

Preparation and Characterization of Nonpolar Fluorinated Carbosilane Dendrimers by APcI Mass Spectrometry and Small-Angle X-ray Scattering

Bamidele A. Omotowa,[#] Keith D. Keefer,[†] Robert L. Kirchmeier,[#] and Jean'ne M. Shreeve^{*,#}

Contribution from the Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343, and William R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352

Received August 5, 1999

Abstract: The following highly fluorinated nonpolar dendrimers were obtained in high yields from multiple hydrosilylation reactions between core hydride terminated carbosilane dendrimers and allyl-1,1-dihydrotri-fluoroethyl ether or allyl-1,1-dihydroheptadecafluorononyl ether through divergent synthetic routes: Si[CH₂-CH₂SiMe₂(CH₂CH₂CH₂OCH₂CF₃)₄] (7), Si{CH₂CH₂SiMe[CH₂CH₂SiMe(CH₂CH₂CH₂OCH₂CF₃)₂]₂}₄ (8), Si[CH₂CH₂Si(CH₂CH₂CH₂OCH₂C₈F₁₇)₃]₄ (9), Si[CH₂CH₂SiMe₂(CH₂CH₂CH₂OCH₂C₈F₁₇)₄] (10), and Si{CH₂-CH₂Si[CH₂CH₂Si(CH₂CH₂CH₂OCH₂C₈F₁₇)₃]₃}₄ (11). These compounds were characterized by elemental and spectroscopic analyses. Valuable mass spectral data were obtained by using atmospheric pressure chemical ionization (APcI). The fluorinated dendrimer molecule and the nonfluorinated core scatter X-ray light differently and present unique slopes on the Guinier Plot of data from small-angle X-ray light scattering (SAXS) in hexafluorobenzene. Glass transition temperatures (*T*_g) and thermogravimetric analyses (TGA) of the dendrimers were determined.

Introduction

Synthesis and characterization of carbosilane dendrimers terminating in polyfluoroalkyl ether units are significant since they are likely to find applications outside the laboratory. Hence, evaluation of alternative synthetic pathways to such compounds and methods of characterizing them and of determining their properties are of interest. Since the first report on cascade molecules by Vögtle et al. in 1978 and subsequent synthesis/characterization by Newkome¹ and Tomalia,¹ more than 1200 papers have been published on this subject.^{1,2} There are many review papers on this very interesting group of polymeric compounds, but the most recent ones are perhaps most comprehensive.^{1,3} Whereas Vögtle and Fischer reviewed the practical applications of these materials, Majoral and Caminade reviewed dendrimers with a focus on heteroatoms in the branching points of the core frame region.^{1,3} The review by Bosman et al. covered the structure, physical properties and applications of dendrimers and Newkome et al. summarized the novel properties of metallodendrimers in their latest review.¹

* Corresponding author: Tel.: (208) 885 6651, Fax: (208) 885 6198, e-mail: jshreeve@uidaho.edu.

[#] University of Idaho.

[†] Pacific Northwest Laboratory.

(1) (a) Majoral, J. P.; Caminade, A. M. *Chem. Rev.* **1999**, *99*, 845–880. (b) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665–1688. (c) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689–1746. (d) Newkome, G. R.; Yao, Z. -Q.; Baker, G. R.; Gupta, K. *J. Org. Chem.* **1985**, *50*, 2003–2004. (e) Tomalia, D. A., Baker, H.; Dewald, J. R., Hall, M.; Kallos, G.; Martins, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J. (Tokyo)* **1985**, *17*, 117–132 (f) Tomalia, D. A., Baker, H.; Dewald, J. R., Hall, M.; Kallos, G.; Martins, S.; Roeck, J.; Ryder, J.; Smith, P. *Macromolecules* **1986**, *19*, 2466–2468.

(2) Chemical Abstract electronic search line.

(3) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 884–905.

Despite the presence of about a dozen papers on fluorinated dendrimers in the literature, the reviews did not mention this subclass.^{4–14} Fluorination imparts some typical properties to dendrimers such as hydrophobicity and very good thermal stabilities.^{4,6,9,13} Fluorinated dendrimers were obtained by incorporation of fluorinated alkyl (or aryl) units into dendritic branches in order to obtain chiral dendrimers.^{4,6,11} Based on results from atomic force microscopy (AFM) micromachining studies, a fluorinated dendrimer performed as a lubricating material superior to the nonfluorinated analogue.⁵ A few amphiphilic fluorinated dendrimers were synthesized, their surfactant properties were evaluated,^{8,12,13} and at least one group

(4) Stark, B.; Steuhn, B.; Frey, H.; Lorenz, K.; Frick, B. *Macromolecules* **1998**, *31*, 5415–5423.

(5) Klug, C.; Kowalewski, T.; Schaefer, J.; Straw, T.; Tasaki, K.; Wooley, K. *Polym. Mater. Sci. Eng.* **1998**, *77*, 99–100.

(6) Grieveldinger, G.; Seebach, D. *Polym. Mater. Sci. Eng.* **1997**, *77*, 134–135.

(7) Michalczyk, M. J.; Sharp, K. G. U.S. Patent 96-663834 19960614 (to E. I. Du Pont De Nemours and Co., U.S.A.), 1997.

(8) Chapman, T. M.; Mahan, E. J. *Polym. Mater. Sci. Eng.* **1995**, *73*, 275–276.

(9) Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018–1025.

(10) Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1991**, *32*, 599–600.

(11) Lorenz, K.; Frey, H.; Stuhn, B.; Mulhaupt, R. *Macromolecules* **1997**, *30*, 6860–6868.

(12) Cooper, A. I.; Londono, J. D.; Wignall, G.; McClain, J. B.; Samulski, E. T.; Lin, J. S.; Dobrynin, A.; Rubinstein, M.; Burke, A. L. C.; Frechet, J. M. J.; DeSimone, J. M. *Nature* **1997**, *389*, 368–370.

(13) Yu, D.; Frechet, J. M. J. *Polymer Preprints* **1998**, *39*, 633.

(14) (a) Dagani, R. *C&EN News* **1999**, February 8, 33–36, and references therein. (b) Balogh, L.; Tomalia, D. A. *J. Am. Chem. Soc.* **1998**, *120*, 7355–7356. (c) Zhao, M., Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 4877–4878. (d) Zhao, M.; Crooks, R. M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 364–365.

has described their surfactant behavior in supercritical CO₂.¹² It thus appears that these fluorine-containing dendrimers have considerable potential application. Dendrimers containing polar groups in the core and terminating in perfluoroalkyl, perfluoroaryl, or perfluoropolyether units are generally very nonpolar and have been characterized solely by elemental analysis and ¹H, ¹³C, or ¹⁹F NMR spectral techniques. Molecular masses of fluorinated dendrimers containing heteroatoms in the polar functionality were determined by MALDI time-of-flight spectrometry. However, no mass spectral characterization of the nonpolar fluorinated dendrimers has been reported to date.

The only results obtained by X-ray and neutron scattering of carbosilane dendrimers terminating in perfluoroalkyl groups suggest that this technique has potential as an additional tool for monitoring the changes in the molecule when they act as surfactants.⁴ X-ray light scattering was used to study physical properties of a number of dendrimers, and the different models for analyzing them have produced a comprehensive background for evaluating the results of scattering experiments.¹⁵ It appears that the Sphere and Guinier models are more applicable than the Zimm plot analysis, despite its strong advantages, because the latter shows poor correlation with experimental deduction.⁶ Hence, evaluation of the response of other models for analysis of fluorinated dendrimers was considered worthwhile.

We report here the syntheses of dendrimers that terminate in polyfluoroalkyl ether groups from their hydride precursor via hydrosilylation. The dendrimer hydrides served only once earlier as substrate precursors for synthetic extensions¹⁶ and were useful for the synthesis of the compounds described in this paper. Interestingly, mass spectral characterizations were not reported for the few fluorinated dendrimers in the literature.^{1,13} It is difficult to generate ions for mass spectral studies by conventional methods, e.g., electrospray and MALDI-TOF, from the nonpolar polyfluoroalkyl ether dendrimers. Solvent ionization from a Corona electric discharge induces the nonpolar fluorinated dendrimers to ionize for mass spectral characterization by atmospheric pressure chemical ionization (APCI). This technique and small-angle X-ray scattering (SAXS) also were used to characterize the carbosilane dendrimers in this work.

Results and Discussion

The carbosilane dendrimers terminating in polyfluoroalkyl ethers (**7–11**) were synthesized by adding two different polyfluorinated ether olefins to dendrimers with multiple terminal hydride functionalities. Although nonfluorinated spacers are usually necessary to prevent expected interactions between silicon and vicinal fluorine atoms, our aim was to introduce as few methylene groups as possible. Researchers in this field have shown preference for dendrimers terminating in olefins (vinyl and allyl) as substrates for developing synthetic extensions through hydrometalation.¹¹ For example, it was convenient to couple a fluorinated alkanethiol to an allyl-terminal in the substrate dendrimer by hydrosulfurylation.¹¹ This is not a

convenient procedure for the synthesis of polyfluoroalkyl ethers because alcohols do not add to olefins in the same manner under mild conditions. Dendrimers terminating in silanes have been useful substrates in a few successful reactions.¹⁶ They were very appropriate for synthesis of compounds in this work.

Reactions of dendrimer silanes with Co₂(CO)₈ and (CH₂=CHC₅H₄)Fe(C₅H₅) have been utilized to produce the respective dendritic derivative ending in –Me₂SiCo(CO)₄ and –Me₂SiCH₂–CH₂C₅H₄)Fe(C₅H₅), respectively.¹⁶ It was possible to monitor the progress and/or completeness of transformation of Si–H bonds to Si–C bonds via hydrosilylation by using a combination of ¹H and ²⁹Si NMR spectra. The latter were particularly helpful. The ²⁹Si NMR signal typical of Si–H remains when conversion to Si–C is incomplete. Thus, progress of the synthesis of the desired dendrimers via reactions of fluoroalkyl ethers was readily monitored.

The synthesis of Si–H terminated carbosilane dendrimers is relatively straightforward.^{17,18} They are a relatively very stable class of organosilicon compounds that are not noticeably changed when handled in open air for short periods.¹⁷ Fully –SiH₃ and partially –Si(Me)H₂ and –Si(Me)₂H terminated hydrides of the first to the fourth generation dendritic carbosilanes can be synthesized, but there is concern for possible cleavage of the Si–H bonds when more drastic reaction conditions are employed to force complete coupling in higher (than second generation) dendrimers. Hence, only first- and second-generation dendrimers were used in this study, and evidence from NMR spectroscopy indicates that no cleavage or any other silyl coupling occurred. Another consideration was the anticipated poor solubility of the higher generation dendrimers as was reported for dendrimers ending in polyfluoroalkylthioethers.¹¹ Two first-generation carbosilane dendritic compounds ending in four (**1**) and 12 (**2**) hydrides and two second-generation analogues ending in 16 (**4**) and 36 (**3**) terminal hydrides were synthesized in this work based on literature procedures.^{17,18} The synthetic pathway for these compounds is shown in Schemes 1–3. Of these, only **4** is a new compound. All the dendrimer hydrides were characterized on the basis of NMR and mass spectral data.

The two polyfluoroalkyl ether olefins used in this work were obtained in high yields by metathetical reactions of the alkali metal derivative of the respective fluoroalkyl alcohol with allyl bromide (see Experimental Section). Allyl-1,1-dihydrotrifluoroethyl ether (**5**), bp = 49 °C and MS (EI) M⁺ = 140, is a low molecular weight species, and addition to terminal silyl hydride in substrate dendrimers **1** and **4** occurs to form **7** and **8**, respectively (Scheme 1). These two new dendrimers that terminate in four and 16 trifluoroalkyl ether units contain relatively small amounts of fluorine and thus were soluble in organic solvents, such as THF, diethyl ether, and dichloromethane. They were isolated as air stable, colorless liquids. Not surprisingly compound **8** is much more viscous than **7**. Any excess of low boiling **5** was removed under vacuum at room temperature. Elemental analysis and nuclear magnetic resonance and mass spectral data were used to satisfactorily characterize the fluorinated dendrimers. After removing any volatile materials, elemental analyses confirmed that the products are analytically pure. Olefin polymerization does not occur with **5**. The hydride substrates **1** and **4** were stable to decomposition in a sealed degassed tube at 75 °C for 24 h. NMR evidence for completed reaction is the disappearance of the allylic signals,

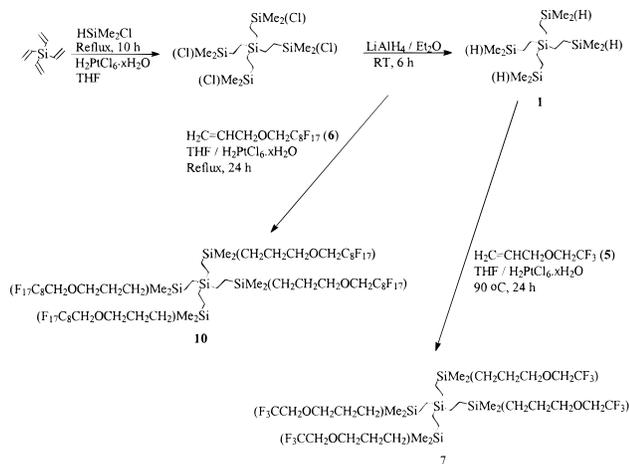
(15) (a) Kleppinger, R.; Reynaers, H.; Desmedt, K.; Forier, B.; Dehaen, W.; Koch, M.; Verhaert, P. *Macromol. Rapid Commun.* **1998**, *19*, 111–114 (b) Prosa, T. J.; Bauer, B. J.; Amis, E. J.; Tomalia, D. A.; Scherrenberg, R. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 2913–2924 (c) Bauer, B. J.; Hammouda, B.; Barnes, J. D.; Briber, R. M.; Tomalia, D. A. *Polym. Mater. Sci. Eng.* **1994**, *71*, 704–5 (d) Bauer, B. J.; Topp, A.; Prosa, T. J.; Amis, E. J.; Yin, R.; Qin, D.; Tomalia, D. A. *Polym. Mater. Sci. Eng.* **1997**, *77*, 87–88 (e) Topp, A.; Bauer, B. J.; Amis, E. J.; Scherrenberg, R. *Polym. Mater. Sci. Eng.* **1997**, *77*, 82–83.

(16) (a) Cuadrado, I.; Moran, M.; Moya, C.; Casado, C. M.; Barranco, M.; Alonso, B. *Inorg. Chim. Acta* **1996**, *251*, 5. (b) Losada, J.; Cuadrado, I.; Moran, M.; Casado, C. M.; Alonso, B.; Barranco, M. *Anal. Chim. Acta* **1997**, *338*, 91. (c) Cuadrado, I.; Casado, C. M.; Alonso, B.; Moran, M.; Losada, J.; Belsky, V., *J. Am. Chem. Soc.* **1997**, *119*, 7613.

(17) Chai, M.; Pi, Z.; Tessier, C.; Rinaldi, P. L. *J. Am. Chem. Soc.* **1999**, *121*, 273–279.

(18) Seyferth, D.; Son, D. Y. *Organometallics* **1994**, *13*, 2682–2690.

Scheme 1



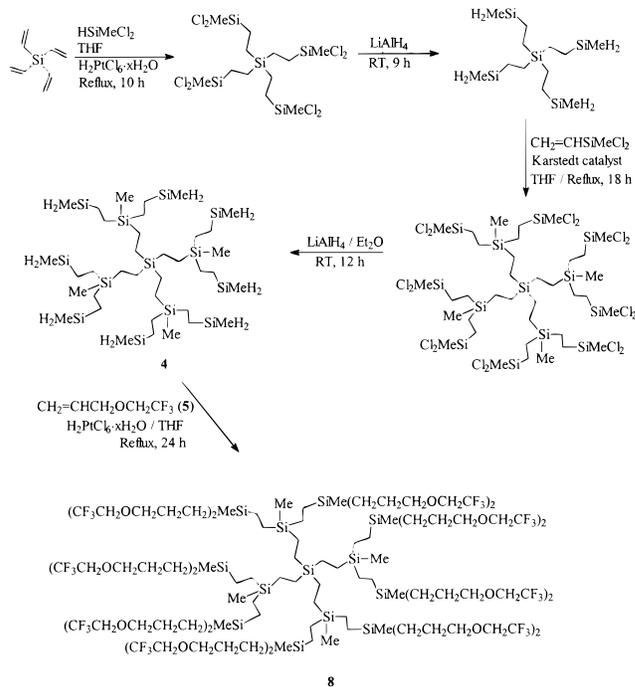
i.e., ^1H : 5.08–5.28 (td), 5.65–5.90 (m) and ^{13}C : 133.1 and 119.4 ppm; however, the ether (CH_2OCH_2) linkage, i.e., ^1H : 3.58–3.94 (t), 4.02 (q) and ^{13}C : 73, 67, 69 ppm, is retained. The peaks for ($\text{Si}-\text{H}$) in the ^1H NMR spectra at ca. 3.5 ppm ($J_{\text{Si}-\text{H}} = 192$ Hz) also disappear completely. New ^1H NMR signals that result from the newly formed $-\text{CH}_2\text{CH}_2-$ linkage as a product of hydrosilylation reactions at the terminal four silicon atoms are observed between 1.20 and 1.80 ppm. Data supporting this linkage are also observed in the ^{13}C NMR signals at ca. 7.0 and 10.0 ppm. The equivalence of the four terminal silicon atoms in the new compounds was monitored by the changed pattern of the ^{29}Si NMR spectra, and these data are reported in the Experimental Section.

The allyl-1,1-heptafluorononyl ether (**6**) is a higher molecular weight, air stable analogue of **5**, bp = 58 °C/0.3 mm, and MS (EI) $M^+ = 490$. This compound was synthesized by utilizing the procedure for the lower homologue, allyl-1,1-pentadecafluoroaoctyl ether.¹⁹ It was characterized in a manner similar to that for **5**. When the dendrimer hydride **2** or **3** was added from a syringe into a mixture of an excess of **6** and catalytic amounts of chloroplatinic acid in 2-propanol and maintained at about 90 °C under anaerobic conditions, viscous, light brown colored oils **9** or **11**, respectively, were obtained. Compound **10** was synthesized from the analogous reaction between **1** and **6**. These highly fluorinated materials were soluble only in fluorinated solvents, such as 1,1,2-trifluoroethane (Freon 113) and hexafluorobenzene. Based on NMR spectral evidence, the three were unreactive toward organic acids, bases, and oxidizing and reducing agents. Since the polyfluoroalkyl ether chains in **9**–**11** are much longer than in **7** and **8**, incomplete coupling of the terminal silane with **6** might be expected but does not occur. Again, the progress of the reaction was monitored by using a combination of ^1H and ^{29}Si NMR spectra.

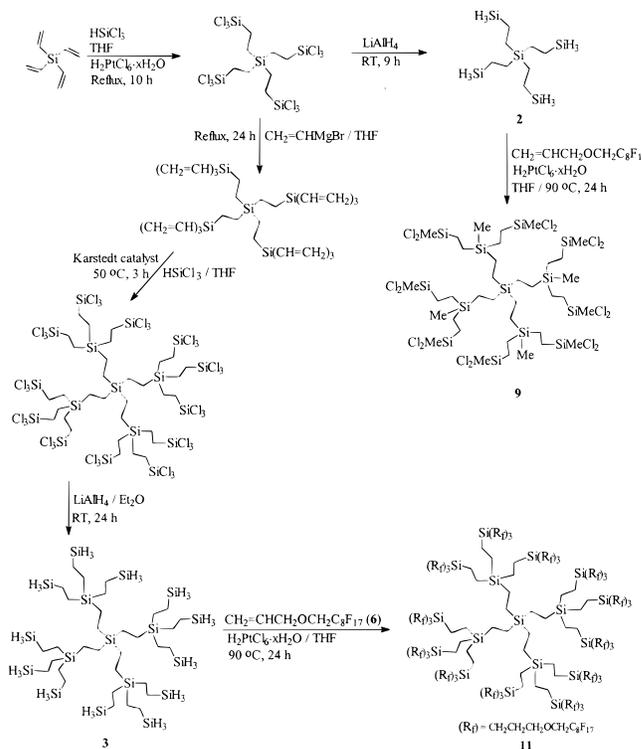
The respective ^{29}Si NMR signals were observed at ca. –53.5 ($-\text{SiH}_3$: **2** and **3**), –29.7 ($-\text{SiMeH}_2$: **4**), or –10.5 ($-\text{SiMe}_2\text{H}$: **1**) for the terminal silicon atoms (Schemes 1–3). The reactions are allowed to continue until the $\text{Si}-\text{H}$ signals had disappeared completely in both the ^1H and ^{29}Si NMR spectra and new ones formed at the expected positions. The ^{29}Si NMR spectra of **3** and **11** are in Figure 1.

New $\text{Si}-\text{CH}_2$ NMR signals that appear between 1.20 and 1.80 ppm in the ^1H NMR spectra confirm successful hydrosilylation. However, it was important to confirm the chemical

Scheme 2



Scheme 3



equivalence of all the terminal silicon atoms (i.e. four atoms in **9** and **10**, 12 in **11**) that would be present when all $\text{Si}-\text{H}$ bonds were displaced. The new signals for the silicon atoms were observed in the ^{29}Si NMR spectra at ca. –22 [$-\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{R}_f)_3$; **9** and **11**], –10 [$-\text{SiMe}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{R}_f)_2$; **8**], or –3.0 [$-\text{SiMe}_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{R}_f)$; **7** and **10**]. However, the intensities of the signals for the terminal silicon atoms are usually very strong. When samples are taken from the reaction system for ^{29}Si NMR measurement, signals of silicon atoms bearing $\text{Si}-\text{CH}_2-$ and $\text{Si}-\text{H}$ were seen along with those of the others in the core of the dendrimer to indicate the degree

(19) Holbrook, G. W.; Steward, O. W. U.S. Patent 3, 012, 006 (to Dow Corning Co., MI), 1961.

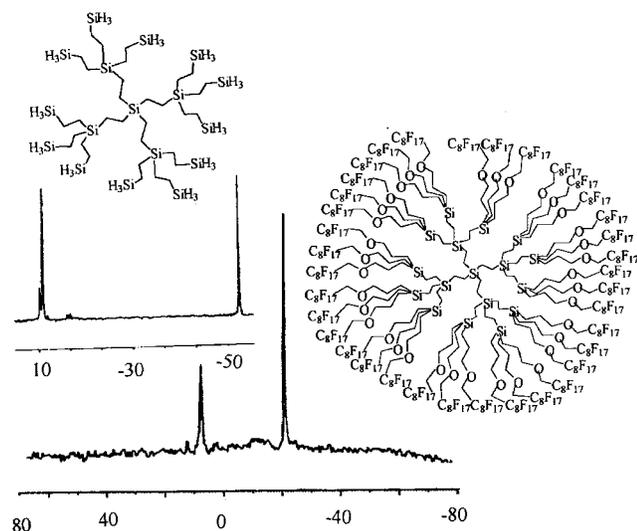


Figure 1. ^{29}Si NMR spectra (ppm) of a second-generation dendrimer hydride substrate (**3**) and the fluorinated derivative (**11**).

of completeness of the reaction. The dendrimers, especially **9** and **11** as the longer polyfluoroalkyl ether chain, were characterized from the combination of $^1\text{H}/^{29}\text{Si}$ NMR and their elemental analyses.

The ^{19}F NMR spectra confirmed the presence of the terminal fluoroalkyl chains in these dendrimers, but not surprisingly the positions of the signals and the multiplicities were not noticeably changed moving from the alcohol to the polyfluoroether olefins (**5** and **6**) to the fluorinated dendrimers (**7–11**). Therefore, the fluorine NMR spectra are not particularly useful in determining the extent of reaction.

Earlier, either size exclusion chromatography (SEC) or small-angle X-ray light scattering (SAXS) was used to determine the molecular masses of fluorinated dendrimers that terminated in perfluoropolyether or polyfluoroether chains.^{4,14} These compounds were generally nonpolar and soluble only in perfluorinated solvents. Hence, they responded poorly to experimental conditions for providing ions in electrospray and MALDI time-of-flight mass spectral studies aimed at determining accurate molecular masses.

In this work, the dendrimers **9–11** that terminate in the long polyfluoroalkyl chains were also insoluble in nonfluorinated solvents, but **7** and **8** that contained a relatively small amount of fluorine were soluble in organic solvents. The latter two compounds were intentionally designed in order to assist in the different maneuvers of mass spectrometry to obtain characteristic data for at least some of the dendrimers by using standard mass spectrometric techniques.

Molecular ions for the dendrimers ending in silanes [**1** (M^+ , 376), **2** (M^+ , 264), **3** (M^+ , 962), and **4** (M^+ , 896)] were obtained by electron ionization (EI) or by MALDI time-of-flight mass spectral analysis. Our experiments that sought to generate both positive and negative ions with three matrices: α -cyano-4-hydroxycinnamic acid, indoleacrylic acid, and 5-chlorosalicylic acid, at two levels of dilution only gave some fairly complex and unexplainable signals in MALDI studies. The dendrimers did not incorporate into the crystallized matrix. The strong positive ion signal obtained for **10** at m/z 2366.4, i.e., $M^+ + 30$, by using 2,4-dihydroxybenzoic acid (DHB) matrix (mass verified with an internal standard) results from our single successful incorporation of the dendrimer into the matrix crystal. Addition of silver trifluoroacetate produced no silver adduct. No other matrix gave the signal at 2366 or as strong and clean

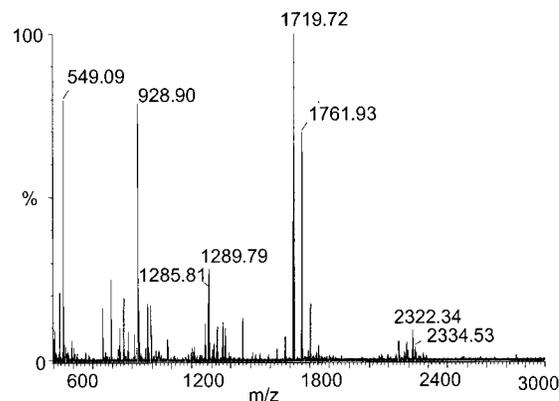


Figure 2. APci mass spectrum for $\text{Si}[\text{CH}_2\text{CH}_2\text{SiMe}_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17})]_4$ (**10**).

spectrum as did DHB. It was not possible to confirm whether the source of the $m/z = 30$ in the $[M^+ + 30]$ signal was the dendrimer or the matrix. Two methyl moieties were assumed to be cleaved and subsequently recombined with another molecular unit, perhaps at the oxygen atom in the ether linkages. Efforts were made to determine if the process that generated the signal at 2366 took place either during the experiment or under mass spectral conditions by using a different mass spectral experimental technique for the same compound. Atmospheric pressure chemical ionization (APci) technique was found to be useful. When APci was used, the signal at 2366 was absent, and signals at 2332–2335 were observed (Figure 2).

The advantage of using APci, an LC-MS technique, is in its ability to produce singly charged protonated or deprotonated molecular ions for a broad range of nonvolatile and thermally labile analytes such as the nonpolar polyfluorinated dendrimers in this work that are only soluble in fluorinated solvents. When the solvent emerges from the LC column into the MS probe it is rapidly expanded into the vapor/gas phase and rapidly reacts with ions from the corona discharge to produce stable reagent ions.²⁰ It is the reaction between this reagent ion and the dendrimers at atmospheric pressure that typically generate the protonated (in the positive mode) or deprotonated species (in the negative mode) that goes into the mass spectrometer.²⁰ Thus the choice of solvent is an important factor that is compound specific in APci studies.

Two other dendrimers, **7** and **8**, containing polyfluoroether chains as terminal groups were examined by using APci. Quasi-molecular masses were obtained in the negative ion mode, and the useful signals were considered as originating from the molecular ion. The $[M^- - \text{CF}_3]$ signal was observed as a strong base peak signal at 867 for compound **7**. The relationship of the higher signal at $m/z = 941$ to M^- expected at $m/z = 935$ for **7** is unclear. In the APci⁻ spectrum for **8**, a significant negative ion signal was observed at ca. 3280. This signal represents an $[M^- + 140]$ mass. Since THF is the solvent mobile phase for **8** in the APci studies, it is assumed that two tetrahydrofuran units more than the expected dendrimer mass are responsible.

Peaks having reasonable signal/noise-level ratio and appearing at m/z values lower than the molecular ion may be arise from either fragmentation of the molecule, the incompletely formed dendrimers or from nonrelated impurities. The mass spectra of dendrimers ending in the trifluoroethyl ether (monomer arm) units, i.e., $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CF}_3$ in **7** and **8** showed few lower mass peaks. These peaks do not arise from loss of monomer

(20) Micromass' users Guide book on Quattro II mass spectrometer.

Table 1. Characterization by Mass Spectrometry

compound	MW (calcd)	MS (obsd)	MS method
Silane Dendrimers			
Si[CH ₂ CH ₂ SiMe ₂ H] ₄ (1)	376	375	EI
Si[CH ₂ CH ₂ SiH ₃] ₄ (2)	264	263	EI
Si[CH ₂ CH ₂ SiMe(CH ₂ CH ₂ SiMeH ₂) ₂] ₄ (4)	896	895	MALDI
Si[CH ₂ CH ₂ Si(CH ₂ CH ₂ SiH ₃) ₃] ₄ (3)	962	961	MALDI
Polyfluoroalkylether Dendrimers			
Si{CH ₂ CH ₂ Si[CH ₂ CH ₂ Si(CH ₂ CH ₂ CH ₂ OCH ₂ C ₈ F ₁₇) ₃] ₃] ₄ (11)	18 600	<i>a</i>	<i>a</i>
Si[CH ₂ CH ₂ SiMe ₂ (CH ₂ CH ₂ CH ₂ OCH ₂ CF ₃) ₄ (7)	936	941 and 867	APcI
Si[CH ₂ CH ₂ SiMe ₂ (CH ₂ CH ₂ CH ₂ OCH ₂ C ₈ F ₁₇) ₄ (10)	2336	2366/2335	MALDI/APcI
Si[CH ₂ CH ₂ Si(CH ₂ CH ₂ CH ₂ OCH ₂ C ₈ F ₁₇) ₃] ₄ (9)	6144	<i>a</i>	<i>a</i>
Si{CH ₂ CH ₂ SiMe ₂ [CH ₂ CH ₂ SiMe(CH ₂ CH ₂ CH ₂ OCH ₂ CF ₃) ₂] ₂] ₄ (8)	3136	3280	APcI
Polyfluoroether Olefins			
CH ₂ =CHCH ₂ OCH ₂ CF ₃ (5)	140	140	EI
CH ₂ =CHCH ₂ OCH ₂ C ₈ F ₁₇ (6)	491	491	EI

^a Mass spectral data were not obtained. See discussions of small angle X-ray scattering.

constituents but agree with calculations of cleavage of each of the fluoroethyl ether chains at the oxygen atom. This occurred irrespective of the dendrimer generation. However, **10**, which terminates in $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17}$ units, showed fewer mass peaks and signals supporting loss of the $\text{CH}_2\text{CH}_2\text{SiMe}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17}$ units ($m/z = 1761$ and 1285 in Figure 2). Since the Si-H signals had completely disappeared in the ¹H and ²⁹Si NMR spectra of **8**, the logical explanation is that these result from loss of arms, rather than being due to incomplete reaction. The spectrum reveals loss of methyl and methylene groups from several ion masses and a loss of one methyl unit from each of the three $-\text{SiMe}_2$ moieties of the species with $m/z = 1761$, accompanied by protonation of the three Si atoms would give the base peak signal at $m/z = 1719$, $\text{HSi}[\text{CH}_2\text{CH}_2\text{Si}(\text{H})\text{MeCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17}]_3$.

There is a concentration of peaks with relatively very high intensities at regions below m/z 800 for **8** (M^+ , 3136) and m/z 1000 for **10** (M^+ , 2336). These signals represent the several fragments from the dendrimer arms or possible nonvolatile impurities, and they could not be completely assigned. A summary of the significant signals from the mass spectrometric studies is shown in Table 1.

Dendrimers that terminate in $\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17}$ (**9**–**11**) in the present work were soluble in Freon 113 and in hexafluorobenzene, and those ending in $\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CF}_3$ (**7** and **8**) dissolved in fluorinated and nonfluorinated solvents as well, e.g., THF, dichloromethane, and diethyl ether. Therefore, Freon 113 (**10**) and tetrahydrofuran (**7** and **8**) were the solvents used in our work. The Micromass user's instruction Guide book on Quatro II mass spectrometer emphasizes that the value of the sample cone determines whether the resulting spectra will be a protonated molecular ion peak or consisting of diagnostic fragment ions.²⁰ Regulating this parameter to 20 V should normally yield soft ionization leading to molecular ion peak, and a setting to 50 V results in a spectrum that contained ion peaks from significant fragmentation of an analyte.²⁰ The cone had to be set at 59 V in order to generate ionization for positively charged signals in the APcI⁺ mode for **10** and partly explains the large number of fragment signals in the resulting spectrum (Figure 2). A setting at 25 V was adequate to generate negative ions in the APcI⁻ mode for **7** and **8**, and the spectra contain relatively fewer significant fragment ions. An evaluation of the spectra for **7** and **8** from the APcI⁺ mode gave no useful information, but the spectra from the APcI⁻ mode were very helpful.

The mass range of its detection window at 4000 molecular mass units is, unfortunately, the limitation of this MS technique.

The signals did not give isotopic patterns that are important for a possible successful deconvolution to reveal the higher than $m/z = 4000$. Therefore, it was not possible to measure the response of the polyfluorinated dendrimers **9** (expected MW = 6144) and **11** (expected MW = 18 600). Thus a combination of elemental analysis and ¹H/²⁹Si NMR were used to characterize the two compounds.

When a 1:9 Freon 113/hexane solution of **10** was allowed to remain in a refrigerator at -15 °C, transparent single crystals grew, but the quality was not adequate for single-crystal X-ray diffraction. The crystal melted in solution at -10 °C. This suggested that there was some order in the structure of these dendrimers. Therefore, an attempt was made to obtain experimental evidence to support this by exposing dilute solutions of **9** and **11** in hexafluorobenzene to small-angle X-ray scattering measurements. Experimental results indicate that the higher generations of polyamidoamine dendrimers have spheroidal shapes and that the smaller relatives are assumed to be similar.¹⁵ The radius of gyration is known to be generation dependent because of different electron density around the nucleus.

Molecular masses (hyperbranched polymers) were deduced from Zimm plot analysis, but the technique was shown to be inaccurate when applied to dendrimers.^{15b} However, the Guinier plot provide accurate and reliable results for evaluating shapes and sizes of dendrimers.^{15b} Over comparable q ranges the reciprocal of the dimension causing the scattering according to Guinier's Approximate Law may be used to analyze the scattering curves.²¹ The law, exact in the limit $q \rightarrow 0$ and stated as $^{21} \ln I(q) = \ln(I_c(q)N[\Delta\rho v]^2) - q^2 R_g^2/3$, was used to analyze our scattering curves¹⁵ (where N is the number of independent scattering particles, $\Delta\rho$ is the electron density contrast between the particle and the matrix in which it is embedded, v is the volume of the particle, and R_g is the electronic radius of gyration of the particle, i.e., the electronically weighted root-mean square radius of the particle about its electronic center of mass).

The plot $\ln(q)$ vs q^2 , according to the Guinier equation, generates some linearity over q ranges where the law is followed and have a slope equal to $-R_g^2/3$. The Guinier plots of the data for **9** and **11** are shown in Figure 3. The plot for **11** has two distinct linear regions, and the lower angle region is regarded to be due to the total size of the dendrimer contrasted with the solvent and gives an R_g of 2.7 ± 0.1 nm. The higher angle part is due to the contrast between the nonfluorinated core of the dendrimer and the surrounding fluorocarbon chains and gives a R_g of 1.1 ± 0.05 nm. A poor signal-to-noise ratio precluded

(21) Guinier, A.; Fournet G. *Small-Angle Scattering of X-rays*; John Wiley & Sons: 1955.

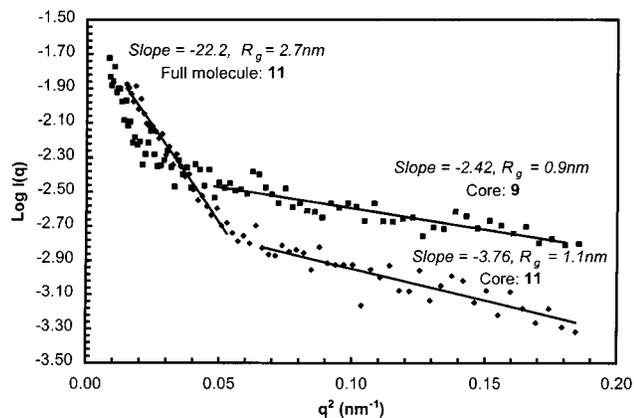


Figure 3. The Guinier plot of the small angle X-ray scattering (SAXS) data for **9** and **11** in hexafluorobenzene.

reliable analysis of the low angle region of the curve for **9**, but the higher angle region corresponds to a core with a R_g of 0.9 ± 0.05 nm.

The dendrimers were assumed to be simple spherical shells for the interpretation of their electron density pair correlation function. The radius of gyration of a sphere, D_s , is related to the algebraic slope value R_g by the equation, $D_s = 2\sqrt{(5/3)R_g}$.

The corresponding diameter of the dendrimer **11** is then 7.0 nm and its core 2.8 nm. The core of **9** is 2.6 nm. Both of these values are in excellent agreement with those that would be predicted from their molecular structure (Figure 4), **11** having the larger core due to its longer nonfluorinated chains. The observed diameter of **11** is close to the maximum it would have if the chains were fully extended which is exactly what would be expected for bulky fluorocarbon chains tethered to a central core. Inward folding and interpenetration of endgroup chains may be expected from third (and higher) generation dendrimers.^{1b,14} The use of very dilute solutions in SAXS experiments minimize the contributions from this phenomenon to the results described in this work. Even though, almost all theoretical models predict backfold branches, the fairly strong correlation of predicted and SAXS experimental deductions on electron density and sizes of the dendritic cores and overall molecules further supports our deductions.^{1b} The combination of evidence from NMR, i.e., that all Si-H had been converted, and SAXS support the proposed composition for these compounds.

Thermal properties of the dendrimers in this work are summarized in Table 2. Glass transition temperatures, T_g , of the dendrimer hydrides were observed at -125 (**2**), -104 (**4**), and -98 °C (**3**), correlating an increase in T_g values with increasing molecular weight. The trend is comparable to that reported for other carbosilane dendrimers.^{11,22} Glass transition temperatures were also observed for the fluorinated dendrimers, **9–11**. Phase and glass transitions in the DSC thermogram **9** were at T_g at -10 and -33 °C, respectively, as shown in Figure 5. The thermogram for **10** and **11** showed a T_g at -26 and -52 °C, respectively. The dendrimer **7** exhibited no mesophase.

The results of thermogravimetric analysis (TGA) data for **8–11** and the results are summarized in Figure 6. The plot relates molecular weight of the compounds and composition to thermal stability. The temperatures for 50% weight loss of **8–11** occur over a range between 196 and 480 °C and are reported in Table 2. The relative position of this value for each compound indicates that their thermal stability correlates directly with increase in molecular weight.

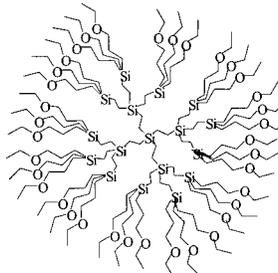
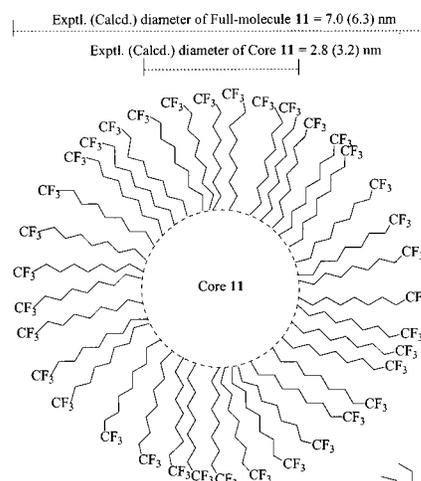
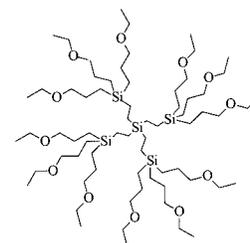
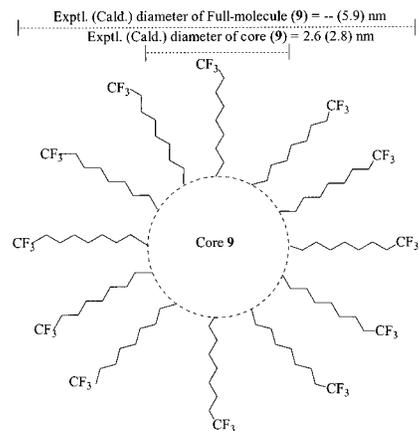


Figure 4. Relative sizes of **9** and **11** as deduced from SAXS.

Conclusions

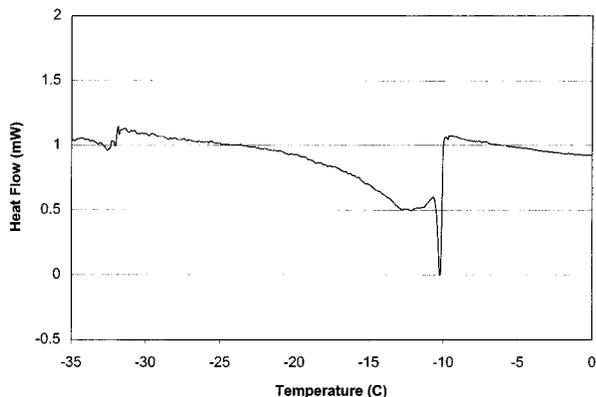
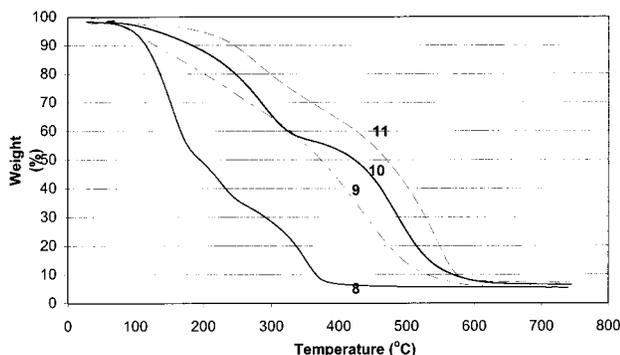
Hydrosilylation reactions between a dendrimer hydride core and polyfluorinated allyl ethers were carried out with completeness of the reaction being monitored by a combination of ^1H and ^{29}Si NMR spectra. Mass spectral characterizations of the nonpolar compounds were obtained by using APcI. Results of small-angle X-ray light scattering of two fluorinated dendrimers in hexafluorobenzene show good correlation of expected values and the experimentally deduced sizes of the nonfluorinated core and the full dendrimer molecule. This level of accuracy makes

(22) Lorenz, K.; Muellhaupt, R.; Frey, H.; Rapp, U.; Mayer-Posner, F. *J. Macromolecules* **1995**, *28*, 6657–6661.

Table 2. Thermal Properties of the Carbosilane Dendrimers

compound	glass transition temp, T_g^b ($^{\circ}\text{C}$)	temp of 50% wt loss in TGA ($^{\circ}\text{C}$)
$\text{Si}[\text{CH}_2\text{CH}_2\text{SiMe}_2\text{H}]_4$ (1)		
$\text{Si}[\text{CH}_2\text{CH}_2\text{SiH}_3]_4$ (2)	-125	
$\text{Si}[\text{CH}_2\text{CH}_2\text{SiMe}(\text{CH}_2\text{CH}_2\text{SiMeH}_2)_2]_4$ (4)	-104	
$\text{Si}[\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{SiH}_3)_3]_4$ (3)	-98	
$\text{Si}[\text{CH}_2\text{CH}_2\text{SiMe}_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17})]_4$ (8)	<i>a</i>	196
$\text{Si}\{\text{CH}_2\text{CH}_2\text{SiMe}_2[\text{CH}_2\text{CH}_2\text{SiMe}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CF}_3)_2]_2\}_4$ (9)	-10	378
$\text{Si}[\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17})_3]_4$ (10)	-26	425
$\text{Si}\{\text{CH}_2\text{CH}_2\text{Si}[\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17})_3]_3\}_4$ (11)	-52	480

^a No mesophase and crystalline; T_g was not observed. ^b T_g values were obtained from Differential Scanning Calorimetry (DSC).

**Figure 5.** DSC thermogram of 9.**Figure 6.** Thermogravimetric data for 8–11.

this technique relevant for determination of any change in the electron density of either the core or in the region of fluorinated terminal chains. The results demonstrate that X-ray scattering is a useful technique with potential application for studying rather complex compounds.

Experimental Section

Materials. The solvents, tetrahydrofuran (THF), diethyl ether, and dichloromethane, were dried with sodium and distilled over purple solution of benzophenone and dimethylsulfoxide (DMSO) over calcium hydride. Allyl-1,1-dihydroheptadecafluorononyl ether was synthesized by a modification of the method for allyl-1,1-dihydropentadecafluorooctyl ether.¹⁹ Three of the four dendrimer precursors ending in silanes, i.e., first-generation ending in four and 12 Si–H groups, $\text{Si}(\text{CH}_2\text{CH}_2\text{SiMe}_2\text{H})_4$ (1) and $\text{Si}(\text{CH}_2\text{CH}_2\text{SiH}_3)_4$ (2), respectively, as well as second-generation ending in 36-H groups, $\text{Si}[\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{SiH}_3)_3]_4$ (3), were synthesized according to literature procedures.^{6,8} The second-generation dendrimer, $\text{Si}[\text{CH}_2\text{CH}_2\text{SiMe}(\text{CH}_2\text{CH}_2\text{SiMeH}_2)_2]_4$ (4), that terminates in 16 silane units was synthesized by the same procedures, and data on this compound are provided below. Karstedt's catalyst (obtained as a 2–3% solution in xylenes) was purchased from PCR-Lancaster and stored under nitrogen. Chloroplatinic acid and all other chemicals were used as received from either of Aldrich.

General. A standard Schlenk line system was used for handling the reactions under anaerobic (dry nitrogen) conditions. Elemental analysis of percentage carbon and hydrogen were performed by Desert Analytics Laboratory, Tucson, AZ. All reactions and manipulations were carried out in an atmosphere of dry nitrogen or argon. The TGA data were collected on a Perkin-Elmer 7 series thermal analyzer under an argon atmosphere with a heating rate of 20 $^{\circ}\text{C}/\text{min}$. Infrared spectra are recorded as neat liquids between KBr plates on a Bio-Rad FTS 3000 Excalibur series infrared spectrometer. ^1H , ^{13}C or $[^{13}\text{C}\{\text{F}\}]$, ^{19}F , and ^{29}Si NMR spectra were obtained on a Bruker AMX (200, 300, or 500 MHz) at 200, 50, 188, and 59 MHz, respectively, using CDCl_3 as locking solvent except where otherwise indicated. Chemical shifts were reported with respect to Me_4Si (^1H , ^{13}C and ^{29}Si) or CFCl_3 (^{19}F). Mass spectra (EI and CI) were obtained from a Finnigan GCQ or a JEOL JMS-AX505HA mass spectrometer connected with a Hewlett-Packard HP 6890 series GC system.

Atmospheric Pressure Chemical Ionization (APCI) Mass Spectrometry. Mass spectral determinations of molecular masses for the fluorinated dendrimers with expected molecular masses under 4000 were done on a Quattro II triple quadrupole mass spectrometer (Micromass Inc., U.K.). The APCI interface consists of a heated nebulizer probe, and the standard atmospheric pressure source configured with a corona discharge pin. Other parameters were corona 1.80 kV (APCI^-) or 3.50 kV (APCI^+), cone 59V (APCI^-) or 25V (APCI^+), Skimmer Lens offset 5V, source temperature 80 $^{\circ}\text{C}$ (APCI^- and APCI^+), APCI probe temperature 20 $^{\circ}\text{C}$ (APCI^-) or 35 $^{\circ}\text{C}$ (APCI^+), and a resolution of 15/15 (MS1/MS2). The samples were dissolved in either THF or 1,1,2-trichlorotrifluoroethane (Freon-113) at a concentration of 0.1 mg/10 mL of solvent. The solutions were normally filtered and stored in clean glass vials with silicon-protected caps to prevent contamination.

MALDI Time-of-Flight Mass Spectrometry. The MALDI-TOF mass spectra were obtained on PerSeptive Biosystems Inc., Voyager-DE RP mass spectrometer (Cambridge, MA), with a nitrogen laser emitting at 337 nm for desorbing the sample ions. The instrument operated in the linear delayed-extraction mode at an accelerating voltage of 25 kV and was internally calibrated. Detection was by means of a microchannel plate detector and a digitizing oscilloscope operating at 250 MHz. Approximately 1 mmol sample solutions were made for the dendrimer hydrides and the polyfluoroether dendrimers in chloroform and Freon-113, respectively. We tried both positive and negative ions out of four matrixes at two levels of dilution: α -cyano-4-hydroxycinnamic acid, indoleacrylic acid, 5-chlorosalicylic acid, and 3,5-dihydrobenzoic acid (DHB) in THF (2.0 M). One microliter of a solution prepared by combining 1.0 μL of matrix solution and 0.1 μL of sample solution was placed on the stainless steel MALDI target and analyzed following evaporation of the solvents. Addition of silver trifluoroacetate produced no silver adduct.

Small-Angle X-ray Scattering. The small-angle X-ray scattering (SAXS) measurements were made on the 7-m, pinhole collimated instrument. This instrument has a Bruker (formerly Siemens) rotating Cu anode X-ray generator with a high brilliance 0.3×0.3 mm focal spot and a set of cross-coupled graded multilayer "mirrors". The output beam divergence is 0.04° fwhm, and its size at the sample position is 0.7×0.7 mm. The sample was contained in a 0.7 mm thick cell with Kapton windows. The data were recorded with a Bruker "Hi-Star" two-dimensional position sensitive proportional counter at point-to-point

resolution of 0.2 mm over an area of 512×512 pixels. The sample-to-detector distance was 2.75 m, and the beam path was fully evacuated. Data were recorded for 3600–5000 s over a scattered wavevector, q , range of 0.12–0.86 nm, where $q = 4\pi \sin\Theta/\lambda$, 2Θ is the scattering angle, and λ is the wavelength of the scattered radiation 0.1541 nm for $\text{Cu}_{K\alpha}$. A background of neat hexafluorobenzene, recorded for 60 000 s was subtracted after correction for detector sensitivity, positional nonlinearity, and transmission. The data were azimuthally averaged into 200 bands having a constant width of q^2 . Data compromised by scatter from the beam stop were removed.

Syntheses. Synthesis of $\text{Si}^{(0)}[\text{CH}_2\text{CH}_2\text{Si}^{(1)}\text{Me}(\text{CH}_2\text{CH}_2\text{Si}^{(2)}\text{MeH}_2)_2]_4$ (4). The procedure used for synthesis of **4** is a modification of the ones described in earlier literature.^{17,18} The following characteristic spectroscopic data were obtained for **4**. IR, 2118 cm^{-1} , $\nu(\text{Si}-\text{H})$. NMR (CDCl_3): ^1H , δ 0.13 (m, 36H, MeSi), 0.66 (s, 16H, $\text{Si}^{(0)}\text{CH}_2\text{CH}_2\text{Si}^{(1)}$), 0.92 (m, 32H, $\text{Si}^{(1)}\text{CH}_2\text{CH}_2\text{Si}^{(2)}$), and 3.6 ppm ($J_{\text{Si}-\text{H}} = 192$ Hz) (s, 16H, Si-H); ^{13}C , δ -3.2, -0.6, 3.8, 5.6, 6.6, 7.8 ($\text{Si}^{(0)}\text{CH}_2\text{CH}_2\text{Si}^{(1)}$ -MeCH₂CH₂Si⁽²⁾(Me) ppm. ^{29}Si , δ 10.3 [$\text{Si}^{(0)}$], 8.9 [$\text{Si}^{(1)}$] and -29.8 ppm [$\text{Si}^{(2)}$]. $\text{Si}^{(0)}\{\text{CH}_2\text{CH}_2\text{Si}^{(1)}\text{Me}_2[\text{CH}_2\text{CH}_2\text{Si}^{(2)}\text{MeH}_2]_2\}_4$; MS (MALDI-TOF): 895 [$\text{M}^+ - 1$].

Synthesis of Allyl-1,1-Dihydrotrifluoroethyl Ether (5), $\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CF}_3$. Solid sodium trifluoroethoxide (25.0 g, 204.9 mmol) was dissolved in 30 mL of DMSO in a flame-dried 250 mL two-necked flask connected with a three-way stopcock for nitrogen gas inlet. This solution was maintained at 10 °C, and allyl bromide (24.7 g, 204.1 mmol) was added dropwise such as to maintain the same temperature throughout the reaction. Sodium bromide precipitated with each drop of the allyl bromide into the stirring reaction mixture. The reaction was allowed to slowly assume room temperature while stirring for another 12 h. The colorless allyl-1,1-dihydrotrifluoroethyl ether was distilled from the reaction mixture; bp = 49 °C in 75% yield. IR, 1642, 992 $\nu(\text{CH}=\text{CH}_2)$, 1297, 1181 $\nu(\text{CH}_2\text{OCH}_2)$, 1142 cm^{-1} $\nu(\text{CF}_3)$. NMR (CDCl_3): ^1H , δ 3.58–3.94 (t, 2H, $\text{CH}_2\text{C}_8\text{F}_{17}$), 4.02 (d, 2H, $\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17}$), 5.08–5.29 (td, 2H, $\text{CH}=\text{CH}_2$), 5.65–5.90 ppm (m, 1H, $\text{CH}=\text{H}_2$); $^{13}\text{C}\{^1\text{H}\}$, δ 133.1 [C(1)], 119.4 [C(2)], 73.0 [C(3)], 66.8, 68.7 [q, C(4)], 121.3 [q, C(5)] in $\text{C}^{(1)}\text{H}_2=\text{C}^{(2)}\text{HC}^{(3)}\text{H}_2\text{OC}^{(4)}\text{H}_2\text{C}^{(5)}\text{F}_3$; ^{19}F , δ -74.6 ppm. MS (EI, 70 eV) (m/z , % intensity); M^+ , 140, 45.5; $\text{M} - \text{CF}_3$, 71, 100.

Synthesis of Allyl-1,1-dihydroheptadecafluorononyl Ether (6), $\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{C}_8\text{F}_{17}$. This procedure is a modification of the one used in the synthesis of allyl-1,1-dihypentadecafluoroctyl ether.¹⁹ In a flame-dried 100 mL two-necked flask, fitted with a magnetic stir-bar and condenser and maintained under nitrogen flow was placed a mixture of 12.50 g (27.78 mmol) of 1,1-dihydroperfluorononanol, 5.6 g (46.28 mmol) of allyl bromide, and 12 g (86.96 mmol) of oven dried anhydrous potassium carbonate. To this was added 15 mL of acetone, and the resulting mixture was refluxed under nitrogen flow for 84 h. Afterward, the salts formed were removed by filtration in a Schlenk system. Benzene (50 mL) was added to the filtrate followed by 10 mL of water. Water was removed azeotropically from the clear solution resulting by using the Dean and Stark system.¹⁹ The product was then fractionated to obtain clear colorless allyl-1,1-dihydroheptadecafluorononyl ether, $\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{C}_8\text{F}_{17}$ (bp 57 °C/5 mmHg) in 70% yield. IR 1637, 991 $\nu(\text{CH}=\text{CH}_2)$, 1297, 1178 $\nu(\text{CH}_2\text{OCH}_2)$. NMR (CDCl_3): ^1H , δ 3.60–3.99 (t, 2H, $\text{CH}_2\text{C}_8\text{F}_{17}$), 4.07 (d, 2H, $\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17}$), 5.14–5.32 (td, 2H, $\text{CH}=\text{CH}_2$), 5.74–5.94 ppm (m, 1H, $\text{CH}=\text{H}_2$); ^{13}C , δ 132.9 [C(1)], 118.2 [C(2)], 73.2 [C(3)], 65.9, 66.4 [C(4)] 106–122 [m, C(5–13)] in $\text{C}^{(1)}\text{H}_2=\text{C}^{(2)}\text{HC}^{(3)}\text{H}_2\text{OC}^{(4)}\text{H}_2\text{C}^{(5-13)}\text{F}_{17}$; ^{19}F , δ -82.4, -120.7, -123.0, -123.8, -124.4, -127.4 ppm. MS (EI, 70 eV) (m/z , % intensity); M^+ , 490, 20; $\text{M} - \text{C}_8\text{F}_{17}$, 71, 100.

Synthesis of the Carbosilane Dendrimers Terminating in Polyfluoroether Units. $\text{Si}^{(0)}(\text{CH}_2\text{CH}_2\text{Si}^{(1)}\text{Me}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CF}_3)_4$ (7). An excess of allyl-1,1-dihydrotrifluoroethyl ether (1.56 g, 11.1 mmol), two drops of 0.1 M chloroplatinic acid solution in 2-propanol, 3 mL of THF, and 0.5 g (0.56 mmol) of the dendrimer hydride **1** were added in that order into a flame-dried glass vessel (50 mL) under nitrogen flow. The mixture was cooled to liquid nitrogen temperature, degassed, sealed under vacuum, and left to gradually warm to room temperature. The mixture was placed in an oven set to 70 °C for 24 h and gradually cooled again to room temperature. The glass reactor was cooled in liquid nitrogen, carefully opened, and connected to a vacuum line to remove

the volatile contents, i.e., THF, 2-propanol, and excess olefin, as the mixture warmed to room temperature. After 6 h under vacuum, the glass reactor was filled with nitrogen and disconnected. Further handling was done in open air. The polyfluoroether dendrimer **7** was obtained as a viscous colorless liquid in 95% yield. IR, 1295, 1170 cm^{-1} $\nu(\text{CH}_2\text{OCH}_2)$. NMR ($\text{CDCl}_3 + \text{Freon 113}$): ^1H , δ 0.28 (s, 24H, $\text{Si}^{(1)}\text{Me}_2$), 0.66 (br, 16H, $\text{SiCH}_2\text{CH}_2\text{Si}$), 1.67 (br, 16H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.59 (br, 8H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.91 ppm (t, 8H, OCH_2CF_3); $^{13}\text{C}\{^1\text{H}\}$, δ 0.4, 2.5, 7.1, 10.3, 24.0, 68.6, 121.3 ppm; ^{19}F , δ -82.4, -120.7, -123.0, -123.8, -124.4, -127.4 ppm. ^{29}Si , δ 9.8 [$\text{Si}^{(0)}$] and -3.2 ppm [$\text{Si}^{(1)}$] in **7**. MS (APCI) (m/z , species): 867, ($\text{M}^+ - \text{CF}_3$). Elemental analysis for $\text{C}_{64}\text{H}_{72}\text{O}_4\text{F}_{68}\text{Si}_5$: Calcd.: C, 32.88; H, 3.06%. Found C, 32.36; H, 2.89%.

$\text{Si}^{(0)}\{\text{CH}_2\text{CH}_2\text{Si}^{(1)}\text{Me}_2[\text{CH}_2\text{CH}_2\text{Si}^{(2)}\text{Me}_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CF}_3)_2]_2\}_4$ (**8**). This procedure for the synthesis of dendrimer **8** is similar to one described for **7**. Yield, 93%. IR, 1290, 1175 cm^{-1} $\nu(\text{CH}_2\text{OCH}_2)$. NMR ($\text{CDCl}_3 + \text{Freon 113}$): ^1H , δ 0.29 (s, 24, $\text{Si}^{(1)}\text{Me}_2$), 0.31 (s, 48H $\text{Si}^{(2)}\text{Me}_2$), 0.66 (br, 16H, $\text{Si}^{(0)}\text{CH}_2\text{CH}_2\text{Si}^{(1)}$), 0.92 (br, 32 H, $\text{Si}^{(1)}\text{Me}_2\text{CH}_2\text{CH}_2\text{Si}^{(2)}$) 1.67 (br, 64H, $\text{Si}^{(2)}\text{Me}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.59 (br, 32H, $\text{Si}^{(2)}\text{Me}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.91 (t, 32H, $\text{Si}^{(2)}\text{Me}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CF}_3$); $^{13}\text{C}\{^1\text{H}\}$, δ -0.6, -0.2, 1.3, 6.8, 9.6, 18.8, 22.5, 24.3, 60.5, 67.6, 123.9; ^{19}F , δ -74.4, ppm. ^{29}Si , δ 9.7 [$\text{Si}^{(0)}$], 8.9 [$\text{Si}^{(1)}$], -8.2 ppm [$\text{Si}^{(2)}$] in **8**. MS (APCI) (m/z , species): 3280, $\text{M}^+ + 140$. Elemental analysis for $\text{C}_{116}\text{H}_{212}\text{O}_{16}\text{F}_{48}\text{Si}_{13}$: Calcd.: C, 44.32; H, 6.70%. Found; C, 44.39; H, 6.76%.

$\text{Si}^{(0)}[\text{CH}_2\text{CH}_2\text{Si}^{(1)}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17})_3]_4$ (**9**). An excess of allyl-1,1-dihydroheptadecafluorononyl ether (13.92 g, 28.4 mmol) and a magnetic stir-bar are placed carefully under inert atmosphere transfer conditions into a flame dried 50 mL three-necked flask fitted with a condenser and connected with a nitrogen flow inlet through a three-way stopcock. Two drops of 0.1 M chloroplatinic acid solution in 2-propanol was added, and the flask temperature was raised to 90 °C. THF (5 mL) and **2** (0.50 g, 1.89 mmol) were added slowly from a syringe needle. The reaction mixture was stored at this temperature for 24 h. The product, $\text{Si}[\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17})_3]_4$ (**9**), was obtained by evaporating excess allyl-1,1-dihydroheptadecafluorononyl ether and other volatile solvents under vacuum (~ 0.05 mmHg) at 40 °C for 3 h. Residues of the catalyst were washed off with chloroform. The fluorinated organosilicon product is insoluble in chloroform, but its solution in 1,1,2-trichlorotrifluoroethane (Freon-113) was filtered through a fine frit Schlenk-type filter. When the Freon-113 was evaporated, the resulting product is a viscous, colorless liquid (yield 10.70 g, 92%). IR 1292, 1169 cm^{-1} $\nu(\text{CH}_2\text{OCH}_2)$. NMR ($\text{CDCl}_3 + \text{Freon 113}$): ^1H , δ 0.64 (br, 16H, $\text{Si}^{(0)}\text{CH}_2\text{CH}_2\text{Si}^{(1)}$), 1.73 (br, 48H, $\text{Si}^{(1)}\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.57 (br, 24H, $\text{Si}^{(1)}\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.91 (t, 24H, $\text{Si}^{(1)}\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17}$); $^{13}\text{C}\{^1\text{H}\}$, δ 6.8, 9.6, 18.7, 22.5, 60.5, 67.6, 104–110 (m), 123.9 (t); ^{19}F , δ -82.4, -120.7, -123.0, -123.8, -124.4, -127.4 ppm. ^{29}Si , δ 10.5 [$\text{Si}^{(0)}$], -21.9 [$\text{Si}^{(1)}$] in **9**. Elemental analysis for $\text{C}_{152}\text{H}_{112}\text{O}_{12}\text{F}_{204}\text{Si}_5$: Calcd.: C, 29.69; 1.82%. Found; C, 28.87; H, 1.65%.

The other fluoroorganosilicon products {i.e., $\text{Si}^{(0)}[\text{CH}_2\text{CH}_2\text{Si}^{(1)}\text{Me}_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17})_3]_4$ (**10**) and $\text{Si}^{(0)}\{\text{CH}_2\text{CH}_2\text{Si}^{(1)}[\text{CH}_2\text{CH}_2\text{Si}^{(2)}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17})_3]_3\}_4$ (**11**)} were obtained from very similar procedure involving the respective carbosilane dendrimer hydride substrate and allyl-1,1-dihydroheptadecafluorononyl ether. Their characteristic data are stated below.

$\text{Si}^{(0)}[\text{CH}_2\text{CH}_2\text{Si}^{(1)}\text{Me}_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17})_3]_4$ (**10**). Yield, 96%. IR, 1290, 1174 cm^{-1} $\nu(\text{CH}_2\text{OCH}_2)$. NMR ($\text{CDCl}_3 + \text{Freon 113}$): ^1H , δ 0.29 (s, 24H, $\text{Si}^{(1)}\text{Me}_2$), 0.64 (br, 16H, $\text{Si}^{(0)}\text{CH}_2\text{CH}_2\text{Si}^{(1)}$), 1.60 (br, 16H, $\text{Si}^{(1)}\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.62 (br, 8H, $\text{Si}^{(1)}\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.88 (t, 8H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17}$); $^{13}\text{C}\{^1\text{H}\}$, δ 0.5, 6.4, 9.2, 19.2, 22.2, 61.3, 66.9, 122.6 (t); ^{19}F , δ -82.5, -120.3, -123.2, -123.8, -124.1, -126.9 ppm; ^{29}Si , δ 9.8 [$\text{Si}^{(0)}$], -3.3 ppm [$\text{Si}^{(1)}$] in **10**. MS (APCI) (m/z , species): 2335, [$\text{M}^+ - 1$]. Elemental analysis for $\text{C}_{64}\text{H}_{72}\text{O}_4\text{F}_{68}\text{Si}_5$: Calcd.: C, 32.88; H, 3.06%. Found; C, 32.36; H, 2.89%.

$\text{Si}^{(0)}\{\text{CH}_2\text{CH}_2\text{Si}^{(1)}[\text{CH}_2\text{CH}_2\text{Si}^{(2)}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17})_3]_3\}_4$ (**11**). Yield, 95%. IR, 1298, 1170 cm^{-1} $\nu(\text{CH}_2\text{OCH}_2)$. NMR ($\text{CDCl}_3 + \text{Freon 113}$): ^1H , δ 0.68 (br, 16H, $\text{Si}^{(0)}\text{CH}_2\text{CH}_2\text{Si}^{(1)}$), 0.96 (br, 48 H, $\text{Si}^{(1)}\text{CH}_2\text{CH}_2\text{Si}^{(2)}$) 1.65 (br, 48H, $\text{Si}^{(1)}\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.64 (br, 72H, $\text{Si}^{(1)}\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.95 (t, 72H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_8\text{F}_{17}$); $^{13}\text{C}\{^1\text{H}\}$, δ 6.3, 9.7 ($\text{SiCH}_2\text{CH}_2\text{Si}$), 21.9, 60.3, 67.3, 124.2 (t); ^{19}F , δ -82.6, -120.5,

−122.7, −123.4, −123.9, −128.1 ppm; ^{29}Si , δ 10.1 [$\text{Si}^{(0)}$], 8.9 [$\text{Si}^{(1)}$], −21.9 ppm [$\text{Si}^{(2)}$] in **11**. Elemental analysis for $\text{C}_{464}\text{H}_{352}\text{O}_{36}\text{F}_{612}\text{Si}_{17}$: Calcd.: C, 29.94; H, 1.89%. Found; C, 28.77; H, 1.80%.

Acknowledgment. Gratitude for financial support of this work is expressed to the National Science Foundation (CHE-9720635) and the ACS-Petroleum Research Fund. We thank Dr. Andrzej Paszczynski of EBI for the APcI experiments and

Dr. Gary Knerr for some high resolution NMR and mass spectral data. The small-angle X-ray scattering experiments described in this manuscript were performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratories, Richland, WA 99352.

JA992794R