# Introduction of per(fluoroorganosilyl) peripheries into carbosilane dendrimers and related core-functionalized monodendrons gives rise to anomalous hydrodynamic and viscosimetric behavior

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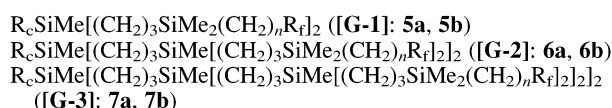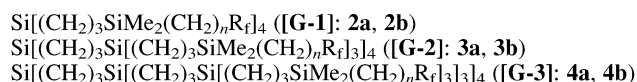**Platinum-catalyzed hydrosilylation of allyl-terminated carbosilane monodendrons using the silanes SiHMe$_2$[(CH$_2$)$_n$R$_f$] (1a, $n$ = 2, R$_f$ = $n$-C$_6$F$_{13}$; 1b, $n$ = 3, R$_f$ = −C$_6$F$_5$) yields fluorous, liquid analogues to [G-3], BrC$_6$H$_4$(CH$_2$)$_3$SiMe[(CH$_2$)$_3$SiMe[(CH$_2$)$_3$SiMe$_2$(CH$_2$)$_n$R$_f$]$_2$]$_2$]$_2$ (7a, $n$ = 2, R$_f$ = $n$-C$_6$F$_{13}$-; 7b, $n$ = 3, R$_f$ = −C$_6$F$_5$), intrinsic viscosities [η] for which are unusually low, resulting in calculated hydrodynamic radii/Å ($ca.$ 6.3, [G-1]; 8.3, [G-2]; 11.5, [G-3]) that imply unusually compact structures.**

The low surface-energy of materials that are required for low-friction coatings and related applications is typically[1] governed by the properties of a fluorine-containing surface layer, a specially effective design for which exposes perfluoroalkyl groups[2] in a microstructural array that[3] minimizes surface disorder. Dendrimer[4] functionalization to prefabricate a suitable hyperbranched subunit, followed by binding of the latter to an appropriate support, is a potentially[5] versatile way of developing such surface coverage; but despite its recent rapid rate of advancement,[4,6] dendrimer chemistry so far offers only a very limited range[7−9] of fluorinated prototypes. Our interest[10,11] in carbosilane[8−12] dendrimers as chemically passive frameworks has led us to explore routes to such species in which a fluorinated organic group is bound to each peripheral silicon atom *directly*, avoiding conjunction through a heteroatom (O or S) as has been reported elsewhere by others.[8,9] We show that by using polyfluoroorgano-substituted silanes in a final convergent step, peripheral modification of allyl-terminated carbosilane dendrimers is possible; and more particularly that, by adaptation of a modular approach[11] to carbosilane monodendrons, members of a family to [G-3] of core *p*-bromophenyl-functionalized analogues may be isolated in high yield. These latter products, in which the unique core functionality can be used for further chemistry including polymer or surface attachment, have been fully characterized by size exclusion chromatography (SEC) and viscosimetry as well as by spectroscopic and analytical data. Dendrimers are known[13] to exhibit low intrinsic viscosities [η] that (in sharp contrast to those for other classes of polymer) tend to a limit with increasing molecular weight. Even by such standards, however, the measured [η] values for the fluorinated carbosilane monodendrons are unusual, generating plots *vs.* SEC elution volume that lie below the[10,14] universal calibration curve. We take this to imply (albeit indirectly[15]) that this type of addendum may be useful for surface coverage to promote non-stick behavior.

In preliminary experiments, we set out to introduce fluorous organic groups directly into carbosilane dendrimers by using organometallic reagents to replace Cl in[10] peripheral −SiMe$_x$Cl$_{3-x}$ units. This led, with Grignard reagents of the type R$_f$CH$_2$CH$_2$MgX (R$_f$ = $n$-C$_6$F$_{13}$ or −C$_6$F$_5$; X = I or Br), to extensive formation of unwanted side-products, as well as to mixtures of products that indicated incomplete substitution at the dendrimer periphery. Platinum-catalyzed hydrosilylation of allyl-terminated carbosilane dendrimer precursors proved to be

a more satisfactory alternative method for building a modified outer layer: thus regiospecific (anti-Markovnikov, γ-substitution of Si-CH$_2$CH=CH$_2$) addition of the silanes[16] SiHMe$_2$[(CH$_2$)$_n$R$_f$] (1a, $n$ = 2, R$_f$ = $n$-C$_6$F$_{13}$; 1b, $n$ = 3, R$_f$ = −C$_6$F$_5$) appeared (through monitoring by NMR) to be essentially quantitative, although limiting the number of fluorous groups to one per silicon atom in the newly-formed periphery. Crude fractions so obtained afforded colorless, viscous liquid products 2a,b–4a,b, see Scheme 1, although the chromatography required to isolate analytically pure samples resulted in significant losses. These new dendrimers possess a branch hierarchy radiating in the archetypal fashion,[4] from a tetra-substituted core silicon atom to a homofunctional periphery that is not amenable to further adaptation. Construction of analogues that can serve as fluorous mesomolecular building blocks may be accomplished, however, by similarly adding the silanes 1a,b across the peripheral allyl groups of the *p*-bromophenyl-substituted trifurcate monodendrons described elsewhere.[11] This routine has been used to synthesize the new monodendrons 5a,b–7a,b, (Scheme 1) which proved to be much easier to purify on flash silica gel than their dendrimer counterparts: like the latter, they remain fluid to [G-3] (glassy transition temperatures $T_g$/0 C: −66, 5a; −58, 5b; −65, 6a; −53, 6b; −59, 7a; −53, 7b) and have likewise been fully characterized.† Prospective use in[11] modular synthesis led us to investigate the physical behavior of these compounds in more detail, using SEC and viscosity measurements.

Variation of intrinsic viscosity [η] (dL g$^{-1}$) with nominal molecular weight $M$ for [G-1], [G-2] and [G-3] homologues (*i.e.* compounds 5a, 6a, 7a; 5b, 6b, 7b), expressed as a double logarithmic relationship, is compared in Fig. 1 with corresponding data for polystyrene standards as well as for unmodified vinyl-terminated, vinyl-derived[10] carbosilane dendrimers (to [G-4]). The successive displacement from one plot to the next highlights the lowering in [η] values that accompanies fluorination, with the effect exaggerated for the *n*-perfluorohexyl-terminated species *vs.* their perfluorophenyl-terminated analogues, *i.e.* decreasing with increasing fluorine content and anticipated changes in surface-energy.[2,3] Calculated hydrodynamic radii are as follows (Å, based on nominal $M$): 6.3, 5a; 6.3, 5b; 8.3, 6a; 8.7, 6b; 11.5, 7a; 11.2, 7b; these are only slightly larger than those for the simple vinyl-terminated prototypes, indicating topology that is unexpectedly compact

Si[(CH$_2$)$_3$SiMe$_2$(CH$_2$)$_n$R$_f$]$_4$ ([G-1]: 2a, 2b)
Si[(CH$_2$)$_3$Si[(CH$_2$)$_3$SiMe$_2$(CH$_2$)$_n$R$_f$]$_3$]$_4$ ([G-2]: 3a, 3b)
Si[(CH$_2$)$_3$Si[(CH$_2$)$_3$Si[(CH$_2$)$_3$SiMe$_2$(CH$_2$)$_n$R$_f$]$_3$]$_3$]$_4$ ([G-3]: 4a, 4b)

R$_c$SiMe[(CH$_2$)$_3$SiMe$_2$(CH$_2$)$_n$R$_f$]$_2$ ([G-1]: 5a, 5b)
R$_c$SiMe[(CH$_2$)$_3$SiMe[(CH$_2$)$_3$SiMe$_2$(CH$_2$)$_n$R$_f$]$_2$]$_2$ ([G-2]: 6a, 6b)
R$_c$SiMe[(CH$_2$)$_3$SiMe[(CH$_2$)$_3$SiMe[(CH$_2$)$_3$SiMe$_2$(CH$_2$)$_n$R$_f$]$_2$]$_2$]$_2$
   ([G-3]: 7a, 7b)

**Scheme 1** For subset a, $n$ = 2, R$_f$ = $n$-C$_6$F$_{13}$−; b, $n$ = 3, R$_f$ = –C$_6$F$_5$; for 5–7 core group R$_c$ = BrC$_6$H$_4$(CH$_2$)$_3$−.
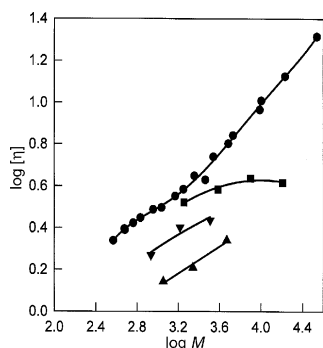
**Fig. 1** Plot of log{intrinsic viscosity/dL g$^{-1}$} *vs.* log{nominal molecular weight}: ● polystyrene standards, ■ vinyl-terminated carbosilane dendrimers (see ref. 10), ▼ pentafluorophenyl-terminated carbosilane monodendrons (**5b**, **6b**, **7b**), ▲ polyfluoroalkyl-terminated carbosilane monodendrons (**5a**, **6a**, **7a**).
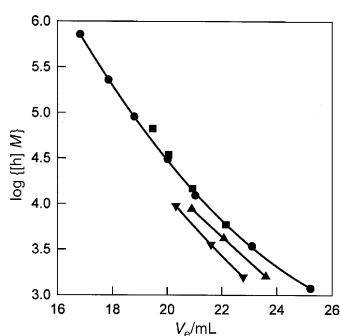


**Fig. 2** Plot of log{(intrinsic viscosity/dL g$^{-1}$)(nominal molecular weight)} *vs.* elution volume $V_e$ (mL): for symbol legend, see Fig. 1.

and very much smaller than dimensions that were calculated[8] for extended structures of polyfluoroalkyl ether analogues. Examination of the relationship between log{[η].$M$} and the SEC elution volume (mL) $V_e$, (Fig. 2) which is the basis[10,14] for the universal calibration curve, shows that while the family of unfluorinated carbosilane dendrimers conform[10] to established expectations, the fluorous monodendrons do not. This is evidence for an anomalous repulsive interaction between the latter and the stationary phase of the SEC column, a phenomenon that may confer resistance to surface penetration on materials that have been treated with reagents like **7a**.

## Notes and references

† Measured $^1$H NMR data were in all cases consistent with the proposed structures. The $^{19}$F{$^1$H} NMR spectra which were essentially identical within each family of compounds were useful for diagnostic purposes. Data for compound **5a**: Yield 88%. Anal. Calcd. for $C_{36}H_{45}BrF_{26}Si_3$: C, 38.07; H, 3.99. Found: C, 38.53; H, 4.23. MALDI-TOF (*m/z*) Calcd. (M + Ag$^+$): 1244. Found: 1244. $^{13}$C{$^1$H} NMR (CDCl$_3$, δ): 143.1, 131.3, 130.2 (s, $C_6H_4$), 121.8 (m, $C_6F_{13}$), 119.6 (s, $C_6H_4$), 119.1, 118.0, 115.8, 111.1, 108.2, (m, $C_6F_{13}$), 39.2 (s, CH$_2$), 25.9 (t, CH$_2$CF$_2$), 25.5, 19.4, 18.4, 18.1, 13.5, 4.4 (s, CH$_2$), −3.9, −5.2 (s, CH$_3$). $^{29}$Si{$^1$H} NMR (CDCl$_3$, δ): 3.09 (s, 2Si), 1.80 (s, 1Si). **5b**: Yield 92%. Anal. Calcd. for $C_{38}H_{49}BrF_{10}Si_3$: C, 53.07; H, 5.74. Found: C, 53.64; H, 5.97. $^{13}$C{$^1$H} NMR (CDCl$_3$, δ): 146.2, 143.4 (m, $C_6F_5$), 141.6 (s, $C_6H_4$), 141.5, 139.2, 138.7, 136.1 (m, $C_6F_5$), 131.2, 130.2, 119.3 (s, $C_6H_5$), 39.3, 31.5, 25.9, 24.1, 19.9, 18.5, 18.3, 15.2, 13.7 (s, CH$_2$), −3.5, −5.2 (s, CH$_3$). $^{29}$Si{$^1$H} NMR (CDCl$_3$, δ): 2.21 (s, 2Si), 1.76 (s, 1Si). **6a**: Yield 94%. Anal. Calcd. for $C_{70}H_{95}BrF_{52}Si_7$: C, 38.20; H, 4.35. Found: C, 38.52; H, 4.47. MALDI-TOF (*m/z*) Calcd. (M + Ag$^+$): 2309. Found: 2309. $^{13}$C{$^1$H} NMR (CDCl$_3$, δ): 141.5, 131.2, 130.1 (s, $C_6H_4$), 121.8 (m, $C_6F_{13}$), 119.2 (s, $C_6H_4$), 119.1, 118.0, 115.8, 111.1, 108.2 (m, $C_6F_{13}$), 39.3 (s, CH$_2$), 25.8 (t, CH$_2$CF$_2$), 25.5, 19.5, 19.0, 18.8, 18.7, 18.6, 18.4, 18.3, 13.7, 4.5 (s, CH$_2$), −3.9, −5.2, −5.3 (s, CH$_3$). $^{29}$Si{$^1$H} NMR (CDCl$_3$, δ):

3.09 (s, 4Si), 1.70 (s, 1Si), 1.05 (s, 2Si). **6b**: Yield 85%. Anal. Calcd. for $C_{74}H_{103}BrF_{20}Si_7$: C, 53.90; H, 6.30. Found: C, 54.15; H, 6.55. $^{13}$C{$^1$H} NMR (CDCl$_3$, δ): 146.2, 143.4 (m, $C_6F_5$), 141.6 (s, $C_6H_4$), 141.5, 139.2, 138.7, 136.1 (m, $C_6F_5$), 131.2, 130.2, 119.3 (s, $C_6H_5$), 39.4, 26.7, 26.0, 24.0, 19.9, 18.9, 18.7, 18.5, 18.4, 15.3, 15.2, 13.8 (s, CH$_2$), −3.4, −3.5, −5.1 (s, CH$_3$). $^{29}$Si{$^1$H} NMR (CDCl$_3$, δ): 2.19 (s, 4Si), 1.72 (s, 1Si), 1.18 (s, 2Si). **7a**: Yield 85%. Anal. Calcd. for $C_{138}H_{195}BrF_{104}Si_{15}$: C, 38.27; H, 4.54. Found: C, 38.43; H, 4.67. MALDI-TOF (*m/z*) Calcd. (M + Ag$^+$): 4439. Found: 4443. $^{13}$C{$^1$H} NMR (CDCl$_3$, δ): 141.5, 131.2, 130.1 (s, CH, $C_6H_4$), 121.8 (m, $C_6F_{13}$), 119.2 (s, $C_6H_4$), 119.1, 118.0, 115.8, 111.1, 108.2 (m, $C_6F_{13}$), 39.3 (s, CH$_2$), 25.8 (t, CH$_2$CF$_2$), 19.5, 18.8, 18.6, 18.5, 18.3, 13.7, 4.5 (s, CH$_2$), −0.19, −3.9, −5.2 (s, CH$_3$). $^{29}$Si{$^1$H} NMR (CDCl$_3$, δ): 3.06 (s, 8Si), 1.66 (s, 1Si), 1.04 (s, 4Si), 0.95 (s, 2Si). **7b**: Yield 82%. Anal. Calcd. for $C_{146}H_{211}BrF_{40}Si_{15}$: C, 54.33; H, 6.59. Found: C, 54.56; H, 6.84. $^{13}$C{$^1$H} NMR (CDCl$_3$, δ): 146.2, 143.4 (m, $C_6F_5$), 141.6 (s, $C_6H_4$), 141.5, 139.2, 138.7, 136.1 (m, $C_6F_5$), 131.2, 130.2, 119.3 (s, $C_6H_5$), 39.4, 26.7, 26.0, 25.9, 24.1, 24.0, 19.9, 19.8, 18.9, 18.7, 18.5, 18.4, 15.3, 15.2 (s, CH$_2$), −3.4, −3.5, −5.1, -5.2 (s, CH$_3$). $^{29}$Si{$^1$H} NMR (CDCl$_3$, δ): 2.18 (s, 8Si), 1.69 (s, 1Si), 1.16 (s, 4Si), 0,99 (s, 2Si).

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