Highly Branched Dendritic Macromolecules with Core Polyhedral Silsesquioxane Functionalities

Bo Hong,* Travis P. S. Thoms, Hunter J. Murfee, and Michael J. Lebrun

Department of Chemistry, University of California, Irvine, California 92697-2025

Received August 14, 1997

Polyhedral silsesquioxanes are well-known molecules that have recently attracted widespread attention as molecular building blocks in the synthesis of various molecular systems and materials, such as ceramic materials and liquid crystalline supramolecular systems. Recently cuboid octasilsesquioxane has also been incorporated in the synthesis of electroactive ferrocenyl-substituted organosilicon dendritic supramolecular systems.[1i] However, the incorporation of silsesquioxanes as cores in dendrimers, highly branched functionalized molecules formed by iterative reaction sequences,[2−4] has not been much explored.[1h−i] We report here the use of a phosphine-substituted polyhedral octasilsesquioxane, $Si_8O_{12}(CH_2CH_2PPh_2)_8$ ([G0]-$Si_8O_{12}P_8$, Figure 1), as a core for building new types of dendritic macromolecules. A total of eight monodendrons can be connected to the octasilsesquioxane center, giving a rapid growth of molecular weight. Different generations of preformed monodendrons can be used to give a controlled growth of molecular weight. In addition, on the external surface of these dendrimers there are terminal 2,2′:6′,2′′-terpyridine (tpy) units, which may allow easy access to the incorporation of multiple active metal centers. In this communication we report the synthesis and characterization of this interesting new type of molecular architecture with a cuboid center. Specifically, electrospray mass spectral analysis (ESI/MS) and $^{31}P\{^1H\}$ NMR spectroscopy are used to study the homogeneity and to establish the purity of this series of dendrimers.

Our approach to the preparation of macromolecules with encapsulated silsesquioxanes and terminal tpy groups began with a convergent synthesis of monodendrons with tpy units, Figure 2. Monodendron tpy_1-[G1]-Br can be prepared according to the literature method.[6] Treatment of tpy_1-[G1]-Br (2 equiv) with 3,5-dihydroxybenzyl alcohol (step i) affords the second-generation monodendron, tpy_2-[G2]-OH. Further bromination with CBr_4/PPh_3 (step ii) gives tpy_2-[G2]-Br. Typically, the reaction yields are in the range 70−80%.

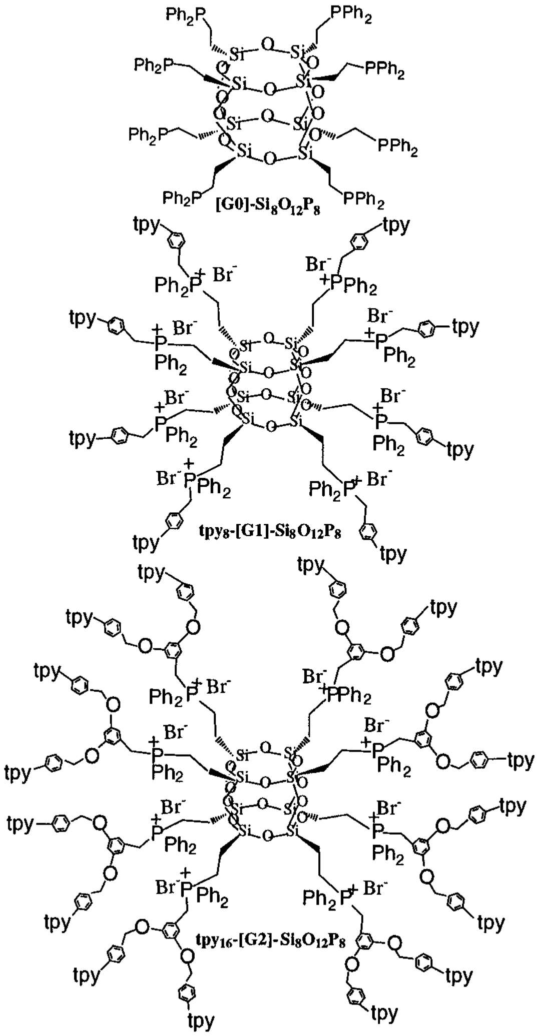

Figure 1. G0, G1, and G2 dendrimers with encapsulated cuboid octasilsesquioxane centers.

All monodendrons have been fully characterized using ^1H and ^{13}C NMR and fast atom bombardment mass spectral (FAB/MS) analysis. Upon conversion from benzylic alcohol to benzylic bromide, the ^1H NMR signal of the benzylic $-CH_2$ groups changes from 4.65 ppm in the former to 4.44 ppm in the latter. Correspondingly, ^{13}C NMR signal of the benzylic $-CH_2$ also changes from 65.11 ppm to 29.72 ppm after the bromination at the focal point. FAB/MS analysis affords clear identification of molecular ion peaks for all monodendrons.[5]

Dendrimers have been prepared by divergently attaching tpy-substituted monodendrons around the periphery of a cuboid silsesquioxane, $Si_8O_{12}(CH_2CH_2PPh_2)_8$.[7] Typically, the coupling reaction is carried out using 1 equiv of this octaphosphine to

---

* To whom the correspondence should be addressed.

[1] (a) Feher, F. J.; Budzichowski, T. A.; Weller, K. J. *J. Am. Chem. Soc.* **1989**, *111*, 7288−7289. (b) Feher, F. J.; Budzichowski, T. A. *Polyhedron*, **1995**, *14*, 3239−3253. (c) Day, V. W.; Klemperer, W. G.; Mainz, V. V.; Millar, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 8262−8264. (d) Agaskar, P. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1024−1026. (e) Yuchs, S. E.; Carrado, K. A. *Inorg. Chem.* **1996**, *35*, 261−262. (f) Mehl, G. H.; Goodby, J. W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2641−2643. (g) Morán, M.; Casado, C. M.; Cuadrado, I.; Losada, J. *Organometallics* **1993**, *12*, 4327−4333. (h) Bassindale, A. R.; Gentle, T. J. *Organomet. Chem.* **1996**, *521*, 391−393. (i) Casado, C. M.; Cuadrodo, I.; Morán, M.; Alonso, B.; Lobete, F.; Losada, J. *Organometallics* **1995**, *14*, 2618−2620.

[2] (a) Steward, G. M.; Fox, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 4354. (b) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635−9644. (c) Gorman, C. B.; Parkhurst, B, L.; Su, W. Y.; Chen, K.-Y. *J. Am. Chem. Soc.* **1997**, *119*, 1141−1142. (d) Gitsov, I.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1996**, *118*, 3785−3786. (e) Miller, T. M.; Neenan, T. X.; Kwock, E. W.; Stein, S. M. *J. Am. Chem. Soc.* **1993**, *115*, 356−357.

[3] (a) Fréchet, J. M. J. *Science* **1994**, *263*, 1710−1715. (b) Tomalia, D. A.; Durst, H. D. *Top. Curr. Chem.* **1993**, *165*, 192−313.

[4] Newkome, G. R.; Moorefield, C. N.; Vögtle, F. Dendritic Molecules: Concepts, Syntheses, Properties; VCH: Weinheim, Germany, 1996.

[5] FAB/MS of monodendrons (with a 3-nitrobenzyl alcohol matrix) *m/z*: tpy_1-[G1]-Br, 401 (M^+); tpy_2-[G2]-OH, 783 (M^+); tpy_2-[G2]-Br, 847 (MH^+).

[6] Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; De Cola, L.; Flamigni, L.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 4230−4238.

[7] The synthesis of $Si_8O_{12}(CH_2CH_2PPh_2)_8$ is reported elsewhere: Feher, F. J.; Eklund, A. G.; Schwab, J. J.; Phillips, S. H. Manuscript in preparation for submission to *Appl. Organomet. Chem.*

S0020-1669(97)01034-3 CCC: $14.00

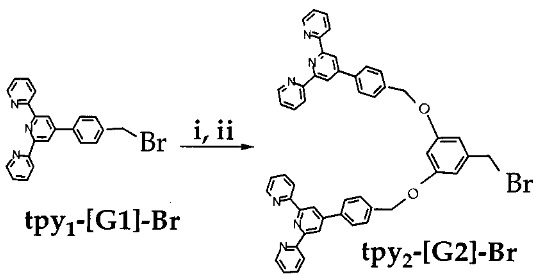

Figure 2. Reagents and conditions: (i) 3,5-dihydroxybenzyl alcohol, K_2CO_3, 18-crown-6, acetone, reflux 24 h; (ii) CBr_4/PPh_3, THF, 2 h.

react, in refluxing tetrahydrofuran for at least 24 h, with an excess amount (usually 9 equiv) of G1 or G2 monodendron with Br at the focal point. An excellent feature of these new dendrimers is that $^{31}P\{^1H\}$ NMR spectroscopy can be readily used to monitor the completion of reaction and also establish the purity of the dendrimers, since the coupling reaction produces phosphonium groups at the points of attachment between the monodendrons and the central core unit, Figure 1. Evidence for the complete transformation from phosphine to phosphonium is provided by the disappearance of the $^{31}P\{^1H\}$ NMR signal of free $-PPh_2$ at -9.37 ppm and the appearance of the $^{31}P\{^1H\}$ NMR signal of phosphonium at 30.99 ppm for tpy$_8$-[G1]-$Si_8O_{12}P_8$ and at 31.80 ppm for tpy$_{16}$-[G2]-$Si_8O_{12}P_8$. At shorter reaction time, an incomplete reaction between all $-PPh_2$ units and benzylic bromine is observed, as evidenced by the presence of a small signal at -9.37 ppm. A solution state $^{29}Si\{^1H\}$ NMR spectroscopic study has also been carried out. Signals at -67.9 and -69.0 ppm are found for tpy$_8$-[G1]-$Si_8O_{12}P_8$ and tpy$_{16}$-[G2]-$Si_8O_{12}P_8$, respectively. These signals, though slightly shifted, are identical to that found for $Si_8O_{12}(CH_2CH_2PPh_2)_8$, -67.1 ppm.[7]

We have incorporated electrospray ionization mass spectrometry (ESI/MS) in the characterization of dendrimers, bearing up to eight positive charges, with encapsulated silsesquioxane centers. ESI/MS, introduced by Fenn and co-workers,[8] has been shown to be a powerful technique in the analysis of multiply charged ions. Contrary to the conventional MS methods, which show many undesirable fragment ions in the MS spectra, ESI/MS often provides a simpler mass pattern and allows the accurate determination of molecular mass with high sensitivity.[9] Only recently has ESI/MS been used in the characterization of dendrimers, such as starburst dendrimers,[10] a polystyrene–poly(propylene imine) dendrimer block copolymer,[11] and a dendritic heptanuclear complex with Ru(II) centers.[9] To our best knowledge, our work here represents the first ESI/MS study of highly charged dendrimers, especially with silsesquioxane centers. Figure 3 shows a representative spectrum of tpy$_8$-[G1]-$Si_8O_{12}P_8$ (MW = 5337) with an inset of the resolution of the peak at *m/z* 1700.7 (isotope peaks separated by 0.3 *m/z* unit). Interestingly, the spectrum is dominated by five sets of peaks, all with $z = 3$. The assignment of peaks is relatively straightforward. The peaks at *m/z* 1700.7 and 1566.1 can be assigned to triply charged species $[M - 3Br]^{3+}$ and $[M - 3Br - (tpy{-}Ph{-}CH_2Br)]^{3+}$. The latter corresponds to the loss of one monodendron (tpy–Ph–CH_2Br) from the former. The third dominating peak at *m/z* 1504.3 corresponds to the fragment $[M - 3Br - (tpy{-}Ph{-}CH_2Br) - PPh_2]^{3+}$, which is the further loss of one PPh_2 unit from the fragment with *m/z* 1566.1. The fourth dominating peak, *m/z* 1370.2, is assigned to a triply charged fragment $[M - 3Br - (2tpy{-}2Ph{-}2CH_2Br) - PPh_2]^{3+}$. This corresponds to the loss of the second monodendron from the fragment with *m/z* 1504.3. The last dominating peak, *m/z* 1307.7, is assigned to the fragment $[M - 3Br - (tpy{-}Ph{-}CH_2Br) - 2PPh_2]^{3+}$, a loss of the second PPh_2 unit. Relative abundance of all other fragments in the full ESI/MS spectrum of tpy$_8$-[G1]-$Si_8O_{12}P_8$ are quite low (<10%). From the ESI/MS study, in correspondence to the aforementioned $^{31}P\{^1H\}$ NMR study, we can conclude that the deposition of monodendrons on the cuboid center is complete and no significant imperfection of the resulting dendrimer is observed.

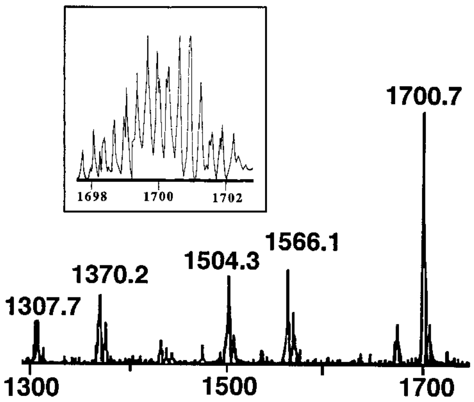

Figure 3. ESI/MS of tpy$_8$-[G1]-$Si_8O_{12}P_8$. Inset: resolution of the peak at *m/z* 1700.7.

All monodendrons and dendrimers with silsesquioxane centers are found to be soluble in $CHCl_3$ and CH_2Cl_2 and sparingly soluble in THF and acetone. Interestingly, the solubility of tpy$_8$-[G1]-$Si_8O_{12}P_8$ in organic solvents (THF specifically) is relatively lower than that of tpy$_{16}$-[G2]-$Si_8O_{12}P_8$. Presumably, when larger monodendrons are used to connect to the center, the hydrophilic cores are surrounded by a loose hydrophobic shell of dendritic wedges extending outward, resulting in the change in solubility.

In conclusion, we have reported a facile route to a novel type of inorganic/organic hybrid dendritic macromolecule with an encapsulated cuboid silsesquioxane. Higher generations of dendrimers can be further obtained using higher generations of preformed dendrons. The incorporation of the external terpyridine units will allow easy access to the introduction of various metal centers in the system. Indeed, the preparation of higher generations of dendrimers and the study of the metalated dendritic macromolecules are underway.

Acknowledgment. This work was supported by startup funds provided by UCI. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. B.H. acknowledges the UCI Faculty Career Development Program. We thank Professor Frank J. Feher for providing us the starting material $Si_8O_{12}(CH_2CH_2PPh_2)_8$ and for helpful discussions during the preparation of the paper. We also thank Dr. John Greaves for his assistance with the FAB/MS and ESI/MS measurements.

Supporting Information Available: Text giving full experimental details and a table listing spectroscopic data (2 pages). See any current masthead page for ordering information.

IC971034J

---

(8) (a) Yamashita, M.; Fenn, J. B. *J. Phys. Chem.* **1984**, *88*, 4451–4459. (b) Yamashita, M.; Fenn, J. B. *J. Phys. Chem.* **1984**, *88*, 4671–4675.

(9) Moucheron, C.; Mesmaeker, A. K.-D. *J. Am. Chem. Soc.* **1996**, *118*, 12834–12835.

(10) Schwarz, B. L.; Rockwood, A. L.; Smith, R. D.; Tomalia, D. A. *Rapid Commun. Mass Spectrom.* **1995**, *9*, 1552–1555.

(11) Van Hest, J. C. M.; Delnoye, D. A. P.; Baars, M. W. P. L.; Elissen-Román, C.; van Genderen, M. H. P.; Meijer, E. W. *Chem. Eur. J.* **1996**, *2*, 1616–1626.