Dumbbell-shaped dendrimers — Synthesis and self-assembly¹

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Abstract: We report on the synthesis and detailed characterization of dendrimers that evolve symmetrically from a linear core of 2-butyne-1,4-diol with 3,5-dihydroxybenzyl alcohol based dendron arms. The divergent layer-by-layer buildup of the dumbbell-shaped dendrimers is based on simple acid–base hydrolytic chemistry of bis(dimethylamino)dimethylsilane with OH-terminated molecules. The self-assembly of these dendrimers in THF and water is significantly influenced by their generation number, the backbone structure, and the solvent.

Key words: dendrimers, divergent synthesis, macromolecules, self-assembly

Résumé : On a effectué la synthèse et une caractérisation totale de dendrimères qui radient à partir d'un noyau linéaire de but-2-yne-1,4-diol avec des ramifications à base d'alcool 3,5-dihydroxybenzylique. La synthèse divergente, faite couche par couche, des dendrimères en forme d'haltère court est basée sur une chimie d'hydrolyse acide–base simple de bis(diméthylamino)diméthylsilanes dans lesquels les molécules se terminent par des groupes OH. L'autoassemblage de ces dendrimères dans un mélange de THF et d'eau est fortement influencé par le nombre de générations, la structure du squelette, et le solvant.

Mots-clés : dendrimères, synthèse divergente, macromolécules, autoassemblage.

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Introduction

Hyperbranched and monodisperse macromolecules that are commonly referred to as dendrimers are becoming increasingly important in designing smart and efficient nanomaterials for a variety of applications in medicine, catalysis, and electronics (1). A significant effort in the design and syntheses of these globular architectures has been invested, which has led to inside-out (divergent) or outside-in (convergent) methodologies (2). Changing the central core leads to many structural variations and novel types of morphologies in the resulting dendrimers (3). We have been investigating the role of the core, backbone, and linking units in the evolving morphology of the dendrimers, and have established a simple and efficient divergent route to the syntheses of such dendritic macromolecules (4), based on the acid-base hydrolytic chemistry of amino-silanes and -stannanes with organic acids (5). We were intrigued by the possibility of developing hyperbranched structures using symmetric growth on either side of a bifunctional linear core, giving rise to dumbbell-

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Dedicated to Professor Robert H. Marchessault for his contributions to Science in general and to Macromolecular Chemistry in particular.

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shaped dendrimers. The synthetic elaboration and detailed investigation of the properties of dumbbell-shaped dendrimers have been much less explored than those of globular dendrimers (6). We report herein a route to the synthesis of dumbbell-shaped dendrimers that are constructed from the bifunctional core 2-butyne-1,4-diol using 3.5dihydroxybenzyl alcohol (DHBA) as wedges. The synthetic elaboration is based on the controlled addition of bis(dimethylamino)dimethylsilane (Me₂Si(NMe₂)₂) to the bifunctional core, followed by the addition of DHBA. The process is then repeated with Me₂Si(NMe₂)₂) and DHBA in sequence, with amine as the only by-product, and the purification of dendrimers can be easily achieved by simple extraction into deuterium oxide. Self-organization of dendrimers by means of suitable peripheral groups continues to be an area of much significance and provides opportunities for designing nanomaterials for molecular encapsulation and delivery (4, 7, 8). The dumbbell-shaped dendrimers reported here have suitably placed OH groups for interdendrimer interactions, and we have examined their self-assembly through such interactions in THF and water, using UV-vis spectroscopy and transmission electron microscopy. In THF, generations 1-3 require a higher critical aggregation concentration (cac) to form aggregates than does generation 4. Because of the open structure in the lower generations, the linear core inhibits selfassembly, whereas in generation 4, the more globular architecture with more prominent hydrogen bonding sites facilitates self-assembly at lower concentrations.

Results and discussion

Dendrimers were synthesized using a quantitative acidbase hydrolytic reaction of aminosilanes with molecules con-

Scheme 1.



taining terminal OH groups (5). The choice of the linear core around which dendrons are built was based on rigidity, solubility, and commercial availability, and 2- butyne-1,4-diol was considered to be an ideal candidate for developing the desired dendrimers. The dendron backbone was chosen to be 3,5-dihydroxybenzyl alcohol because it has been successfully employed in our laboratory in the past to synthesize globular dendritic architectures (4). For synthesizing the first generation dendrimer, 1 molar equivalent of 2-butyne-1,4 diol was added dropwise over a period of 2 h to an ice-bath-cooled solution of 2 equivalents of bis(dimethylamino)dimethylsilane in THF. The solution was stirred at ice-bath temperature for an additional six hours, and then left to warm to room temperature. The solution was transferred to an addition funnel, and added slowly to a solution of 2 equivalents of DHBA in THF, and stirred overnight. After removal of the solvent in vacuo, the product was extracted into deuterium oxide (D₂O). The solution was filtered and D₂O was then removed under vacuum, to afford a light pink powder **1**. Continuation of this methodology by carrying out reactions under controlled conditions led to the synthesis of dendrimers **2–4** in very good yields. Dendrimers were characterized using a combination of

Fig. 1. (A) UV-vis absorption spectra of dendrimer 1 at concentrations of 1 to 10 mg/mL in THF and (B) plot of absorbance vs concentration of dendrimer 1 in THF at 340 nm.



¹H and ¹³C{¹H} NMR, matrix-assisted laser desorption/ionization time of flight (MALDI-TOF), and FT-IR spectroscopies, and elemental analyses. These data confirmed the identity of the dendrimers as shown in Scheme **1**.

Self-assembly of dendrimers via intermolecular interactions between peripheral groups is a topic of current interest (7, 8), and we have also investigated the aggregation behaviour of globular DHBA based dendrimers in solution and at interfaces (4). We were intrigued by the self-assembly behaviour of dendrimers in which the linear core as well as the evolving shape of the dendrimers could influence their association. In addition, dendrimers 1-4 contain peripheral hydroxyl groups that increase in number exponentially from 4 to 32, and are expected to contribute to enhanced interdendrimer interactions as the generation number increases.

The aggregation behaviour of dendrimers was first investigated using UV-vis spectroscopy at concentrations of 1 to 10 mg/mL in THF. The dendrimers generally depicted three peaks around 240, 260, and 290 nm at 1 mg/mL (Fig. 1A), which become broad as the concentrations were increased and the solutions become turbid. The cac for each generation was calculated by plotting the intensity of scattered light at a given wavelength against concentration (Fig. 1B), and it was found to be 4.9 mg/mL for dendrimers 1-3. The latter is much higher than the globular DHBA based dendrimers of generations 1-3, which was calculated to be 3.7 mg/mL (4g). This suggests that the more open structure of dendrimers, constructed around the linear core, allows more freedom for these molecules. In addition, the central core in these open structures might participate in packing via π - π interactions, and these competing interactions might create an association-dissociation equilibrium which will delay aggregation.

The dendrimer 4 showed a *cac* of 4.1 mg/mL, which was quite comparable to the DHBA based dendrimers, suggesting clearly that the structure was becoming more globular at generation 4. The aggregation of dendrimers through participation of terminal OH groups in hydrogen bonding was also confirmed by FT-IR that showed a broad peak at approximately 3300 cm⁻¹ for the terminal OH groups. The latter clearly suggested that terminal OH groups in these dendrimers are strongly hydrogen-bonded at concentrations above *cac*; below this concentration, a peak at around 3500 cm⁻¹ is commonly observed, which is indicative of the absence of hydrogen bonds.

Transmission electron microscopy is a useful technique for examining the self-assembly of macromolecules, and can provide essential information related to the morphology of the resulting aggregates (9). We first studied the aggregation behaviour of dendrimers 1–4 in THF at concentrations of 4 and 8 mg/mL (concentrations below and above *cac*). At 4 mg/mL, a general globular morphology for the aggregates (Fig. 2) was observed for dendrimers 1-4. The particle size distribution in these aggregates showed that, whereas the size distribution for dendrimer 1 aggregates was found to range between 30 and 135 nm (Fig. 2A), dumbbell dendrimers 2-4 formed mostly small aggregates of 5 to 25 nm in size, below cac (Figs. 2B-2D). The largest aggregates for those from generation 4, for example, were 55 nm in size. This type of behavior has also been observed earlier (10), and can be explained by considering that, generally, dendrimers of lower generations have a more open structure. This facilitates their interaction with other dendrimers.

When the concentration was increased to 8 mg/mL in THF, it was observed that the globular shape of dumbbell dendrimers **1–4** was generally retained. However, there were quite significant differences in particle size distribution of the aggregates from those at 4 mg/mL. For example, dendrimer **1** formed a larger number of smaller aggregates, in the range of 5 to 15 nm in size (Fig. 3). This can be explained by considering that at much higher concentrations, large aggregates can collapse, yielding small-size clusters.

We also studied the aggregation of these dendrimers in a more polar solvent at a concentration of 4 mg/mL and found that aggregation behaviour changed significantly with the change in the solvent from THF to water. The dumbbell-shaped dendrimers possess a hydrophobic interior with polar OH groups at the periphery. In lower generations, there may be hydrophobic-hydrophilic repulsion between dendrimers that enhances their coagulation in water. Water will also compete with interdendritic hydrogen bonding, and it is expected that much smaller aggregates will emerge. The transmission electron microscopy (TEM) study confirmed these expectations, and the effects were quite evident especially in generations 1 and 2 of dendrimers 1 and 2, which seem to avoid any contact with water, and yield random assemblies of various confirmations (Fig. 4). In addition, the size of these aggregate assemblies was much smaller than in THF at 4 mg/mol.

Self-assembly of dendrimers **3** and **4** in water was found to be quite different from that of first and second generation dendrimers. It suggested that small aggregates of 5 to 25 nm are first formed, which then assemble into larger clusters of 55 to 75 nm size (Fig. 4D). This is in agreement with the obFig. 2. Transmission electron micrographs and particle-size distributions of dendrimers (A) 1, (B) 2, (C) 3, and (D) 4 in THF at 4 mg/mL



servation that generation 3 and 4 dendrimers will start to adopt a more globular structure, and there will be much less contact of the hydrophobic interior with hydrophilic exterior (water), thereby reducing repulsion.

Conclusions

Symmetric growth of DHBA based dendrons on a linear core has been successfully carried out to construct dumbbell-

shaped dendrimers of generations 1–4. These dendrimers evolve from a very open structure in lower generations to a more globular architecture in higher generations. Molecular self-assembly of these dendrimers is influenced by their backbone structure, as indicated by much higher critical aggregation concentration for generations 1–3 in THF, compared to that for globular dendrimer counterparts, and for generation 4. The influence of the solvent in their self-assembly was examined using THF and water; in lower generations, the inability



Fig. 3. Transmission electron micrographs and particle-size distributions of dendrimers (A) 1, (B) 2, (C) 3, and (D) 4 in THF at 8 mg/mL.

of the more polar solvent to interact with dendrimer backbones leads to aggregates that are formed by minimizing the repulsive forces. In higher generations, the major interaction of the solvent with the dendrimer is at the periphery which has a higher concentration of polar OH groups, and it does not interfere significantly with their ability to self-associate. The influence of the solvent in controlling morphology and sizes of dendrimer aggregates is of interest, as it allows one to tailor their properties for molecular encapsulation and release.

Experimental

Materials and Measurements

2-butyne-1,4-diol (Sigma-Aldrich), 3,5-dihydroxybenzyl alcohol (Sigma-Aldrich), and bis(dimethylamino)dimethylsilane (Gelest) were used as received. All manipulations were performed under a nitrogen atmosphere using either standard Schlenk line techniques or an Innovative Technology (Braun) Labmaster MB-150-M dry box. All solvents were stored unFig. 4. Transmission electron micrographs and particle-size distributions of dendrimers (A) 1, (B) 2, (C) 3, and (D) 4 in H₂O at 4 mg/mL.



der nitrogen and used after distillation over sodium-benzophenone. NMR spectra were measured on a 270 MHz JEOL spectrometer at ambient temperature. The samples were prepared inside the dry box using deuterated solvents (Cambridge Isotope laboratories, Inc.), and the chemical shifts in ppm are reported relative to tetramethylsilane as an internal standard for ¹H and ¹³C spectra. Mass spectra were obtained on a Hewlett Packard 5973 mass spectrometer and MALDI-TOF spectra on a Kratos Kompact Maldi 3.v.4.0.0 spectrometer using LiBr–dithranol as the matrix. Elemental analyses were performed by Laboratoire d'Analyse Elementaire de l'Université de Montréal. Infrared spectra were measured on a Bruker IFS-48 Fourier transform infrared spectrometer using a standard resolution of 4 cm⁻¹ for transmission. UV–vis spectra were recorded in water on a Hewlett Packard 8453 with a resolution of 2 nm. TEM measurements were carried out on a JEOL 2000FX microscope operating at an acceleration voltage of 80 kV.

First generation dendrimer (1)

A solution of 2-butyne-1,4-diol (0.200 g, 2.32 mmol) dissolved in 5 mL of dry THF was added dropwise to a solution of 2 equiv. of bis(dimethylamino)dimethylsilane (0.852 mL, 4.65 mmol) in 5 mL of dry THF cooled to 0°C. Stirring at ice bath temperature was maintained for an additional 6 h, and the resulting solution was subsequently warmed to room temperature. The solution was then added dropwise to a solution of 2 equiv. of DHBA (0.651 g, 4.65 mmol) in 10 ml of dry THF. The resulting solution was stirred overnight, and the THF was then removed under vacuum to afford a sticky gel. D₂O (2-3 mL) was added to the gel and was stirred for 5-10 minutes. The solution was filtered and the D₂O was then removed under vacuum to afford a light pink powder (778 mg, 70%). ¹H NMR (270 MHz, D_2O-d_2 , ppm) & 0.05 (s, 12H, OSiMe₂O), 4.11 (s, 4H, OCH₂C), 4.36 (s, 4H, C₆H₃-CH₂O), 6.18 (s, 2H, C₆H₂ para), 6.30 (t, 4H, C₆ H_2 ortho).¹³C NMR (68 MHz, D₂O- \tilde{d}_2) & -1.7, -0.7 (SiCH₃), 49.7 (OCH₂C), 63.6 (C₆H₃-CH₂), 83.6 (OCH₂C), 101.9, 106.4, 143.8, 157.1 (C₆H₃). FT-IR (KBr, cm⁻¹): 3243 (v_{OH}), 2896 (v_{C-H arom}), 1242 (δ_{si-CH3}), 1041 (v_{si-O}). EI-MS *m*/*z*: 479.1 (expected: 478.6). Anal. calcd. for C₂₂H₃₀O₈Si₂: C 55.21, H 6.32; found: C 55.36, H 5.96.

Second generation dendrimer (2)

A solution of 1 equiv. of 2-butyne-1,4-diol (50 mg, 0.581 mmol) in 10 mL of THF was added to a solution of 2 equiv. of bis(dimethylamino)dimethylsilane (0.213 mL, 1.161 mmol) in 5 mL of THF, and stirred for 6 h at ice bath temperature. The resulting solution was added dropwise over a period of 1h to 2 equiv. of DHBA (163 mg, 1.161 mmol) dissolved in 10 mL of THF. After stirring overnight, the mixture was then added dropwise (1h) to a solution of 4 equiv. of bis(dimethylamino)dimethylsilane (0.426 mL, 2.323 mmol) in 5 mL of THF. The resulting solution was added dropwise (1h) to 4 equiv. of DHBA (325 mg, 2.323 mmol) dissolved in 15 mL of THF, and stirred overnight. The removal of the solvent under vacuum afforded a sticky gel. D₂O (4-5 mL) was added to the gel and stirred for 5-10 minutes. The solution was filtered and the D₂O was then removed under vacuum to afford a light pink powder (455 mg, 62%). ¹H NMR (270 MHz, D_2O-d_2) & 0.05 (m, 36H, OSiMe₂O), 4.15 (s, 4H, OCH₂C), 4.36 (s, 12H, C₆H₃- CH_2O), 6.18 (s, 6H, C_6H para), 6.30 (m, 12H, C_6H_2 ortho). ¹³C NMR (68 MHz, D₂O-d₂, ppm) & -1.7, -0.1 (SiCH₃), 50.3 (OCH₂C), 64.3 (C₆H₃-CH₂), 83.6 (OCH₂C), 102.6, 107.0, 144.5, 157.8 (C_6H_3). FT-IR (KBr, cm⁻¹): 3378 (v_{OH}), 2962 (v_{C-H arom.}), 1262 (δ_{Si-CH3}), 1084, 890 (v_{Si-O}). MALDI-TOF m/z: 1261.3 (expected 1263.7, including m/z Li⁺). Anal. calcd. for C₅₈H₇₈O₂₀Si₆: C 55.11, H 6.22; found: C 55.95, H 6.26.

Third generation dendrimer (3)

A similar procedure as described above for the second generation was used to prepare the third generation. A solution of 1 equiv. of 2-butyne-1,4-diol (20 mg, 0.232 mmol) in 10 mL of THF was added to a solution 2 equiv. of bis(dimethylamino)dimethylsilane (0.085 mL, 0.465 mmol) in 5 ml THF, and stirred for 6 h at ice bath temperature. The mixture was added dropwise (1h) to a solution of 2 equiv. of DHBA (65.1 mg, 0.465 mmol) in 10 mL of THF, and stirred overnight at room temperature. It was then added dropwise

(1h) to а solution of 4 equiv. of bis(dimethylamino)dimethylsilane (0.170 mL, 0.929 mmol) in 5 mL of THF, and stirred overnight at room temperature. The solution was added dropwise (1h) to a solution of 4 equiv. of DHBA (130 mg, 0.929 mmol) in 10 mL of THF, and after stirring overnight, it was added dropwise (1h) to a solution of 8 equiv. of bis(dimethylamino)dimethylsilane (0.341 mL, 1.858 mmol) in 5 mL of THF, and stirred for 14 h. Finally it was added to a solution of 8 equiv. of DHBA (260 mg, 1.858 mmol) in 15 mL of THF, and stirred overnight. THF was removed under vacuum to afford a gel. D₂O (4–5 mL) was added to the gel and stirred for 5–10 minutes. The solution was filtered and the D₂O was then removed under vacuum to afford a light pink powder (402 mg, 61%). ¹H NMR (270 MHz, D_2O-d_2) & 0.01, 0.05 (m, 84H, $OSiMe_2O$), 4.10 (s, 4H, OCH₂C), 4.34 (s, 28H, C₆H₃-CH₂O), 6.18 (s, 14H, C_6H para), 6.30 (m, 28H, C_6H_2 ortho). ¹³C NMR (68 MHz, D₂O-d₂, ppm) & -1.7, -0.77 (SiCH₃), 49.6 (OCH₂C), 63.6 (C₆H₃-CH₂), 83.5 (OCH₂C), 101.8, 106.3, 143.7, 157.0 (C_6H_3). FT-IR (KBr, cm⁻¹): 3378 (v_{OH}), 2892 $(v_{C-H arom.})$, 1154 (δ_{Si-CH3}), 1042, 954 (v_{Si-O}). MALDI-TOF m/z: 2837.9 (expected 2833.9, including m/z Li⁺). Anal. calcd. for C₁₃₀H₁₇₄O₄₄Si₁₄: C 55.10, H 6.19; found: C 55.12, H 6.38.

Fourth generation dendrimer (4)

A solution of 1 equiv. of 2-butyne-1,4-diol (20 mg, 0.232 mmol) in 10 mL of THF, was added to a solution 2 equiv. of bis(dimethylamino)dimethylsilane (0.085 mL, 0.465 mmol) in 5 ml THF, and stirred for 6 h at ice bath temperature. The mixture was added dropwise (1h) to a solution of 2 equiv. of DHBA (65.1 mg, 0.465 mmol) in 10 mL of THF, and stirred overnight at room temperature. It was then added dropwise (1h) to a solution of 4 equiv. of bis(dimethylamino)dimethylsilane (0.170 mL, 0.929 mmol) in 5 mL of THF, and stirred overnight at room temperature. The latter was added dropwise (1h) to a solution of 4 equiv. of DHBA (130 mg, 0.929 mmol) in 10 mL of THF, and after stirring overnight, it was added dropwise (1h) to a solution of 8 equiv. of bis(dimethylamino)dimethylsilane (0.341 mL, 1.858 mmol) in 5 mL of THF, and stirred for 14 h. Then it was added to a solution of 8 equiv. of DHBA (260 mg, 1.858 mmol) in 15 mL of THF, and stirred overnight. The resulting solution was added dropwise to 16 equiv. of bis(dimethylamino)dimethylsilane (0.681 mL, 3.717 mmol) in 10 mL of THF. Stirring was continued overnight at room temperature. The resulting solution was then added dropwise (1h) to a solution of 16 equiv. of DHBA (521 mg, 3.717 mmol) in 10 mL of THF. The reaction mixture was stirred for 36 h at room temperature. Solvent removal under vacuum afforded a sticky gel. D₂O (4-5 mL) was added to the gel and was stirred for 5-10 minutes. The solution was filtered and D₂O was then removed under vacuum to afford a pink powder (833 mg, 60%). ¹H NMR (270MHz, D₂O-d₂) & -0.06, 0.00, 0.22 (m, 180H, OSiMe₂O), 4.10 (s, 4H, OCH_2C), 4.31 (s, 60H, C_6H_3 - CH_2O), 6.15 (s, 30H, C_6H para), 6.25 (m, 60H, C_6H_2 ortho). ¹³C NMR (68 MHz, D_2O d₂, ppm) & -1.54, -1.033, 0.40 (SiCH₃), 49.5 (OCH₂C), 63.9 $(C_6H_3-CH_2)$, 83.7 (OCH₂C), 100.5, 105.9, 143.1, 158.8 $(C_{6}H_{3})$. FT-IR (KBr, cm⁻¹): 3379 (v_{OH}), 2889 (v_{C-H arom}), 1263 ($\delta_{\text{Si-CH3}}$), 1042, 970 ($v_{\text{Si-O}}$). MALDI-TOF *m/z*: 5978.8

(expected: 5974.3, including m/z Li⁺). Anal. calcd. for $C_{274}H_{366}O_{92}Si_{30}$: C 55.14, H 6.18; found: C 55.26, H 6.31.

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