JOURNAL OF Materials CHEMISTRY

Dendritic polymers containing a dimethylsilyl linked dihydroxybenzyl alcohol backbone: divergent synthesis, aggregation, functionalization, and an evaluation of their applications in catalysis

Olivier Bourrier and Ashok K. Kakkar*

Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, H3A 2K6, Canada. E-mail: ashok.kakkar@mcgill.ca

Received 13th February 2003, Accepted 26th March 2003
First published as an Advance Article on the web 17th April 2003

A divergent synthetic approach to the construction of dimethylsilyl linked dihydroxybenzyl alcohol based dendrimers *via* acid–base hydrolytic chemistry of bis(dimethylamino)dimethylsilane with 3,5-dihydroxybenzyl alcohol, is reported. The peripheral OH groups lead to significant aggregation that was studied using FT-IR and UV-Vis spectroscopies, light scattering and transmission electron microscopy. Different generations of dendrimers could be easily functionalized at the periphery with phosphorus donor groups that were subsequently bound to $RhCl(1,5\text{-}C_8H_{12})$. Such organometallic dendrimers were found to be active and recoverable catalysts for hydrogenation of decene. The catalytic efficiency was found to be dependent on the number of generations and reaction time. An uncontrolled reaction of $Me_2Si(NMe_2)_2$ with 3,5-dihydroxybenzyl alcohol in a multi-step addition process or one-pot reaction, led to the formation of hyperbranched polymers in which the build-up of the polymeric backbone was found to be dependent on the preferential reactivity and sterics at the benzylic center, as observed during dendrimer construction.

Introduction

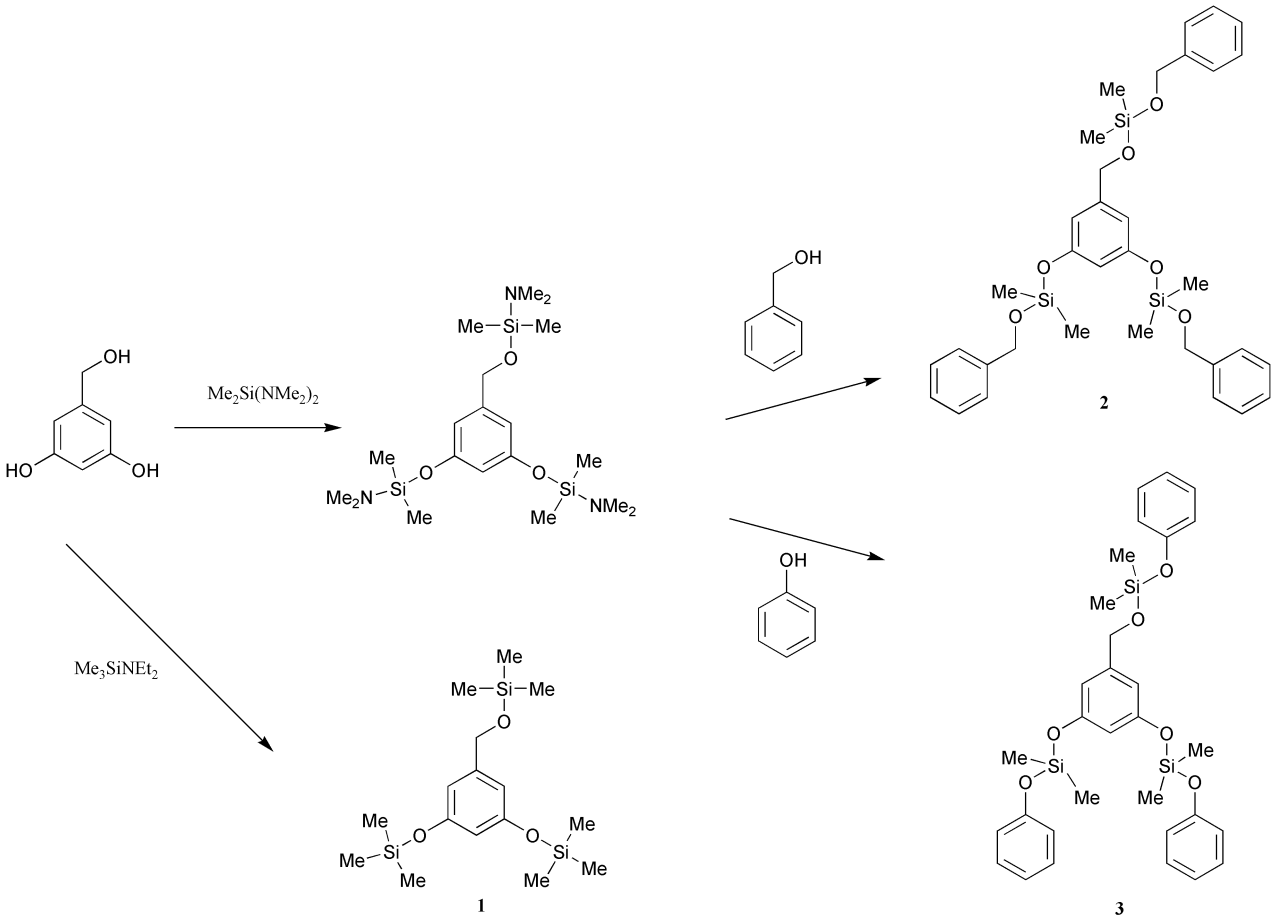
Dendrimers constitute an important and intriguing class of bulky monodisperse macromolecules that can offer a potentially defect-free structure for a diverse range of applications.[1] Due to their unique properties and enormous significance, much effort has been devoted to the development of synthetic routes that can lead to large quantities of these materials, and incorporate required functionalities in the core or at the periphery of a desired backbone.[2] Numerous methodologies have been proposed to synthesize these dendrimers, and employ a divergent step-by-step approach or a convergent one-step reaction. The divergent route has the advantage of providing maximum control on the growth of the dendrimer, and macromolecules with a higher number of generations can be obtained. We have been investigating new divergent synthetic routes to dendrimers, utilizing commercially available or easily accessible reagents with high yield reactions,[3] and have reported the synthesis of dendrimers containing phosphorus and nitrogen based donor groups distributed throughout their backbone.[3a,c] These globular macromolecules containing donor sites are important precursors in the synthesis of metallodendrimers due to the strong ability of phosphines to ligate with a variety of transition metal centers. Studies of the efficiency of dendrimer supported metal catalysts, in terms of their activity, selectivity and recyclability in important organic transformations, continue to emerge.[3a,d]

Poly(aryl ether) dendrimers developed by Hawker and Frechet[4] using 3,5-dihydroxybenzyl alcohol as the monomer and a convergent synthetic methodology, constitute some of the widely studied dendrimers due to their suggested applications in areas such as light amplification and harvesting.[4c] The construction of similar dendrimers with a tailorable architecture is an important goal in achieving desired functions attributable to the specific properties of the dendritic frameworks. We were intrigued by the design of dendritic polymers in which the 3,5-dihydroxybenzyl alcohol based backbone units are linked by flexible dimethylsilyl groups using a simple and controlled coupling reaction in a divergent synthetic route. Such dendritic materials are of considerable value due to their ease of synthesis using a divergent methodology and versatility in manipulating the peripheral architecture by functionalization with a variety of useful moieties for targeted applications. We demonstrate here a simple and highly tailorable synthetic route to dendritic polymers containing a dimethylsilyl linked 3,5-dihydroxybenzyl alcohol (DHBA) backbone, examine their physical properties, and the functionalization of their peripheries with a variety of end-groups including organometallic centers for applications in supported metal catalysis. The methodology is based on acid–base hydrolytic chemistry, and capitalizes on the repetitive and controlled addition of an aminosilane ($Me_2Si(NMe_2)_2$) to backbones containing terminal OH groups (DHBA), leading to the formation of Si–O links with amine as the only by-product. It is an attractive route to prepare a diverse range of dendritic polymers since the peripheries of any generation can be easily functionalized with, for example, trimethylsilyl groups, and phosphorus donors for binding transition metal centers. An investigation of the uncontrolled addition of dimethylaminosilane to DHBA was also carried out in one pot, and step-by-step reactions, and it led to the formation of hyperbranched polymers that typically follow a dendritic growth.

The secondary interactions among the suitable periphery situated end-groups of a dendrimer often affect its overall shape.[1i] It has been demonstrated that the non-polar terminal groups in poly(aryl ether) based dendrimers lead to a mesogenic assembly while the polar end units lead to structures resembling that of a micelle.[5] The dendrimers reported here contain OH groups at the periphery, and may undergo extensive intermolecular hydrogen bonding at appropriate dilutions. We have examined the behavior of these dendrimers in THF using UV-Vis and FT-IR spectroscopies, transmission electron microscopy and multi-angle light scattering studies, and a discussion of their aggregation depending on the concentration of the solutions, is reported.

Dendrimers functionalized with active transition metal centers are gaining ongoing importance in the development of efficient recyclable catalysts.[3a,c,d] Different generations of

 DOI: 10.1039/b301778h



Scheme 1

dimethylsilyl linked 3,5-dihyroxybenzyl alcohol dendrimers were functionalized on the periphery with phosphine donor ligands by reacting them first with $Me_2Si(NR_2)_2$ followed by $HO–(CH_2)_3PPh_2$. The phosphine terminated dendrimers were then metallated *via* a bridge splitting reaction with $[RhCl(cod)]_2$, and the catalytic activity of these dendrimers was investigated for the hydrogenation of decene. The catalytic activity was found to be dependent on factors such as the number of generations in the dendrimer core, and the duration of the hydrogenation reaction. After one batch of the reaction, the organometallic dendrimer was precipitated and reintroduced into a fresh loading of decene in the hydrogenation reactor. The activity was retained in the case of the third generation dendrimer, however, it was found to increase upon recycling of the functionalized dendrimers of generation 1 and 2.

Results and discussion

Dendrimers

Acid–base hydrolysis of aminosilanes with molecules containing acidic groups *e.g.*, terminal OH groups in alcohols, leading to almost quantitative conversion to the corresponding Si–OR with elimination of amine, is well known.[6] We have used this chemistry to prepare a variety of supramolecular structures ranging from simple monolayers to complex sol–gel networks.[3b,7] The generality of this simple reaction has enabled us to develop an efficient synthetic route to dendritic polymers. A bifunctional linking unit [bis(dimethylamino)dimethylsilane] and trifunctional backbone 3,5-dihydroxybenzyl alcohol (DHBA) were chosen as reacting partners in a divergent step-by-step build-up of dendrimers. To demonstrate the reactivity of the aminosilanes with OH terminated molecules, DHBA was reacted with 3 equivalents of a mono-aminosilane, $Me_3Si–NEt_2$, in tetrahydrofuran (THF) at room temperature overnight. It led to a clean and almost quantitative conversion to the corresponding trimethylsilyl terminated compound **1** (Scheme 1) as a grey liquid, with the elimination of NEt_2H.

Since the DHBA backbone contains a benzylic OH and two phenolic OH groups, we decided to first prepare model compounds **2** and **3** containing DHBA at the core and benzylic or phenolic terminal units. In the model studies, 1 equivalent of DHBA was added slowly in a dropwise fashion to a solution of 3 equivalents of bis(dimethylamino)dimethylsilane in THF, cooled to ice-bath temperatures. After stirring the mixture for 5 h, a solution of 3 equivalents of benzyl alcohol or phenol in THF was added, and the stirred mixture was left to warm to room temperature overnight. The removal of the solvent yielded compounds **2** and **3** as colorless and highly viscous liquids in good yields. The above reaction established that we could tailor the reactivity of bis(dimethylamino)dimethylsilane with DHBA using controlled temperature conditions and slow dropwise additions, and avoid any side reactions leading to hyperbranched polymer growth.

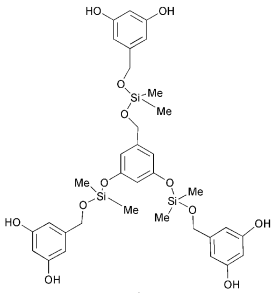
To prepare the first generation of dendrimers, a similar reaction sequence was adopted. To an ice-bath cooled solution of 3 equivalents of bis(dimethylamino)dimethylsilane in THF, 1 equivalent of DHBA was added dropwise over a period of 2–3 h. The stirred solution was then left to warm to room temperature over a period of 5 h, and then transferred to an addition funnel. This was then added slowly to a solution of 3 equivalents of DHBA in THF and stirred overnight. Removal of the solvent and characterization by ^1H, ^{13}C and ^{29}Si NMR, MS and C & H analysis confirmed the synthesis of first-generation dendrimer **4** as a solid in a good yield. Continuation of this methodology of carrying out reactions under controlled additions at room temperature at each step

led to the preparation of second and third generation dendrimers **5** and **6**. The dendrimers remained in solution during their syntheses, but their ability to go back into solution upon isolation was reduced with an increasing in the number of generations, most probably due to the kinetics of dissolution getting slower with an increasing number of generations.

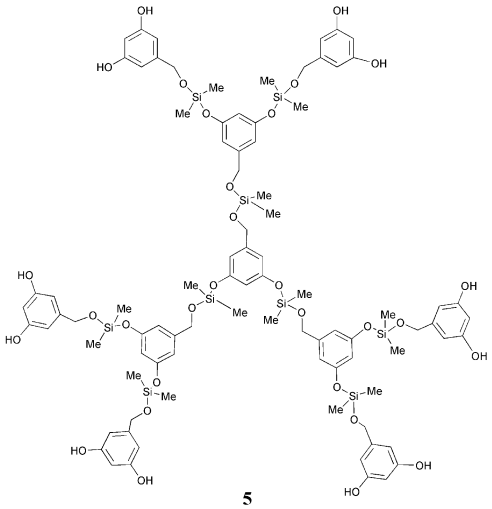
^{1}H NMR spectroscopy and MALDI-TOF MS proved to be extremely useful in the characterization of these dendrimers. DHBA has an asymmetric location of OH groups, and although the pK_a of phenolic hydroxy group (10) is lower than that of benzylic analog (15), the reactivities of benzylic and phenolic OH groups were expected to be indistinguishable under the reaction conditions employed. If there is no preferential attack site on DHBA, one would expect that the structures of the above dendrimers will have a random distribution of benzylic and phenolic links to dimethylsilane. However, it was noted from the ^{1}H NMR spectra that in generations 1–3, the residual OH groups on the periphery were almost exclusively phenolic in nature and not benzylic. This reactivity pattern could be explained using steric arguments. The steric strain will be much less at the benzylic center in these dendrimers making it the preferential site of attachment. It becomes manifested more in the synthesis of hyperbranched polymers, and will be discussed in detail in the later sections.

Aggregation

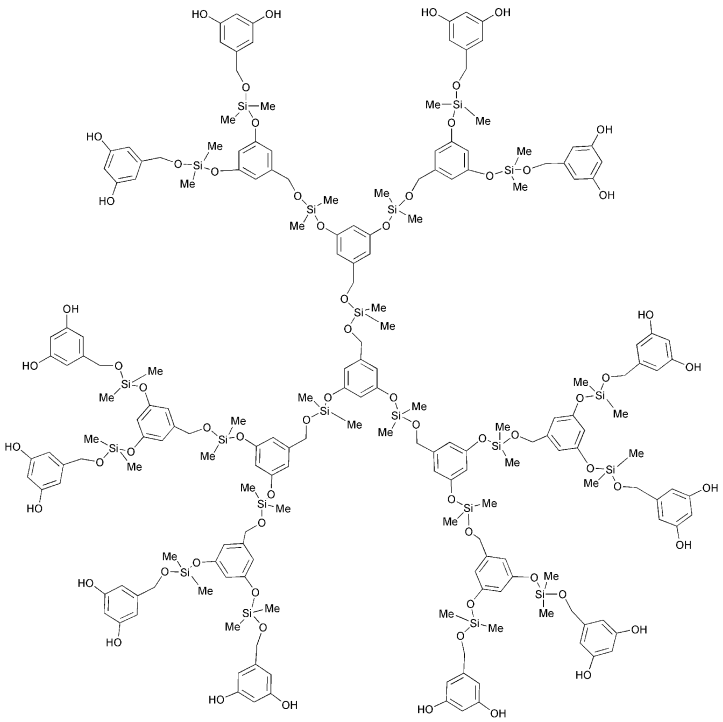
The interactions among dendritic molecules *via* suitable periphery situated end groups impart interesting physical properties, and may lead to aggregation in solution when their concentration exceeds a certain threshold, often referred to as the *critical micellar concentration* (c.m.c.). DHBA based dendrimers (**4–6**) contain terminal OH groups (6, 12 and 24 respectively), and individual molecules may interact with each other through hydrogen bonding, yielding aggregates. This phenomenon was first examined using UV-Vis spectroscopy. A steady decrease in turbidity of the solution was observed upon successive dilutions, and upon reaching the c.m.c., the absorption decreased dramatically. The scattering part of each UV-Vis spectrum remained quite similar at c.m.c. and below, suggesting that it was not affected very much by a decrease in concentration of the dendrimers in solution. By



4



5



6

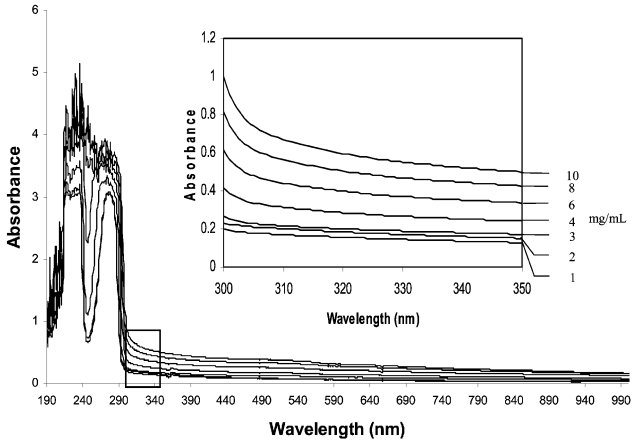


Fig. 1 UV-Vis spectra of dendrimer **6** including the region of scattering (300–350 nm) at concentrations of 1–10 mg mL^{-1} in THF.

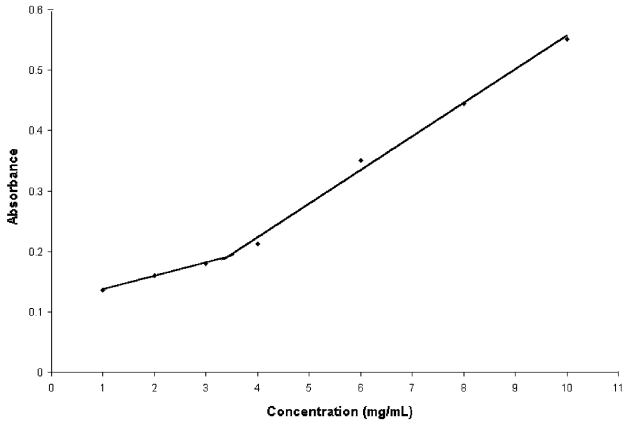


Fig. 2 Absorbance *vs.* concentration of dendrimer **6** (in mg mL^{-1}) in THF at 340 nm.

plotting the intensity of scattered light at a given wavelength against the concentration (Figs. 1 and 2), we were able to determine the c.m.c. for the dendrimer generations 2 and 3. The aggregation was seen to begin at a concentration of 3.7 mg mL^{-1} for dendrimer generation 2 as well as generation 3.

As mentioned earlier, the aggregate formation in DHBA based dendrimers may be attributed to intermolecular hydrogen bonds between dendrimer molecules. Infrared spectroscopy is a valuable tool in examining the existence of hydrogen bonds, and it has been used to ascertain their presence in dendrimers containing peripheral carbamate N–H groups.[8] It was reported that there is a difference of 120 cm^{-1} in the N–H absorption between hydrogen bonded and non-hydrogen bonded compounds. We obtained FT-IR spectra of dendrimer generations 2 and 3 at different concentrations (1–10 mg mL^{-1}). Fig. 3 highlights the evolution of the IR spectrum in the hydroxy group region at these concentrations. A broad peak at 3300 cm^{-1} for the terminal OH groups was clearly observed at concentrations of 4–10 mg mL^{-1}. This peak position suggests strong hydrogen bonding between peripheral OH groups. At concentrations of 1–3 mg mL^{-1} which are below the c.m.c., a peak due to OH stretching appeared at 3570 cm^{-1}, which is indicative of the absence of any hydrogen bonding between the peripheral OH groups.

Dynamic light scattering (DLS) has been extensively used to assess the particle size of polymeric materials in solution, and in particular micelles.[9] DLS is also a useful technique to estimate the radii of the particles in solution, and to study the effect of the concentration of the solutions on the radii. If the formation of aggregates is dependent on concentration, a noticeable change in

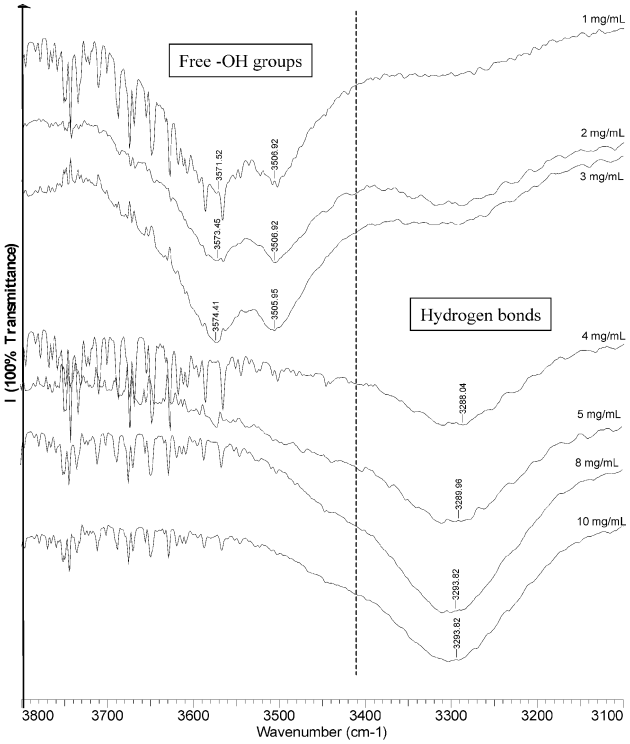


Fig. 3 FT-IR spectra of dendrimer **5** (3100–3800 cm^{-1}) in THF at concentrations of 1–10 mg mL^{-1}.

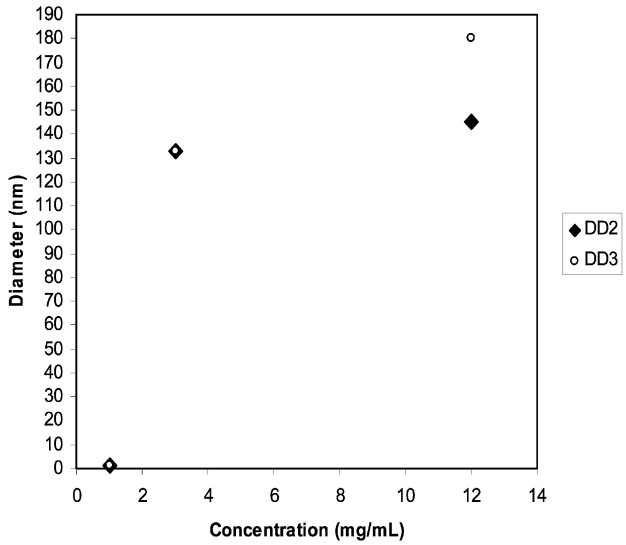


Fig. 4 Diameter (as determined from light scattering measurements) *vs.* concentration in mg mL^{-1} in THF for dendrimers **5** and **6**.

the size of the aggregates is expected. An evaluation of the size of the DHBA based dendrimers was carried out using DLS measurements at different concentrations of dendrimers of generations 2 and 3: one below the c.m.c. (1 mg mL^{-1}), one close to the c.m.c. (3 mg mL^{-1}), and one well above the c.m.c. (12 mg mL^{-1}). Calculation of the diameter (Fig. 4) was done using the CONTIN method.[10] For dendrimer generations 2 and 3 at a concentration of 1 mg mL^{-1}, only one peak with a particle size of 1.33 nm was observed. At 3 mg mL^{-1}, particles of size 133 nm were detected, which indi- cated the formation of aggregates. At 12 mg mL^{-1} of dendrimer generation 2, a major peak at 145 nm was observed. For dendrimer generation 3, at a concentration of 12 mg mL^{-1}, similar aggregation was seen with particles of 180 nm diameter. These experiments clearly suggested that dendrimers of generations 2 and 3 show a

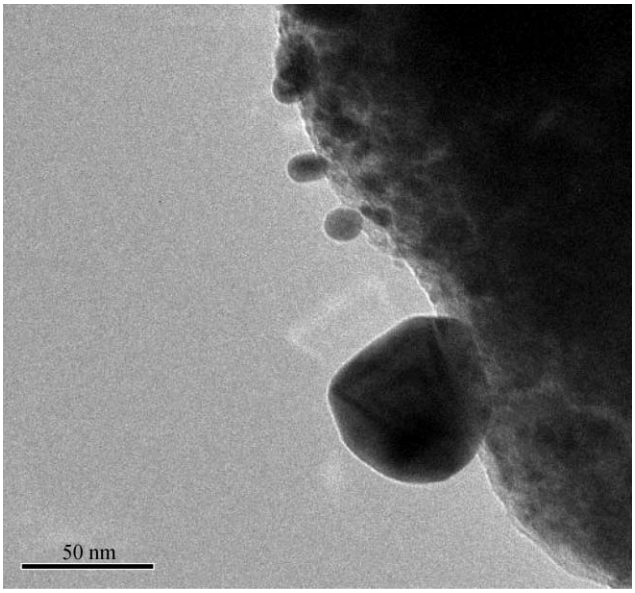


Fig. 5 Transmission electron micrograph of dendrimer **5** in a solution (3 mg mL^{-1}) of THF.

strong tendency to interact with each other through hydrogen bonding that leads to the formation of large aggregates.

Transmission electron microscopy is another useful tool to assess the physical characteristics of particles in solution.[10] We have also used this technique to evaluate the size of aggregates formed by dendrimers reported here. A transmission electron micrograph of dendrimer generation 2 is shown in Fig. 5. It shows the presence of two particles of globular shapes and sizes 65 nm (major) and ~10 nm (minor component). A detailed evaluation of different generations of these dendrimers is continuing.

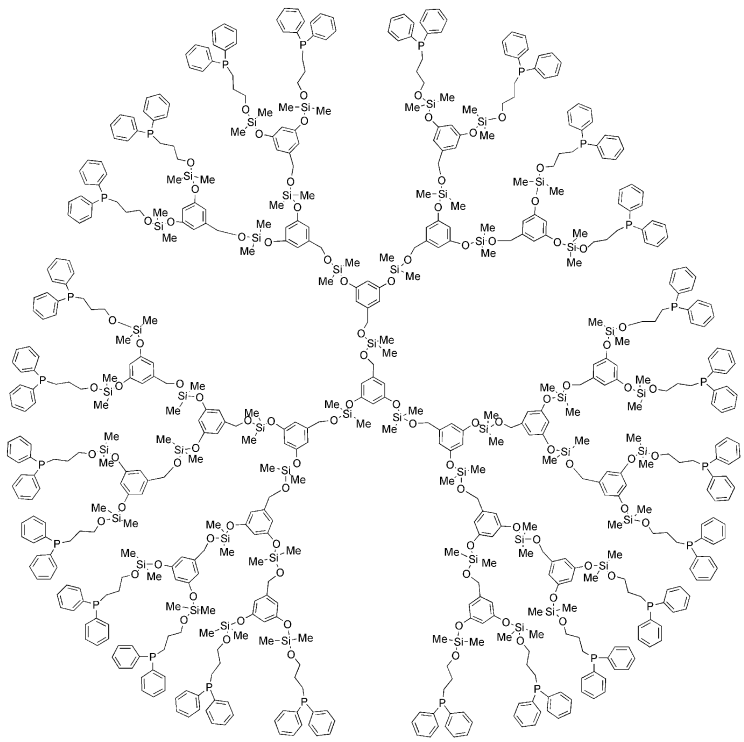
Functionalization of dendrimers

The terminal OH groups in the DHBA based dendrimers offer opportunities to functionalize them with a variety of peripheral moieties. Since the ability to redissolve dendrimers **4–6** upon isolation as powders decreased with an increase in the number of generations, we attempted to improve their solubility by introducing Me_3Si functionalities at the periphery. This could easily be achieved by reacting, for example, dendrimer **4** with 6 equivalents of $Me_3Si–NEt_2$ at room temperature overnight, leading to a clean and quantitative capping of the latter dendrimer with Me_3Si groups. The resulting compound (**7**) was isolated as a liquid that was found to be soluble in common organic solvents.

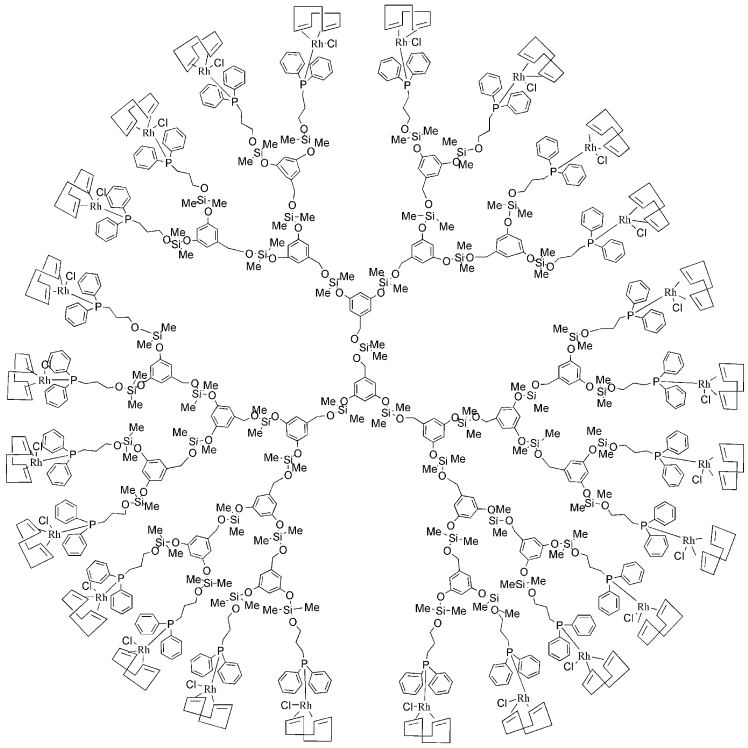
The terminal OH groups in dendrimers **4–6** were then used to introduce donor phosphine groups at the periphery. The latter could then bind transition metal centers for heterogenizing homogeneous catalysts.[5j] To test this methodology, after reacting 6 equivalents of $Me_2Si(NMe_2)_2$ with 1 equivalent of the first-generation dendrimer **4** in THF at room temperature, 6 equivalents of $HO(CH_2)_3PPh_2$ in THF were added, and the solution was warmed to room temperature. The solution mixture was stirred at room temperature overnight, and the solvent was then removed under vacuum to yield compound **8**. The latter showed a single peak in its $^{31}P\{^1H\}$ NMR spectrum at −15.9 ppm. Phosphinated first-generation dendrimer **8** was then reacted with $[RhCl(cod)]_2$ in a bridge-splitting reaction to link donor phosphine units to Rh(I) centers. This led to a complete functionalization with metal centers (**9**) with no residual free phosphine units on the periphery, as indicated by the appearance of a doublet at 27.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum due to Rh–P coupling (J_{Rh-P} = 150 Hz). Using the same reaction sequence as described above for generation 1, dendrimers of generations 2 and 3 were functionalized with $HO(CH_2)_3PPh_2$ to give dendrimers functionalized at the periphery with phosphines (**10** and **11**). Complete functionalization with terminal phosphine units required stirring at 55 °C to graft 12 equivalents of $HO(CH_2)_3PPh_2$ to the second generation dendrimer backbone (**10**), and a week of stirring at 55 °C to graft 24 equivalents on the third generation dendrimer (**11**). Compounds **10** and **11** were then reacted with $[RhCl(cod)]_2$ to yield organometallic dendrimers **12** and **13**.

Hydrogenation of decene

Dendrimers offer unique opportunities to design supports for recoverable heterogenized homogenous catalysts.[3a,d] Much effort has been devoted to the synthesis of organometallic



11



13

dendrimers in which active transition metal centers are present in the core, corona or the entire backbone. A study of the catalytic efficiency of DHBA based organometallic dendrimers of generations 1–3 functionalized at the periphery with phosphines ligated to $RhCl(1,5\text{-}C_8H_{12})$ was carried out for the catalytic hydrogenation of decene. The hydrogen pressure reactor was loaded with the organometallic dendrimer and decene (1:200 molar ratio) dissolved in benzene, and catalysis was carried out at room temperature at 20 bars of H_2 for periods of 0.5 to 5 h. The organometallic dendrimers were found to be active catalysts for the hydrogenation of decene, and the activity of the catalyst was found to increase with an increase in the number of generations and the reaction time (Table 1). For example, with the generation 1 organometallic dendrimer, only 19% of decene was found to be converted to decane after 0.5 h of the reaction which gradually increases to 97% after 5 h reaction time. The reactivity of the generation 2 organometallic dendrimer was found to be higher than that of generation 1, and followed a similar pattern of increasing activity with time (Table 1). Generation 3 dendrimer showed a maximum conversion after 2 h of contact time, and was retained upon further increase in time. Catalyst recovery and its recycling ability were also investigated for generations 1–3 (Table 1). The recycled catalysts retained their efficiency, and surprisingly, the recovered catalysts showed an increase in activity upon recycling.

Table 1 Hydrogenation of decene using functionalized dendrimers of generation 1–3

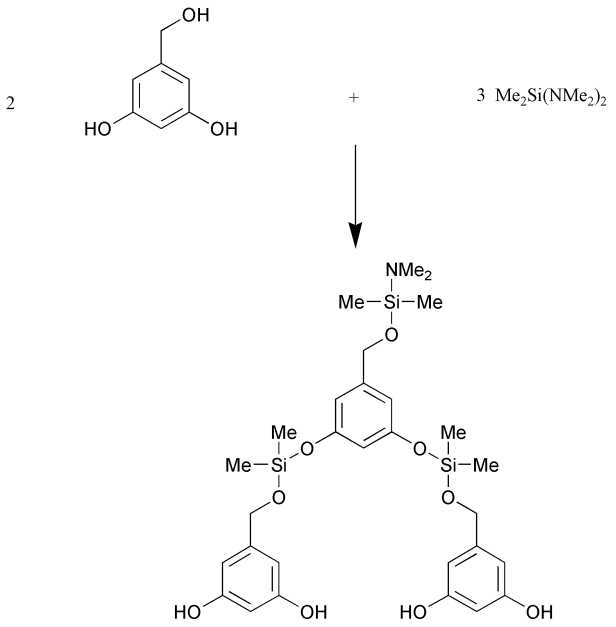
	Time of Reaction/h	Conversion (%)
9, [G-1]-$[Rh(cod)Cl]_6$	0.5	19
	1	47
	2	48
	5	97
12, [G-2]-$[Rh(cod)Cl]_{12}$	0.5	23
	1	65
	2	71
	5	98
13, [G-3]-$[Rh(cod)Cl]_{24}$	0.5	26
	1	65
	2	93
	5	93
9, [G-1]-$[Rh(cod)Cl]_6$	2	48
Recycle **9**, [G-1]-($[Rh(cod)Cl]_6$	2	85
12, [G-2]-$[Rh(cod)Cl]_{12}$	2	71
Recycle **12**, [G-2]-$[Rh(cod)Cl]_{12}$	2	93
13, [G-3]-$[Rh(cod)Cl]_{24}$	2	93
Recycle **13**, [G-3]-$[Rh(cod)Cl]_{24}$	2	98

Hyperbranched polymers

The synthesis of globular macromolecules with defect free structures has been the driving force for all the activity in the field of dendrimers. It requires a careful execution of the steps involved in the build-up of generations in a divergent manner, and is a lengthy and cumbersome process. This could be a handicap in any industrial scale synthesis and applications of these otherwise very valuable materials. We made a compromise and carried out the synthesis using our acid–base hydrolytic chemistry under uncontrolled conditions, which lead to macromolecules that have a hyperbranched structure but with more defects than their corresponding dendrimers. To achieve this goal, two sets of reactions were designed: i) a one-step process in which equimolar quantities of reactive groups are put together with the evolution of the macromolecule examined after a set period of time; and ii) a multi-step reaction of partners, as in the synthesis of dendrimers, but without the dropwise addition or control of temperature.

In the one-pot reaction, solutions of 2 equivalents of DHBA and 3 equivalents of $Me_2Si(NMe_2)_2$ in THF were mixed together, and stirred at room temperature overnight. Removal of the solvent yielded a solid, the MALDI-TOF MS of which showed a major peak at a mass of 589. This corresponds to the species shown in Scheme 2, the formation of which could be explained by considering a reaction pattern in which molecules of DHBA first react with 1 equivalent of $Me_2Si(NMe_2)_2$ each preferably at the benzylic OH group position. One molecule of the resulting compound then reacts with the other at the phenolic OH group yielding a compound with MALDI-TOF mass of 589 (after losing a NMe_2 group).

In the two-step uncontrolled methodology to prepare



Scheme 2

hyperbranched polymers, a solution of 1 equivalent of DHBA in THF was added directly to the solution of 3 equivalents of $Me_2Si(NMe_2)_2$ in THF. The mixture was stirred at room temperature overnight. Then 3 equivalents of DHBA were added, and the solution was left to stir at room temperature overnight. Removal of the solvent yielded a sticky brown gel, the ^1H NMR spectrum of which indicated the presence of a substantial amount of residual phenolic OH groups. The MALDI-TOF MS of the product showed the expected mass of 728 for the first generation dendrimer, however, there were additional peaks up to a maximum noticeable mass of 1910, corresponding to the second generation dendrimer. A very interesting feature to be noted in the MALDI-TOF MS was the appearance of peaks that were separated by a unit mass of 197 which corresponds to the linking unit $\{(HO)_2[C_6H_3](OCH_2\text{-}Si(CH_3)_2)\}$. Once again, this suggests a reaction pattern based on the domination of the higher rate of reaction of $Me_2Si(NMe_2)_2$ with the benzylic OH groups, leading to the formation of a molecular species, $\{(HO)_2[C_6H_3](OCH_2\text{-}Si(CH_3)_2)NMe_2\}$. The latter then reacts with DHBA one OH at a time to yield a dendritic polymer.

Conclusions

It is demonstrated here that the simple acid–base hydrolytic chemistry of 3,5-dihydroxybenzyl alcohol with $Me_2Si(NMe_2)_2$, is a versatile divergent synthetic methodology for the construction of dendrimers and hyperbranched polymers containing aryl ether units linked by dimethylsilyl units. Preferential attack at the benzylic OH group by the aminosilane during the synthesis of hyperbranched polymers leads to an unexpected control of the evolution of these macromolecules. The terminal OH groups in the dendrimers yield to hydrogen bonding, and lead to significant aggregation at concentrations above 3 mg mL^{-1}. The peripheral OH groups in the dendrimers of *n*th generations were functionalized with i) Me_3Si groups leading to significant improvements in their solubilities; and ii) phosphine donor groups that were subsequently used to bind Rh(I) centers. The resulting organometallic dendrimers were found to be active and recyclable catalysts for the hydrogenation of decene. The catalytic efficiency was found to be dependent on dendrimer generation and reaction time. Further evaluation of these dendrimers as traps for important organic molecules during aggregation and blocking the escape of the guest molecules by using Me_3Si locks at the periphery after entrapment are currently being pursued.

Experimental section

Materials and measurements

All manipulations were performed under a nitrogen atmosphere using either standard Schlenk line techniques or an Innovative Technology (Braun) Labmaster MB-150-M dry box. All solvents were stored under nitrogen and used after distillation over sodium. Chemicals were purchased from the following and used as received: 3,5-dihydroxybenzyl alcohol (Aldrich), trimethylsilyldiethylamine (Aldrich), bis(dimethylamino)dimethylsilane (Gelest), 3-hydroxypropyldiphenylphosphine (Organometallics, Inc.), chloro(1,5-cyclooctadiene)rhodium(I) dimer (Pressure Chemicals). NMR spectra were measured on a 270 MHz JEOL spectrometer at ambient temperature. NMR samples were prepared inside the dry box using deuterated solvents (Cambridge Isotope laboratories, Inc.). The chemical shifts in ppm are reported relative to tetramethylsilane as an internal standard for ^1H, ^{13}C and ^{29}Si NMR spectra, and to H_3PO_4 for $^{31}P\{^1H\}$ NMR spectra. Mass spectra were obtained on a Hewlett Packard 5973 mass spectrometer, and MALDI-TOF spectra on a Kratos Kompact Maldi 3.v.4.0.0 spectrometer using LiBr–dithranol or α-cyano-4-hydroxycinamic acid as the matrices. Elemental analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada. Infrared spectra were measured on a Bruker IFS-48 Fourier transform infrared spectrometer using a standard resolution of 4 cm^{-1} for transmission. UV-Vis spectra were recorded on a Hewlett Packard 8453 with a resolution of 2 nm using quartz cuvettes. For dynamic light scattering experiments, a system from Brookhaven Instruments Corporation equipped with their BI-200SM goniometer, BI-9000AT digital correlator, and a Compass 315-150 CW laser light source from Coherent Inc. (operating at 532 nm, 150 mW), was used. The DLS experiments were carried out at an angle of 90°. Transmission electron microscopy (TEM) was carried out on a JEOL 2000FX microscope operating at an acceleration voltage of 80 kV. Copper EM grids (400 mesh) were precoated with carbon.

Reaction of 3,5-dihydroxybenzyl alcohol with $Me_3Si\text{-}NEt_2$

3,5-Dihydroxybenzyl alcohol (DHBA) (304 mg, 2.17 mmol) was dissolved in 1 mL of dry THF, and added to a solution of 3 equivalents of trimethylsilyldiethylamine (1.22 mL, 6.51 mmol) in 10 mL of dry THF. The mixture was stirred at room temperature overnight. The solvent was removed under vacuum, yielding a brown liquid (**1**, 714 mg, 96%). ^1H NMR (270 MHz, C_6D_6): δ (ppm) 0.07 (s, 9H, $CH_2O\text{-}Si\mathit{Me}_3$), 0.18 (s, 18H, $C_6H_3\text{-}OSi\mathit{Me}_3$), 4.51 (s, 2H, $C_6H_3\text{-}C\mathit{H}_2OSiMe_3$), 6.49 (s, 1H, $C_6\mathit{H}_3$), 6.67 (s, 2H, $C_6\mathit{H}_3$). ^{13}C NMR (68 MHz, C_6D_6): δ (ppm) −0.6, 0.0 ($C_6H_3\text{-}OSi\mathit{C}H_3$ and $C_6H_3\text{-}\mathit{C}H_2\text{-}OSi\mathit{C}H_3$), 64.2 ($C_6H_3\text{-}\mathit{C}H_2$), 110.7, 111.4, 144.0, 156.7 (C_6H_3). ^{29}Si NMR (54 MHz, C_6D_6): δ (ppm) 18.1 and 18.7 ($C_7H_5\text{-}O\mathit{Si}Me_3$ and $C_6H_3\text{-}O\mathit{Si}Me_3$). EI-MS: *m*/*z* 356. Anal. Calcd. for $C_{16}H_{32}O_3Si_3$: C, 53.93; H, 8.98. Found: C, 53.93; H, 8.71%.

Reaction of 3,5-dihydroxybenzyl alcohol first with $Me_2Si(NMe_2)_2$ and then benzyl alcohol

A solution of DHBA (104 mg, 0.74 mmol) in 10 mL of THF was added dropwise to a solution of 3 equivalents of bis(dimethylamino)dimethylsilane (0.40 mL, 2.22 mmol) in 5 mL of THF at ice-bath temperature. After stirring for 5 hours, a solution of 3 equivalents of benzyl alcohol (0.24 mL, 2.22 mmol) in 5 mL of dry THF was added dropwise to the above mixture, which was then stirred overnight. The solvent

was removed under vacuum yielding a colorless liquid (**2**, 1.215 g, 89%). ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 0.13 (s, 12H, OSiMe_2O), 0.20 (s, 6H, OSiMe_2O), 4.67 (s, 6H, O-CH_2-C_6H_3), 4.74 (s, 2H, C_6H_3-CH_2-O), 6.90–7.30 (m, 18H, C_6H_3). ^{13}C NMR (68 MHz, C_6D_6): δ (ppm) −4.0, −2.3 (SiCH_3), 62.3, 66.5 (C_6H_3-CH_2), 111.6, 140.9, 156.0 (C_6H_3), 125.9, 127.4, 128.2, 143.9 (C_6H_5). EI-MS: *m*/*z* 632. Anal. Calcd. for $C_{34}H_{44}O_6Si_3$: C, 64.56; H, 6.96. Found: C, 65.50; H, 7.34%.

Reaction of 3,5-dihydroxybenzyl alcohol with $Me_2Si(NMe_2)_2$ and then phenol

A solution of DHBA (106 mg, 0.76 mmol) in 10 mL of dry THF was added dropwise to a solution of 3 equivalents of bis(dimethylamino)dimethylsilane (0.43 mL, 2.28 mmol) in 5 mL of dry THF. During the addition and the 6 hours of stirring that followed, the solution was maintained at ice-bath temperature. A solution of 3 equivalents of phenol (223 mg, 2.28 mmol) was prepared in 15 mL of dry THF. The latter was stored on molecular sieves for about 5 hours, and then added dropwise to the above mixture. It was stirred overnight at room temperature, and then the solvent was removed under vacuum. A clear grey liquid was obtained as the product (**3**, 1.16 g, 91%). ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 0.18 (s, 6H, OSiMe_2O), 0.23 (s, 12H, OSiMe_2O), 4.47 (s, 2H, C_6H_3-CH_2O), 6.80–7.08 (m, 18H, C_6H_3, C_6H_5). ^{13}C NMR (68 MHz, C_6D_6): δ (ppm) −2.6 (SiCH_3), 64.3 (C_6H_3-CH_2), 102.1, 105.3, 143.5, 156.2 (C_6H_3), 117.0, 120.5, 128.7, 131.0 (C_6H_5). ^{29}Si NMR (54 MHz, C_6D_6): δ (ppm) −5.4, −3.3, (C_6H_3-OSiO-C_6H_5, $C_6H_3CH_2$-OSiO-C_6H_5). CI-MS: *m*/*z* 590. Anal. Calcd. for $C_{31}H_{38}O_6Si_3$: C, 63.05; H, 6.44. Found: C, 62.87; H, 6.60%.

First generation dendrimer: [G-1]-$(OH)_6$ (4)

A solution of DHBA (0.200 g, 1.43 mmol) in 5 mL of dry THF was added dropwise to a solution of 3 equivalents of bis(dimethylamino)dimethylsilane (0.774 mL, 4.29 mmol) in 5 mL of dry THF cooled to 0 °C. Stirring at ice-bath temperature was maintained for an additional 6 hour period, and the resulting solution was then warmed to room temperature. The latter was then added to a solution of 3 equivalents of DHBA (0.600 g, 4.29 mmol) in 10 mL of dry THF. The resulting solution was stirred overnight, and THF was then removed under vacuum to afford a sticky gel (**4**, 0.936 g, 90%). ^{1}H NMR (270 MHz, DMSO-d_6): δ (ppm) 0.10 (s, 6H, OSiMe_2O), 0.23 (s, 12H, OSiMe_2O), 4.65 (s, 8H, C_6H_3-CH_2O), 6.09–6.54 (m, 12H, C_6H_3), 9.07 (s, 6H, C_6H_3OH). ^{13}C NMR (68 MHz, DMSO-d_6): δ −2.4, −0.1, 1.4 (SiCH_3), 63.6, 64.0 (C_6H_3-CH_2), 101.4, 104.7, 143.3, 158.8 (C_6H_3). ^{29}Si NMR (54 MHz, DMSO-d_6): δ (ppm) −19.9, −11.1, −1.6 (C_7H_5-OSiMe$_2$O-C_7H_5, C_7H_5-OSiMe$_2$O-C_6H_3, C_6H_3-OSiMe$_2$O-C_6H_3). Mass spectrum (MALDI-TOF) *m*/*z* 734.7 (including *m*/*z* Li^+). Anal. Calcd for $C_{34}H_{38}O_{12}Si_3$: C, 56.04; H, 6.04. Found: C, 55.55; H, 6.57%.

Second generation dendrimer: [G-2]-$(OH)_{12}$ (5)

A solution of 1 equivalent of DHBA (50 mg, 0.357 mmol) in 10 mL of THF was added to a solution of 3 equivalents of bis(dimethylamino)dimethylsilane (0.194 mL, 1.071 mmol) in 5 mL of THF, and stirred for 6 hours at ice-bath temperature. The resulting solution was added to 3 equivalents of DHBA (150 mg, 1.071 mmol) dissolved in 10 mL of THF. After stirring overnight, the mixture was then added dropwise to a solution of 6 equivalents of bis(dimethylamino)dimethylsilane (0.388 mL, 2.142 mmol) in 5 mL of THF. The resulting solution was then added to 6 equivalents of DHBA (300 mg, 2.142 mmol) dissolved in 15 mL of THF, and stirred overnight. The removal of the solvent under vacuum afforded a sticky gel. (**5**, 0.587, 86%). ^{1}H NMR (270 MHz, DMSO-d_6) δ 0.11, 0.21 (m, 54H, OSiMe_2O), 4.60 (s, 20H, C_6H_3-CH_2O), 6.18 (m, 30H, C_6H_3), 9.13 (s, 12H, C_6H_3-OH). ^{13}C NMR (68 MHz, DMSO-d_6): δ (ppm) −2.5, −0.5, 1.4 (SiCH_3), 63.5, 64.2, 67.5 (C_6H_3-CH_2), 143.1, 145.2, 158.7 (C_6H_3). ^{29}Si NMR (54 MHz, DMSO-d_6): δ (ppm) −19.9, −11.1, −10.9, −1.6 (C_7H_5-OSiMe$_2$O-C_7H_5, C_7H_5-OSiMe$_2$O-C_6H_3, C_6H_3-OSiMe$_2$O-C_6H_3). Mass spectrum (MALDI-TOF) *m*/*z* 1912. Anal. Calcd for $C_{88}H_{116}O_{30}Si_9$: C, 53.26; H, 6.07. Found: C, 53.06; H, 6.68%.

Third generation dendrimer: [G-3]-$(OH)_{24}$ (6)

A similar procedure as described above for [G-2]-$(OH)_{12}$ was used to prepare the third generation dendrimer. A solution of 1 equivalent of DHBA (20 mg, 0.143 mmol) in 10 mL of THF was added to a solution of 3 equivalents of bis(dimethylamino)-dimethylsilane (0.0755 mL, 0.429 mmol) in 5 mL THF, and stirred for 6 hours at ice bath temperature. The above mixture was added to a solution of 3 equivalents of DHBA (60 mg, 0.429 mmol) in 10 mL of THF, and stirred overnight at room temperature. It was then added to a solution of 6 equivalents of bis(dimethylamino)dimethylsilane (0.155 mL, 0.858 mmol) in 5 mL of THF, and stirred overnight at room temperature. This was then added to a solution of 6 equivalents of DHBA (120 mg, 0.858 mmol) in 10 mL of THF, and after stirring overnight, this solution was added to a solution of 12 equivalents of bis(dimethylamino)dimethylsilane (0.310 mL, 1.716 mmol) in 5 mL of THF, and stirred for 14 hours. Finally this solution was added to a solution of 12 equivalents of DHBA (240 mg, 1.716 mmol) in 15 mL of THF, and stirred overnight. THF was removed under vacuum to afford a gel (**6**, 0.550 g, 91%). ^{1}H NMR (270 MHz, DMSO-d_6): δ (ppm) 0.12–0.24 (m, 126H, OSiMe_2O), 4.66 (s, 44H, C_6H_3-CH_2O), 6.14, 6.17, 6.26, 6.73 (m, 66H, C_6H_3), 9.36 (s, 24H, C_6H_3-OH). ^{13}C NMR (68 MHz, DMSO-d_6): δ (ppm) −2.2 (m, SiCH_3), 64.3, 67.6 (C_6H_3-CH_2), 143.1, 155.4, 158.7 (C_6H_3). ^{29}Si NMR (54 MHz, DMSO-d_6): δ (ppm) −20.5 −11.8, −1.7 (C_7H_5-OSiMe$_2$O-C_7H_5, C_7H_5-OSiMe$_2$O-C_6H_3). Mass spectrum (MALDI-TOF) *m*/*z* 4245.7 (including *m*/*z* Li^+). Anal. Calcd for $C_{196}H_{260}O_{66}Si_{21}$: C, 55.48; H, 6.13. Found: C, 55.02; H, 6.65%.

[G-1]-$(SiMe_3)_6$ (7)

To a solution of the first generation dendrimer (**4**, 520 mg, 0.714 mmol) in 20 mL of THF, 6 equivalents of trimethylsilyldiethylamine (0.811 mL, 4.286 mmol) were added *via* syringe, and the mixture was stirred overnight. THF was removed under vacuum to afford a dark brown liquid (**7**, 0.801 g, 96%). ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 0.17 (s, 6H), 0.22 (s, 12H and s, 54H, OSiMe_2O and OSiMe_3), 4.68 (br s, 8H, C_6H_3-CH_2O), 6.61–6.81 (m, 12H, C_6H_3). ^{13}C NMR (C_6D_6) δ −2.9, −0.1, 0.4 (SiCH_3), 64.0 (C_6H_3-CH_2),111.4, 111.5, 156.6 (C_6H_3). ^{29}Si NMR (54 MHz, C_6D_6): δ (ppm) −3.7, −3.3, −1.8, −1.8 (OSiMe$_2$O), 18.86, 18.92 (OSiMe$_3$). Mass spectrum (MALDI-TOF) *m*/*z* 1168.8 (including *m*/*z* Li^+). FAB-MS: *m*/*z* 1160.

[G-1]-$(PPh_2)_6$ (8)

To a solution of 6 equivalents of bis(dimethylamino)dimethylsilane (0.755 mL, 4.302 mmol) in THF, a solution of **4** (520 mg, 0.714 mmol) in 10 mL of THF was added dropwise over a period of 3 hours. Once the addition was complete, the mixture was stirred overnight at room temperature. A solution of 6 equivalents of 3-hydroxypropyldiphenylphosphine (1.051 g, 4.302 mmol) in 10 mL of THF was then added dropwise to the above mixture. Stirring was continued overnight at room temperature. The removal of THF afforded a white gel (**8**, 1.570 g, 87%). ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 0.09, 0.21 (br s, 54H, OSiMe_2O), 1.75 (m, 12H, -O-CH$_2$-CH_2-), 2.07 (t, J_{H-H} = 8.3 Hz, 12H, -CH$_2$- PPh$_2$), 3.63 (t, J_{H-H} = 6.3 Hz, 12H, -O-CH_2-CH$_2$-), 4.69 (m, 8H, C_6H_3-CH_2O), 6.86 (m, 12H,

C_6H_3), 7.08, 7.44 (m, 60H, $P(C_6H_5)_2$). $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6): δ (ppm) −15.9 (s, PPh_2). Mass spectrum (MALDI-TOF) *m/z* 2529.5. Anal. Calcd for $C_{136}H_{164}O_{18}Si_9P_6$: C, 57.41; H, 6.72. Found: C, 56.94; H, 6.89%.

[G-1]-[Rh(cod)Cl]$_{16}$ (9)

To a solution of **8** (362 mg, 0.143 mmol) in 10 mL of THF, a solution of 3 equivalents of chloro(1,5-cyclooctadiene)rhodium(I) dimer (211 mg, 0.429 mmol) in 15 mL of THF was added dropwise. THF was then removed under vacuum to give a yellow solid (**9**, 0.544 g, 95%). ^1H NMR (270 MHz, C_6D_6): δ (ppm) 0.17 (br m, 60H, OSiMe_2O), 1.70 (br, 12H, -O-CH_2-CH_2-), 2.10 (br, 48H, -CH_2-CH_2-), 2.30 (br, 12H, -CH_2-PPh_2), 3.67 (br, 12H, -O-CH_2-CH_2-), 4.60 (br m, 8H, C_6H_3-CH_2O), 5.77 (s, 24H, -CH=CH-), 6.86 (m, 12H, C_6H_3), 7.06, 7.69 (m, 60H, $P(C_6H_5)_2$). $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6): δ (ppm) 27.3 (d, J_{Rh-P} = 150.4 Hz). Mass spectrum (MALDI-TOF) *m/z* 4008.2.

[G-2]-(PPh_2)$_{12}$ (10)

To a solution of 12 equivalents of bis(dimethylamino)dimethylsilane (0.755 mL, 4.285 mmol) in 5 mL of THF, a solution of **5** (682 mg, 0.357 mmol) in 15 mL of THF was added dropwise. The mixture was stirred overnight. Then 1.05 g of 3-hydroxypropyldiphenylphosphine (12 equivalents, 4.285 mmol) in 15 mL of THF were added. The reaction mixture was heated for a period of 24 hours at a temperature of 55 °C. The solvent was then removed under vacuum to afford a white gel (**10**, 1.593 g, 81%). ^1H NMR (270 MHz, C_6D_6): δ (ppm) 0.11 (br m, 126H, OSiMe_2O), 1.71 (m, 24H, -O-CH_2-CH_2-), 2.08 (m, 24H, -CH_2-PPh_2), 3.54 (t, J_{H-H} = 6.29 Hz, 24H, -O-CH_2-CH_2-), 4.70 (m, 20H, C_6H_3-CH_2O), 6.86 (m, 30H, C_6H_3), 7.15, 7.46 (m, 120H, $P(C_6H_5)_2$). $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6): δ (ppm) 16.0 (s, PPh_2). Mass spectrum (MALDI-TOF, LiBr, dithranol) *m/z* 5518.7 (including *m/z* Li^+).

[G-3]-(PPh_2)$_{24}$ (11)

A solution of 170 mg of **6** (0.040 mmol) in 10 mL of THF was added dropwise to a solution of 24 equivalents of bis(dimethylamino)dimethylsilane (0.174 mL, 0.960 mmol) in 5 mL of THF. The mixture was then stirred overnight at room temperature. 24 equivalents of 3-hydroxypropyldiphenylphosphine (0.235 mg, 0.960 mmol) in 10 mL of THF were added dropwise to the latter solution. Once the addition was complete, the mixture was stirred at 55 °C under nitrogen for 7 days to allow all the phosphine compounds to be grafted on the dendritic backbone (**11**, 0.375 g, 87%). ^1H NMR (270 MHz, C_6D_6): δ (ppm) 0.16 (br m, 270H, OSiMe_2O), 1.75 (m, 48H, -O-CH_2-CH_2-), 2.10 (m, 48H, -CH_2-PPh_2), 3.69 (t, J_{H-H} = 6.2 Hz, 48H, -O-CH_2-CH_2-), 4.79 (m, 44H, C_6H_3-CH_2O), 6.86 (m, 66H, C_6H_3), 7.06, 7.45 (m, 240H, $P(C_6H_5)_2$). $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6): δ (ppm) −15.9 (s, PPh_2). Mass spectrum (MALDI-TOF) *m/z* 11465.6 (including *m/z* Na^+).

[G-2]-[Rh(cod)Cl]$_{12}$ (12)

211 mg of chloro(1,5-cyclooctadiene)rhodium(I) dimer (6 equivalents, 0.428 mmol) were dissolved in 15 mL of THF, and added dropwise to a solution of **10** (393 mg, 0.0714 mmol) in 10 mL of THF. The yellow solution was stirred overnight at room temperature. The solvent was then removed under vacuum to give a yellow solid (**12**, 0.588 g, 93%). ^1H NMR (270 MHz, C_6D_6): δ (ppm) 0.21 (br m, 126H, OSiMe_2O), 1.70 (br, 24H, -O-CH_2-CH_2-), 2.10 (br, 96H, -CH_2-CH_2-), 2.30 (br, 24H, -CH_2- PPh_2), 3.67 (br, 24H, -O-CH_2-CH_2-), 4.76 (m, 20H, C_6H_3-CH_2O), 5.84 (s, 48H, -CH=CH-), 6.86 (m, 30H, C_6H_3), 7.15, 7.73 (m, 120H, $P(C_6H_5)_2$). $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6): δ (ppm) 27.1 (d, J_{Rh-P} = 149.0 Hz). Mass spectrum (MALDI-TOF) *m/z* 8488.7 (including *m/z* Na^+).

[G-3]-[Rh(cod)Cl]$_{24}$ (13)

An orange solution of 12 equivalents of the chloro(1,5-cyclooctadiene)rhodium(I) dimer (106 mg, 0.215 mmol) in 15 mL of THF was added dropwise to a solution of **11** (311 mg, 1.793×10^{-5} mol). The mixture was left to stir overnight before removing the solvent to afford an orange sticky solid (**13**, 0.230 g, 74%). ^1H NMR (270 MHz, C_6D_6): δ (ppm) 0.15 (br m, 270H, OSiMe_2O), 1.67 (br, 48H, -O-CH_2-CH_2-), 2.11 (br, 192H, -CH_2-CH_2-), 2.34 (br, 48H, -CH_2-PPh_2), 3.56 (br, 48H, -O-CH_2-CH_2-), 4.69 (br m, 44H, C_6H_3-CH_2O), 5.74 (s, 96H, -CH=CH-), 6.84 (m, 66H, C_6H_3), 7.00, 7.63 (m, 240H, $P(C_6H_5)_2$). $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6): δ (ppm) 27.3 (d, J_{Rh-P} = 150.4 Hz). Mass spectrum (MALDI-TOF) *m/z* 17368.7.

Synthesis of hyperbranched polymers

One-pot reaction. 2 Equivalents of DHBA (151.6 mg, 1.083 mmol) were dissolved in 10 mL of THF, and 3 equivalents of bis(dimethylamino)dimethylsilane (0.294 mL, 1.624 mmol) were directly added to the DHBA solution *via* syringe. The mixture was stirred overnight at room temperature, and the solvent was then removed under vacuum to yield a grey gel (293 mg, 92%). ^1H NMR (270 MHz, C_6D_6): δ (ppm) 0.07, 0.20, 0.29 (s, 18H, OSiMe_2O), 2.42 (s, -SiNMe_2), 4.72 (br m, 6H, C_6H_3-CH_2O), 6.89 (br, 9H, C_6H_3-CH_2O),. Mass spectrum (MALDI-TOF, LiBr, dithranol) *m/z* 596.2 (including *m/z* Li^+). Anal. Calcd for $C_{29}H_{43}O_9Si_3N$: C, 53.94; H, 6.84. Found: C, 53.38; H, 7.06%.

2-Step preparation of hyperbranched polymers. 3 Equivalents of bis(dimethylamino)dimethylsilane (0.774 mL, 4.286 mmol) were directly added *via* syringe to a solution of DHBA (200 mg, 1.429 mmol) in 10 mL of THF, and the mixture was stirred overnight at room temperature. Then a solution of 3 equivalents of DHBA (600 mg, 1.429 mmol) in 15 mL of THF was added, and the mixture was stirred overnight at room temperature. The solvent was then removed under vacuum to afford a grey–brown gel (1.150 mg, 80%). ^1H NMR (270 MHz, DMSO-d_6): δ (ppm) 0.12, 0.23, 0.35 (m, OSiMe_2O), 2.30 (s, -SiNMe_2), 4.65 (m, C_6H_3-CH_2O), 6.16 (m, C_6H_3-CH_2O), 9.17 (br, C_6H_3-OH). Mass spectrum (MALDI-TOF, LiBr, dithranol) *m/z* 539, 735.1, 931.1, 1127.7, 1324, 1521, 1719.5, 1917.5 (including *m/z* Li^+).

Hydrogenation of 1-decene

All of the hydrogenation reactions were performed using a Parr 4560 Mini-reactor with constant experimental conditions: p_{H_2} = 20 bar, room temperature, ratio $n_{dendrimer}$:n_{decene} = 1:200. The product analysis was carried out using a GC-MS spectrometer (Hewlett Packard 6840 GC and HP 5973 mass spectrometer) using He as the carrier gas and an initial temperature of 50 °C with a ramp of 12 °C min^{-1} stopping at 300 °C. Both the catalyst and the decene were mixed in 20 mL of benzene inside the pressure reactor. After the catalysis run, the solvent and the decene–decane mixture were distilled by static vacuum distillation, leaving the dendritic catalyst behind. The benzene was then removed by distillation to afford a colourless liquid. ^1H NMR (270 Hz, C_6D_6): δ (ppm) 0.91 (6H, t, J_{H-H} = 6.7 Hz, CH_3), 1.28 (16H, br m, CH_2). GC-MS: *m/z* 142, 7.45 min.

Acknowledgements

We would like to thank the NSERC of Canada and FCAR of Quebec, Canada, for financial support.

References

1 (*a*) D. Astruc and F. Chardac, *Chem. Rev.*, 2001, **101**, 2991; (*b*) H. Ma and A. K.-Y. Jen, *Adv. Mater.*, 2001, **13**, 1201; (*c*) A. Cordova and K. D. Janda, *J. Am. Chem. Soc.*, 2001, **123**, 8248; (*d*) D. de Groot, B. F. M. de Waal, J. N. H. Reek, A. P. H. J. Schenning, P. C. J. Kamer, E. W. Meijer and P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.*, 2001, **123**, 8453; (*e*) V. Balzani, P. Ceroni, A. Juris, M. Venturi, S. Campagna, F. Puntoriero and S. Serroni, *Coord. Chem. Rev.*, 2001, **219-221**, 545; (*f*) C. Marmillon, F. Gauffre, T. Gulik-Krzywicki, C. Loup, A.-M. Caminade, J.-P. Majoral, J.-P. Vors and E. Rump, *Angew. Chem., Int. Ed.*, 2001, **40**, 2626; (*g*) G. E. Oosterom, J. N. H. Reek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Angew. Chem., Int. Ed.*, 2001, **40**, 1828; (*h*) M. Fischer and F. Vogtle, *Angew. Chem., Int. Ed.*, 1999, **38**, 884; (*i*) A. W. Bosman, H. M. Janssen and E. W. Meijer, *Chem. Rev.*, 1999, **99**, 1665; (*j*) M. A. Hearshaw, A. T. Hutton, J. R. Moss and K. J. Naidoo, *Adv. Dendritic Macromol.*, 1999, **4**, 1; (*k*) O. A. Matthews, A. N. Shipway and J. F. Stoddart, *Prog. Polym. Sci.*, 1998, **23**, 1; (*l*) J. F. G. A. Jansen den Brabander-van der Berg and E. W. Meijer, *Science*, 1994, **266**, 1226.

2 (*a*) J. P. Majoral and A.-M. Caminade, *Chem. Rev.*, 1999, **99**, 845; (*b*) F. Vogtle, *Top. Curr. Chem.*, 1998, 197; (*c*) G. R. Newkome, C. N. Moorefield and F. Vogtle, *Dendritic Molecules*, Wiley, Weinheim, 1996.

3 (*a*) M. Dasgupta, M. B. Peori and A. K. Kakkar, *Coord, Chem. Rev.*, 2002, **233–234**, 223; (*b*) M. B. Peori and A. K. Kakkar, *Organometallics*, 2002, **21**, 3860; (*c*) M. Petrucci-Samija, V. Guillemette, M. Dasgupta and A. K. Kakkar, *J. Am. Chem. Soc.*, 1999, **121**, 1968; (*d*) R. van Heerbeek, P. C. J. Kamer, P. W. N. M. van Leeuwen and J. N. H. Reek, *Chem. Rev.*, 2002, **102**(10), 3717.

4 (*a*) C. J. Hawker and J. M. J. Frechet, *J. Am. Chem. Soc.*, 1990, **112**, 7638; (*b*) C. J. Hawker and J. M. J. Frechet, *J. Chem. Soc., Chem. Commun.*, **1990**, 1010; (*c*) S. M. Grayson and J. M. J. Frechet, *Chem. Rev.*, 2001, **101**, 3819.

5 (*a*) M. J. Laufersweiler, J. M. Rhode, J.-L. Chaumette, D. Sarazin and J. R. Parquette, *J. Org. Chem.*, 2001, **66**, 6440; (*b*) V. Percec, C.-H. Ahn, T. K. Bera, G. Ungar and D. J. P. Yeardley, *Chem. Eur. J.*, 1999, **5**, 1070; (*c*) R.-M. Sebastian, G. Margo, A.-M. Caminade and J.-P. Majoral, *Tetrahedron*, 2000, **56**, 6269; (*d*) M. W. P. L. Baars, R. Kleppinger, M. H. J. Koch, S.-L. Yeu and E. W. Meijer, *Angew. Chem., Int. Ed.*, 2000, **39**, 1285; (*e*) Y. Pan and W. T. Ford, *Macromolecules*, 2000, **33**, 3731; (*f*) M. Brettreich, S. Burghardt, C. Bottcher, T. S. Bayerl and A. Hirsch, *Angew. Chem., Int. Ed.*, 2000, **39**, 1845.

6 R. Fessenden and J. S. Fessenden, *Chem. Rev.*, 1961, **61**, 361.

7 (*a*) A. K. Kakkar, *Chem. Rev.*, 2002, **102**(10), 3579; (*b*) A. J. Dickie, A. K. Kakkar and M. A. Whitehead, *Langmuir*, 2002, **18**, 5657; (*c*) C. M. Yam, A. J. Dickie and A. K. Kakkar, *Langmuir*, 2002, **18**, 8481; (*d*) F. Chaumel, H. Jiang and A. K. Kakkar, *Chem. Mater.*, 2001, **13**, 3389; (*e*) H. Jiang and A. K. Kakkar, *J. Am. Chem. Soc.*, 1999, **121**, 3657; (*f*) C. M. Yam and A. K. Kakkar, *Langmuir*, 1999, **15**, 3807; (*g*) M. G. L. Petrucci and A. K. Kakkar, *Chem. Mater.*, 1999, **11**, 269; (*h*) C. M. Yam, A. Dickie, A. Malkhasian, A. K. Kakkar and M. A. Whitehead, *Can. J. Chem.*, 1998, **76**, 1766; (*i*) H. Jiang and A. K. Kakkar, *Adv. Mater.*, 1998, **10**, 1093; (*j*) C. M. Yam, S. S. Y. Tong and A. K. Kakkar, *Langmuir*, 1998, **14**, 6941; (*k*) H. Jiang and A. K. Kakkar, *Macromolecules*, 1998, **31**, 2501; (*l*) M. G. L. Petrucci and A. K. Kakkar, *Organometallics*, 1998, **17**, 1798; (*m*) H. Jiang and A. K. Kakkar, *Macromolecules*, 1998, **31**, 4170; (*n*) M. G. L. Petrucci and A. K. Kakkar, *Adv. Mater.*, 1996, **8**, 251; (*o*) H. Jiang, A. K. Kakkar, A.-M. Lebuis, H. Zhou and G. K. Wong, *J. Mater. Chem.*, 1996, **6**, 1075; (*p*) C. M. Yam and A. K. Kakkar, *J. Chem. Soc., Chem. Commun.*, **1995**, 907; (*q*) M. G. L. Petrucci and A. K. Kakkar, *J. Chem. Soc., Chem. Commun.*, **1995**, 1577.

8 A. Bosman, M. J. Bruining, H. Koojman, A. L. Spek, R. A. J. Janssen and E. W. Meijer, *J. Am. Chem. Soc.*, 1998, **120**, 8547.

9 (*a*) B. Chu, *Laser Light Scattering: Basic Principles and Practice*, Academic Press, New York, 2nd edn., 1991; (*b*) R. Finsy, *Adv. Colloid Interface Sci.*, 1994, **52**, 79.

10 (*a*) F. M. Ottaviani, P. Favuzza, B. Sacchi, N. J. Turro, S. Jockusch and D. A. Tomalia, *Langmuir*, 2002, **18**(6), 2347; (*b*) P. N. Floriano, C. O. Noble, M. J. Schoonmaker, E. D. Poliakoff and R. L. McCarley, *J. Am. Chem. Soc.*, 2001, **123**(43), 10545.