Fast and Convenient Divergent Synthesis of Aliphatic Ester Dendrimers by Anhydride Coupling

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Abstract: A novel divergent approach was developed for the synthesis of dendritic aliphatic polyester structures using an acetal-protected anhydride derivative of 2,2-bis(hydroxymethyl)propionic acid as the acylating agent. This divergent synthesis is remarkable, because unlike all others, it only requires a small excess of reagent to achieve quantitative growth, and it requires no means of purification other than a simple solvent extraction or precipitation. A monodisperse sixth generation dendrimer with molecular weight of 30 711 Dalton and 192 masked hydroxyl groups was prepared in high yield and purity using 1,1,1-tris(hydroxyphenyl)ethane as the core molecule. Linear and star-shaped poly(ethylene glycol) (PEG) derivatives of narrow polydispersity were also used as core molecules in the divergent synthesis of dendritic-linear copolymer hybrids up to the fourth generation without requiring any chromatographic purification.

Introduction

Over the past decade, chemists have developed a large number of synthetic routes to a variety of dendritic macromolecules using different chemistries and monomers.[1] The ability to precisely control the three-dimensional structure, functionality, and material properties of a molecule has always been a challenge for chemists. Today, most of the well-defined macromolecules in existence are still supplied by nature itself. Dendrimers represent one of the very few families of synthetic macromolecules that possess a structural precision approaching that of proteins. As a result of their structural precision, globular shape, and high functionality, dendrimers have found use in a large number of applications that are frequently inspired from natural systems. For instance, dendrimers have demonstrated unique properties that enable their use in molecular encapsulation,[2] light-harvesting systems,[3] biomedical applications[4] and catalysis.[5] However, the synthetic procedures used for their preparation involve multiple steps with intermediate purifications that detract from their widespread use.

Two different synthetic strategies are employed to construct regular dendritic frameworks. The first is the divergent approach introduced independently by Tomalia[6] and Newkome[7] in their synthesis of PAMAM and arborol dendrimers; the second is the convergent approach of Hawker and Fréchet.[8] The two approaches complement each other and neither is generally better. The choice of synthetic approach is usually justified by the features of the target molecule, the chemistry available for growth, and the specific building blocks used in the construction of the dendritic framework. The convergent approach is generally acknowledged to provide better overall structural control, in part as a result of its enhanced potential for purification at intermediate stages of the synthesis, and in part as a result of its innate ability to introduce differentiated functionalities at the focal point and the periphery of the dendrimer. In the divergent approach, structural uniformity is harder to maintain, because the number of reactions that must be completed at each step of growth increases exponentially, thus requiring large excesses of reagents, but the process is better suited not only for syntheses

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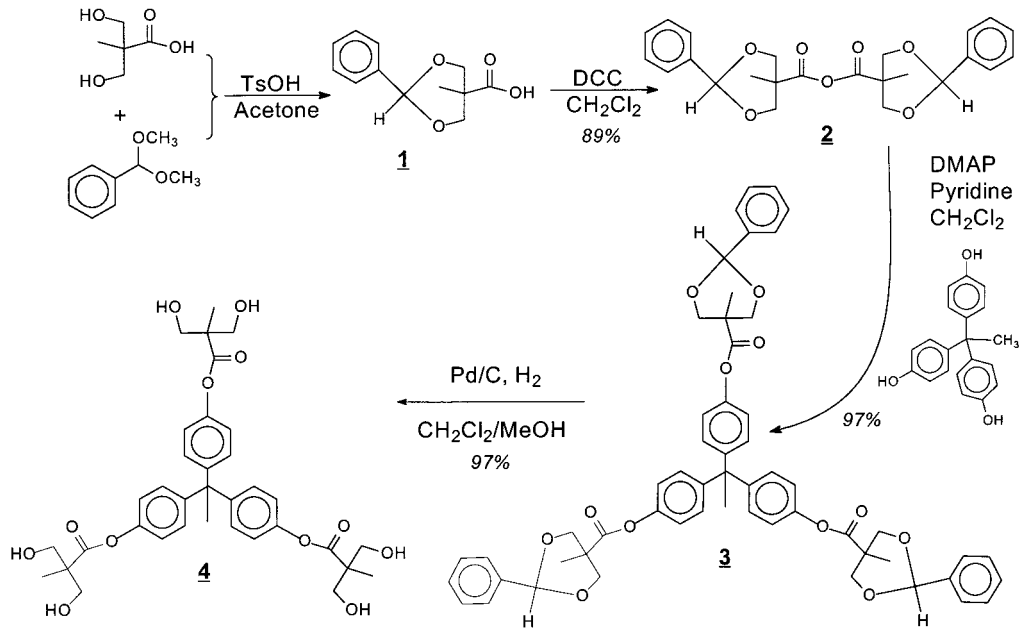
Scheme 1



on a larger scale but also for the preparation of high-generation dendrimers.

As part of a program in targeted drug delivery,[9] we have been interested in the development of biocompatible aliphatic dendrimers lacking the toxicity[10] associated with the two commercial families of amine-containing dendrimers. Here, we present a divergent synthesis of aliphatic ester dendrimers by anhydride coupling, based on readily available 2,2-bis(hydroxymethyl)propionic acid as the repeating unit. Using this approach, the sixth generation benzylidene-protected dendrimer with a molecular weight of 30 711 was obtained in high yields and purity. Linear and star-shaped poly(ethylene glycol) (PEG) of narrow polydispersity (PDI $\sim$ 1.03) were also used as cores for the divergent growth of novel linear-dendritic hybrids. This novel route is noteworthy for its rapidity and ability to rapidly produce high-generation aliphatic ester dendrimers of high purity with no means of purification other than solvent extraction and precipitation.

Results and Discussion

Synthesis of Polyether Dendrimers from a Tris-Phenolic Core. In previous work, acetate-terminated polyester dendrons based on 2,2-bis(hydroxymethyl)propionic acid ranging from generations one to four were synthesized according to a strictly convergent growth approach;[11] however, the original design suffered from a lack of versatility, because the desirable deprotection of the terminal acetate groups to obtain the corresponding hydroxyl-terminated dendrimers could not be achieved without some concomitant cleavage of the dendrimer itself. In addition, coupling of the fourth generation dendrons to the core molecule could only be achieved in a yield significantly lower than that obtained in the coupling steps that were used to prepare the lower generation dendrons. Access to the hydroxyl-terminated polyester dendrons was eventually achieved with a double-stage convergent approach using acetonide-protected building blocks and *N*,*N*′-dicyclohexylcarbodiimide (DCC) for the coupling steps.[12] Once deprotected, the hydroxyl-functionalized dendrons can easily undergo "surface" functionalization in reactions, such as the growth of ϵ-caprolactone via controlled ring-opening polymerization to afford dendritic star structures.[13]

Given the compact nature of the building block and the specific chemistry used in these synthetic routes, the main drawbacks of these syntheses rest in the repeated purifications by column chromatography and the increased steric inhibition to growth that are observed at higher generations. In addition, one implementation of our drug delivery target application requires that the polyfunctional drug be attached in a last synthetic step to the periphery of the fully constituted dendritic carrier; therefore, a new synthetic route alleviating these problems was developed. It involves a divergent growth based on a novel anhydride derivative of 2,2-bis(hydroxymethyl)-propionic acid **2**.

The building block used as the acylating agent in this divergent synthesis is the benzylidene-protected anhydride derivative **2** of 2,2-bis(hydroxymethyl)propionic acid. The preparation of **2**, shown in Scheme 1, starts with the protection of the diol group of 2,2-bis(hydroxymethyl)propionic acid by reaction with benzaldehyde dimethyl acetal and a catalytic amount of *p*-toluenesulfonic acid (TsOH) in dry acetone to afford **1**. Although benzaldehyde itself can be used for this reaction, use of its dimethyl acetal derivatives provides for easier workup and higher yields of **1**. Anhydride **2** is then obtained by self-condensation of **1** in CH_2Cl_2 using *N*,*N*′-dicyclohexylcarbodiimide (DCC) as the dehydrating agent. DCC provides mild, rapid, and high-yielding access to the symmetrical anhydride, but other reagents, such as P_2O_5 or acetic anhydride, are more difficult to use given the presence of acid-labile acetal protective groups. The crude anhydride **2** is easily purified from remaining *N*,*N*′-dicyclohexylurea (DCU) and excess DCC by

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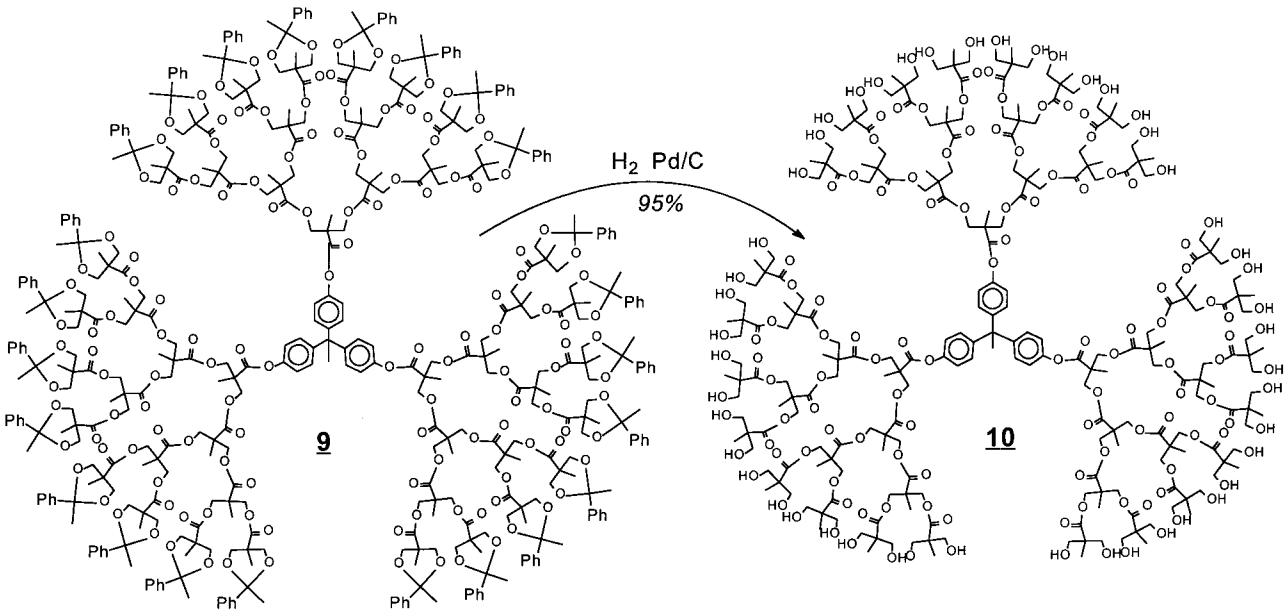
Scheme 2



precipitation of the CH_2Cl_2 solution into hexane under vigorous stirring to afford an essentially pure product.

Coupling of **2** with the triphenolic core molecule 1,1,1-tris-(hydroxyphenyl)ethane is readily accomplished using only 1.25 equivs of **2**/hydroxyl group to afford a 94% isolated yield of **3**. The esterification reaction is best performed in a 1:3 mixture of pyridine and CH_2Cl_2 at a concentration of ~0.3 M using 20−25 mol % of DMAP as the acylating catalyst. Attempts to perform the esterifications either without DMAP or in a very dilute solution resulted in low conversions and long reaction times. Other solvents such as THF, DMF, and MeCN are also suitable as solvents in the formation of dendritic aliphatic esters using anhydride **2** as the acylating agent; however, because higher generation hydroxyl functional dendrimers are sparingly soluble in these solvents, it was found most efficient to predissolve the hydroxyl-functional dendrimer in pyridine and then dilute the reaction mixture with a solvent such as CH_2Cl_2. After stirring at room temperature for 3 h, the excess of the anhydride **2** was quenched by stirring the reaction mixture with a solution (1:1) of pyridine and water overnight. The reaction mixture was then diluted with CH_2Cl_2 and extracted with $NaHSO_4$ (1 M), then Na_2CO_3 (10% w/v), and finally, with brine to remove pyridine, DMAP, and the benzylidene-protected acid **1** that is formed as a byproduct. The reaction is so clean that the product obtained after this simple workup is essentially pure. As will be seen below, the next step of the synthesis involves a Pd catalyst for the removal of the benzylidene protecting groups. It is, therefore, essential to ensure that all of the pyridine and DMAP are removed from the dendrimers in the extraction and washing steps to avoid catalyst deactivation.

To prepare larger dendrimers, the sequence of the anhydride coupling step and the subsequent deprotection by hydrogenolysis is repeated until a dendrimer of the desired size is obtained. The extractive workup procedure described above is fully satisfactory for the first three generations of polyester dendrimers. At higher generations, a small amount of DCU present in the anhydride **2** accumulates in the system and can be detected both by ^{1}H NMR spectroscopy and by size exclusion chromatography (SEC); therefore, the extraction procedure is complemented by an additional step of precipitation of the crude benzylidene functional dendrimers from a CH_2Cl_2 solution into hexane under vigorous stirring. The precipitate is then redissolved in CH_2Cl_2 and evaporated to afford a high-purity benzylidene-protected dendrimer as a glass.

The benzylidene protecting groups of **3** and larger dendrimers such as the fourth generation dendrimer **9** (Scheme 2) can be selectively removed in very high yields by catalytic hydrogenolysis in a process that does not affect the ester bonds of the dendritic backbone. Hydrogenolysis is best carried out by stirring overnight under medium pressure of H_2 using 10% w/w of Pd/C (10%) as catalyst; therefore, deprotection of **3** affords the corresponding first generation hydroxyl-functional dendrimer **4** in 97% yield, and deprotection of **9** affords dendrimer **10** with 48 peripheral hydroxyls in 95% yield after purification by precipitation. The deprotection reaction is easily monitored by ^{1}H NMR spectroscopy using DMSO-d_6 as solvent, and the pure product is isolated almost quantitatively after removal of the catalyst by filtration. Removal of the protecting groups by hydrogenolysis was preferred over alternate routes involving hydrolysis, because the latter required very long reaction times and the use of more difficult workup procedures.

Using this iterative divergent growth process, the sixth generation benzylidene-functional dendrimer with a molecular weight of 30 711 and 192 masked terminal hydroxyl groups was obtained in high yields and purity using no means of purification other than extraction and precipitation. The process is noteworthy, because it is unlike all other divergent syntheses that require a large excess of reagent to be used in the growth steps. Here, only a small excess of the anhydride (at most, 1.25 equivs of **2**/hydroxyl group) is needed to drive each growth step to completion, even at high generation. Both the quantitative nature of the coupling reaction and the fact that the only side product formed is the benzylidene-protected acid **1** greatly facilitate product isolation after a trivial workup procedure.

We also explored the alternate approach involving the direct DCC coupling of acid **1** rather than anhydride **2** using either 4-(dimethylamino)pyridine (DMAP) or 4-(dimethylamino)-pyridinium *p*-toluenesulfonate (DPTS)[14] as the acylation catalyst for the preparation of higher generation dendrimers. This approach led to product mixtures, including partially acylated molecules, that proved very difficult to purify by column chromatography. In addition, because a large excess of reagent

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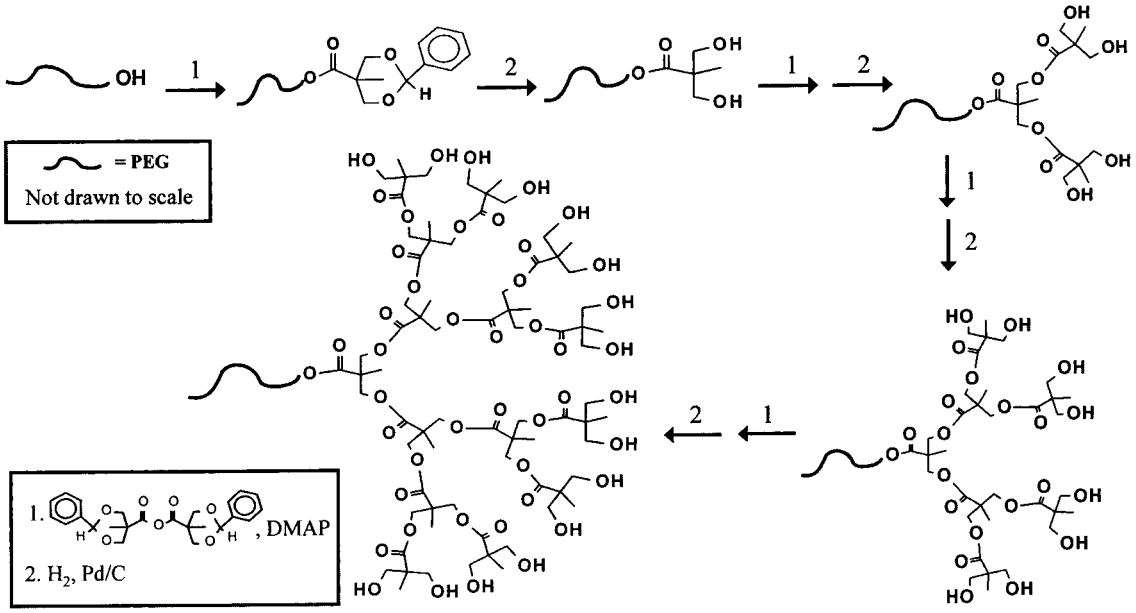
Scheme 3



had to be used at higher generations in order to attempt complete coupling, significant amounts of the rearranged *N*-acylurea byproduct were formed.

Preparation of Dendritic Linear Hybrids. The versatility and simple experimental implementation of this novel and extremely efficient divergent approach to dendritic aliphatic ester structures was further demonstrated by syntheses in which the dendrons were built from the chain-ends of narrow polydispersity linear and star-shaped poly(ethylene glycols) (PEGs) used as core molecules (Scheme 3). Dendritic PEG hybrids have been prepared previously using both convergent and divergent growth.[13] These hybrids have interesting properties as a result of the intrinsic differences that exist between the core and dendritic portions of the molecules, leading to amphiphilic properties and to their use as surface modifiers,[16] "stimulus-responsive" materials,[17] and drug carriers,[18] for instance.

The specific features of our target polyester-PEG structure are fully compatible with the divergent growth approach, because the PEG core may be used to assist in product purification through simple precipitation, but the terminal functionalities of the dendritic-linear hybrid remain available for the direct attachment of a functional molecule, such as a drug or a chromophore.

Three different low-polydispersity (PDI $\sim$ 1.03) PEGs were used as starting materials to prepare the dendritic PEG hybrids: a linear monomethyl ether PEG alcohol (5500 Da), a linear telechelic PEG diol (10 604 Da), and a four-arm star PEG tetraol (20 330 Da). After growth of fourth generation dendrons from their terminal hydroxyl groups, these should afford hybrid molecules displaying a total of 16, 32, and 64 benzylidene acetal-protected hydroxyl groups, respectively, at their surfaces (Figure 1). Once again, the preparation procedure that was used is very simple and amenable to operation on a rather large scale. The hydroxyl-functional PEG and DMAP (20 mol % with respect to the anhydride) predissolved in CH_2Cl_2 at a concentration of 10−40 mM was treated with an excess of anhydride **2** added as the neat reagent. In view of the dilution effect caused by the presence of the large PEG moiety, the use of an excess of **2** larger than the 1.25-fold excess used earlier is desirable to avoid excessively long reaction times; typically, 2−4 equivs of **2** may be used. After stirring at room temperature for 5−18 h, the excess of anhydride was quenched with methanol. Because both side-products, the benzylidene protected acid and its methyl ester formed during the coupling and quenching reactions, are readily soluble in diethyl ether, but the PEG hybrids are not, purification is readily accomplished by precipitation of the reaction mixture into diethyl ether. The quenching procedure is necessary, because anhydride **2** is insoluble in ether, and it would contaminate the precipitated PEG hybrids isolated by precipitation in that solvent. After filtration and washing with diethyl ether, the highly pure dendritic hybrids are isolated as white powders in yields of >90%. Once again, removal of the benzylidene protecting groups was achieved by catalytic hydrogenolysis and the alcohol-terminated hybrids were isolated in near quantitative yield by precipitation in ether.

General Characterization. The techniques that were used for the characterization of the various dendrimers were ^{1}H NMR, ^{13}C NMR, size exclusion chromatography (SEC), and MALDI-TOF; however, the characterization of especially high-generation dendrimers may be somewhat troublesome, as pointed out in a recent review.[19] Examination of the ^{1}H NMR spectra reveals unique generation-related features, such as the methyl resonance of the building block that shifts downfield for the successive generational layers, most clearly for the low-generation numbers. As expected, all of these methyl resonances are seen as singlets, but of significantly different chemical shifts reflecting the generation: from 1.21 for the benzylidene-protected G-1 to 0.79 for G-6. In addition, ^{1}H NMR spectroscopy proved invaluable for monitoring the removal of the benzylidene protective groups, because thin-layer chromatography is ineffective for the differentiation of fully and partial deprotected species because of the very small differences in R_f values expected for closely related molecules with large numbers of reaction sites. For the

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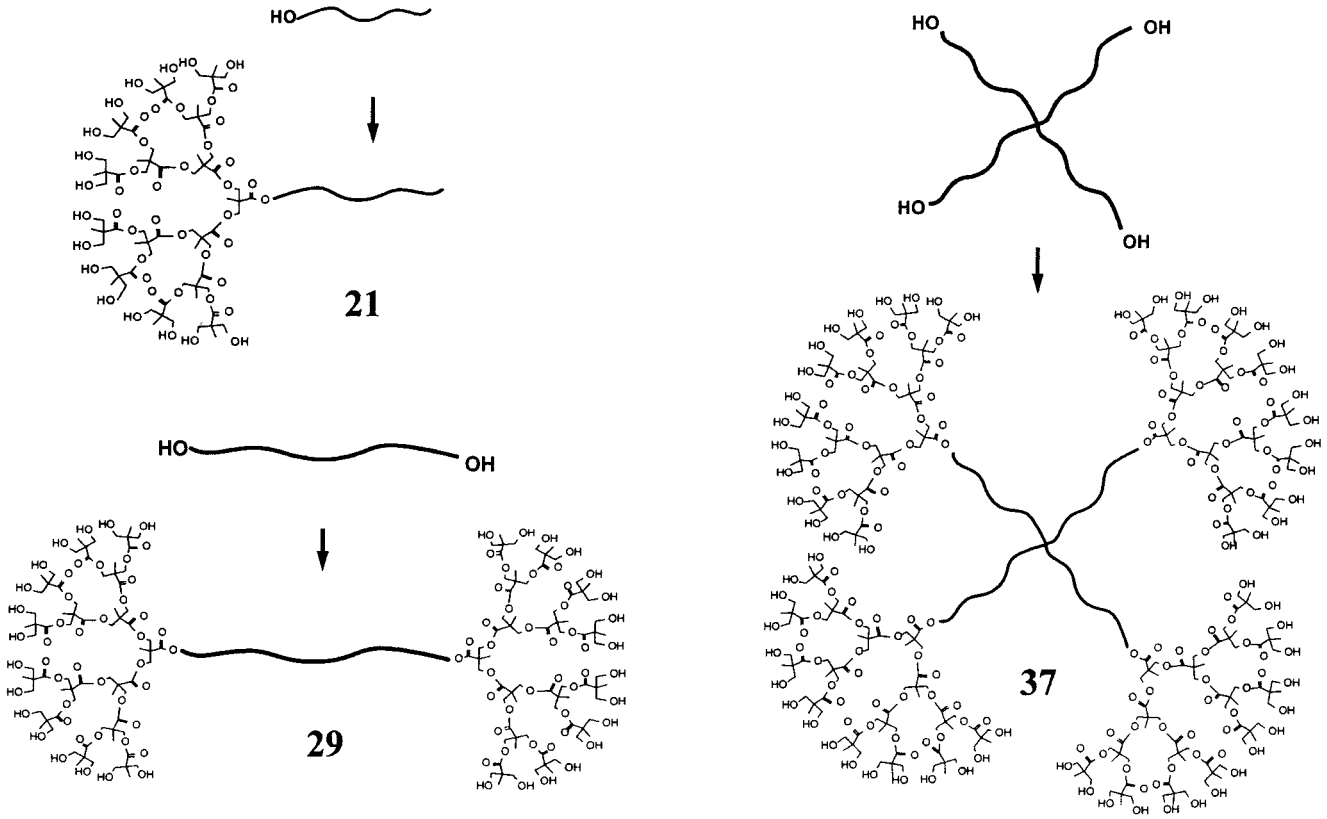

Figure 1. Three types of hybrids of PEG and [G-4] polyester dendrons obtained from PEGs with one, two, or four reactive ends.

sixth generation polyester dendrimer, the symmetry of the two doublets emanating from the core molecule at 7.05−7.14 ppm suggests a fully substituted core molecule. In contrast, resonances between 6.6 and 6.8 ppm would indicate a partly substituted core molecule. As expected, the molecular weights determined by SEC for these polymeric systems were not in agreement with those calculated using calibration with linear polystyrene. This phenomenon, which is related mainly to the highly globular shape adopted by these very compact dendrimers, has been observed previously in our work with polyether dendrimers for a comparable range of generations;[20] therefore, the fifth generation dendrimer **11**, with a theoretical molecular weight of 15 334 Dalton shows a polystyrene-equivalent molecular weight of only 6012 by SEC (Figure 2). MALDI-TOFMS analysis proved invaluable in confirming that complete reaction of all peripheral groups was achieved during early generation growth. In the synthesis of dendrimers of higher generations, SEC analysis showed polydispersity values (M_w/M_n) below those of the linear polystyrene standards used for column calibration, and MALDI-TOFMS analysis was used effectively to monitor coupling, because the technique is capable of detecting instances of incomplete reactions during the formation of the next higher generation. In a kinetic study, MALDI-TOF analysis was used to monitor the formation of the fifth generation dendrimer **11**, prepared from the fourth generation dendrimer with 48 reactive hydroxyl groups (Figure 3). Although the reaction was complete after 7 h of reaction time, there was no observable trace of any product having undergone less than 44 of the possible 48 coupling reactions even after only 1 h of reaction. This finding is somewhat surprising, considering the large number of reactive sites and the steric implications resulting from the very compact nature

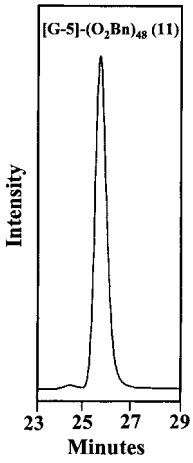

Figure 2. SEC trace of the fifth generation benzylidene-terminated dendrimer with M_n (theory) = 15 334 Da and M_n (SEC) = 6012 Da.

of the dendrimers. It is clear that the kinetics of this reaction are significantly faster than those for the single ether-forming divergent growth step of the synthesis we developed 10 years ago to prepare very large polyether dendrimers via a double-stage growth method.[21] In this earlier instance, we had also noticed a scarcity of partially reacted molecules while starting material and near-fully reacted products coexisted.

Although SEC analysis is clearly extremely valuable, its resolution limits are such that it is not possible to distinguish between fully and near-fully reacted dendrimers during generation growth. For example, SEC analysis of the sample obtained after 1 h of reaction time during growth of the fifth generation dendrimer shows a single peak with a polydispersity index of 1.008, confirming that SEC is not the optimal technique for

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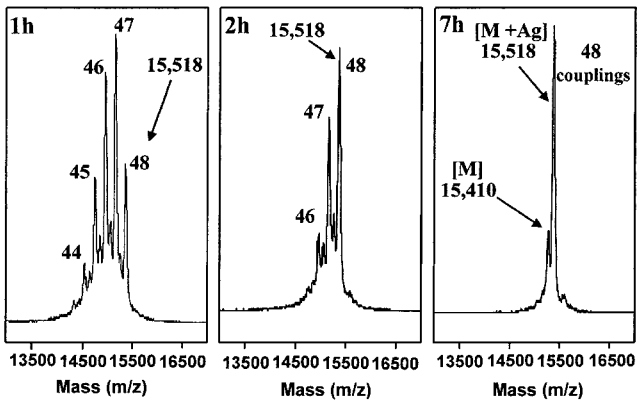

Figure 3. MALDI-TOFMS trace for the formation of the fifth generation dendrimer **11** with a theoretical molecular weight of 15 334 Da after 1, 2, and 7 h.

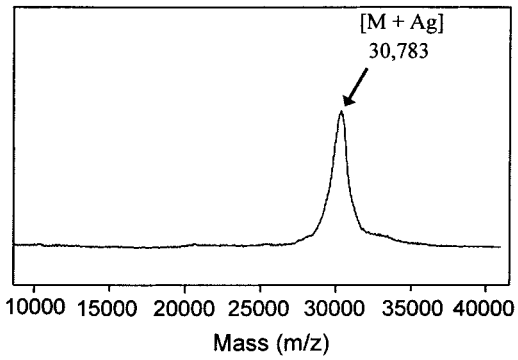

Figure 4. MALDI-TOFMS trace of the sixth generation dendrimer **13** with a theoretical molecular weight of 30 711 Da.

validating the purity of high-generation dendrimers. For the sixth generation dendrimer with a molecular weight of 30 711 Dalton, slight peak broadening was observed in the MALDI spectrum (Figure 4), but the data suggests that even at such high generation, full coupling was achieved within the detection limits of our instrumentation.

The PEG−polyester dendron hybrids were characterized using both ^{1}H NMR and MALDI-TOFMS. In the ^{1}H NMR spectrum, the integration of signals corresponding to the single benzylic and aromatic protons at ∼5.5 ppm and ∼7.0−7.5 ppm, respectively, can be compared with those between 0.8 and 1.5 ppm, corresponding to the isolated methyl groups of the building blocks that are characteristic of each generation. Any defect on the dendron resulting from incomplete coupling reactions would be observed near the methyl (0.8−1.5 ppm) and methylene (∼4.5 ppm) resonances of the building block, within the limits of detection of the NMR technique. Because of the intrinsic polydispersity of the PEG used for these hybrids, the SEC peaks are broader than for the pure dendrimers; however, as reported previously for analogous dendritic-linear hybrids,[22] MALDI-TOF provides invaluable data for the characterization of these macromolecules and suggests that dendrimer growth is highly regular (Figure 5).

Although it must be emphasized that NMR and, to a lesser extent, MALDI-TOF suffer from resolution limitations that would preclude the detection of very low levels of impurities if such were present, it is clear that the coupling and deprotection that we report proceed in remarkably high conversions, leading to rather pure products.

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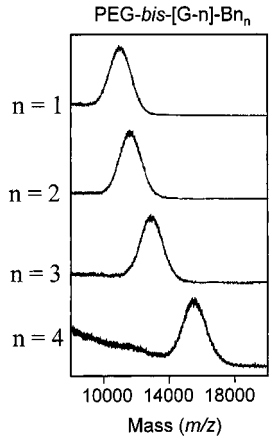

Figure 5. MALDI-TOFMS traces showing the generational increment for the telechelic PEGs in hybrids with benzylidene-protected [G-n] dendrons ($n = 1-4$).

Conclusion

A novel, very simple, and highly efficient divergent approach for the synthesis of aliphatic polyester dendrimers based on anhydride coupling has been developed and shown to be successful with a variety of cores. A monodispersed [G-6] polyester tridendron dendrimer with a molecular weight of 30 711 Dalton was synthesized as well as three different families of PEG−[G-4] polyester dendron hybrids. In all cases, the only purification that was used involved extraction and precipitation, thus affording very high purity materials. The simplicity and experimental ease of this novel divergent route to aliphatic ester dendrimers make it extremely attractive for the preparation of high-generation dendrimers at a reasonable cost. We are currently exploiting several families of dendrimers derived from this chemistry for applications in the fields of catalysis[5b] and polymer therapeutics.[9,10]

Experimental Section

General Procedures. All chemicals were purchased from Aldrich and used without any further purification. Solvents (Fischer) were reagent grade (99.9%). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 300, AM 400, or DRX 500, as specified. The solvents used were $CDCl_3$ and DMSO-d_6. The solvent signals were used as internal standards for both ^{1}H NMR and ^{13}C NMR recordings. Size-exclusion chromatography (SEC) with double detection was performed at 45 °C on a chromatography line calibrated with linear polystyrene standards and fitted with with three 7-μm ultra-Styragel columns having pore sizes 100 and 500 Å and a linear column, a differential refractive index (DRI) detector M410, and a photodiode array (PDA) detector M991 (Waters). THF was used as eluent at a nominal flow of 1 mL/min. Corrections for the flow rate fluctuation were made by using toluene as an internal standard. For compounds having a molecular mass <1000 Da and all polyol dendritic species, mass spectral data was collected by a Micromass LC−TOF instrument in positive mode. For benzylidene protected dendrimers, MALDI-TOFMS data was collected on a PerSeptive Biosystems Voyager-DE instrument in positive ion mode using a 9-nitroanthracene matrix with silver trifluoroacetate and calibration against bovine insulin standards. For PEG−polyester dendron hybrids, the matrix used was α-cyano-4-hydroxycinnamic acid, and no silver trifluoroacetate was used. M-H-W Laboratories (Phoenix, AZ) performed the elemental analyses.

Preparation of Benzylidene-2,2-bis(oxymethyl)propionic Acid (1). 2,2-Bis(hydroxymethyl)-propionic acid 20.00 g (149 mmol), 34.04 g (222 mmol) benzaldehyde dimethyl acetal, and 1.42 g (7.4 mmol) *p*-toluenesulfonic acid monohydrate (TsOH) were mixed in 150 mL of acetone. The reaction mixture was stirred for 4 h at room temperature. After storage of the reaction mixture in the refrigerator overnight, the

solids were filtered off and washed with cold acetone to give **1** as white crystals: 21.0 g, (64%). IR (cm^{-1}, thin film from $CHCl_3$): 3400−2300 (br), 1699 (s). ^1H NMR (500 MHz, $CDCl_3$): δ 1.11 (s, 3), 3.70 (d, 2, $J = 11.7$), 4.63 (d, 2, $J = 11.4$), 5.49 (s, 1), 7.37 (m, 3), 7.48 (m, 2). ^{13}C NMR (500 MHz, $CDCl_3$): δ 17.58, 41.58, 72.65, 100.37, 126.10, 128.01, 128.70, 138.39, 175.58. Calcd.: $[M]^+$ $m/z = 222.24$. Found: TOFMS-ES: $[M + Na]^+ = 245.10$. Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35; O, 28.80. Found: C, 64.89; H, 6.52.

Preparation of Benzylidene-2,2-bis(oxymethyl)propionic Anhydride (2). Compound **1** (20.00 g, 90 mmol) and 10.21 g (49.5 mmol) of *N*,*N*′-dicyclohexylcarbodiimide (DCC) were mixed in 150 mL of CH_2Cl_2. The reaction mixture was stirred overnight at room temperature. The precipitated urea DCC byproduct was filtered off in a glass filter and washed with a small volume of CH_2Cl_2. The crude product was purified by precipitating the filtrate into 1000 mL of hexane under vigorous stirring. After filtration, **2** was isolated as white crystals: 17.1 g (89%). IR (cm^{-1}, thin film from $CHCl_3$): 3050, 1814 (s), 1746 (s). ^1H NMR (300 MHz, $CDCl_3$): δ 1.12 (s, 6), 3.69 (d, 4, $J = 10.5$), 4.66 (d, 4, $J = 10.5$), 5.47 (s, 2), 7.35 (m, 6), 7.45 (m, 4). ^{13}C NMR (400 MHz, $CDCl_3$): δ 16.85, 44.18, 73.17, 102.11, 126.27, 128.22, 129.09, 137.56, 169.12. Calcd.: $[M]^+$ $m/z = 426.46$. Found: TOFMS-ES: $[M + Na]^+ = 449.20$. Anal. Calcd for $C_{24}H_{26}O_7$: C, 67.59; H, 6.15. Found: C, 67.37; H, 6.30.

Preparation of the First Generation Benzylidene-Protected Dendrimer [G-1]-(O_2Bn)$_3$ and General Esterification Procedure by Anhydride Coupling (3). 1,1,1-Tris(hydroxyphenyl)ethane 100 mg (326 μmol) and 20 mg (160 μmol) of 4-(dimethylamino)pyridine (DMAP) were dissolved in 2 mL of dry pyridine and then diluted with 6 mL of CH_2Cl_2. Solid anhydride **2** (556 mg, 1.3 mmol) was added, and the reaction mixture was stirred at room temperature for 5 h. After completion, according to MALDI-TOF, the excess benzylidene-2,2-bis(oxymethyl)propionic anhydride (**2**) was quenched by stirring the reaction mixture with 2 mL of a 1:1 pyridine:water solution overnight. The organic phase was diluted with 100 mL of CH_2Cl_2 and extracted with 2 × 40 mL of $NaHSO_4$ (1 M), 2 × 40 mL of Na_2CO_3 (10%) and 1 × 40 mL of brine. The organic phase was dried using $MgSO_4$ and evaporated to give **3** as a white glass: 292 mg, (97%). IR (cm^{-1}, thin film from $CHCl_3$): 3036, 1755 (s). ^1H NMR (300 MHz, $CDCl_3$): δ 1.21 (s, 9), 2.17 (s, 3), 3.75 (d, 6, $J = 11.4$), 4.78 (d, 6, $J = 11.4$), 5.52 (s, 3), 7.04 (d, 6, $J = 8.7$), 7.11 (d, 6, $J = 9.0$), 7.35 (m, 9), 7.46 (m, 6). ^{13}C NMR (500 MHz, $CDCl_3$): δ 17.67, 30.84, 42.85, 51.58, 73.50, 101.99, 120.83, 126.20, 128.25, 129.04, 129.62, 137.73, 146.12, 149.03, 172.69. Calcd.: $[M]^+$ $m/z = 919.03$. Found: TOFMS-ES: $[M + Na]^+ = 941.56$, MALDI-TOFMS $[M + Ag]^+ = 1033$. Anal. Calcd for $C_{56}H_{54}O_{12}$: C, 73.19; H, 5.92. Found: C, 72.91; H, 5.95.

Preparation of the First Generation Hydroxyl-Terminated Dendrimer [G-1]-$(OH)_6$ (4) and General Procedure for the Removal of the Benzylidene Group. [G-1]-(O_2Bn)$_3$ (**3**) (268 mg, 292 μmol) was dissolved in 20 mL of CH_2Cl_2 and diluted with 15 mL of methanol. 50 mg Pd/C (10%) was added to the solution. The apparatus for catalytic hydrogenolysis was evacuated and filled with H_2 three times. After vigorous stirring overnight, the catalyst was filtered off in a glass filter and carefully washed with methanol. The filtrate was evaporated to give **4** as white crystals: 185 mg, (97%). IR (cm^{-1}, thin film from THF): 3369 (br), 1744 (s). ^1H NMR (300 MHz, DMSO-d_6): δ 1.18 (s, 9), 2.14 (s, 3), 3.53 (dd, 6, $J = 10.5$, 5.4), 3.65 (dd, 6, $J = 10.5$, 5.4), 4.92 (t, 6, $J = 10.8$), 7.04 (q, 12, $J = 18.9$, 8.7). ^{13}C NMR (500 MHz, DMSO-d_6): δ 16.92, 30.42, 50.88, 51.27, 64.00, 121.32, 129.17, 145.77, 149.00, 173.63. Calcd.: $[M]^+$ $m/z = 654.71$. Found: TOFMS-ES: $[M + Na]^+ = 677.43$. Anal. Calcd for $C_{35}H_{42}O_{12}$: C, 64.21; H, 6.47. Found: C, 64.12; H, 6.39.

[G-2]-(O_2Bn)$_6$ (5). [G-1]-$(OH)_6$ (**4**), 328 mg (500 μmol), and 122 mg (1 mmol) of DMAP were dissolved in 2 mL of dry pyridine and diluted with 6 mL of CH_2Cl_2. Following addition of 1.71 g (4.0 mmol) of anhydride **2**, the reaction mixture was stirred at room temperature for 5 h. Excess anhydride was quenched with 2 mL of 1:1 pyridine: water overnight. The organic phase was diluted with 100 mL of CH_2Cl_2 and extracted with 2 × 40 mL of $NaHSO_4$ (1 M), 2 × 40 mL of Na_2CO_3 (10%) and 1 × 40 mL of brine. The organic phase was dried with $MgSO_4$ and evaporated to give **5** as a white glass: 850 mg, (90%). IR(cm^{-1}, thin film from $CHCl_3$): 3050, 1741 (s). ^1H NMR (300 MHz, $CDCl_3$): δ 0.98 (s, 18), 1.42 (s, 9), 1.97 (s, 3), 3.63 (d, 12, $J = 11.5$), 4.52 (s, 12), 4.63 (d, 12, $J = 11.5$), 5.43 (s, 6), 6.80 (d, 6, $J = 8.9$), 6.88 (d, 6, $J = 8.9$), 7.25 (m, 18), 7.39 (m, 12). ^{13}C NMR (500 MHz, $CDCl_3$): δ 17.72, 17.17, 42.65, 47.06, 51.39, 65.60, 73.42, 73.49, 101.77, 120.76, 126.11, 128.08, 128.83, 129.55, 137.62, 146.11, 148.45, 171.41, 173.29. Calcd.: $[M]^+$ $m/z = 1880.06$. Found: MALDI-TOF: $[M + Ag]^+ = 1984$. Anal. Calcd for $C_{107}H_{114}O_{30}$: C, 68.36; H, 6.11. Found: C, 68.39; H, 6.26.

[G-2]-$(OH)_{12}$ (6). [G-2]-(O_2Bn)$_6$ (**5**) (778 mg, 410 μmol) was dissolved in 20 mL of CH_2Cl_2 and diluted with 20 mL of methanol. 50 mg Pd/C (10%) was added to the solution. The procedure described above was repeated to give **6** as a white glass: 544 mg, (97%). IR (cm^{-1}, thin film from THF): 3416 (br), 1734 (s). ^1H NMR (500 MHz, DMSO-d_6): δ 1.09 (s, 18), 1.33 (s, 9), 2.17 (s, 3), 3.44 (d, 12, $J = 8.5$), 3.50 (d, 12, $J = 10.5$), 4.26 (dd, 12, $J = 22.8$, 10.5), 7.11 (m, 12). ^{13}C NMR (500 MHz, DMSO-d_6): δ 16.83, 17.16, 46.73, 50.49, 51.35, 63.87, 65.17, 121.28, 129.40, 146.21, 148.55, 171.50, 174.23. Calcd.: $[M]^+$ $m/z = 1351.41$. Found: TOFMS-ES: $[M + Na]^+ = 1374.61$, $[M + Na]^{2+} = 698.28$. MALDI-TOF: $[M + Ag]^+ = 1447$. Anal. Calcd for $C_{65}H_{90}O_{30}$: C, 57.77; H, 6.71. Found: C, 57.52; H, 6.86.

[G-3]-(O_2Bn)$_{12}$ (7). Generation growth was carried out using [G-2]-$(OH)_{12}$, **6**, (426 mg, 315 μmol), and 154 mg (1.2 mmol) of DMAP in 3 mL of dry pyridine and 6 mL of CH_2Cl_2, followed by addition of 2.15 g (5.0 mmol) of anhydride **2**, and stirring at room temperature for 5 h. Following workup as above, **7** was obtained as a white glass: 1100 mg, (92%). IR (cm^{-1}, thin film from $CHCl_3$): 3048, 1742 (s). ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (s, 36), 1.12 (s, 9), 1.22 (s, 18), 2.04 (s, 3), 3.55 (d, 24, $J = 11.7$), 4.15 (dd, 12, $J = 18.2$, 11.2), 4.37 (s, 24), 4.54 (d, 24, $J = 11.4$), 5.38 (s, 12), 6.90 (d, 6, $J = 9$), 7.03 (d, 6, $J = 9$), 7.27 (m, 36), 7.39 (m, 24). ^{13}C NMR (500 MHz, $CDCl_3$): δ 14.09, 17.28, 17.61, 17.69, 22.62, 25.24, 31.55, 34.63, 42.53, 46.79, 46.89, 65.13, 65.61, 73.39, 73.46, 101.61, 120.73, 126.13, 128.08, 128.81, 129.68, 137.79, 146.23, 148.49, 170.80, 171.89, 173.17. Calcd.: $[M]^+$ $m/z = 3802.11$. Found: MALDI-TOF: $[M + Ag]^+ = 3901$. Anal. Calcd for $C_{209}H_{234}O_{66}$: C, 66.02; H, 6.20. Found: C, 66.02; H, 6.39.

[G-3]-$(OH)_{24}$ (8). [G-3]-(O_2Bn)$_{12}$ (**7**) (942 mg, 248 μmol) in 20 mL of CH_2Cl_2 diluted with 20 mL of methanol and 50 mg Pd/C (10%) were used for the deprotection to afford **8** as a white glass: 637 mg, (94%). IR (cm^{-1}, thin film from THF): 3424 (br), 1732 (s). ^1H NMR (500 MHz, DMSO-d_6): δ 0.99 (s, 36), 1.19 (s, 18), 1.37 (s, 9), 2.15 (s, 3), 3.42 (m, 24), 4.14 (m, 24), 4.35 (dd, 12, $J = 26.5$, 11), 4.65 (t, 24, $J = 5.5$), 7.05 (d, 6, $J = 9$), 7.12 (d, 6, $J = 9$). ^{13}C NMR (500 MHz, DMSO-d_6): δ 16.75, 17.03, 17.22, 46.42, 46.60, 50.33, 63.73, 64.60, 65.89, 121.05, 129.49, 146.24, 148.35, 170.98, 171.95, 174.13. Calcd.: $[M]^+$ $m/z = 2744.81$. Found: TOFMS-ES: $[M + Na]^+ = 2767.30$, $[M + Na]^{2+} = 1395.23$. Anal. Calcd for $C_{125}H_{186}O_{66}$: C, 54.70; H, 6.83. Found: C, 54.68; H, 7.02.

[G-4]-(O_2Bn)$_{24}$ (9). Compound 9 was prepared as above using [G-3]-$(OH)_{24}$ (**8**) (443 mg, 161 μmol), 157 mg (1.29 mmol) of DMAP, 3 mL of dry pyridine, and diluting with 6 mL of CH_2Cl_2, followed by the addition of 2.20 g (5.0 mmol) of anhydride **2**. Following the reaction, **9** was purified by precipitation into 200 mL of hexane under vigorous stirring. After decantation, the precipitate was redissolved in CH_2Cl_2 and evaporated to give **7** as a white glass: 1150 mg, (93%). IR (cm^{-1}, thin film from $CHCl_3$): 3047, 1741 (s). ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (s, 72), 1.01 (s, 18), 1.17 (s, 36), 1.25 (s, 9), 2.06 (s, 3), 3.52 (d, 48, $J = 10.8$), 4.07 (m, 24), 4.32 (m, 60), 4.52 (d, 48, $J = 11.4$), 5.35 (s, 24), 6.92 (d, 6, $J = 8.4$), 7.07 (d, 6, $J = 8.7$), 7.26 (m, 72), 7.36 (m, 48). ^{13}C NMR (500 MHz, $CDCl_3$): δ 17.24, 17.44, 17.63, 17.66, 42.51, 46.49, 46.82, 46.85, 65.01, 65.27, 65.60, 73.36, 73.41, 101.58, 120.77, 126.17, 128.09, 128.82, 137.86, 146.36, 148.55, 170.71, 171.44, 171.85, 173.17. Calcd.: $[M]^+$ $m/z = 7646.22$. Found: MALDI -TOF $[M + Ag]^+ = 7742$. Anal. Calcd for $C_{413}H_{474}O_{138}$: C, 64.88; H, 6.25. Found: C, 65.05; H, 6.40.

[G-4]-$(OH)_{48}$ (10). Debenzylation of [G-4]-(O_2Bn)$_{12}$ (**9**) (760 mg, 99 μmol) was carried out as above to give **10** as a white glass: 522 mg, (95%). IR (cm^{-1}, thin film from THF): 3439 (br), 1736 (s). ^1H NMR (500 MHz, DMSO-d_6): δ 0.97 (s, 72), 1.12 (s, 36), 1.18 (s, 18), 1.35 (s, 9), 2.14 (s, 3), 3.44 (m, 48), 4.08 (m, 48), 4.22 (m, 24), 4.36 (dd, 12, $J = 24.5$, 10.0), 4.63 (t, 48, $J = 5.5$), 7.05 (d, 6, $J = 8.0$), 7.12

(d, 6, $J = 7.5$). ^{13}C NMR (500 MHz, DMSO-d_6): δ 16.73, 16.97, 17.18, 46.27, 46.56, 50.26, 63.69, 64.37, 65.28, 65.56, 121.02, 129.48, 146.25, 148.29, 170.80, 171.49, 171.88, 174.08. Calcd.: $[M]^+$ $m/z = 5531.61$. Found: TOFMS-ES: $[M + Na]^+ = 5553.58$, $[M + Na]^{2+} = 2788.54$, $[M + Na]^{3+} = 1866.94$. Anal. Calcd for $C_{245}H_{378}O_{138}$: C, 53.20; H, 6.89. Found: C, 53.06; H, 7.06.

[G-5]-(O_2Bn)$_{48}$ (11). Generation growth for [G-4]-(OH)$_{48}$ (**10**) (391 mg, 71 μmol) was carried out as above to afford **12** as a white glass (after purification by precipitation): 972 mg, (90%). IR (cm^{-1}, thin film from $CHCl_3$): 3050, 1738 (s). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.83 (s, 144), 1.00 (s, 36), 1.15 (s, 90), 1.34 (s, 9), 2.01 (s, 3), 3.49 (d, 96, $J = 10.5$), 4.06 (m, 60), 4.31 (m, 120), 4.49 (d, 96, $J = 10.5$), 5.32 (s, 48), 6.95 (d, 6, $J = 7$), 7.06 (d, 6, $J = 7$), 7.24 (m, 144), 7.36 (m, 96). ^{13}C NMR (500 MHz, $CDCl_3$): δ 17.25, 17.47, 17.60, 17.65, 42.47, 46.41, 46.48, 46.76, 47.00, 51.72, 64.93, 73.29, 73.34, 101.52, 120.81, 126.18, 128.07, 128.80, 137.93, 146.37, 148.65, 170.65, 171.41, 171.83, 173.15. Calcd.: $[M]^+$ $m/z = 15\,334.29$. Found: MALDI-TOFMS: $[M + Ag]^+ = 15\,518$. Anal. Calcd for $C_{821}H_{954}O_{282}$: C, 64.31; H, 6.27. Found: C, 63.12; H, 6.24.

[G-5]-(OH)$_{96}$ (12). Deprotection of [G-5]-(O_2Bn)$_{48}$ (**11**) (300 mg, 19 μmol) as above afforded **12** as a white glass: 200 mg, (92%). IR (cm^{-1}, thin film from THF): 3419 (br), 1734 (s). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.97 (s, 144), 1.13 (s, 108), 1.21 (s, 18), 1.35 (s, 9), 2.11 (s, 3), 3.40 (m, 192), 4.05 (m, 180), 4.56 (m, 96), 7.04 (d, 6, $J = 7$), 7.10 (d, 6, $J = 7$). ^{13}C NMR (500 MHz, DMSO-d_6): δ 16.80, 17.05, 17.29, 46.23, 46.28, 50.29, 63.74, 64.00, 64.35, 65.04, 121.13, 129.52, 146.34, 148.39, 170.79, 171.50, 171.95, 174.15. Calcd.: $[M]^+$ $m/z = 11\,105.07$. Found: TOFMS-ES: $[M + Na]^{2+} = 5571.71$, $[M + Na]^{3+} = 3724.09$, $[M + Na]^{+4} = 2799.73$. Anal. Calcd for $C_{485}H_{762}O_{282}$: C, 52.45; H, 6.92. Found: C, 51.42; H, 6.94.

[G-6]-(O_2Bn)$_{96}$ (13). Reaction of [G-5]-(OH)$_{96}$ (**12**) (402 mg, 36 μmol) and 132 mg (1.1 mmol) DMAP with 1.85 g (4.3 mmol) of anhydride **2**, followed by quenching the excess anhydride, extracting, and precipitating, afforded **13** as a white glass: 800 mg, (92%). IR (cm^{-1}, thin film from $CHCl_3$): 3051, 1741 (s). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.79 (s, 288), 0.99 (s, 72), 1.12 (s, 144), 1.23 (s, 18), 1.36 (s, 9), 1.92 (s, 3), 3.42 (d, 192, $J = 10.5$), 4.05 (m, 132), 4.28 (m, 240), 4.44 (d, 192, $J = 10.5$), 5.28 (s, 96), 6.93 (d, 6, $J = 7$), 7.00 (d, 6, $J = 7$), 7.23 (m, 288), 7.34 (m, 192). ^{13}C NMR (500 MHz, $CDCl_3$): δ 17.25, 17.54, 17.64, 42.41, 46.34, 46.69, 64.81, 73.22, 101.41, 126.20, 128.04, 128.76, 138.00, 171.43, 171.81, 173.12. Calcd.: $[M]^+$ $m/z = 30\,710.56$. Found: MALDI-TOFMS: $[M + Ag]^+ = 30\,783$. Anal. Calcd for $C_{1637}H_{1914}O_{570}$: C, 64.02; H, 6.28. Found: C, 63.86; H, 6.13.

Preparation of the First Generation Benzylidene-Protected PEG-mono[G-1]-(O_2Bn) (14). The PEG monomethyl ether (Mn = 5500, PDI = 1.03; 10.00 g, 2.0 mmol, 1 equiv) was dissolved in 30 mL of CH_2Cl_2, anhydride **2** (1.71 g, 4.0 mmol, 2.0 equiv), and DMAP (0.10 g, 0.8 mmol, 0.4 equiv) was added. After stirring the reaction mixture for 6 h at room temperature, 5 mL of MeOH was added to quench the excess anhydride. After stirring for 5 h, the product was precipitated into 1 L of diethyl ether. The precipitate was filtered through a glass filter to afford 9.89 g of product as a white powder (95%). IR (cm^{-1}, thin film from $CHCl_3$): 2888, 1737, 1125. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05 (s, 3), 3.38 (s, 3), 3.42 (m, 3), 3.61 (bs, ~600), 3.87 (t, 4, $J = 4.8$), 4.36 (t, 2, $J = 4.8$), 4.66 (d, 2, $J = 11.4$), 5.44 (s, 1), 7.32 (m, 3), 7.42 (m, 2). ^{13}C NMR (500 MHz, $CDCl_3$): δ. 17.85, 42.38, 58.87, 63.67, 64.15, 69.00, 70.50, 71.87, 73.45, 101.69, 126.14, 128.12, 128.89, 137.81, 173.87. Calcd.: $[M]^+$ $m/z = 5705$. Found: MALDI-TOFMS: $[M]^+ = 5694$. PDI = 1.03. Anal. for **14**: Found: C, 53.41; H, 8.76.

PEG-mono[G-1]-(OH)$_2$ (15). Polymer **14** (3.79 g, 0.73 mmol) was dissolved in 25 mL of a 1:2 mixture of CH_2Cl_2 and MeOH, and the catalyst (Pd/C 10%, 0.04 g) was added to the reaction mixture, followed by evacuation of the system. The reaction mixture was stirred vigorously for 6 h at room temperature under H_2 atmosphere. After removal of the catalyst by filtration, the product was precipitated in 500 mL of diethyl ether, affording 3.57 g of a white powder (95%). IR (cm^{-1}, thin film from $CHCl_3$): 3476, 2893, 1726, 1129. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (s, 3), 3.37 (s, 3), 3.63 (bs, ~600), 4.33 (t, 2, $J = 4.8$). ^{13}C NMR (500 MHz, $CDCl_3$): δ 16.97, 49.49, 56.68, 58.83, 63.16, 63.53, 67.11, 68.59, 70.35, 71.72, 84.02, 175.44. Calcd.: $[M]^+$ $m/z = 5,617$. Found: MALDI-TOFMS: $[M]^+ = 5610$. PDI = 1.03. Anal. for **15**: Found: C, 53.86; H, 9.08.

PEG-mono[G-2]-(O_2Bn)$_2$ (16). This was prepared as above using **15** (8.00, 1.5 mmol, 1.0 equiv), 18 mL of CH_2Cl_2, **2** (5.32 g, 12.5 mmol, 8.0 equiv), and DMAP (0.30 g, 2.5 mmol, 1.6 equiv) 15 h at room temperature, followed by quenching with 5 mL of MeOH with 7 h of stirring. Precipitation of the reaction mixture into 1,L of diethyl ether afforded 7.82 g of product as a white powder (91%). IR (cm^{-1}, thin film from $CHCl_3$): 2888, 1737, 1096. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.95 (s, 6), 1.26 (s, 3), 3.36 (s, 3), 3.63 (bs, ~600), 3.79 (s, 4), 3.87 (t, 2, $J = 4.8$), 4.12 (t, 2, $J = 4.8$), 4.39 (s, 4), 4.58 (d, 4, $J = 11.4$), 5.41 (s, 2), 7.32 (m, 6), 7.39 (m, 4). ^{13}C NMR (500 MHz, $CDCl_3$): δ. 17.68, 42.51, 46.70, 58.97, 64.15, 65.43, 68.62, 70.50, 71.86, 73.38, 101.63, 126.10, 128.04, 128.78, 137.74, 172.54, 173.16. Calcd.: $[M]^+$ $m/z = 6025$. Found: MALDI-TOFMS: $[M]^+ = 6020$. PDI = 1.03. Anal. for **16**: Found: C, 55.10; H, 8.90.

PEG-mono[G-2]-(OH)$_4$ (17). Polymer **16** (3.08 g, 0.56 mmol) was deprotected as described above using 15 mL of 1:2 CH_2Cl_2:MeOH and 0.3 g of Pd/C catalyst for 10 h at room temperature under H_2 atmosphere. After filtration and precipitation in 500 mL of diethyl ether, 2.76 g of **17** was obtained as a white powder (93%). IR (cm^{-1}, thin film from $CHCl_3$): 3464, 2904, 1735, 1154. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (s, 6), 1.31 (s, 3), 3.37 (s, 3), 3.46 (m, 4), 3.64 (bs, ~600), 3.81 (t, 8, $J = 5.2$), 4.31 (m, 4), 4.40 (d, 2, $J = 10.8$). ^{13}C NMR (500 MHz, $CDCl_3$): δ. 17.08, 17.96, 46.40, 49.70, 58.95, 63.64, 64.33, 64.84, 67.39, 68.79, 70.47, 71.84, 84.15, 172.97, 174.97. Calcd.: $[M]^+$ $m/z = 5849$. Found: MALDI-TOFMS: $[M]^+ = 5848$. PDI = 1.03. Anal. for **17**: Found: C, 55.51; H, 9.07.

PEG-mono[G-3]-(O_2Bn)$_4$ (18). This was prepared as above with **17** (5.58 g, 1.0 mmol, 1 equiv), 30 mL of CH_2Cl_2, anhydride **2** (8.6 g, 20.20 mmol, 20 equiv), and DMAP (0.25 g, 2 mmol, 2 equiv) stirred for 18 h at room temperature. Following quenching with 5 mL of MeOH for 8 h, the product was precipitated into 1 L of diethyl ether, affording 5.68 g of product as a white powder (91%). IR (cm^{-1}, thin film from $CHCl_3$): 2886, 1739, 1106. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (s, 12), 1.04 (s, 3), 1.20 (s, 6), 3.38 (s, 3), 3.46 (m, 4), 3.64 (bs, ~600), 3.81 (t, 3, $J = 4.8$), 4.06 (q, 4, $J = 5.2$), 4.17 (t, 2, $J = 4.8$), 4.34 (m, 8), 4.56 (d, 8, $J = 11.6$), 5.40 (s, 4), 7.30 (m, 12), 7.38 (m, 8). ^{13}C NMR (400 MHz, $CDCl_3$): δ 17.18, 17.57, 17.61, 42.30, 46.34, 46.80, 58.94, 64.15, 65.06, 65.75, 70.49, 71.85, 73.35, 73.43, 101.95, 126.08, 128.02, 128.75, 137.75, 171.79, 172.01, 173.11. Calcd.: $[M]^+$ $m/z = 6665$. Found: MALDI-TOFMS: $[M]^+ = 6678$. PDI = 1.03. Anal. for **18**: Found: C, 56.00; H, 8.44.

PEG-mono[G-3]-(OH)$_8$ (19). Deprotection of **18** (2.14 g, 0.35 mmol) in 10 mL of 1:2 CH_2Cl_2:MeOH with Pd/C (10%, 0.2 g) for 15 h at room temperature under a H2 atmosphere followed by filtration and precipitation in 500 mL of diethyl ether afforded 1.84 g of **19** as a white powder (91%). IR (cm^{-1}, thin film from $CHCl_3$): 3455, 2885, 1737, 1106. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.01 (s, 12), 1.16 (s, 6), 1.19 (s, 3), 3.24 (s, 3), 3.51 (bs, ~600), 3.66 (s, 4), 3.74 (t, 3, $J = 4.8$), 4.16 (m, 16), 4.63 (t, 8, $J = 5.4$). ^{13}C NMR (400 MHz, DMSO-d_6): δ 16.68, 16.97, 17.08, 46.09, 46.30, 50.24, 58.02, 63.65, 64.06, 64.47, 68.00, 69.57, 69.77, 71.37, 171.80, 171.98, 174.03. Calcd.: $[M]^+$ $m/z = 6313$. Found: MALDI-TOFMS: $[M]^+ = 6302$. PDI = 1.03. Anal. for **19**: Found: C, 55.79; H, 8.75.

PEG-mono[G-4]-(O_2Bn)$_8$ (20). This was prepared as above using **19** (2.63 g, 0.45 mmol, 1 equiv) in 25 mL of CH_2Cl_2, anhydride **2** (6.14 g, 14.40 mmol, 32 equiv) and DMAP (0.35 g, 2.9 mmol, 6.4 equiv) with stirring for 18 h at room temperature. After quenching with 5 mL of MeOH (7 h), the product was precipitated into 1 L of diethyl ether, affording 2.97 g of **20** as a white powder (89%). IR (cm^{-1}, thin film from $CHCl_3$): 2873, 1741, 1117. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (s, 24), 1.01 (s, 6), 1.14 (s, 3), 1.19 (s, 12), 3.38 (s, 3), 3.62 (bs, ~600), 3.88 (t, 2, $J = 4.8$), 4.05 (s, 6), 4.15 (m, 6), 4.33 (m, 16), 4.55 (d, 16, $J = 11.7$), 5.38 (s, 8), 7.29 (m, 24), 7.38 (m, 16). ^{13}C NMR (400 MHz, $CDCl_3$): δ 17.10, 17.24, 17.58, 24.45, 46.42, 46.76, 58.92, 64.17, 64.97, 65.34, 66.04, 70.48, 71.84, 73.32, 73.38, 101.55, 126.08, 128.00, 128.73, 137.78, 171.30, 171.76, 173.07. Calcd.: $[M]^+$ $m/z = 7945$. Found: MALDI-TOFMS: $[M]^+ = 7950$. PDI = 1.03. Anal. for **20**: Found: C, 56.94; H, 8.19.

PEG-mono[G-4]-(OH)$_{16}$ (21). Compound **20** (1.21 g, 0.16 mmol) in 12 mL of 1:2 CH_2Cl_2/MeOH was deprotected as described above to 0.90 g of **21** as a white powder (83%). IR (cm^{-1}, thin film from $CHCl_3$): 3447, 2886, 1736, 1127. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.00 (s, 24), 1.16 (s, 12), 1.18 (s, 6), 1.21 (s, 3), 3.24 (s, 3), 3.51 (bs, ~600), 3.72 (t, 3, J = 4.8), 4.15 (m, 30), 4.63 (t, 16, J = 5.4). ^{13}C NMR (400 MHz, DMSO-d_6): δ 16.68, 16.83, 17.10, 46.19, 46.24, 50.21, 58.02, 63.64, 64.36, 69.77, 71.26, 171.35, 171.80, 174.01. Calcd.: [M]$^+$ m/z = 7241. Found: MALDI-TOFMS: [M]$^+$ = 7240. PDI = 1.03. Anal. for **21**: Found: C, 54.34; H, 8.46.

Preparation of the First Generation Benzylidene-Protected Telechelic PEG-bis[G-1]-(O$_2$Bn) (22). The telechelic PEG diol (M_n = 10 604 Da, PDI = 1.03; 10.00 g, 0.91 mmol, 1 equiv) dissolved in 25 mL of CH_2Cl_2 was treated with anhydride **2** (2.40 g, 5.5 mmol, 6 equiv) and DMAP (0.67 g, 0.55 mmol, 0.6 equiv). After stirring the reaction mixture for 6 h at room temperature, 5 mL of MeOH was added to quench the excess of anhydride. The mixture was stirred for 5 h, and the product was precipitated directly from the reaction mixture into 1 L of diethyl ether to afford 9.86 g of product as a white powder (95%). IR (cm^{-1}, thin film from $CHCl_3$): 2891, 1737, 1146. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.04 (s, 6), 3.40 (t, 6, J = 5.0), 3.63 (bs, ~1100), 3.87 (t, 6, J = 5.0), 4.35 (t, 4, J = 5.0), 4.66 (d, 4, J = 11.4), 5.44 (s, 2), 7.32 (m, 6), 7.41 (m, 4). ^{13}C NMR (500 MHz, $CDCl_3$): δ 17.80, 42.34, 56.78, 63.63, 64.11, 68.96, 70.46, 73.40, 101.65, 126.10, 128.07, 128.85, 137.77, 173.82. Calcd.: [M]$^+$ m/z = 11 014. Found: MALDI-TOFMS: [M]$^+$ = 11 032. PDI = 1.03. Anal. for **22**: Found: C, 54.65; H, 8.82.

Removal of the Protecting Groups: Preparation of Telechelic PEG-bis[G-1]-(OH)$_2$ (23). The protecting groups at both ends of **22** (7.95 g, 0.7 mmol) dissolved in 40 mL of 1:2 CH_2Cl_2:MeOH were removed as described above (Pd/C 10%, 0.2 g, 8 h at room temperature under H_2). After precipitation in 1 L of diethyl ether, 7.36 g of **23** were obtained as a white powder (94%). IR (cm^{-1}, thin film from $CHCl_3$): 3479, 2889, 1728, 1148. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (s, 6), 3.64 (bs, ~1100), 4.33 (t, 4, J = 5.0). ^{13}C NMR (500 MHz, $CDCl_3$): δ 17.02, 49.52, 56.60, 63.34, 63.44, 66.64, 68.65, 70.17, 83.94, 175.45. Calcd.: [M]$^+$ m/z = 10 838. Found: MALDI-TOFMS: [M]$^+$ = 10 838. PDI = 1.03. Anal. for **23**: Found: C, 53.16; H, 8.27.

Telechelic PEG-bis[G-2]-(O$_2$Bn)$_2$ (24). Generation growth was carried out as above using **23** (12.19 g, 1.1 mmol, 1 equiv) in 40 mL of CH_2Cl_2 anhydride **2** (7.44 g, 17.4 mmol, 16 equiv) and DMAP (0.43 g, 3.5 mmol, 3.2 equiv). Yield: 11.74 g of white powder (89%). IR (cm^{-1}, thin film from $CHCl_3$): 2887, 1738, 1097. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (s, 12), 1.26 (s, 6), 3.64 (bs, ~1100), 3.81 (t, 4, J = 4.8), 4.13 (t, 4, J = 4.8), 4.39 (s, 8), 4.59 (d, 8, J = 11.6), 5.42 (s, 4), 7.40 (m, 12), 7.47 (m, 8). ^{13}C NMR (500 MHz, $CDCl_3$): δ 17.55, 17.58, 42.41, 46.60, 58.86, 63.57, 64.05, 65.32, 68.52, 70.40, 71.76, 73.28, 73.37, 83.96, 101.52, 126.01, 127.94, 128.68, 137.65, 172.44, 173.06. Calcd.: [M]$^+$ m/z = 11 654. Found: MALDI-TOFMS: [M]$^+$ = 11 631. PDI = 1.03. Anal. for **24**: Found: C, 54.70; H, 8.46.

Telechelic PEG-bis[G-2]-(OH)$_4$ (25). Deprotection of **24** (11.45 g, 0.95 mmol) in 70 mL of (1:2) CH_2Cl_2:MeOH was carried out as above for 16 h at room temperature under H_2 atmosphere. Yield: 10.27, white powder (92%). IR (cm^{-1}, thin film from $CHCl_3$): 3466, 2886, 1730, 1147. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.07 (s, 12), 1.31 (s, 6), 3.26 (m, 8), 3.40 (t, 6, J = 4.8), 3.64 (bs, ~1100), 4.32 (m, 8), 4.40 (d, 4, J = 11.1). ^{13}C NMR (500 MHz, $CDCl_3$): δ 17.04, 17.92, 46.35, 49.67, 56.75, 63.60, 64.28, 64.79, 67.27, 68.74, 70.42, 84.10, 172.93, 174.89. Calcd.: [M]$^+$ m/z = 11 302. Found: MALDI-TOFMS: [M]$^+$ = 11 292. PDI = 1.03. Anal. for **25**: Found: C, 53.31; H, 8.39.

Telechelic PEG-bis[G-3]-(O$_2$Bn)$_4$ (26). Generation growth was carried out as described above with **25** (8.02 g, 0.7 mmol, 1 equiv) in 60 mL of CH_2Cl_2, anhydride **2** (9.36 g, 22 mmol, 32 equiv) and DMAP (0.54 g, 4.4 mmol, 6.4 equiv) for 15 h at room temperature. Yield 8.44 g, white powder (92%). IR (cm^{-1}, thin film from $CHCl_3$): 2894, 1741, 1128. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (s, 24), 1.04 (s, 6), 1.20 (s, 12), 3.46 (t, 6, J = 4.8), 3.64 (bs, ~1100), 3.81 (t, 3, J = 4.8), 4.08 (q, 6, J = 5.8), 4.28 (t, 3, J = 4.8), 4.34 (m, 16), 4.56 (d, 16, J = 11.6), 5.40 (s, 8), 7.30 (m, 24), 7.39 (m, 16). ^{13}C NMR (400 MHz, $CDCl_3$): δ 17.07, 17.46, 17.50, 42.36, 46.23, 46.68, 64.04, 64.94, 65.61, 68.48, 70.37, 73.23, 73.31, 101.46, 125.97, 127.90, 128.62, 137.66, 171.67, 171.90, 172.98. Calcd.: [M]$^+$ m/z = 12 934. Found: MALDI-TOFMS: [M]$^+$ = 12 946. PDI = 1.03. Anal. for **26**: Found: C, 56.06; H, 8.33.

Telechelic PEG-bis[G-3]-(OH)$_8$ (27). Deprotection of **26** (8.10 g, 0.61 mmol) in 45 mL of 1:2 CH_2Cl_2:MeOH, for 18 h at room temperature under H_2 atmosphere afforded 6.82 g of a white powder (89%). IR (cm^{-1}, thin film from $CHCl_3$): 3461, 2886, 1735, 1104. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.07 (s, 24), 1.29 (s, 6), 1.30 (s, 12), 3.28 (t, 5, J = 5.8), 3.35 (t, 5, J = 5.8), 3.50 (t, 6, J = 5.8), 3.64 (bs, ~1100), 3.78 (m, 25), 4.30 (m, 20), 4.36 (dd, 10, J = 11.0, 5.0). ^{13}C NMR (500 MHz, DMSO-d_6): δ 16.71, 16.99, 17.10, 46.11, 46.32, 50.26, 62.96, 63.65, 64.09, 64.50, 65.70, 68.02, 69.78, 76.61, 83.46, 171.83, 172.01, 174.06. Calcd.: [M]$^+$ m/z = 12 230. Found: MALDI-TOFMS: [M]$^+$ = 12 229. PDI = 1.03. Anal. for **27**: Found: C, 53.38; H, 8.19.

Telechelic PEG-bis[G-4]-(O$_2$Bn)$_8$ (28). Generation growth was carried out as above using **27** (4.61 g, 0.37 mmol, 1 equiv) in 50 mL of CH_2Cl_2, anhydride **2** (9.96 g, 23.3 mmol, 64 equiv), and DMAP (0.57 g, 4.6 mmol, 13 equiv), for 18 h at room temperature. After precipitation in diethyl ether, 5.01 g of product was obtained as a white powder (86%). IR (cm^{-1}, thin film from $CHCl_3$): 2885, 1741, 1105. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (s, 48), 1.01 (s, 12), 1.14 (s, 6), 1.19 (s, 24), 3.40 (t, 10, J = 5.8), 3.64 (bs, ~1100), 3.80 (s, 5), 3.87 (t, 3, J = 5.8), 4.04 (s, 12), 4.13 (m, 12), 4.33 (dd, 32, J = 11.7, 5.0), 4.54 (d, 32, 11.4), 5.38 (s, 16), 7.29 (m, 48), 7.38 (m, 32). ^{13}C NMR (400 MHz, $CDCl_3$): δ 17.15, 17.63, 42.50, 46.42, 46.45, 46.79, 63.68, 64.22, 64.99, 65.35, 66.07, 70.51, 73.37, 73.43, 101.60, 126.13, 128.06, 128.79, 137.81, 171.34, 171.81, 173.12. Calcd.: [M]$^+$ m/z = 15 494. Found: MALDI-TOFMS: [M]$^+$ = 15 510. PDI = 1.03. Anal. for **28**: Found: C, 57.08; H, 7.91.

Telechelic PEG-bis[G-4]-(OH)$_{16}$ (29). Deprotection of **28** (4.50 g, 0.28 mmol) as above afforded 3.26 g of a white powder (80%). IR (cm^{-1}, thin film from $CHCl_3$): 3454, 2883, 1738, 1107. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.00 (s, 48), 1.16 (s, 24), 1.17 (s, 12), 1.21 (s, 6), 3.27 (t, 8, J = 5.8), 3.64 (bs, ~1100), 3.66 (s, 16), 3.74 (t, 12, J = 5.0), 4.15 (m, 68), 4.63 (t, 32, J = 5.4). ^{13}C NMR (500 MHz, DMSO-d_6): δ 16.71, 16.86, 17.14, 46.21, 46.27, 50.24, 62.98, 63.64, 64.14, 64.37, 65.33, 66.11, 68.01, 69.80, 76.62, 171.39, 171.83, 174.05. Calcd.: [M]$^+$ m/z = 14 086. Found: MALDI-TOFMS: [M]$^+$ = 14 090. PDI = 1.03. Anal. for **29**: Found: C, 52.79; H, 7.70.

Preparation of the First Generation Benzylidene-Protected Four-Arm Star PEG-tetra[G-1]-(O$_2$Bn) (30). The 4-arm PEG star (M_n = 20 330 Da, PDI = 1.10; 10.00 g, 0.50 mmol, 1 equiv) dissolved in 30 mL of CH_2Cl_2 was treated with anhydride **2** (1.71 g, 4.0 mmol, 8 equiv) and DMAP (0.10 g, 0.8 mmol, 1.6 equiv), and the mixture was stirred for 15 h at room temperature. After quenching the excess anhydride with 5 mL of MeOH and stirring for 7 h, the product was precipitated directly from the reaction mixture into 1 L of diethyl ether. The precipitate was filtered through a glass filter, affording 10.02 g of product as a white powder (96%). IR (cm^{-1}, thin film from $CHCl_3$): 2884, 1736, 1106. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.03 (s, 12), 3.39 (m, 20), 3.62 (bs,), 3.77 (s, 22), 3.86 (t, 14, J = 4.5), 4.34 (t, 8, J = 4.8), 4.65 (d, 8, J = 10.5), 5.43 (s, 4), 7.31 (m, 12), 7.40 (m, 8). ^{13}C NMR (500 MHz, $CDCl_3$): δ 17.85, 42.39, 64.16, 69.01, 70.50, 73.45, 101.70, 126.15, 128.13, 128.90, 137.81, 173.88. Calcd.: [M]$^+$ m/z = 21 150. Found: MALDI-TOFMS: [M]$^+$ = 21 139. PDI = 1.10. Anal. for **30**: Found: C, 54.42; H, 8.71.

Deprotection of 30, Preparation of Four-Arm PEG-tetra[G-1]-(OH)$_2$ (31). Removal of the benzylidene groups of **30** (10.40 g, 0.5 mmol) dissolved in 60 mL of 1:2 CH_2Cl_2:MeOH was achieved using Pd/C (10%, 0.25 g) for 18 h at room temperature under H_2 atmosphere. The catalyst was removed from the reaction mixture by filtration using a glass filter. The product was precipitated in 1 L of diethyl ether, affording 10.02 g of a white powder (98%). IR (cm^{-1}, thin film from $CHCl_3$): 3477, 2885, 1733, 1104. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.11 (s, 12), 3.06 (t, 10, J = 4.5), 3.41 (s, 10), 3.46 (t, 10, J = 4.0), 3.64 (bs, ~2100), 3.80 (m, 18), 4.34 (t, 8, J = 4.8). ^{13}C NMR (500 MHz, $CDCl_3$): δ 17.01, 45.20, 49.52, 63.23, 63.60, 67.21, 68.63, 70.24, 80.10, 175.50. Calcd.: [M]$^+$ m/z = 20 798. Found: MALDI-TOFMS: [M]$^+$ = 20 812. PDI = 1.11. Anal. for **31**: Found: C, 54.28; H, 8.61.

Four-Arm PEG-tetra[G-2]-(O$_2$Bn)$_2$ (32). Generation growth of **31** (6.78 g, 0.33 mmol, 1 equiv) was carried out as above with anhydride

2 (5.65 g, 13.2 mmol, 40 equiv) and DMAP (0.16 g, 1.3 mmol, 4 equiv) for 16 h at room temperature. Yield: 7.01 g, white powder (96%). IR (cm^{-1}, thin film from $CHCl_3$): 2887, 1739, 1130. ^1H NMR (300 MHz, $CDCl_3$): δ 0.95 (s, 24), 1.26 (s, 12), 3.63 (bs, ~2100), 3.79 (m, 20), 3.87 (m, 8), 4.13 (t, 6, $J = 4.8$), 4.39 (s, 16), 4.58 (d, 16, $J = 11.7$), 5.41 (s, 8), 7.30 (m, 24), 7.38 (m, 16). ^{13}C NMR (500 MHz, $CDCl_3$): δ 17.50, 17.53, 42.36, 45.30, 46.55, 56.65, 63.55, 64.01, 65.27, 68.47, 70.35, 73.23, 73.31, 84.10, 101.47, 125.96, 127.89, 128.63, 137.61, 172.39, 173.01. Calcd.: $[M]^+$ m/z = 22 430. Found: MALDI-TOFMS: $[M]^+ = 22\,397$. PDI = 1.11. Anal. for **32**: Found: C, 55.17; H, 8.48.

Four-Arm PEG-tetra[G-2]-$(OH)_4$ (33). Deprotection of **32** (3.35 g, 0.15 mmol) in 16 mL of (1:2) CH_2Cl_2/MeOH afforded 3.09 g of a white powder (95%). IR (cm^{-1}, thin film from $CHCl_3$): 3462, 2883, 1734, 1107. ^1H NMR (300 MHz, $CDCl_3$): δ 1.07 (s, 24), 1.31 (s, 12), 3.38 (m, 20), 3.64 (bs, ~2100), 3.83 (s, 32), 3.87 (m, 16), 4.30 (m, 16), 4.40 (d, 8, $J = 11.1$). ^{13}C NMR (400 MHz, $CDCl_3$): δ 17.10, 17.95, 46.43, 49.74, 64.34, 64.88, 67.39, 68.81, 70.56, 172.98, 174.98. Calcd.: $[M]^+$ $m/z = 21\,726$. Found: MALDI-TOFMS: $[M]^+ = 21\,728$. PDI = 1.11. Anal. for **33**: Found: C, 53.54; H, 8.67.

Four-Arm PEG-tetra[G-3]-$(O_2Bn)_4$ (34). Generation growth of **33** (2.93 g, 0.14 mmol, 1 equiv) in 30 mL of CH_2Cl_2 was carried out as above using anhydride **2** (4.67 g, 11 mmol, 80 equiv) and DMAP (0.13 g, 1.1 mmol, 8 equiv) to afford 3.10 g of product as a white powder (92%). IR (cm^{-1}, thin film from $CHCl_3$): 2885, 1741, 1126. ^1H NMR (400 MHz, $CDCl_3$): δ 0.92 (s, 48), 1.04 (s, 12), 1.20 (s, 24), 3.63 (bs, ~2100), 4.07 (m, 8), 4.18 (s, 4), 4.34 (s, 32), 4.55 (d, 32, $J = 11.7$), 5.40 (s, 16), 7.29 (m, 48), 7.38 (m, 32). ^{13}C NMR (400 MHz, $CDCl_3$): δ 17.23, 17.62, 17.66, 42.52, 46.40, 46.85, 64.19, 65.11, 65.80, 70.53, 73.41, 73.48, 101.65, 126.14, 128.07, 128.79, 137.81, 171.85, 173.14. Calcd.: $[M]^+$ $m/z = 24\,490$. Found: MALDI-TOFMS: $[M]^+ = 24\,984$. PDI = 1.11. Anal. for **34**: Found: C, 55.53; H, 8.18.

Four-Arm PEG-tetra[G-3]-$(OH)_8$ (35). Deprotection of **34** (2.87 g, 0.12 mmol) afforded 2.10 g of a white powder (78%). IR (cm^{-1}, thin film from $CHCl_3$): 3455, 2885, 1737, 1124. ^1H NMR (400 MHz, DMSO-d_6): δ 1.01 (s, 48), 1.16 (s, 24), 1.19 (s, 12), 3.51 (bs, ~2100), 4.14 (m, 54), 4.63 (t, 32, $J = 5.4$)). ^{13}C NMR (400 MHz, DMSO-d_6): δ 16.68, 16.95, 17.08, 46.09, 46.30, 50.24, 63.65, 64.47, 69.77, 171.81, 171.98, 174.03. Calcd.: $[M]^+$ m/z = 23 582. Found: MALDI-TOFMS: $[M]^+ = 23\,582$. PDI = 1.16. Anal. for **35**: Found: C, 53.59; H, 8.44.

Four-Arm PEG-tetra[G-4]-$(O_2Bn)_8$ (36). Generation growth of **35** (1.94 g, 0.08 mmol, 1 equiv) dissolved in 25 mL of CH_2Cl_2 was carried out as above using anhydride **2** (4.53 g, 10.6 mmol, 128 equiv) and DMAP (0.13 g, 1.1 mmol, 12.8 equiv) with stirring for 18 h at room temperature. After quenching and precipitation into 500 mL of diethyl ether, 1.73 g of product was obtained as a white powder (70%). IR (cm^{-1}, thin film from $CHCl_3$): 2883, 1741, 1126. ^1H NMR (300 MHz, $CDCl_3$): δ 0.90 (s, 96), 1.01 (s, 24), 1.14 (s, 12), 1.19 (s, 48), 3.64 (bs, ~2100), 3.87 (t, 8, $J = 5.1$), 4.04 (s, 28), 4.14 (m, 22), 4.34 (dd, 64, $J = 15.2, 3.3$), 4.54 (d, 64, $J = 11.4$), 5.38 (s, 32), 7.29 (m, 96), 7.38 (m, 64). ^{13}C NMR (500 MHz, $CDCl_3$): δ 17.13, 17.61, 42.48, 46.40, 46.43, 46.77, 64.97, 65.34, 66.06, 70.27, 70.50, 73.35, 73.41, 101.58, 126.11, 128.05, 128.78, 137.79, 171.33, 171.80, 173.11. Calcd.: $[M]^+$ $m/z = 30\,110$. Found: MALDI-TOFMS: $[M]^+ = 30\,094$. PDI = 1.08. Anal. for **36**: Found: C, 56.95; H, 8.02.

Four-Arm PEG-tetra[G-4]-$(OH)_{16}$ (37). Deprotection of **36** (1.54 g, 0.05 mmol) as above followed by precipitation in 500 mL of diethyl ether afforded 1.19 g of a white powder (85%). IR (cm^{-1}, thin film from $CHCl_3$): 3456, 2883, 1737, 1108. ^1H NMR (300 MHz, DMSO-d_6): δ 1.01 (s, 96), 1.16 (s, 48), 1.17 (s, 24), 1.21 (s, 12), 3.50 (bs, ~2100), 3.74 (t, 12, $J = 5.1$), 4.14 (m, 116), 4.63 (t, 64, $J = 5.4$). ^{13}C NMR (500 MHz, DMSO-d_6): δ 17.07, 17.38, 17.49, 17.87, 46.51, 46.53, 46.65, 49.93, 64.74, 66.21, 70.49, 172.44, 174.94. Calcd.: $[M]^+$ $m/z = 27\,294$. Found: MALDI-TOFMS: $[M]^+ = 27\,280$. PDI = 1.10. Anal. for **37**: Found: C, 54.19; H, 8.20.

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