Electronic Supplementary Material (ESI) for Soft Matter

Synthesis and Thermal Studies of Aliphatic Polyurethane Dendrimers: A Geometric Approach to the Flory-Fox equation for Dendrimer Glass Transition Temperature.

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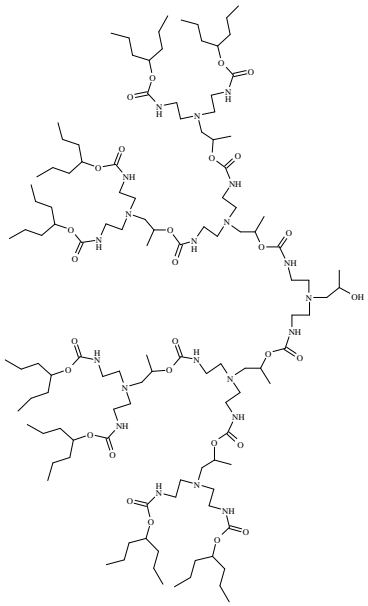
Electronic Supporting Information

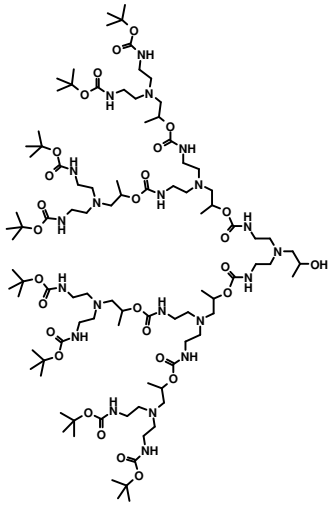
Synthetic Details

Synthesis of **6a**:



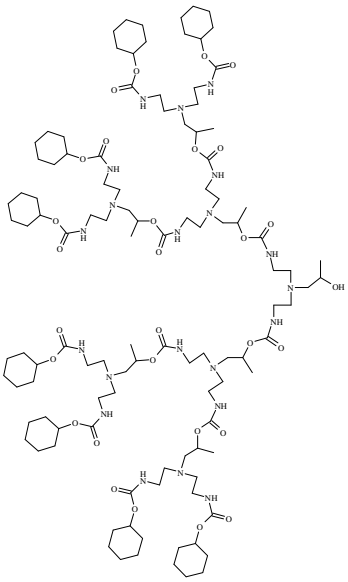
CDI (0.75 g, 4.62 mmol) was added to a stirred solution of **5a** (4.3 g, 3.89 mmol) in toluene (50 mL). The mixture was heated at 60°C for 4 hrs. Subsequently, the reaction mixture was analysed by ^{1}H NMR spectroscopy and interpretation of the spectrum indicated there was no evidence of the starting materials. The branching unit **4** (0.31 g, 1.95 mmol) was added and the solution was heated for 1 day at 60°C. The reaction mixture was concentrated *in vacuo* and redissolved in CH_2Cl_2 (100 mL). The organic phase was subsequently washed with water (3 x 100 mL), dried over $MgSO_4$ and the solvent removed using a rotary evaporator. The resulting pale yellow oil was purified by column chromatography (silica gel, eluting with EtOAc increasing to EtOAc:MeOH 100:5) and the colourless oil obtained was dried under vacuum (10^{-1} mbar) to give **6a** as a colourless oil (2.1 g, 44%). T_g = 11°C. Found C, 59.08; H, 9.72; N, 12.02%. $C_{119}H_{233}O_{29}N_{21}$ requires, C, 59.01; H, 9.70; N, 12.14%. ^{13}C NMR (62.9 MHz, CD_3OD) δ(ppm)= 14.5, 19.0, 19.6, 21.0, 37.9, 40.1, 55.6, 61.0, 64.1, 66.1, 70.7, 75.2, 158.7, 159.2. ^{1}H NMR (250 MHz, CD_3OD) δ(ppm)= 0.92 (t, J=7Hz, 48H), 1.12 (d, J=6Hz, 3H), 1.20 (d, J=6Hz, 18H), 1.36 (m, 32H), 1.49 (m, 32H), 2.45-2.62 (m, 42H), 3.10-3.27 (m, 28H), 3.78 (m, 1H), 4.73 (m, 8H), 4.81 (m, obscured by water peak, 6H), 6.64 (s, br, O(CO)N*H*CH_2CH_2), 6.71 (s, br, O(CO)N*H*CH_2CH_2), 6.85 (s, br, O(CO)N*H*CH_2CH_2). *m/z* (MALDI TOF (Voyager) MS) 2423.6 $[M+H]^+$, 2445.2 $[M+Na]^+$, 2461.2 $[M+K]^+$, calculated M_w = 2422.25. GPC; M_w = 2830, PDI = 1.02.

Synthesis of **6b**:



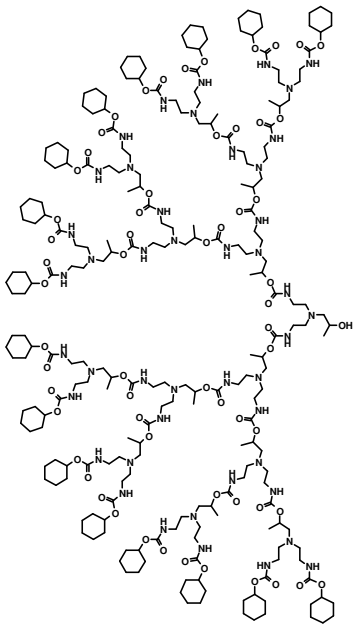
The procedure was similar to that described for the synthesis of, but using **5b** as the starting material. The oil obtained was purified by column chromatography (silica gel, eluting with EtOAc increasing to EtOAc:MeOH, 100:5) and then purified by preparative GPC (Biobeads, eluting with toluene) to give **6b** as a colourless amorphous solid (48%). T_g = 40°C. Found C, 54.16; H, 9.08; N, 13.83%. $C_{95}H_{185}O_{29}N_{21}$ requires, C, 54.71; H, 8.94; N, 14.10%. ^{13}C NMR (62.9 MHz, CD_3OD) δ(ppm)= 19.0, 21.0, 28.9, 39.6, 40.0, 55.6, 55.9, 61.0, 64.0, 66.0, 70.7, 79.9, 158.3, 158.7, 158.8. ^{1}H NMR (400 MHz, CD_3OD) δ(ppm)= 1.12 (d, J=6Hz, 3H), 1.20 (d, J=6.4Hz, 18H), 1.44 (s, 72H), 2.41-2.64 (m, 42H), 3.04-3.24 (m, 28H), 3.78 (m, 1H), 4.85 (m, obscured by water peak, 6H), 6.42 (s, br, O(CO)N*H*CH_2CH_2), 6.71 (s, br, O(CO)N*H*CH_2CH_2), 6.85 (s, br, O(CO)N*H* CH_2CH_2). *m/z* (ES MS) 2108.2 $[M+Na]^+$, 1054.4 $[M+H]^{2+}$, 1065.4 $[M+Na]^{2+}$. *m/z* (MALDI TOF (Voyager) MS) 2086 $[M+H]^+$, 2108 $[M+Na]^+$, 2124 $[M+K]^+$ – and sets of similar peaks at 100 mass intervals below the molecular ion, calculated M_w = 2085.61. GPC; M_w = 2300, PDI = 1.01.

Synthesis of **6c**:



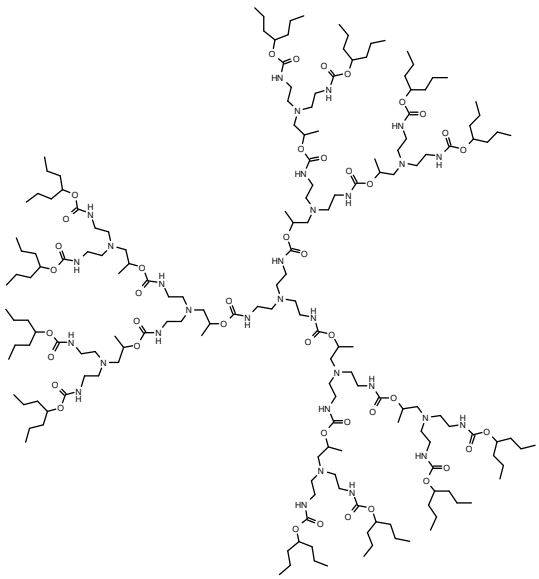
The procedure was similar to that described above, but using **5c** as the starting material. The colourless oil obtained after silica gel chromatography (eluting with EtOAc increasing to EtOAc:MeOH 100:5) was purified further by preparative GPC (Biobeads, eluting with toluene) to give **6c** as a colourless amorphous solid (28%). T_g = 40°C. Found C, 58.05; H, 8.85; N, 12.69%. $C_{111}H_{201}O_{29}N_{21}$ requires, C, 58.12; H, 8.83; N, 12.82%. ^{13}C NMR (100 MHz, CD_3OD) δ(ppm)= 19.0, 21.0, 24.9, 26.6, 33.2, 39.9, 40.1, 40.5, 55.5, 55.7, 55.9, 60.9, 64.1, 66.0, 70.7, 73.9, 157.6, 157.7, 157.8. ^{1}H NMR (400 MHz, CD_3OD) δ(ppm)= 1.12 (d, J=6.4Hz, 3H), 1.45 (d, J=5.6Hz, 18H), 1.25-1.42 (m, 40H), 1.56 (m, 8H), 1.75 (m, 16H), 1.85 (m, 16H), 2.42-2.69 (m, 42H), 3.15-3.25 (m, 28H), 3.78 (m, 1H), 4.57 (m, 8H), 4.84 (m, obscured by water peak, 6H), 6.59 (s, br, O(CO)N*H*CH_2CH_2), 6.71 (s, br, O(CO)N*H*CH_2CH_2), 6.86 (s, br, O(CO)N*H*CH_2CH_2). *m/z* (MALDI TOF (Voyager) MS) 2294.0 $[M+H]^+$, 2316.2 $[M+Na]^+$, 2331.2 $[M+K]^+$, calculated M_w = 2293.91. GPC; M_w = 2440, PDI = 1.01.

Synthesis of **7c**:



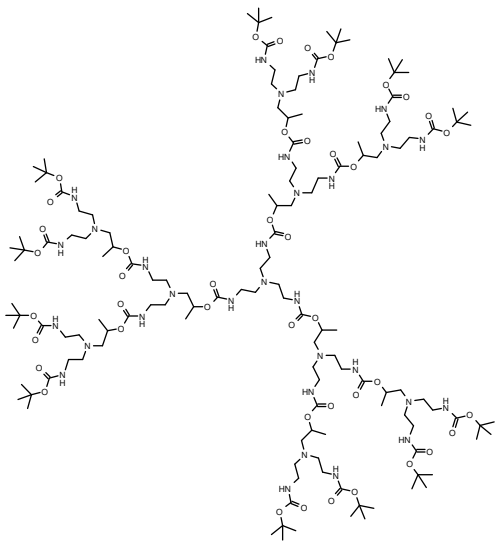
The procedure was similar to that described for the synthesis of **6a**, but using **6c** as the starting material. The crude product obtained was purified by column chromatography (silica gel, eluting with EtOAc:MeOH, 100:5) and the colourless solid obtained was purified by preparative GPC (Biobeads, eluting with toluene) to give *compound* ***CG4OH*** as a colourless amorphous solid (14%). T_g = 48°C. Found C, 56.95; H, 8.66; N, 12.57%. $C_{231}H_{417}O_{61}N_{45}$ requires, C, 57.79; H, 8.75; N, 13.13%. ^{13}C NMR (100 MHz, CD_3OD) δ(ppm)= 19.0, 19.1, 21.1, 24.9, 26.6, 33.2, 39.9, 40.1, 40.4, 40.5, 55.5, 55.7, 60.9, 64.1, 66.0, 70.7, 74.0, 158.6, 158.7, 158.8. ^{1}H NMR (400 MHz, CD_3OD) δ(ppm)= 1.12 (d, J=6Hz, 3H), 1.19-1.45 (m, 122H), 1.56 (m, 16H), 1.74 (m, 36H), 1.85 (m, 36H), 2.44-2.68 (m, 88H), 3.11-3.20 (m, 60H), 3.78 (m, 1H), 4.57 (m, 16H), 4.84 (m, 14H), 6.59 (s, br, O(CO)N*H*CH_2CH_2), 6.70 (s, br, O(CO)N*H*CH_2CH_2), 6.85 (s, br, O(CO)N*H*CH_2CH_2). *m/z* (MALDI TOF (Voyager) MS) 4801.4 $[M+H]^+$, 4823.4 $[M+Na]^+$, 4839.3 $[M+K]^+$, calculated M_w = 4801.05. GPC; M_w = 4190, PDI = 1.02.

Synthesis of G2-4-heptyl Dendrimer TAEA:



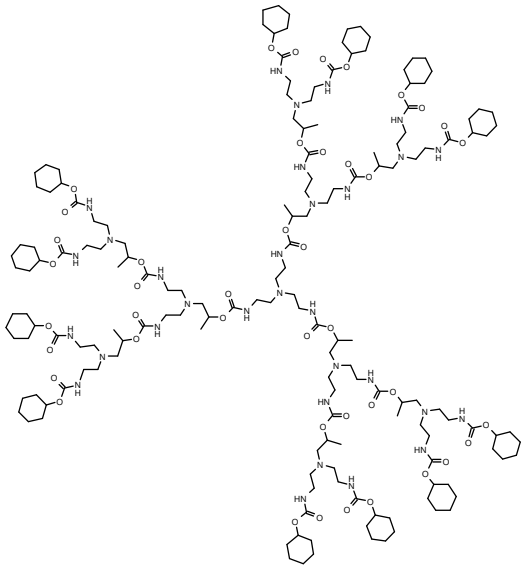
CDI (0.52 g, 3.21 mmol) was added to a stirred solution of **5a** (3.2 g, 2.90 mmol) in toluene (100 mL). The mixture was heated at 60°C for 4 hrs. Subsequently, the reaction mixture was analysed by ^{1}H NMR spectroscopy and interpretation of the spectrum indicated there was no evidence of the starting materials. Tris(2-aminoethyl)amine (0.14 g, 0.96 mmol) was added and the solution was heated for 20 hrs at 60°C. The reaction mixture was concentrated *in vacuo* and redissolved in CH_2Cl_2 (150 mL). The organic phase was subsequently washed with water (3 x 150 mL), dried over $MgSO_4$ and the solvent removed using the rotary evaporator. The crude product was purified by column chromatography (silica gel, eluting with EtOAc increasing to EtOAc:MeOH 100:5) and the colourless oil obtained was purified further by preparative GPC (Biobeads, eluting with toluene) to give G2-4-heptyl Dendrimer TAEA as a sticky colourless oil (0.86 g, 24%). T_g = 17°C. Found C, 58.38; H, 9.55; N, 12.15%. $C_{174}H_{339}O_{42}N_{31}$ requires, C, 59.07; H, 9.66; N, 12.27%. ^{13}C NMR (62.9 MHz, CD_3OD) δ(ppm)= 14.5, 19.1, 19.6, 37.9, 40.0, 55.2, 55.6, 60.9, 70.7, 75.1, 158.6, 159.1. ^{1}H NMR (400 MHz, CD_3OD) δ(ppm)= 0.92 (t, J=7.2Hz, 72H), 1.20 (d, J=6Hz, 27H), 1.36 (m, 48H), 1.50 (m, 48H), 2.50-2.62 (m, 60H), 3.16 (m, 42H), 4.73 (m, 12H), 4.86 (m, 9H), 6.65 (s, br, OC(O)N*H*CH_2), 6.76 (s, br, OC(O)N*H*CH_2). *m/z* (ES MS) 3558.5 $[M+Na]^+$, 1791.5 $[M+2Na]^{2+}$. *m/z* (MALDI TOF (Kratos) MS) 3558 $[M+Na]^+$, calculated M_w = 3537.74. GPC; M_w = 3680, PDI = 1.01.

Synthesis of G2-*t*-butyl Dendrimer TAEA:



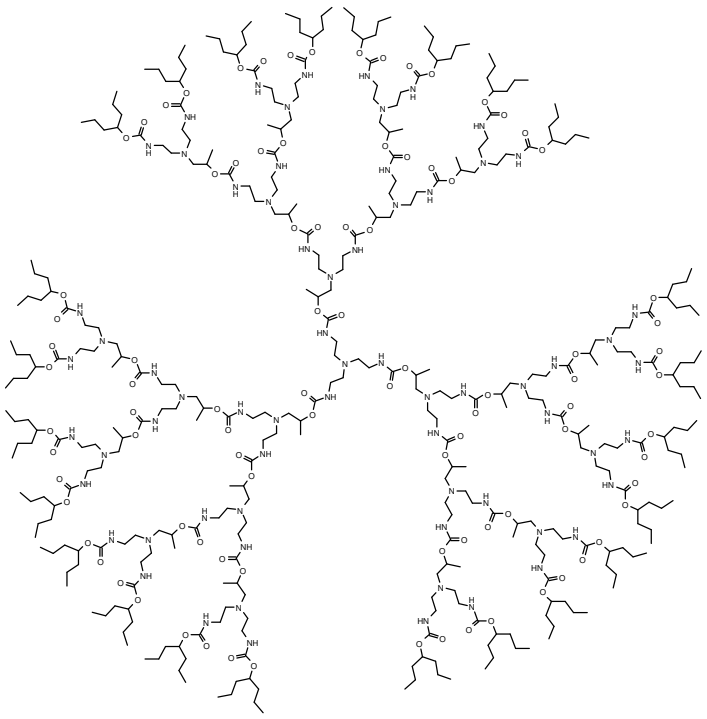
The procedure was the same as that described for the synthesis and purification of G2-4-heptyl Dendrimer TAEA but **5b** was used as the starting material to give G2-cyclohexyl Dendrimer TAEA as colourless oil (32%). T_g = 47°C. Found C, 55.11; H, 8.79; N, 13.46%. $C_{138}H_{267}O_{42}N_{31}$ requires, C, 54.65; H, 8.87; N, 14.32%. ^{13}C NMR (62.9 MHz, CD_3OD) δ(ppm)= 19.0, 28.9, 39.5, 40.0, 55.2, 55.7, 60.9, 70.6, 80.0, 158.4, 158.7. ^{1}H NMR (250 MHz, CD_3OD) δ(ppm)= 1.21 (d, J=6Hz, 27H), 1.45 (s, 108H), 2.50-2.75 (m, 60H), 3.05-3.25 (m, 42H), 4.85 (m, obscured by water peak, 9H), 6.46 (s, br, OC(O)N*H*CH_2), 6.76 (s, br, OC(O)N*H*CH_2). *m/z* (ES MS) 3055.1 $[M+Na]^+$, 1539.0 $[M/2+Na]^+$. *m/z* (MALDI TOF (Kratos) MS) 3039 $[M+H]^+$, calculated M_w = 3032.78. GPC; M_w = 3120, PDI = 1.02.

Synthesis of G2-cyclohexyl Dendrimer TAEA:

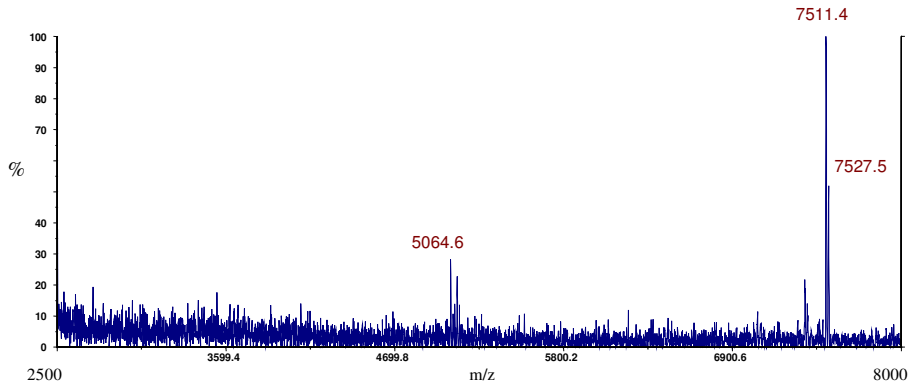


The procedure was similar to that described for the synthesis of G2-4-heptyl Dendrimer TAEA but **5c** was used as the starting material. The purification step was achieved by column chromatography (silica gel, eluting with EtOAc increasing to EtOAc:MeOH 100:5) and the oil obtained was purified further by preparative GPC (Biobeads, eluting with toluene) to give G2-cyclohexyl Dendrimer TAEA as a colourless amorphous solid (41%). T_g = 44°C. Found C, 57.43; H, 8.70; N, 12.75%. $C_{162}H_{291}O_{42}N_{31}$ requires, C, 58.16; H, 8.77; N, 12.98%. ^{13}C NMR (62.9 MHz, CD_3OD) δ(ppm)= 19.0, 24.8, 26.5, 33.1, 39.9, 55.5, 60.9, 70.7, 73.9, 158.57, 158.62, 158.7. ^{1}H NMR (250 MHz, CD_3OD) δ(ppm)= 1.19 (d, J=5.5Hz, 27H), 1.39 (m, 60H), 1.55 (m, 12H), 1.75 (m, 24H), 1.85 (m, 24H), 2.48-2.61 (m, 60H), 3.16 (m, 42H), 4.57 (m, 12H), 4.84 (m, obscured by water peak, 9H), 6.58 (s, br, OC(O)N*H*CH_2), 6.70 (s, br, OC(O)N*H*CH_2). *m/z* (MALDI TOF (Voyager) MS) 3370.2 $[M+Na]^+$, 3386.1 $[M+K]^+$, calculated M_w = 3345.23. GPC; M_w = 2780, PDI = 1.05.

Synthesis of G3-4-heptyl Dendrimer TAEA:

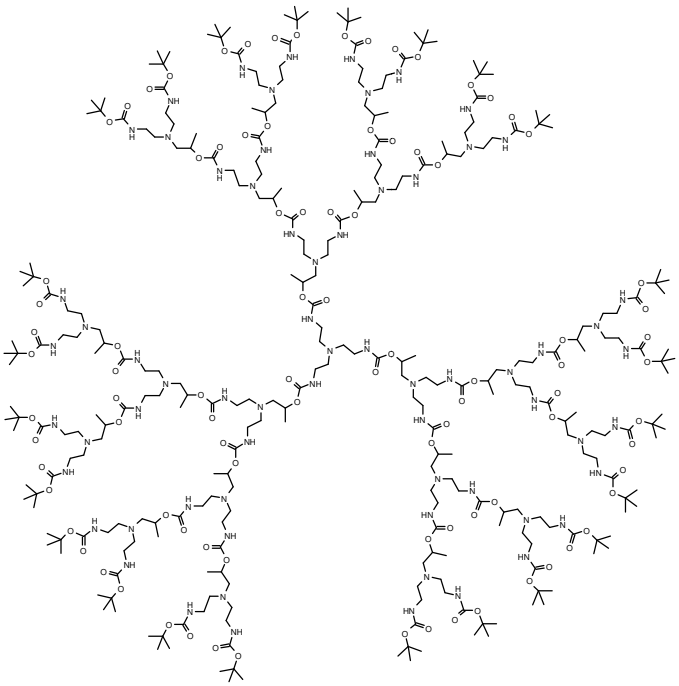


CDI (92 mg, 0.57 mmol) was added to a stirred solution of **6a** (1.15 g, 0.47 mmol) in toluene (40 mL) and the mixture was heated at 60°C for 4 hours. Subsequently, the reaction mixture was analysed by ^{1}H NMR spectroscopy and interpretation of the spectrum indicated no evidence of the presence of starting materials. Tris(2-aminoethyl)amine (23 mg, 0.16 mmol) was added to the solution and the mixture was heated for 1 day at 60°C. The reaction mixture was concentrated *in vacuo* and redissolved in CH_2Cl_2 (100 mL). The organic phase was subsequently washed with water (3 x 100 mL), dried over $MgSO_4$ and the solvent removed using the rotary evaporator. The yellow oil obtained was purified by column chromatography (silica gel, eluting with EtOAc:MeOH 100:5 increasing to EtOAc:MeOH 100:10). The colourless oil obtained was purified further by preparative GPC (Biobeads, eluting with toluene) to give G3-4-heptyl Dendrimer TAEA as an extremely sticky oil (280 mg, 24%). T_g = 19°C. Found C, 57.37; H, 9.50; N, 11.88%. $C_{366}H_{711}O_{90}N_{67}$ requires, C, 58.68; H, 9.57; N, 12.53%. ^{13}C NMR (100 MHz, CD_3OD) δ(ppm)= 14.6, 19.1, 19.7, 40.0, 40.1, 55.7, 61.0, 70.7, 75.2, 158.7, 158.8, 159.3. ^{1}H NMR (400 MHz, CD_3OD) δ(ppm)= 0.92 (t, J=7.2Hz, 144H), 1.20 (d, J=6Hz, 63H), 1.36 (m, 96H), 1.50 (m, 96H), 2.51-2.66 (m, 132H), 3.12-3.20 (m, 90H), 4.74 (m, 24H), 4.85 (m, obscured by water peak, 9H), 6.46 (s, br, OC(O)N*H*CH_2), 6.76 (s, br, OC(O)N*H*CH_2). *m/z* (MALDI TOF (Kratos) MS) 7511.4 $[M+Na]^+$, 7527.5 $[M+K]^+$, calculated M_w = 7490.96 and an impurity at 5063.6 corresponding to the two-armed dendrimer. GPC; M_w = 6410, PDI = 1.01.

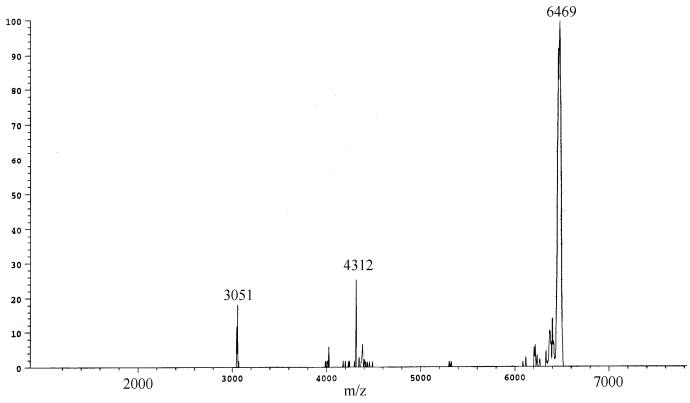


MALDI TOF – MS of G3-4-heptyl Dendrimer TAEA

Synthesis of G3-*t*-butyl Dendrimer TAEA:

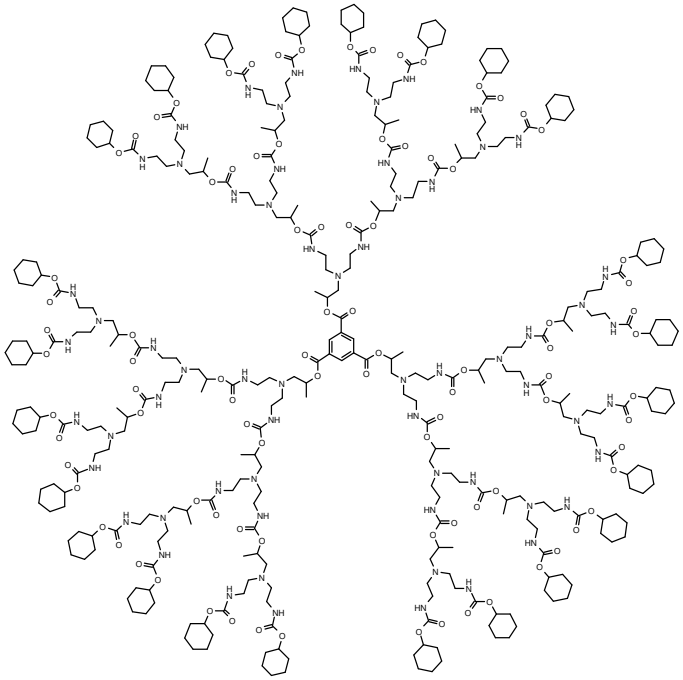


The procedure was similar to that described for the synthesis of G3-4-heptyl Dendrimer TAEA, but **6b** was used as the starting material. After the same purification method G3-*t*-butyl Dendrimer TAEA was isolated as a white amorphous solid (20%). T_g = 49°C. Found C, 54.46; H, 8.74; N, 13.41%. $C_{294}H_{567}O_{90}N_{67}$ requires, C, 54.48; H, 8.82; N, 14.48%. ^{13}C NMR (125 MHz, CD_3OD) δ(ppm)= 19.1, 29.0, 39.9, 40.2, 55.6, 55.7, 61.1, 70.9, 80.0, 158.3, 158.6. ^{1}H NMR (400 MHz, CD_3OD) δ(ppm)= 1.20 (d, J=6.4Hz, 63H), 1.44 (s, 216H), 2.48-2.63 (m, 132H), 3.05-3.25 (m, 90H), 4.85 (m, obscured by water peak, 21H), 6.42 (s, br, OC(O)N*H*CH_2), 6.71 (s, br, OC(O)N*H*CH_2). *m/z* (ES MS) 3235.8 $[M+H]^{2+}$, 3246.9 $[M+Na]^{2+}$, 3257.9 $[M+2Na]^{2+}$. *m/z* (MALDI TOF (Kratos) MS) 6469 $[M+H]^+$, calculated M_w = 6481.05. GPC; M_w = 4980, PDI = 1.06.

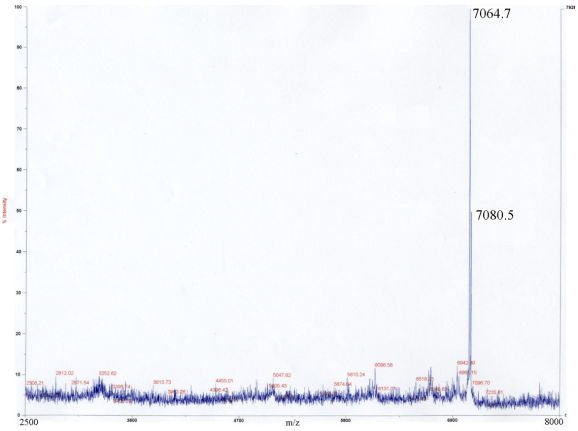


MALDI TOF-MS of G3-*t*-butyl Dendrimer TAEA

Synthesis of G3-cyclohexyl Dendrimer BTT:

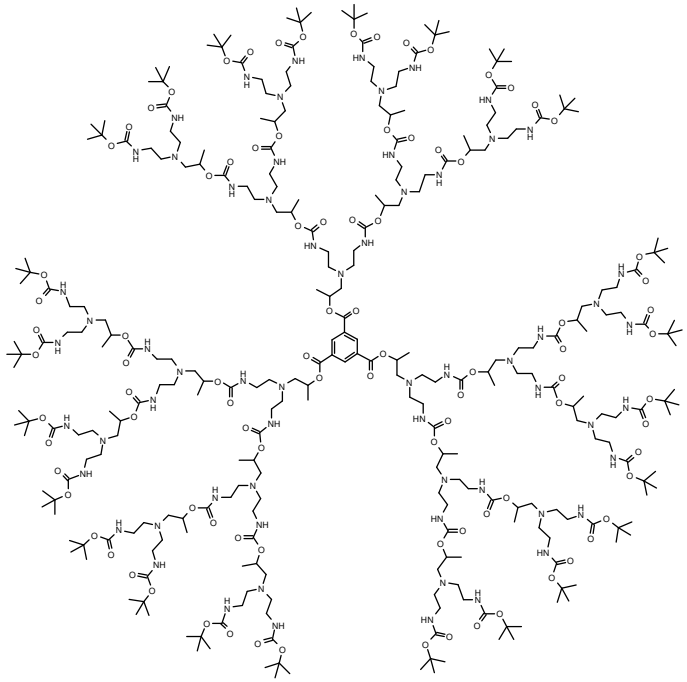


A solution of **6c** (0.64 g, 0.28 mmol) and DMAP (90 mg, 0.74 mmol) in benzene (50 mL) was refluxed for 4 hrs with a Dean-Stark trap filled with molecular sieves attached. The mixture was cooled to room temperature and 1,3,5-benzenetricarbonyl trichloride (22 mg, 8.29 x 10^{-2} mmol) was added. The reaction mixture was stirred and heated at reflux temperature (81°C) for 22 hrs and then concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, eluting with EtOAc:MeOH, 100:5) and by preparative GPC (Biobeads, eluting with toluene) to give G3-cyclohexyl Dendrimer BTT as a white amorphous solid (290 mg, 50%). T_g = 50°C. Found C, 57.00; H, 8.52; N, 12.92%. $C_{342}H_{603}O_{90}N_{63}$ requires, C, 58.37; H, 8.64; N, 12.54%. ^{13}C NMR (100 MHz, CD_3OD) δ(ppm)= 18.9, 19.1, 24.9, 26.6, 33.2, 40.0, 40.5, 55.5, 55.8, 60.5, 61.0, 70.7, 72.3, 74.0, 133.1, 135.4, 158.6, 158.7, 158.8, 165.7. ^{1}H NMR (400 MHz, CD_3OD) δ(ppm)= 1.19 (d, J=6Hz, 54H), 1.24-1.41 (m, 129H), 1.55 (m, 24H), 1.73 (m, 48H), 1.84 (m, 48H), 2.48-2.86 (m, 126H), 3.10-3.26 (m, 84H), 4.56 (m, 24H), 4.86 (m, obscured by water peak, 18H), 5.28 (m, 3H), 6.58 (s, br, OC(O)N*H*CH_2), 6.71 (s, br, OC(O)N*H*CH_2), 8.81 (s, 3H). *m/z* (MALDI TOF (Voyager) MS) 7064.6 $[M+Na]^+$, 7080.5 $[M+K]^+$, calculated M_w = 7037.82. GPC; M_w = 6410, PDI = 1.01.



MALDI TOF-MS of G3-cyclohexyl Dendrimer BTT

Synthesis of G3-*t*-butyl Dendrimer BTT:

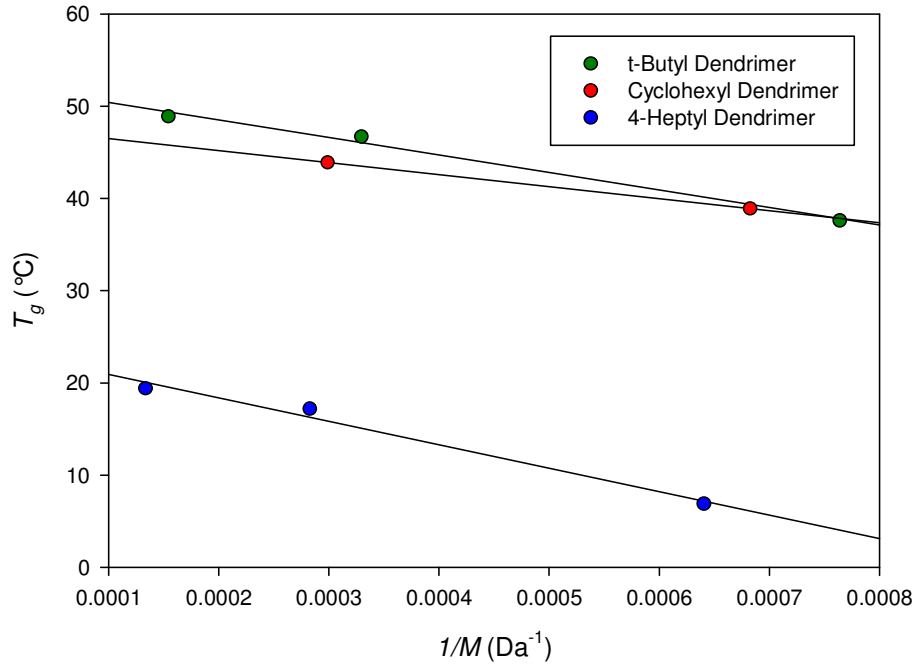


The procedure was similar to that described for the synthesis of G3-cyclohexyl Dendrimer BTT, but **6b** was used as the starting material. After the same purification method G3-*t*-butyl Dendrimer BTT was isolated as a white amorphous solid (48%). T_g = 49°C. Found C, 55.17; H, 8.67; N, 12.52%. $C_{294}H_{555}O_{90}N_{63}$ requires, C, 55.06; H, 8.72; N, 13.76%. ^{13}C NMR (100 MHz, CD_3OD) δ(ppm)= 18.9, 19.1, 29.0, 30.9, 40.0, 40.1, 55.7, 61.0, 70.7, 72.3, 80.0, 133.1, 135.4, 158.4, 158.7, 158.8, 165.7. ^1H NMR (400 MHz, CD_3OD) δ(ppm)= 1.20 (d, 54H), 1.44 (m, 225H), 2.49-2.86 (m, 126H), 3.08-3.21 (m, 84H), 4.85 (m, obscured by water peak, 18H), 5.28 (m, 3H), 6.43 (s, br, OC(O)N*H*CH_2), 6.73 (s, br, OC(O)N*H*CH_2), 8.80 (s, 3H). GPC; M_w = 5650, calculated M_w = 6412.92, PDI = 1.03.

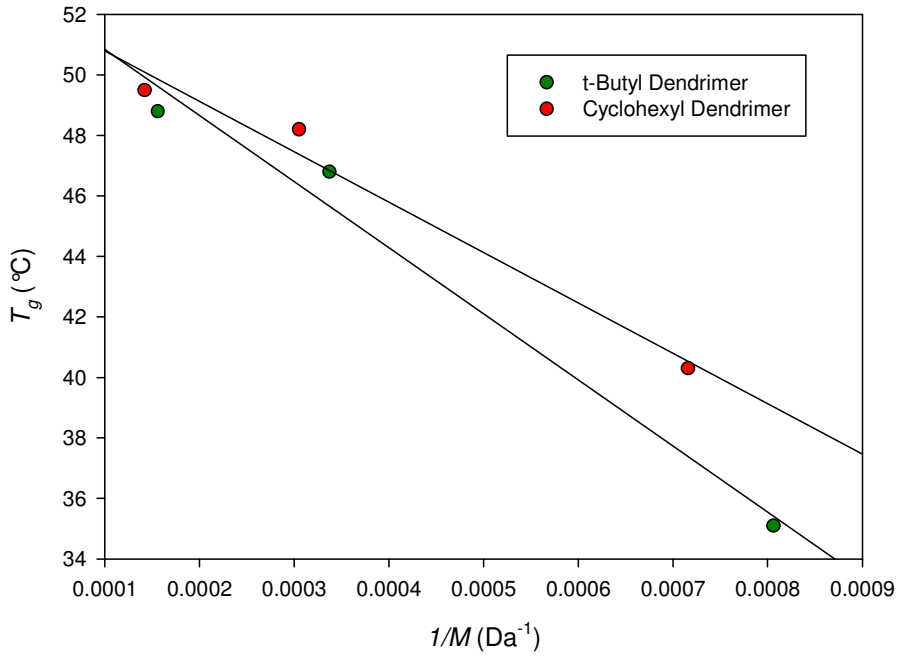
Graphical Analysis

Conventional Flory-Fox analysis

Dendrimers comprising TAEA cores

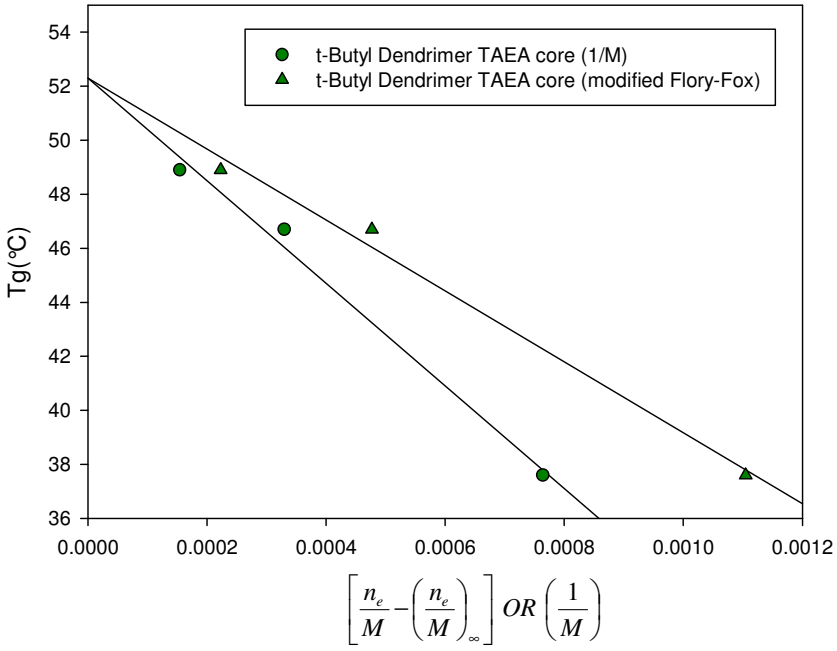


Dendrimers comprising BTT cores

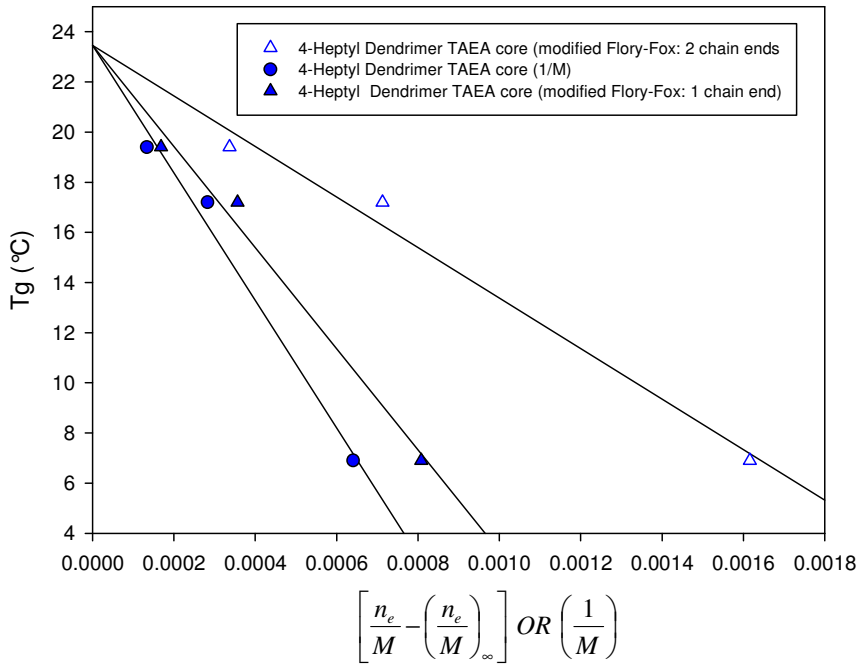


Comparison of modified Flory-Fox vs Flory-Fox analysis

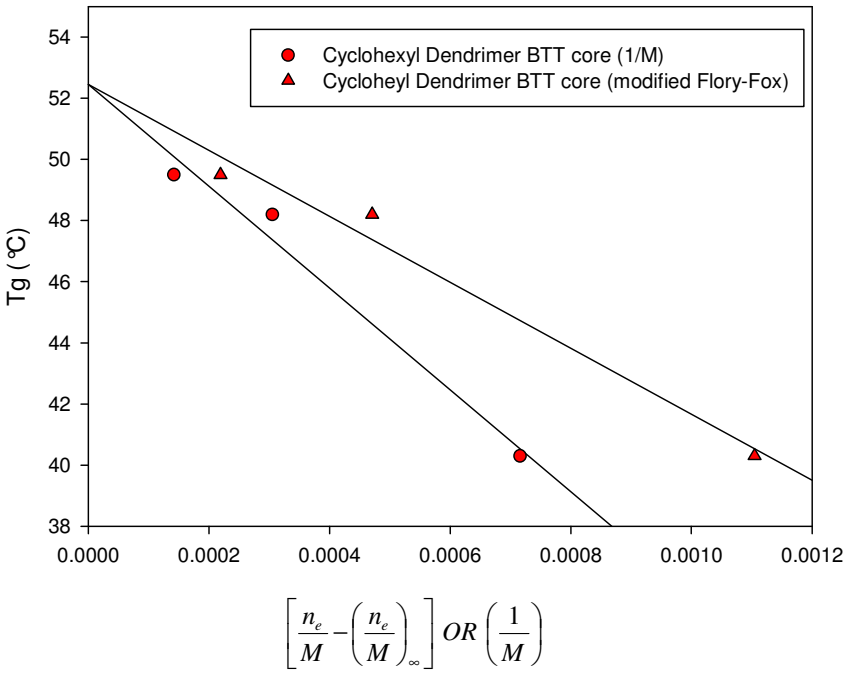
Dendrimers comprising TAEA cores and *t*-butyl surface functionality



Dendrimers comprising TAEA cores and 4-heptyl surface functionality



Dendrimers comprising BTT cores and cyclohexyl surface functionality



Example calculations of $(ne/M)_\infty$

Cyclohexyl functional dendrons (GREY = experimental data, blue = $(ne/M)_\infty$ values)

Generation	Molecular Weight	number of end groups (ne)	ne/M	ne/M – $(ne/M)_\infty$
1	413.56	2	4.83610E-03	1.65E-03
2	1040.36	4	3.84480E-03	6.54E-04
3	2293.96	8	3.48740E-03	2.97E-04
4	4801.16	16	3.33250E-03	1.42E-04
5	9815.56	32	3.26010E-03	
6	19844.36	64	3.22510E-03	
7	39901.96	128	3.20790E-03	
8	80017.16	256	3.19930E-03	
9	160247.56	512	3.19510E-03	
10	320708.36	1024	3.19290E-03	
11	641629.96	2048	3.19190E-03	
12	1283473.16	4096	3.19130E-03	
13	2567159.56	8192	3.19110E-03	
14	5134532.36	16384	3.19090E-03	
15	10269277.96	32768	3.19090E-03	
16	20538769.16	65536	3.19080E-03	
17	41077751.56	131072	3.19080E-03	
18	82155716.36	262144	3.19080E-03	
19	164311646	524288	3.19080E-03	
20	328623505.2	1048576	3.19080E-03	
21	657247223.6	2097152	3.19080E-03	
22	1314494660	4194304	3.19080E-03	
23	2628989534	8388608	3.19080E-03	
24	5257979281	16777216	3.19080E-03	
25	10515958776	33554432	3.19080E-03	
26	21031917764	67108864	3.19080E-03	
27	42063835742	134217728	3.19080E-03	
28	84127671697	268435456	3.19080E-03	
29	1.68255E+11	536870912	3.19080E-03	
30	3.36511E+11	1073741824	3.19080E-03	

4-Heptyl functional TAEA Dendrimers (GREY = experimental data, blue = (ne/M)∞ values)

Generation	Molecular Weight	number of end groups (ne)	ne/M	ne/M – (ne/M)∞
1	1561.17	6	3.84330E-03	8.08E-04
2	3537.82	12	3.39190E-03	3.56E-04
3	7491.14	24	3.20380E-03	1.68E-04
4	15397.77	48	3.11730E-03	
5	31211.03	96	3.07580E-03	
6	62837.55	192	3.05550E-03	
7	126090.59	384	3.04540E-03	
8	252596.67	768	3.04040E-03	
9	505608.83	1536	3.03790E-03	
10	1011633.15	3072	3.03670E-03	
11	2023681.79	6144	3.03610E-03	
12	4047779.07	12288	3.03570E-03	
13	8095973.63	24576	3.03560E-03	
14	16192362.75	49152	3.03550E-03	
15	32385140.99	98304	3.03550E-03	
16	64770697.47	196608	3.03540E-03	
17	129541810.4	393216	3.03540E-03	
18	259084036.4	786432	3.03540E-03	
19	518168488.2	1572864	3.03540E-03	
20	1036337392	3145728	3.03540E-03	
21	2072675199	6291456	3.03540E-03	
22	4145350814	12582912	3.03540E-03	
23	8290702043	25165824	3.03540E-03	
24	16581404502	50331648	3.03540E-03	
25	33162809420	100663296	3.03540E-03	
26	66325619256	201326592	3.03540E-03	
27	1.32651E+11	402653184	3.03540E-03	
28	2.65302E+11	805306368	3.03540E-03	
29	5.30605E+11	1610612736	3.03540E-03	
30	1.06121E+12	3221225472	3.03540E-03	

t-Butyl functional BTT Dendrimers (GREY = experimental data, blue = (ne/M)∞ values)

Generation	Molecular Weight	number of end groups (ne)	ne/M	ne/M – (ne/M)∞
1	1240.56	6	4.83650E-03	1.36E-03
2	2964.73	12	4.04760E-03	5.68E-04
3	6413.07	24	3.74240E-03	2.62E-04
4	13309.75	48	3.60640E-03	
5	27103.11	96	3.54200E-03	
6	54689.83	192	3.51070E-03	
7	109863.27	384	3.49530E-03	
8	220210.15	768	3.48760E-03	
9	440903.91	1536	3.48380E-03	
10	882291.43	3072	3.48180E-03	
11	1765066.47	6144	3.48090E-03	
12	3530616.55	12288	3.48040E-03	
13	7061716.71	24576	3.48020E-03	
14	14123917.03	49152	3.48010E-03	
15	28248317.67	98304	3.48000E-03	
16	56497118.95	196608	3.48000E-03	
17	112994721.5	393216	3.48000E-03	
18	225989926.6	786432	3.47990E-03	
19	451980336.9	1572864	3.47990E-03	
20	903961157.4	3145728	3.47990E-03	
21	1807922798	6291456	3.47990E-03	
22	3615846080	12582912	3.47990E-03	
23	7231692644	25165824	3.47990E-03	
24	14463385772	50331648	3.47990E-03	
25	28926772027	100663296	3.47990E-03	
26	57853544538	201326592	3.47990E-03	
27	1.15707E+11	402653184	3.47990E-03	
28	2.31414E+11	805306368	3.47990E-03	
29	4.62828E+11	1610612736	3.47990E-03	
30	9.25657E+11	3221225472	3.47990E-03	

Analysis of Wooley *et al*[1] data and comparison of geometric progression, Flory-Fox and modified Flory-Fox approaches

	Tg (K)	M	1/M	n_e	n_e/M	(ne/M)-(ne/M)$_\infty$	2^{Gn}	$2^{Gn}C^2$	$1/(2^{Gn}C^2\text{-}CA)$
[G1]-OH	255	320	0.00313	3	0.00938	0.004658	2	89888	1.47406×10^{-5}
[G2]-OH	285	744	0.00134	5	0.00672	0.002003	4	179776	6.34003×10^{-6}
[G3]-OH	305	1592	0.00063	9	0.00565	0.000936	8	359552	2.96293×10^{-6}
[G4l-OH	312	3288	0.0003	17	0.00517	0.000453	16	719104	1.4346×10^{-6}
[G5l-OH	315	6680	0.00015	33	0.00494	0.000223	32	1438208	7.06135×10^{-7}
[G6l-OH	316	13464	7.4E-05	65	0.00483	0.000111	64	2876416	3.5034×10^{-7}

The polybenzylether dendrons exhibit a geometric progression of molecular weight that is described by the equation 5 (see manuscript)

$$M_{Gn} = 2\left(M_{Gn-1}\right) + A$$

The factor A can therefore be determined as A = 104Da

The factor B is determined by equation 6 (see manuscript) as the generation 1 molecular weight minus the factor A, ie

$$B = M_{G1} - A$$

B is readily determined to be B = 320 – A = 216 Da

Using equation 8 (see manuscript) it is possible to determine the molecular weight of any generation *n*.

$$M_{Gn} = B2^{Gn-1} + A2^{Gn} - A$$

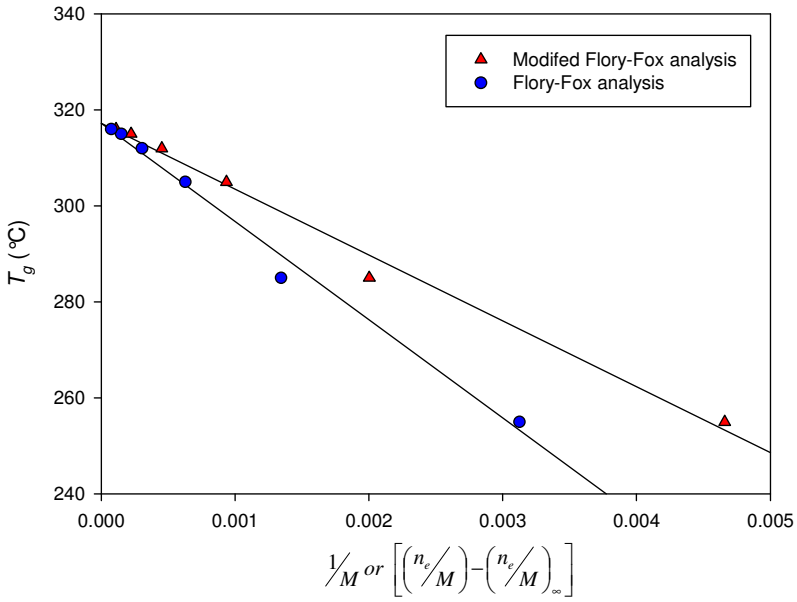
eg Generation 6 = $216(2^5) + 104(2^6) - 104 = 6912 + 6656 - 104 = 13464$ Da

Factor C is defined a C=B/2+A and is therefore C = 212 Da

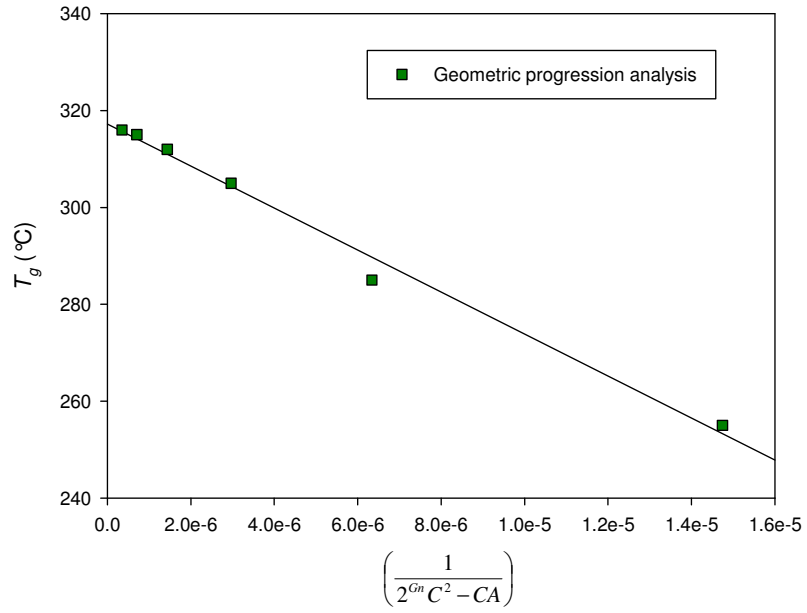
With these values (A = 104 Da; B = 216 Da; C = 212 Da), equation 18 (see manuscript) may be used to determine $T_{g\infty}$ through a plot of $T_{g,Gn}$ *vs.* $1/(2^{Gn}C^2\text{-}CA)$.

$$T_{g,Gn} = T_{g\infty} - K''\left(\frac{1}{2^{Gn}C^2 - CA}\right)$$

Comparative graphs for the dendrons of the Wooley *et al*[1] paper are shown below.



Calculated $T_{g\infty}$ values: Flory-Fox analysis gives 317.17072K; Modified Flory-Fox analysis gives 317.16857K.



Calculated $T_{g\infty}$ values: Geometric progression analysis gives 317.17072K.

Data for all materials described in Wooley *et al*[1] report with calculations for geometric progression analysis

Generation	Surface	MW[b]	2^{Gn}	A	B	C	$1/(2^{Gn}C^2-CA)$	1/M	$(ne/M)-(ne/M)_\infty$	Tg (K)
1	H	320	2	104	216	212	1.47×10^{-5}	3.13×10^{-3}	4.66×10^{-3}	255
2	H	744	4	104	216	212	6.34×10^{-6}	1.34×10^{-3}	2.00×10^{-3}	285
3	H	1592	8	104	216	212	2.96×10^{-6}	6.28×10^{-4}	9.36×10^{-4}	305
4	H	3288	16	104	216	212	1.43×10^{-6}	3.04×10^{-4}	4.53×10^{-4}	312
5	H	6680	32	104	216	212	7.06×10^{-7}	1.50×10^{-4}	2.23×10^{-4}	315
6	H	13464	64	104	216	212	3.50×10^{-7}	7.43×10^{-5}	1.11×10^{-4}	316
1	Br	478	2	104	374	291	7.19×10^{-6}	2.09×10^{-3}	2.84×10^{-3}	271
2	Br	1060	4	104	374	291	3.24×10^{-6}	9.43×10^{-4}	1.28×10^{-3}	309
3	Br	2224	8	104	374	291	1.55×10^{-6}	4.50×10^{-4}	6.10×10^{-4}	316
4	Br	4552	16	104	374	291	7.55×10^{-7}	2.20×10^{-4}	2.98×10^{-4}	325
1	CN	370	2	104	266	237	1.14×10^{-5}	2.70×10^{-3}	3.89×10^{-3}	287
2	CN	844	4	104	266	237	5.00×10^{-6}	1.18×10^{-3}	1.70×10^{-3}	327
3	CN	1792	8	104	266	237	2.35×10^{-6}	5.58×10^{-4}	8.03×10^{-4}	334
4	CN	3688	16	104	266	237	1.14×10^{-6}	2.71×10^{-4}	3.90×10^{-4}	349
1	C-2[a]	366[a]	2	58	308	212	1.29×10^{-5}	2.73×10^{-3}	7.47×10^{-4}	270
2	C-2	790	4	58	308	212	5.97×10^{-6}	1.27×10^{-3}	3.46×10^{-4}	287
3	C-2	1656 (1638)	8	58	308	212	2.88×10^{-6}	6.11×10^{-4}	1.67×10^{-4}	306
4	C-2	3354 (3334)	16	58	308	212	1.41×10^{-6}	3.00×10^{-4}	8.20×10^{-5}	311
5	C-2	6750 (6726)	32	58	308	212	7.01×10^{-7}	1.49×10^{-4}	4.07×10^{-5}	311
6	C-2	13542 (13510)	64	58	308	212	3.49×10^{-7}	7.40×10^{-5}	2.02×10^{-5}	312
1	C-3	576	2	60	516	318	5.46×10^{-6}	1.74×10^{-3}	4.90×10^{-4}	282
2	C-3	1212	4	60	516	318	2.59×10^{-6}	8.25×10^{-4}	2.32×10^{-4}	298
3	C-3	2484	8	60	516	318	1.27×10^{-6}	4.03×10^{-4}	1.12×10^{-4}	309
4	C-3	5026	16	60	516	318	6.25×10^{-7}	1.99×10^{-4}	5.63×10^{-5}	312
5	C-3	10126	32	60	516	318	3.11×10^{-7}	9.89×10^{-5}	2.80×10^{-5}	314
6	C-3	20292	64	60	516	318	1.55×10^{-7}	4.93×10^{-5}	1.40×10^{-5}	315
1	C-OH	714	2	102	612	408	3.43×10^{-6}	1.40×10^{-3}	1.05×10^{-3}	446
2	C-OH	1530	4	102	612	408	1.60×10^{-6}	6.54×10^{-4}	4.90×10^{-4}	458
3	C-OH	3162	8	102	612	408	7.75×10^{-7}	3.16×10^{-4}	2.37×10^{-4}	467
4	C-OH	6426	16	102	612	408	3.81×10^{-7}	1.56×10^{-4}	1.17×10^{-4}	474

[a] This molecule is a core rather than a dendrimer

[b] Values in brackets are corrected molecular weights; values without brackets are molecular weights reported from measurement

[1] K. L. Wooley, C. J. Hawker, J. M. Pochan and J. M. J. Fréchet, Macromolecules, 1993, **26**, 1514.