Supplementary Material

Synthesis of novel AB_2 monomers for the construction of highly branched macromolecular architectures

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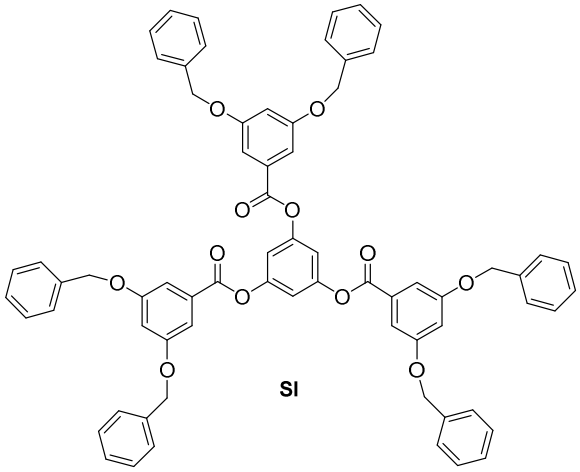
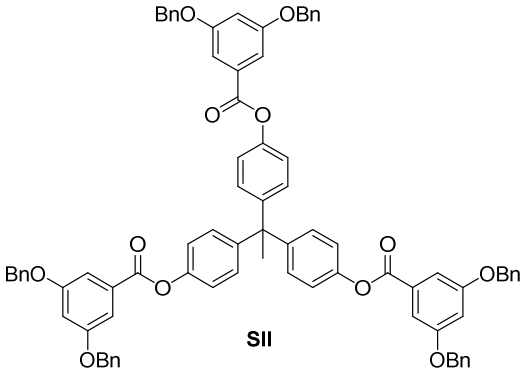
1. Structures of Additional Branched Materials

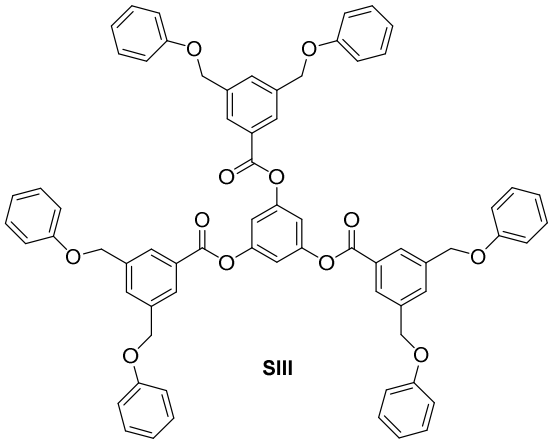
Additional branched systems were prepared using monomers **1**-**3** and cores **19**-**20** using the methods described in this work. The structures of the resulting compounds are shown below:



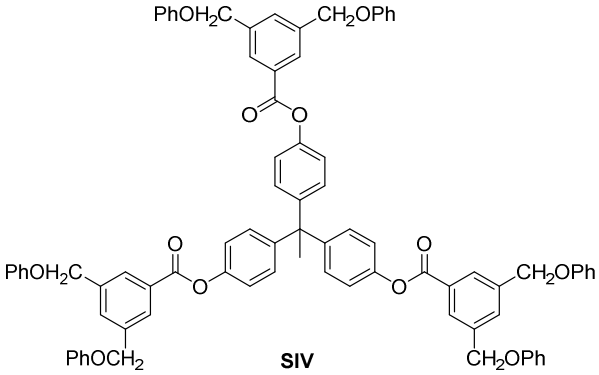
SI



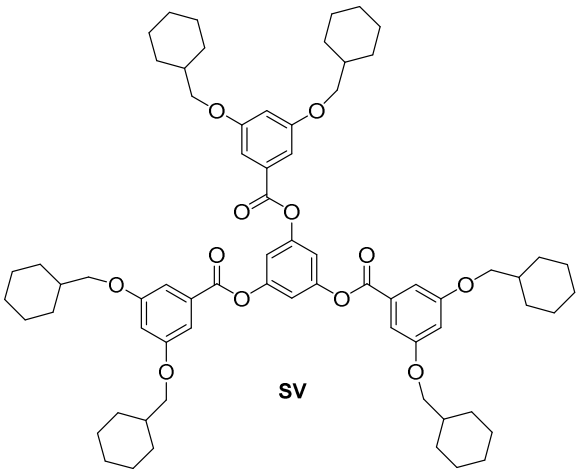
SII



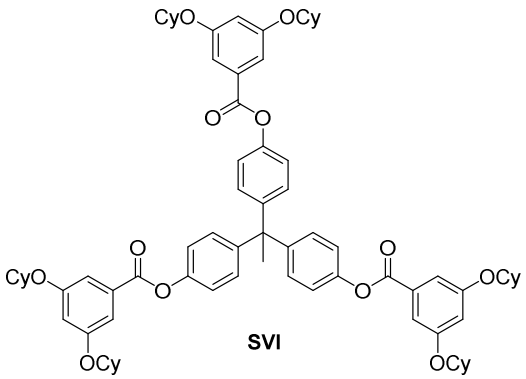
SIII



SIV



SV



SVI

2. Experimental Procedures and Characterization Data for SIII-SVI

Benzyl Ether Branched Material Synthesis

The synthesis of benzyl ether **SI** and **SII** proceeded according to procedures which were previously reported.[1]

Synthesis of "Reverse" Benzyl Ether SIII-SIV

General Procedure. To a solution of 0.25 g (0.75 mmol) of **2** in 2.5 mL of CH_2Cl_2 was added 0.24 mmol of the core and 0.23 g (0.82 mmol) of DPTS. After 15 min, 0.17 g (0.82 mmol) of DCC was added, and the reaction mixture was stirred at 25 ˚C until TLC (10% MeOH in CH_2Cl_2) indicated that the reaction had reached completion. The reaction mixture was passed through a short silica gel plug and washed with 100 mL of CH_2Cl_2. After the solvent was removed *in vacuo*, the resulting solid was purified by SEC in $PhCH_3$ to obtain the desired product.

"Reverse" Benzyl Ether SIII. The general procedure was followed to produce 0.14 g (67%) of **SIII** as a pale yellow foam. ^{1}H NMR ($CDCl_3$) δ 8.25 (s, 6H, ArH), 7.85 (s, 3H, ArH), 7.30 (t, *J* 8.0, 12H, ArH), 7.22 (s, 3H, ArH), 7.01 (app d, *J* 7.7, 18H, ArH), 5.05 (s, 12H, CH_2OPh). ^{13}C NMR ($CDCl_3$) δ 164.0, 158.3, 151.4, 138.4, 131.6, 129.6, 129.6, 128.6, 121.3, 114.8, 113.3, 69.0. HRMS-FAB: *m/z* $[M]^+$ calcd for $C_{69}H_{54}O_{12}$ 1074.3616; found 1074.3618.

"Reverse" Benzyl Ether SIV. The general procedure was followed to produce 0.16 g (54%) of **SIV** as a colorless foam. ^{1}H NMR ($CDCl_3$) δ 8.20 (s, 6H, ArH), 7.77 (s, 3H, ArH), 7.28-7.21 (t, *J* 8.0, 12H, ArH), 7.15 (app quart, *J* 7.5, 12H, ArH), 6.95 (app d, *J* 7.2, 18H, ArH), 5.10 (s, 12H, CH_2OPh), 2.31 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$) δ 164.7, 158.4, 149.1, 146.2, 138.3, 131.3, 130.2, 129.8, 129.5, 128.5, 121.3, 121.1, 114.8, 69.1, 51.7, 30.9. HRMS-ESI: *m/z* $[M+Na]^+$ calcd for $C_{83}H_{66}O_{12}Na$ 1277.4452; found 1277.4390.

Synthesis of Cyclohexane Based Branched Systems SV-SVI

General Procedure. To a solution of 0.25 g (0.72 mmol) of **3** in 10 mL of CH_2Cl_2 was added 0.24 mmol of the core and 0.20 g (0.72 mmol) of DPTS. After 15 min, 0.15 g (0.72 mmol) of DCC was added, and the reaction mixture was stirred at 25 ˚C for 15 min until TLC (1:1 pet ether:EtOAc) indicated that the reaction had reached completion. The reaction mixture was filtered and washed with cold CH_2Cl_2. After the solvent was removed *in vacuo*, the resulting solid was purified by silica gel column chromatography (1:1 pet ether:EtOAc) to obtain the desired product.

Cyclohexane Based SV. The general procedure was followed to produce 0.072 g (19%) of **SV** as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.28 (d, *J* 2.3, 6H, ArH), 7.13 (s, 3H, ArH), 6.71 (t, *J* 2.3, 3H, ArH), 3.79 (d, *J* 6.2, 12H, OCH_2Cy), 1.89-1.69 (m, 42H, Cy), 1.37-1.18 (m, 22H, Cy), 1.12-1.01 (m, 12H, Cy). ^{13}C NMR ($CDCl_3$) δ 164.4, 160.5, 151.5, 130.5, 113.3, 108.1, 107.5, 73.8, 37.6, 29.8, 26.5, 25.8. HRMS-ESI: *m/z* $[M + H]^+$ calcd for $C_{69}H_{90}O_{12}$ 1111.6511; found 1111.6516.

Cyclohexane Based Dendrimer SVI. The general procedure was followed to produce 0.18 g (19%) of **SVI** as a white solid. ^{1}H NMR ($CDCl_3$) δ 7.30 (d, *J* 2.5, 6H. ArH), 7.13 (app quart, *J* 8.0, 12H, ArH), 6.70 (t, *J* 2.5, 3H, ArH), 3.79 (d, *J* 6.1, 12H, OCH_2Cy), 2.18 (s, 3H, CH_3), 1.89-1.69 (m, 42H, Cy), 1.37-1.18 (m, 22H, Cy), 1.11-1.00 (m, 12H, Cy). ^{13}C NMR ($CDCl_3$) δ 165.3, 160.4, 145.0, 146.8, 129.8, 129.7, 120.9, 108.1, 107.1, 73.8, 51.3, 37.6, 30.9, 29.8, 26.5, 25.8. HRMS-FAB: *m/z* $[M]^+$ calcd for $C_{83}H_{102}O_{12}$ 1290.7372; found 1290.7368.

3. Estimation of Molecular Weight by SEC

A calibration curve for analytical SEC data was constructed by obtaining the retention times of linear polystyrene standards of the following molecular weights on the analytical SEC: 1.2×10^3, 2.6×10^3, 7.35×10^3, 5.25×10^4, and 3.7×10^5 molecular weight units. The natural log of retention times were plotted against the molecular weight to give the following equation to convert retention time (*t*) in minutes to molecular weight ln(*m*): $\ln(m) = -0.7952(t) + 20.796$.

4. Literature Citation

1. Hawker, C. J. Fréchet, J. M. J. *J. Chem. Soc. Perkin Trans. 1* **1992**, 2459-2469.

