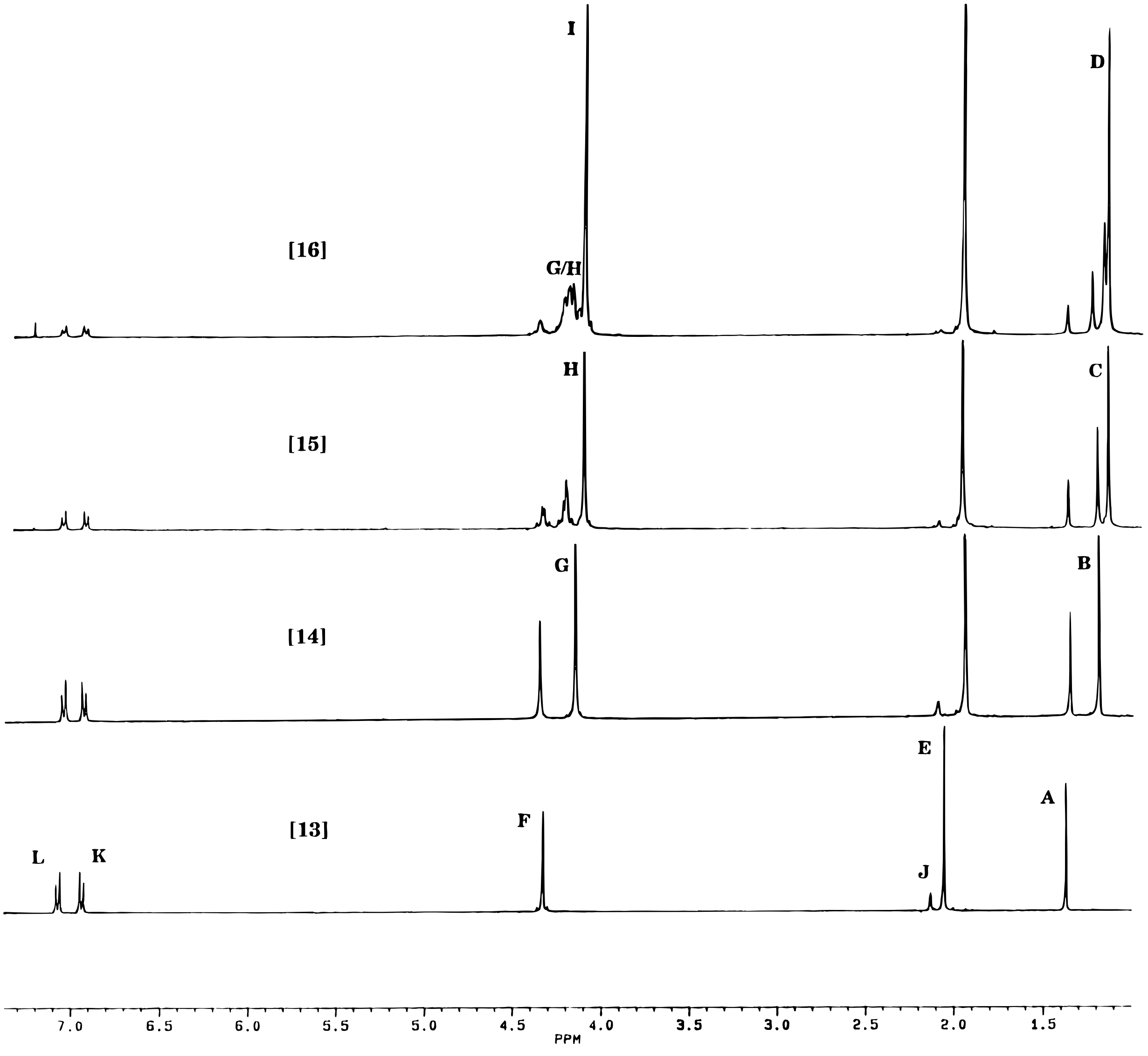


Figure 1. ^{1}H NMR spectra in $CDCl_3$ of dendritic polyesters **13**−**16**.

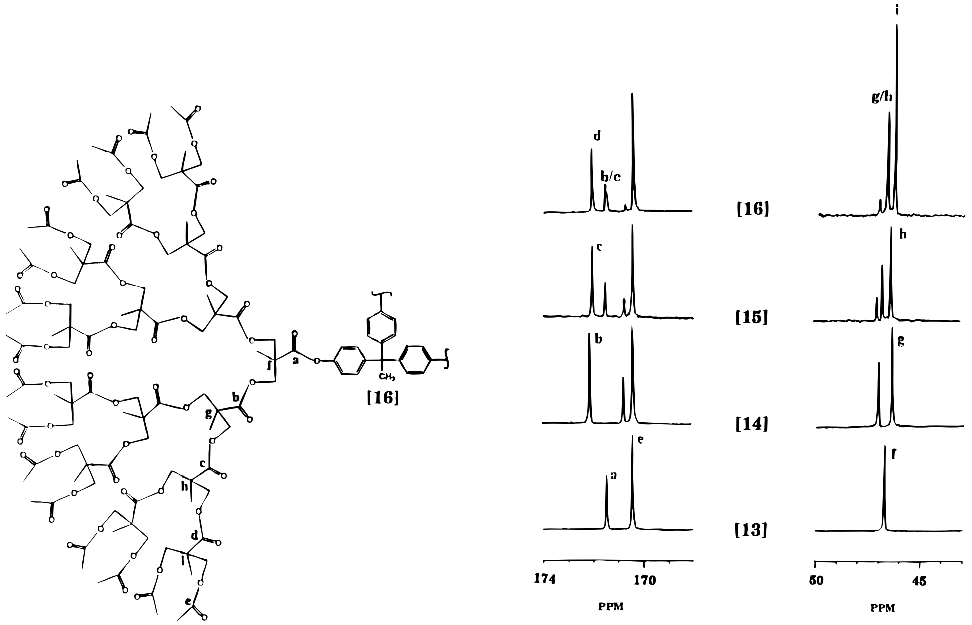


Figure 2. ^{13}C NMR spectra in $CDCl_3$ of four generations of dendrimers.

In a polydisperse system the observed NMR signal becomes a superposition of all individual signals, weighted by the volume fraction of each size of molecule. From the NMR experiment alone, the functional form of the size distribution function cannot

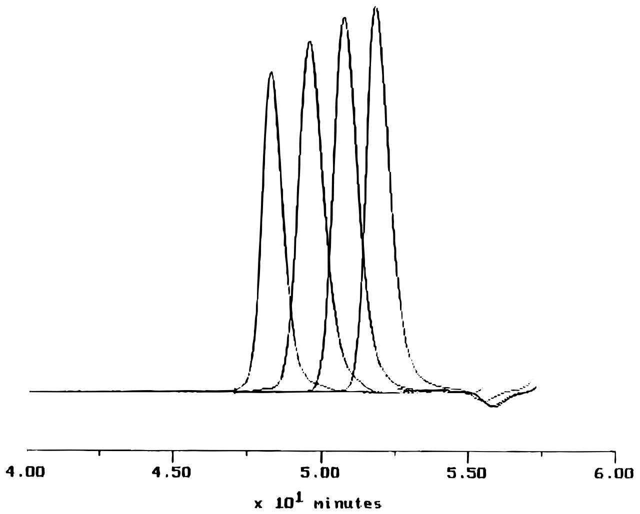


Figure 3. SEC-trace of dendritic polyesters **13**−**16**.

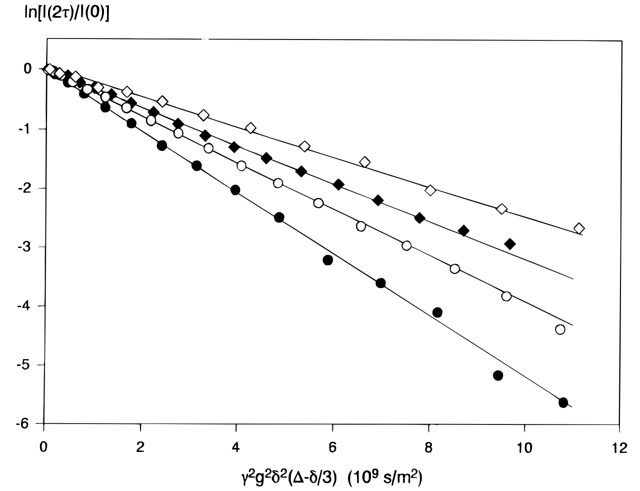


Figure 4. Normalized echo intensities, plotted on a logarithmic scale, of the four different dendrimers, generation 1 (●), 2 (○), 3 (■), and 4 (□), vs $\gamma^2 g^2 \delta^2(\Delta\text{-}\delta/3)$ (see eqs 1 and 2).

be determined. However, given a functional form, its characteristic parameters may be determined. Here it is assumed that the Kohlrausch−Williams−Watts[17] distribution describes the diffusion coefficients, if there is a distribution of sizes. This leads to a modified Stejskal−Tanner expression[12]

$$I(2\tau) = I(0)e^{-(\gamma^2 g^2 \delta^2(\Delta-\delta/3)D_{\mathrm{app}})^{\beta}} \tag{2}$$

In this equation D_{app} represents an apparent diffusion coefficient, while β is a measure of the width of the distribution ($0 < \beta \leq 1$). A mean diffusion coefficient D_{mean} may be obtained through the transformation

$$D_{\mathrm{mean}} = D_{\mathrm{app}}/(1/\beta \cdot \Gamma(1/\beta)) \tag{3}$$

where $\Gamma(1/\beta)$ is the γ function of $1/\beta$. For a monodisperse system $\beta = 1$, and the obtained D becomes the true diffusion coefficient. By applying a nonlinear least-squares fitting of a function according to eq 2 to the experimental data, the parameters $I(0)$, D_{app}, and β are easily extracted.

Figure 4 shows the amplitude decays of dendrimers **13**−**16**. In the figure, the logarithms of the normalized signal intensities are plotted versus $\gamma^2 g^2 \delta^2(\Delta-\delta/3)$. The linear relationship obtained for the four samples indicates that they are pure and monodisperse. This is also confirmed by the parameters extracted from the fitting procedure, these parameters are given in Table 1.

For spheres diffusing in a continuous medium of viscosity η, the relation between the self-diffusion coefficient, D, and the effective radius of the sphere, R, is given by the Stokes−Einstein equation

$$R = k_{\mathrm{B}}T/6\pi\eta D \tag{4}$$

where k_{B} is the Boltzmann constant and T the temperature. Equation 4 only holds for diffusion of single species, *i.e.*, obstruction effects are not accounted for. Although obstructed diffusion, i.e., the interactions between the diffusing species, has been treated before,[18] such effects have been neglected here. For dilute systems, such as those considered here, the interactions between the diffusing species are negligible, and eq 4 may be used without modifications.

The effective radii of the four dendrimers were calculated using this equation, and the obtained values are given in Table 1. In these calculations isotope effects on the viscosity of the solvent were neglected, and the viscosity of protonated chloroform, η(25 °C) = 0.542 cp was used. As seen in Table 1, the radius increases from 7.8 to 17.1 Å. for dendrimers **13**−**16**. These figures correlate well with estimations from molecular modeling, using SYBYL 6.1, data not presented here. This study has only been concerned with the sizes of the dendrimers in one particular solvent, chloroform. However, one may expect the size of the dendrimers to be dependent on type of solvent, due to different swelling behavior. Similar effects have previously been observed in water soluble dendritic macromolecules, whose hydrodynamic radius were shown to be strongly pH-dependent.[13] The NMR diffusion experiment is, therefore, an excellent tool for the study of swelling of dendrimers in different solvents, an issue we hope to address in a later study.

Conclusions

The convergent growth approach is useful for the synthesis of monodisperse dendritic structures. The use of bis-MPA as a building block results in dendrimers that have simple ^{1}H NMR and ^{13}C NMR spectra in which the different generations are easily distinguished.

Molecular self-diffusion studies by pulsed field spin echo ^{1}H NMR is a convenient method to estimate the hydrodynamic radii of dendrimers, in solution, of different generations.

Experimental Section

General Procedures. Bis-MPA was obtained from Perstorp Polyols AB, Sweden. All other chemicals were purchased from Aldrich and Merck and used without any further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 400, at 400 and 100 MHz, respectively, using $CDCl_3$ as solvent. The solvent signals were used as internal standards for both ^{1}H NMR and ^{13}C NMR recordings. SEC measurements were performed on a Waters GPC-system using a solvent delivery system (Model 510), automatic injector (WISP 710B), and a differential refractometer (Waters 410) as a detector. All measurements were made at 25 °C with one μ-styragel column (100 Å). THF was used as a solvent at a flow rate of 0.5 mL/min. All recordings and calculations were made with a Copam PC-501 turbo unit.

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The self-diffusion of the dendrimers was studied by means of NMR spectroscopy, using the well-known pulsed field-gradient spin echo (PGSE) method.[13] The measurements were performed on a JEOL FX-100 spectrometer, operating at 100 MHz for protons, equipped with a 5-mm ^1H probe. An internal field/frequency lock was provided by the deuterons in the solvent, $CDCl_3$. The gradient driver was homemade and produced gradients (g) in the range $g \approx 50-70$ mT/m. The gradient strength was calibrated using literature data for water diffusion in ^1H_2O/^2H_2O mixtures.[19] The temperature was kept at 25 °C in all experiments. In this work, each set of experimental data was obtained by varying the duration of the gradient pulse ($\delta = 1-19$ ms) keeping the radio frequency pulse interval ($\tau = \Delta = 140$ ms) and the gradient strength (g) constant. The attenuation of the signal intensities from the terminal methyl protons (chemical shift, $\delta \approx 2.1$ ppm) was monitored, and from a nonlinear least-squares fitting procedure the diffusion coefficient (D) could be evaluated (from eqs 1−3).

2,2-Bis(acetoxymethyl)propionic Acid [1]. Bis-MPA (5.00 g, 37.28 mmol), 9.40 g (93.07 mmol) of TEA and 0.23 g (1.88 mmol) of DMAP were dissolved in 100 mL of dry CH_2Cl_2. Acetylchloride (6.20 g, 78.98 mmol) was added drop by drop to the reaction mixture. After 30 min of stirring, the reaction mixture was extracted with three portions (40 mL) of Na_2CO_3 (10%). The combined aqueous phase was acidified with HCl (concentrated) and extracted with three portions (40 mL) of CH_2Cl_2. The combined organic phase was dried with $MgSO_4$ and evaporated to give **1** as white crystals: 8.0 (98%); ^1H NMR ($CDCl_3$) δ 1.29 (s, 3H, $-CH_3$), 2.07 (s, 6H, $-CH_3$), 4.24 (d, 4H, $-CH_2C$); ^{13}C NMR ($CDCl_3$) δ 17.63, 20.60, 45.66, 65.15, 170.84, 177.96.

Benzyl-2,2-bis(methylol)propionate [2]. Bis-MPA (9.00 g, 67.11 mmol) and 4.30 g (76.79 mmol) of KOH were dissolved in 50 mL of DMF. The potassium salt was allowed to form at 100 °C for 1 h. Benzylbromide (13.80 g, 80.71 mmol) was added. After 15 h of stirring at 100 °C the DMF was evaporated. The residue was dissolved in 200 mL of diethyl ether and extracted with two portions (50 mL) of water. The crude product was purified by liquid chromatography on silica gel eluating with hexane gradually increasing to 20:80 hexane/ethyl acetate. **2** was obtained as white crystals: 10.0 g (67%); ^1H NMR ($CDCl_3$) δ 1.08 (s, 3H, $-CH_3$), 3.74 (d, 2H, $-CH_2OH$), 3.95 (d, 2H, $-CH_2OH$), 5.22 (s, 2H, $-CH_2Ar$), 7.36 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.16, 49.35, 66.64, 67.49, 127.84, 128.28, 128.63, 175.69.

2,2-Bis(acetoxymethyl)propionic Acid Chloride [3] and a General Procedure for Acid Chloride Formation. Oxalylchloride (6.30 g, 49.61 mmol) was added drop by drop to a solution of 5.40 g (24.77 mmol) of 2,2-bis(acetoxymethyl)propionic acid [**1**] and 3 drops of DMF in 40 mL of CH_2Cl_2. The reaction was allowed to reach completion for 2 h at 25 °C. The excess oxalylchloride was removed on the rotary evaporator by a stripping procedure with several portions of chloroform to give **3** as a yellow oil that was used without any further purification: 5.8 g (99%); ^1H NMR ($CDCl_3$) δ 1.38 (s, 3H, $-CH_3$), 2.08 (s, 6H, $-CH_3$), 4.28 (s, 4H, CH_2C); ^{13}C NMR ($CDCl_3$) δ 17.79, 20.51, 55.77, 64.88, 170.07, 175.06.

[G#2]-$CO_2CH_2C_6H_5$ [4] and a General Esterification Procedure. 2,2-Bis(acetoxymethyl)propionic acid chloride [**3**] (5.90 g, 24.95 mmol), diluted in a small amount of dry CH_2Cl_2, was added drop by drop to a solution of 2.60 g (11.61 mmol) benzyl-2,2-bis(methylol)propionate [**2**], 0.14 g (0.60 mmol) of DMAP, and 3.00 g of (29.70 mmol) of TEA in 30 mL of dry CH_2Cl_2 at 0 °C under argon atmosphere. After stirring at 0 °C for 1 h the temperature was raised to 25 °C, and the reaction was allowed to reach completion over night. The CH_2Cl_2 was evaporated and the dark brown crude product was purified by liquid chromatography on silica gel eluating with hexane gradually increasing to 60:40 hexane/ethyl acetate to give **4** as a colorless viscous oil: 5.9 g (82%); ^1H NMR ($CDCl_3$) δ 1.16 (s, 6H, $-CH_3$), 1.26 (s, 3H, $-CH_3$), 2.03 (s, 12H, $-CH_3$), 4.14 (s, 8H, $-CH_2C$), 4.27 (d, 4H, $-CH_2C$), 5.15 (s, 2H, $-CH_2Ar$), 7.35 (m, 5H, $-ArH$); ^{13}C NMR ($CDCl_3$) δ 17.52, 17.62, 46.23, 46.62, 65.22, 65.57, 67.06, 128.32, 128.46, 128.63, 135.31, 170.37, 171.96, 172.01.

[G#2]-CO_2H [5] and a General Procedure for Removal of the Benzyl Ester Group. 0.4 g Pd/C (10%) was added to a solution of 4.00 g (6.41 mmol) of [G#2]-$CO_2CH_2C_6H_5$ [**4**] in 30 mL of ethyl acetate. The apparatus for catalytic hydrogenolysis was evacuated from air and filled with H_2. Approximately 170 mL of H_2 were consumed. The Pd/C was filtered off and carefully washed with ethyl acetate. The filtrate was evaporated to give **5** as white crystals. 3.3 g (96%); ^1H NMR ($CDCl_3$) δ 1.24 (s, 6H, $-CH_3$), 1.31 (s, 3H, $-CH_3$), 2.05 (s, 12H, $-CH_3$), 4.20 (s, 8H, $-CH_2C$), 4.28 (s, 4H, $-CH_2$); ^{13}C NMR ($CDCl_3$) δ 17.46, 17.65, 20.60, 65.38, 170.71, 172.02, 176.44.

[G#2]-COCl [6]. Oxalylchloride (2.90 g, 22.83 mmol) and 6.00 g (11.23 mmol) of [G#2]-CO_2H [**5**] were reacted according to the general procedure for acid chloride formation to give **6** as a slightly yellow oil: 6.0 g (97%); ^1H NMR ($CDCl_3$) δ 1.24 (s, 6H, $-CH_3$), 1.40 (s, 3H, $-CH_3$), 2.05 (s, 12H, $-CH_3$), 4.19 (s, 8H, $-CH_2C$), 4.33 (d, 4H, $-CH_2C$); ^{13}C NMR ($CDCl_3$) δ 17.21, 17.52, 17.63, 20.60, 46.23, 48.39, 48.46, 64.92, 65.41, 65.64, 65.81, 170.65, 171.40, 172.06, 172.26, 173.43, 173.54, 175.96, 176.25.

[G#3]-$CO_2CH_2C_6H_5$ [7]. [G#2]-COCl [**6**] (5.70 g, 10.32 mmol), 1.10 g (4.91 mmol) of benzyl-2,2-bis(methylol)propionate [**2**], 0.06 g (0.5 mmol) of DMAP and 1.2 g (12.3 mmol) of TEA were reacted according to the general esterification procedure over night to give a slightly yellow crude product that was purified by liquid chromatography on silica gel eluating with hexane gradually increasing to 20:80 hexane/ethyl acetate to give **7** as a colorless viscous oil: 5.3 g (86%); ^1H NMR ($CDCl_3$) δ 1.16 (s, 6H, $-CH_3$), 1.22 (s, 12H, $-CH_3$), 1.30 (s, 3H, $-CH_3$), 2.04 (s, 24H, $-CH_3$), 4.18 (m, 24H, $-CH_2C$), 4.26 (q, 4H, $-CH_2C$), 5.16 (s, 2H, $-CH_2Ar$), 7.35 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.31, 17.46, 17.66, 20.59, 46.24, 46.58, 65.18, 66.09, 67.09, 128.34, 128.46, 128.61, 135.3, 170.31, 171.37, 171.79, 171.94.

[G#3]-CO_2H [8]. Pd/C (0.5 g, 10%) and 5.00 g (3.98 mmol) of [G#3]-$CO_2CH_2C_6H_5$ [**4**] were reacted according to the general procedure for removal of the benzyl ester group, approximately 100 mL H_2 were consumed, to give **8** as a colorless viscous oil: 4.55 g (98%); ^1H NMR ($CDCl_3$) δ 1.23 (s, 12H, $-CH_3$), 1.25 (s, 6H, $-CH_3$), 1.33 (s, 3H, $-CH_3$), 2.06 (s, 24H, $-CH_3$), 4.17 (s, 17H, $-CH_2C$), 4.25 (s, 8H, $-CH_2C$), 4.29 (m, 4H, $-CH_2C$); ^{13}C NMR ($CDCl_3$) δ 17.35, 17.45, 17.69, 20.63, 46.13, 46.24, 46.66, 65.23, 66.46, 170.71, 171.46, 171.96, 173.57.

[G#3]-COCl [9]. Oxalylchloride (1.00 g, 7.87 mmol) and 4.30 g (3.69 mmol) of [G#3]-CO_2H [**8**] were reacted according to the general procedure for acid chloride formation to give **9** as a slightly yellow oil: 4.30 g (98%); ^1H NMR ($CDCl_3$) δ 1.23 (s, 12H, $-CH_3$), 1.26 (s, 6H, $-CH_3$), 1.45 (s, 3H, $-CH_3$), 2.05 (s, 24H, $-CH_3$), 4.16 (s, 16H, $-CH_2C$), 4.25 (s, 8H, $-CH_2C$), 4.33 (q, 4H, $-CH_2C$); ^{13}C NMR ($CDCl_3$) δ 17.31, 17.45, 17.66, 20.60, 46.24, 46.71, 56.03, 65.19, 65.82, 170.34, 170.61, 171.22, 171.45, 171.94, 174.66.

[G#4]-$CO_2CH_2C_6H_5$ [10]. [G#3]-COCl [**9**] (4.55 g, 3.84 mmol), 287 mg (1.28 mmol) of benzyl-2,2-bis(methylol)propionate [**2**], 47 mg (0.38 mmol) of DMAP, and 452 mg (4.48 mmol) of TEA were reacted according to the general esterification procedure for 24 h to give a slightly yellow crude product that was purified by liquid chromatography on silica gel eluating with hexane gradually increasing to 20:80 hexane/ethyl acetate to give **10** as a colorless viscous oil: 2.60 g (81%); ^1H NMR ($CDCl_3$) δ 1.20 (s, 6H, $-CH_3$), 1.22 (s, 24H, $-CH_3$), 1.23 (s, 12H, $-CH_3$), 1.31 (s, 3H, $-CH_3$), 2.08 (s, 48H, $-CH_3$), 4.18 (s, 32H, $-CH_2C$), 4.20−4.34 (m, 28H, $-CH_2C$), 5.15 (s, 2H, $-CH_2Ar$), 7.35 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.34, 17.50, 17.77, 20.72, 46.31, 46.66, 46.80, 65.14, 65.24, 65.67, 66.53, 67.20, 128.26, 128.55, 128.72, 135.44, 170.46, 171.40, 171.49, 171.83, 172.06.

[G#4]-CO_2H [11]. Pd/C (0.26 g, 10%) and 2.60 g (1.03 mmol) of [G#4]-$CO_2CH_2C_6H_5$ [**10**] were reacted according to the general procedure for removal of the benzyl ester group, approximately 25 mL of H_2 were consumed, to give **11** as a colorless viscous oil: 2.48 g (98.8%); ^1H NMR ($CDCl_3$) δ 1.23 (s, 24H, $-CH_3$), 1.25 (s, 12H, $-CH_3$), 1.29 (s, 6H, $-CH_3$), 1.33 (s, 3H, $-CH_3$), 2.05 (s, 48H, $-CH_3$), 4.19 (s, 32H, $-CH_2C$), 4.21−4.31 (m, 28H, $-CH_2C$); ^{13}C NMR ($CDCl_3$) δ 17.52, 17.77, 20.74, 46.35, 46.70, 65.31, 65.84, 66.88, 170.59, 171.49, 172.02.

[G#4]-COCl [12]. Oxalylchloride (0.32 g, 2.54 mmol) and 3.08 g (1.27 mmol) of [G#4]-CO_2H [**11**] were reacted according to the general procedure for acid chloride formation to give **12** as a slightly yellow oil: 3.1 g (99.7%); ^1H NMR ($CDCl_3$) δ 1.23 (s, 24H, $-CH_3$), 1.25 (s, 12H, $-CH_3$), 1.29 (s, 6H, $-CH_3$), 1.47 (s, 3H, $-CH_3$), 2.04 (s, 48H, $-CH_3$), 4.17 (s, 32H, $-CH_2C$), 4.21−4.29 (m, 24H, $-CH_2C$), 4.28−4.40 (m, 4H, $-CH_2C$); ^{13}C NMR ($CDCl_3$) δ 17.34, 17.50, 17.77, 20.72, 46.32, 46.69, 46.75, 65.25, 65.76, 66.25, 170.48, 171.24, 171.49, 172.07, 174.75.

Dendritic Polyester [13]. 2,2-Bis(acetoxymethyl)propionic acid chloride [**3**] (2.50 g, 10.57 mmol), 1.03 g (3.36 mmol) of 1,1,1-tris-(hydroxyphenyl)ethane, 0.06 g (0.50 mmol) of DMAP, and 1.08 g (10.70 mmol) of TEA in 20 mL of dry CH_2Cl_2 were reacted according to the general esterification procedure for 2 h. The dark brown crude product was purified by liquid chromatography on silica gel eluating with hexane gradually increasing to 40:60 hexane/ethyl acetate to give **13** as a colorless viscous oil: 2.85 g (93%); ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 9H, $-CH_3$), 2.09 (s, 18H, $-CH_3$), 2.15 (s, 3H, $-CH_3$), 4.35 (s, 12H, $-CH_2C$), 6.95 (d, 6H, $-$ArH), 7.08 (d, 6H, $-$ArH); ^{13}C NMR ($CDCl_3$) δ 17.93, 20.75, 30.83, 46.70, 51.67, 65.50, 120.78, 129.75, 146.32, 148.73, 170.49, 171.50. Anal. Calcd for $C_{47}H_{54}O_{18}$: C, 62.24; H, 6.00. Found: C, 62.15; H, 6.02.

Dendritic Polyester [14]. [G#2]-COCl [**6**] (1.59 g, 1.88 mmol), 280 mg (0.92 mmol) of 1,1,1-tris(hydroxyphenyl)ethane, 17 mg (0.14 mmol) of DMAP, and 0.32 g (3.21 mmol) of TEA in 10 mL of dry CH_2Cl_2 were reacted according to the general esterification procedure for 4 h. The slightly yellow crude product was purified by liquid chromatography on silica gel eluating with hexane gradually increasing to 20:80 hexane/ethyl acetate to give **14** as a colorless viscous oil: 1.51 g (89%); ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 18H, $-CH_3$), 1.41 (s, 9H, $-CH_3$), 2.01 (s, 36H, $-CH_3$), 2.15 (s, 3H, $-CH_3$), 4.21 (s, 24H, $-CH_2C$), 4.41 (s, 12H, $-CH_2C$), 6.97 (d, 6H, $-$ArH), 7.19 (d, 6H, $-$ArH); ^{13}C NMR ($CDCl_3$) δ 17.55, 17.74, 20.57, 30.76, 46.35, 47.00, 51.62, 65.31, 65.60, 120.70, 129.69, 146.32, 148.56, 170.33, 170.75, 172.09. Anal. Calcd for $C_{89}H_{114}O_{42}$: C, 57.60; H, 6.19. Found: C, 57.48; H, 6.29.

Dendritic Polyester [15]. ([G#3]-COCl) [**9**] (1.34 g, 1.14 mmol), 105 mg (0.344 mmol) of 1,1,1-tris(hydroxyphenyl)ethane, 6.3 mg (0.052 mmol) of DMAP, and 122 mg (1.2 mmol) of TEA in 5 mL of dry CH_2Cl_2 were reacted according to the general esterification procedure for 15 h. The slightly yellow crude product was purified by liquid chromatography on silica gel eluating with hexane gradually increasing to 20:80 hexane/ethyl acetate to give **15** as a colorless viscous oil: 0.95 g (74%); ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 36H, $-CH_3$), 1.27 (s, 18H, $-CH_3$), 1.44 (s, 9H, $-CH_3$), 2.04 (s, 72H, $-CH_3$), 2.14 (s, 3H, $-CH_3$), 4.15 (s, 48H, $-CH_2C$), 4.22$-$4.30 (m, 24H, $-CH_2C$), 4.37$-$4.39 (m, 12H, $-CH_2C$), 6.98 (d, 6H, ArH), 7.20 (d, 6H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.44, 17.49, 17.59, 20.53, 30.77, 46.23, 46.65, 46.88, 51.62, 65.18, 66.01, 120.68, 129.68, 146.32, 148.56, 170.24, 170.75, 171.45, 171.95. Anal. Calcd for $C_{173}H_{234}O_{90}$: C, 55.36; H, 6.28. Found: C, 55.26; H, 6.44.

Dendritic Polyester [16]. ([G#4]-COCl) [**12**] (2.60 g, 1.06 mmol), 81.2 mg (0.265 mmol) of 1,1,1-tris(hydroxyphenyl)ethane, 9.7 mg (0.08 mmol) of DMAP, and 120 mg (1.19 mmol) TEA in 5 mL of dry CH_2Cl_2 were reacted according to the general esterification procedure for 72 h. The slightly yellow crude product was purified by liquid chromatography on silica gel eluating with hexane gradually increasing to 20:80 hexane/ethyl acetate to give **16** as a colorless viscous oil: 600 mg (30%); ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 72H, $-CH_3$), 1.22 (s, 36H, $-CH_3$), 1.28 (s, 18H, $-CH_3$), 1.42 (s, 9H, $-CH_3$), 2.00 (s, 144H, $-CH_3$), 2.14 (s, 3H, $-CH_3$), 4.15 (s, 96H, $-CH_2C$), 4.21$-$4.31 (m, 72H, $-CH_2C$), 4.39$-$4.40 (m, 12H, $-CH_2C$), 6.98 (d, 6H, ArH), 7.10 (d, 6H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.51, 17.74, 20.67, 46.32, 46.67, 47.04, 65.11, 65.23, 65.50, 120.83, 129.79, 146.25, 148.66, 170.38, 170.72, 171.46, 171.52, 172.04. Anal. Calcd for $C_{341}H_{474}O_{186}$: C, 54.25; H, 6.33. Found: C, 53.97; H, 6.40.

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