## **Silane Dendrimers**

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A wide variety of silane dendrimers with up to 972 end groups has been synthesised in excellent yields using repetitive alkenylation-hydrosilylation cycles.

Over the past few years much interest has developed in a group of macromolecules known as dendrimers.<sup>1</sup> These tree-like molecules are the result of a controlled repetitive growth starting from a polyfunctional core. From the core, two or more identical branches emanate, each branch containing further branch sites at its end. With successive generations a fractal, ball-like structure evolves until further growth is limited by surface congestion.

Ever since the first successful syntheses were reported a variety of new routes has been described and it is some of these newer, silicon-based routes that have prompted us to disclose some of our own results.<sup>2–5</sup>

The synthesis<sup>†</sup> of our silane dendrimers starts with the exhaustive allylation of tetrachlorosilane with a 10% excess of



<sup>†</sup> Full experimental details will appear elsewhere but the following may serve as examples: *Alkenylation*: 59 g (0.35 mol) of SiCl<sub>4</sub> in 50 cm<sup>3</sup> of Et<sub>2</sub>O was slowly added over a period of 2 h to 1.05 dm<sup>3</sup> of 1.4 mol dm<sup>-3</sup> CH<sub>2</sub>=CHCH<sub>2</sub>MgBr (1.47 mol) in Et<sub>2</sub>O. The mixture was refluxed for 4 h, cooled to 0°C and hydrolysed with 10% aqueous NH<sub>4</sub>Cl. The organic layer was washed with water, dried on MgSO<sub>4</sub> and concentrated. Yield 66.5 g (99%) of tetraallylsilane (100% pure according to GC). *Hydrosilylation*: a mixture of 10 g of tetraallylsilane, 25 cm<sup>3</sup> of HSiCl<sub>3</sub> and 2 × 10<sup>-7</sup> mol of a common platinum-based hydrosilylation catalyst, *e.g.* H<sub>2</sub>PtCl<sub>6</sub> in propan-2-ol (Speier's catalyst) or platinum divinylsiloxane complex (Karstedt's catalyst), was stirred for 24 h at room temp. When the reaction was complete (<sup>1</sup>H NMR), excess HSiCl<sub>3</sub> was removed under vacuum. Yield: 38.2 g (100%) of **G1–Cl** as a white solid.

allylmagnesium bromide in diethyl ether (reflux, 4 h) to produce tetraallylsilane (**G0**) (see Scheme 1). Then the allyl groups of tetraallylsilane are hydrosilylated (room temp.; 1–2 days) with trichlorosilane (25% excess) in the presence of a platinum catalyst ( $10^{-4}$ – $10^{-5}$  mol per double bond) to give in quantitative yield **G1–CI** with four SiCl<sub>3</sub> functional groups. Next, all the SiCl<sub>3</sub> groups are reacted with allylmagnesium bromide in diethyl ether (reflux; overnight) to produce a dendrimer with 12 allyl end-groups (**G1**). This first generation can be converted into a second generation (**G2**, 36 allyl



Compound	Formula	Molecular mass	End groups
G0	C <sub>12</sub> H <sub>20</sub> Si	192	4
G1	$C_{48}H_{84}Si_5$	802	12
G2	C156H276Si17	2624	36
G3	C480H852Si53	8113	108
G4	C1452H2580Si161	24562	324
G5	C4368H7764Si485	73912	972
<b>G6</b> <sup><i>a</i></sup>			

<sup>*a*</sup> This generation is no longer monodisperse since not all of the allyl end groups of **G5** could be hydrosilylated owing to surface congestion.



end-groups) by a repetition of the hydrosilylation–alkenylation cycle. Repeating these reactions gives third (G3), fourth (G4) and fifth (G5) generation dendrimers (see Table 1). In line with molecular modelling calculations, higher generation dendrimers could not be prepared due the phenomenon of surface congestion.

Each of the two steps (alkenylation and hydrosilylation) provided almost quantitative yields after a simple flashchromatographic purification (silica; hexane) of pure dendrimers, as is evident from <sup>1</sup>H (see Fig. 1), <sup>13</sup>C, and <sup>29</sup>Si NMR spectra as well as from gel-permeation chromatography (GPC) traces and elemental analyses (C, H, Si). **G0**, **G1**, and **G2** are clear colourless liquids whose viscosity increases with the generation number, **G3** is a wax-like solid, and **G4** and **G5** are white solids. All generations exhibit a ready solubility in, or miscibility with, a wide range of solvents including hexane, diethyl ether, chloroform, acetonitrile, ethyl acetate and dimethylformamide.

Our route is attractive in that it produces, because of the branching degree of four, in a limited number of steps very compact surface-congested dendrimers, compounds which are not easily accessible *via* conventional routes.‡ Moreover, this

route offers a unique flexibility: not only the degree of branching can be adjusted by replacing  $HSiCl_3$  with  $HSiCl_2Me$  or  $HSiClMe_2$ , but also the length of the branches can be varied. With similar high yields, for example, we also prepared vinyl-based silane dendrimers up to the fourth generation by using vinylmagnesium chloride in tetrahydrofuran (THF) in the alkenylation step. As an additional benefit the reactive Si–Cl end groups allow an easy functionalisation of the dendrimer surface.

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 $<sup>\</sup>ddagger$  For example, surface congestion seems not to have been reached even in the tenth generation of Tomalia's PAMAN dendrimers (*i.e.* after 20 reaction steps, see ref. 1).