3672 *Macromolecules* **2010**, *43*, 3672–3681
DOI: 10.1021/ma1004056

Macromolecules
ARTICLE

Synthesis of 1,4-Polybutadiene Dendrimer−Arborescent Polymer Hybrids

Mario Gauthier* **and Abdul Munam**

Institute for Polymer Research, Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada

Received February 19, 2010; Revised Manuscript Received March 18, 2010

ABSTRACT: A divergent synthetic scheme was developed for the preparation of high branching functionality hybrid polymers from carbosilane dendrimer substrates and polybutadiene side chains. Carbosilane dendrimers with 32, 64, or 128 peripheral Si−Cl functional groups were first coupled with 1,2-polybutadienyllithium chains having a number-average molecular weight $M_n \approx 1000$. The polybutadiene-grafted substrates were then hydrosilylated with dichloromethylsilane and reacted with high 1,4-microstructure content polybutadienyllithium chains to generate high branching functionality dendrimer−arborescent hybrids. Three series of hybrid polymers were synthesized containing 1,4-polybutadiene side chains with $M_n \approx 1500$, 5000, or 30 000. Size exclusion chromatography analysis of the polymers confirmed that a narrow molecular weight distribution was maintained ($M_w/M_n \leq 1.14$). The branching functionality of the arborescent hybrids varied from 140−335, 160−1110, and 360−2830 for the 32-, 64-, and 128-site coupling precursors, respectively. The experimental branching functionalities attained were lower than the theoretical values due to decreased coupling efficiency within each series, in particular for polymers with longer polybutadiene side chains, apparently due to steric limitations in the grafting reaction.

Introduction

Branched polymers are of interest, among others, because of their peculiar physical properties[1−3] and their potential usefulness as rheological modifiers for other polymers.[4] Star-branched and arborescent (dendrigraft) polymers are two families of branched polymers of particular importance because their controllable architecture enables fundamental investigations of structure−property relations. The physical properties of these materials can be fine-tuned through variations in parameters such as their side-chain molecular weight and composition, branching functionality, the presence of functional end groups, etc. The molecular weight distribution (MWD) of star-branched and arborescent polymers is often very narrow because their synthesis typically relies on living polymerization techniques. As a result, these polymers are ideal to elucidate the influence of structural parameters on the molecular (polymeric) and intermolecular (colloidal) properties of branched polymers.

Different methods have been developed for the synthesis of star-branched polybutadiene, but the coupling reaction of living polybutadienyllithium chains with chlorosilane substrates is clearly most successful.[5] This technique was extended to the synthesis of 32-, 64-, and 128-arm regular star polybutadiene from carbosilane dendrimers with chlorosilane functionalities as coupling agents.[6,7] The dendrimer path is versatile, but grafting on these substrates eventually restricts further growth of the molecules due to steric limitations. Grafting of 1,4-polybutadiene chains onto linear and 18-arm star-branched 1,2-polybutadiene substrates hydrosilylated with dichloromethylsilane has also been explored for the synthesis of high branching functionality stars,[8] leading to branching functionalities of up to 270. An alternate core-first strategy using dendrimeric initiators carrying hydroxyl end groups was reported for the synthesis of 4-, 8-, and 16-arm star polymers with poly(ethylene oxide) arms.[9] The synthesis of dendrimer−linear polymer hybrids was also achieved with lithiated carbosilane substrates to initiate the anionic polymerization of styrene, ethylene oxide, or hexamethylcyclotrisiloxane.[10] Unfortunately, the core-first methods are only practical if rapid exchange exists between the active and dormant anionic propagating centers, and characterization of the side chains cannot be carried out unless they are linked to the core through selectively cleavable bonds.

The synthesis of arborescent polymers (a subclass of dendrigraft polymers) relies on a generation-based scheme to obtain a dendritic (multilevel) graft polymer architecture.[11] A linear polymer substrate is modified to introduce coupling sites serving in a grafting reaction for linear chains. The comb polymer (also called the generation zero or G0 arborescent polymer) thus obtained is then subjected to additional cycles of functionalization and grafting reactions to yield higher generation (G1, G2, ...) arborescent polymers, with a branching functionality and molecular weight increasing geometrically for each cycle. The random distribution of coupling sites on the substrates makes these molecules less sensitive to incomplete reactions because all the molecules are affected to the same extent when a large number of coupling sites are present. Consequently, a narrow MWD ($M_w/M_n \sim 1.1$) is achieved even for very high branching functionalities.

A strategy combining carbosilane dendrimer substrates and arborescent polymer chemistry is now presented for the synthesis of high branching functionality dendrimer−arborescent polybutadiene hybrids, characterized by a much denser core structure than analogous arborescent systems derived from linear polymer substrates.[12] Carbosilane dendrimer substrates bearing 32, 64, or 128 peripheral Si−Cl functional groups are first coupled with short 1,2-polybutadienyllithium segments and hydrosilylated with dichloromethylsilane. The polyfunctional substrates are then reacted with polybutadienyllithium chains of different number-average molecular weights (M_n = 1500, 5000, and 30 000) with a high 1,4-microstructure content. This approach yields polymers with up to 2830 side chains, much higher than for the star-branched polymer structures reported previously.

---

*Corresponding author: e-mail gauthier@uwaterloo.ca; Ph +1-519-888-4567; Fax +1-519-746-0435.

Experimental Section

Solvent and Reagent Purification. Tetrahydrofuran (THF; Caledon, reagent grade) and cyclohexane (BDH, HPLC grade) were purified by distillation under nitrogen (N_2) from sodium benzophenone ketyl and oligostyryllithium, respectively. The dry solvents were introduced directly from the stills into the polymerization reactor or ampule preparation manifolds through polytetrafluoroethylene (PTFE) tubing. *n*-Butyllithium (*n*-BuLi, Aldrich, 2.5 M in hexane) and *tert*-butyllithium (*tert*-BuLi, Aldrich, 1.7 M in heptane) solutions were used as received; the exact activity of the *tert*-BuLi solution was determined by the method of Lipton et al.[13] 2,2′-Bipyridyl (Aldrich, 99+%) was dissolved in dry cyclohexane to give a 0.10 M solution. All reagent ampules serving in the polymerization and coupling procedures were prepared by high-vacuum techniques and filled with dry N_2.[14] The ampules, equipped with PTFE stopcocks and ground glass joints, were designed to be mounted directly on the polymerization reactor. 1,3-Butadiene (Praxair, 99%) was purified by stirring with *n*-butyllithium (1 mL for 20 mL of monomer) for 30 min at 0 °C and condensation to an ampule under vacuum. The monomer was diluted by condensing an equal volume of dry THF or cyclohexane under vacuum, and the ampule was stored at −20 °C until used. Dichloromethylsilane (Aldrich, 99%) was purified on a high-vacuum manifold by three freezing−evacuation−thawing cycles and slow distillation to a glass ampule. Tetravinylsilane (Gelest, 95%), vinylmagnesium chloride (Aldrich, 1.6 M solution in THF), and platinum(0)−1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Aldrich, 3 wt % solution in xylene) were used as received.

Synthesis of Carbosilane Dendrimers. All carbosilane dendrimer generations (i.e., 8-, 16-, 32-, and 64-arm) were synthesized by a modification of the method reported by Zhou and Roovers.[15] Only procedures differing significantly from those reported previously are described. A detailed procedure for the synthesis of an 8-arm carbosilane dendrimer is described below as an example.

8-Arm (G1) Carbosilane Dendrimer. Tetravinylsilane (4.4 mL, 3.5 g, 26 mmol) was transferred with a syringe to an ampule previously flamed under vacuum and purged with N_2 on a high-vacuum manifold.[14] The compound was dried by three azeotropic distillation cycles with dry THF from the purification still and redissolved in 40 mL of dry THF. Freshly distilled dichloromethylsilane (17.7 mL, 19.6 g, 170 mmol, 1.6 equiv vs vinyl groups) contained in a second ampule was then recondensed under vacuum to the first ampule. The apparatus was filled with N_2, and the platinum(0)−1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylene (75 μL) was added to the ampule with a syringe through the stopcock opening. The ampule was sealed again and heated to 50 °C in an oil bath until the reaction started refluxing (< 5 min). The oil bath was then removed and replaced with an ice−water bath to cool the reaction. After 30 min, the ampule was heated again in the oil bath at 50 °C for 4 h. After cooling to room temperature, excess dichloromethylsilane and the solvent (THF) were removed under vacuum, and two portions of dry THF (40 mL) were condensed and distilled from the ampule to remove excess reagent. A last 40 mL portion of dry THF was condensed to the ampule, which was filled with N_2. Vinylmagnesium chloride (1.6 M in THF, 230 mL, 370 mmol, 1.8 equiv vs Si−Cl groups) was then added through the stopcock opening over ca. 30 min. The ampule was sealed, and the reaction was allowed to proceed at room temperature for 7 days. The reaction mixture was transferred to a separatory funnel, hexane (200 mL) was added, and the mixture was washed twice with 200 mL of water and once with 200 mL of saturated aqueous NaCl solution. The organic solution was dried over anhydrous $MgSO_4$, the solvent was removed on a rotary evaporator, and the solid residue (14 g) was purified by flash chromatography on a silica gel column (230−400 mesh, 15 cm length × 6 cm diameter) by eluting with a solution of 0.25% ethyl acetate in hexane to give 7.2 g of the pure 8-arm carbosilane dendrimer (or the first generation, G1) in 52% yield as an oily product.

The conditions for the synthesis of the 16-, 32-, and 64-arm carbosilane dendrimers were identical with those described above, using the reagent amounts specified below.

16-Arm (G2) Carbosilane Dendrimer. G1 carbosilane dendrimer 3.8 g (7.2 mmol); dichloromethylsilane 11.3 g (10.2 mL, 98 mmol, 1.7 equiv vs vinyl groups); total hydrosilylation reaction time 5 h; vinylmagnesium chloride 173 mL (277 mmol, 2.4 equiv vs Si−Cl groups); reaction time 15 days. Raw product (10 g) purified on silica gel column (230−400 mesh, 15 cm length × 6 cm diameter), eluting with 0.25% ethyl acetate in hexane to give 4.6 g of the pure 16-arm (G2) carbosilane dendrimer in 48% yield as an oily product.

32-Arm (G3) Carbosilane Dendrimer. G2 carbosilane dendrimer 2.6 g (2.0 mmol); dichloromethylsilane 6.5 g (5.8 mL, 57 mmol, 1.8 equiv vs vinyl groups); total hydrosilylation reaction time 5 h; vinylmagnesium chloride 120 mL (190 mmol, 3.0 equiv vs Si−Cl groups); total reaction time 30 days. Raw product (6 g) purified on silica gel column (230−400 mesh, 8 cm length × 6 cm diameter), eluting with 8 drops of ethyl acetate in 500 mL of hexane to give 2.5 g of the pure 32-arm (G3) carbosilane dendrimer in 44% yield as a viscous liquid.

64-Arm (G4) Carbosilane Dendrimer. G3 carbosilane dendrimer 1.0 g (0.35 mmol); dichloromethylsilane 3.0 g (2.7 mL, 26 mmol, 2.3 equiv vs vinyl groups); total hydrosilylation reaction time 6 h; vinylmagnesium chloride (1.6 M in THF) 42.5 mL (68 mmol, 3.0 equiv vs Si−Cl groups), total reaction time 60 days. Raw product (2.2 g) purified on silica gel column (230−400 mesh, 5 cm length × 6 cm diameter), eluting with 8 drops of ethyl acetate in 500 mL of hexane to give 0.5 g of the pure 64-arm (G4) carbosilane dendrimer in 24% yield as a viscous liquid.

Synthesis of Carbosilane-*graft*-1,2-polybutadiene Starlike Hybrids. The starlike hybrid polymers were synthesized from the 16-, 32-, and 64-arm carbosilane dendritic cores and side chains with a number-average molecular weight $M_n \approx 1000$ by adapting a reported procedure.[7] The synthesis of a 32-arm starlike hybrid is described below as an example.

The G2 (16-arm) carbosilane dendrimer (0.25 g, 0.19 mmol) in 10 mL of THF was hydrosilylated in an ampule as described above with dichloromethylsilane (0.63 g, 0.57 mL, 5.5 mmol, 1.7 equiv vs vinyl groups) and platinum divinyltetramethyldisiloxane complex (25 μL); total reaction time 5 h. After purification, the substrate was dissolved in 10 mL of THF and stored at room temperature under N_2 until the coupling reaction.

The anionic polymerization of 1,3-butadiene was carried out in THF to yield a mixed microstructure (52% of 1,2-units). 1,3-Butadiene (7.7 g, 140 mmol, 12 mL at 0 °C) was purified on a high-vacuum manifold by stirring with *n*-butyllithium (0.6 mL) for 30 min at 0 °C, condensed into a calibrated ampule, and diluted with 15 mL of THF. The ampule was stored at −20 °C until the polymerization. Ampules containing the G2 starlike chlorosilane coupling agent (6.4 mequiv Si−Cl groups) in THF, 1,3-butadiene (140 mmol in THF), the dry THF inlet, and a septum were mounted on the polymerization reactor.[14] After evacuation, flaming, and purging with N_2, THF (150 mL) and a few drops of 1,3-butadiene were added, and residual impurities were titrated at −78 °C with *tert*-BuLi to a persistent light yellow color. The calculated amount of *tert*-BuLi (4.5 mL, 7.7 mmol, for a target $M_n = 1000$) was then added, followed by the monomer over 5 min; the light yellow color changed to deep yellow. After 5 min the reactor was warmed to 0 °C, the polymerization was allowed to proceed for 4 h, and a side-chain sample was removed and terminated with N_2-purged methanol (measured side chain $M_n = 540$). The reactor was warmed to 23 °C, and the coupling agent solution was added over 5 min. Fading of the deep yellow color of the polybutadienyllithium solution was noticeable within 2 min, and after 30 min the reaction mixture was light yellow. The coupling reaction was allowed to proceed further for 24 h at 23 °C, and residual macroanions were terminated with N_2-purged methanol. The crude product (5.0 g) was recovered by precipitation in methanol, filtration, and drying under vacuum. The pure graft polymer (2.5 g, absolute $M_n = 19\,000$, $M_w/M_n = 1.02$, branching functionality $f_n = 31$) was isolated from the crude product by precipitation fractionation from *n*-hexane/methanol. The polymer was dried under vacuum and stored at −80 °C. The same conditions were used for the synthesis of 64- and 128-arm carbosilane-*graft*-1,2-polybutadiene hybrids, using the reagent amounts specified below.

64-Arm Starlike Hybrid. Chlorosilane substrate: G3 (32-arm) carbosilane dendrimer (0.25 g, 0.08 mmol) in 10 mL of THF; dichloromethylsilane (0.72 g, 0.65 mL, 6.2 mmol, 2.4 equiv vs vinyl groups); platinum divinyltetramethyldisiloxane (25 μL); total hydrosilylation reaction time 5 h. Coupling reaction: G3 chlorosilane coupling agent (5.5 mequiv chlorosilane groups) in 10 mL of THF; 1,3-butadiene (11 g, 18 mL, 200 mmol); *tert*-BuLi (6.5 mL, 11 mmol). Crude product yield 10 g, fractionated polymer yield 4.0 g (absolute $M_n = 61\,000$, $M_w/M_n = 1.03$, branching functionality $f_n = 57$).

128-Arm Starlike Hybrid. Chlorosilane substrate: G4 (64-arm) carbosilane dendrimer (0.25 g, 0.04 mmol) in 10 mL of THF; dichloromethylsilane: (0.80 g, 0.73 mL, 7.0 mmol, 2.7 equiv vs vinyl groups); platinum divinyltetramethyldisiloxane complex (25 μL); total hydrosilylation reaction time 6 h. Coupling reaction: G4 chlorosilane coupling agent (5.3 mequiv Si−Cl groups) in 10 mL of THF; 1,3-butadiene (10.6 g, 16.5 mL, 196 mmol); *tert*-BuLi (6.2 mL, 10.6 mmol, for a target $M_n = 1000$). Crude product yield 9.5 g, fractionated polymer yield 2.0 g (absolute $M_n = 160\,000$, $M_w/M_n = 1.16$, branching functionality $f_n = 126$).

Synthesis of Dendrimer−Arborescent Polybutadiene Hybrids. Three series of arborescent hybrids were synthesized by hydrosilylation of the carbosilane-*graft*-1,2-polybutadiene starlike hybrids and coupling with 1,4-polybutadienyllithium side chains having a $M_n \approx 1500$, 5000, or 30 000. The 1,2-polybutadiene hybrid substrates derived from the G2−G4 carbosilane dendrimers all had a microstructure with 52% of 1,2-units. A procedure for the synthesis of an arborescent hybrid using the G2 substrate and $M_n \approx 1500$ side chains is provided as an example.

The G2 (32-arm) starlike hybrid (0.25 g, dried for 24 h under high vacuum; 2.04 mmol 1,2-vinyl groups) in 10 mL of THF was hydrosilylated in an ampule with dichloromethylsilane (0.47 g, 0.42 mL, 4.1 mmol, 2.0 equiv vs vinyl groups) and platinum divinyltetramethyldisiloxane complex (50 μL) as described above; total hydrosilylation reaction time 24 h. The chlorosilane coupling agent was dried under high vacuum overnight, redissolved in 10 mL of THF, and stored under N_2 at room temperature. The same conditions were used for the hydrosilylation of the G3 and G4 starlike hybrids, but the total reaction time required for complete conversion at 50 °C was 30 and 36 h, respectively.

High *cis*-1,4-content polybutadiene was prepared in cyclohexane at 23 °C after purifying the monomer as described earlier.[14] Ampules containing the 32-arm chlorosilane coupling agent (4.1 mequiv of chlorosilane groups) in 10 mL of THF, purified 1,3-butadiene (9.2 g, 14.3 mL, 170 mmol) in 15 mL of cyclohexane, the dry cyclohexane inlets, and a septum were mounted on a 2 L glass reactor equipped with a vacuum-tight mechanical stirrer.[14] After evacuation, flaming, and purging with N_2, cyclohexane (300 mL) and 0.5 mL of 0.10 M 2,2′-bipyridyl solution in cyclohexane were added, and the solvent was titrated with *tert*-BuLi to give a persistent light orange color.[16] The reactor was then cooled to 0 °C, and the calculated amount of *tert*-BuLi (3.6 mL, 6.1 mmol, for a target $M_n = 1500$) was added, followed by the monomer over 5 min. The reactor was warmed to room temperature (23 °C), polymerization was allowed to proceed for 24 h, and a side-chain sample was removed and terminated with N_2-purged methanol (measured side chain $M_n = 1200$). The coupling agent solution was added to the reactor over 5 min. Fading of the orange color of the polybutadienyllithium solution was noticeable within 5 min, and after 2 h the reaction mixture became almost colorless and hazy. The coupling reaction was allowed to proceed further for 24 h at 23 °C, and residual macroanions were terminated with N_2-purged methanol. The crude product (8.7 g) was recovered by precipitation in methanol, filtration, and drying under vacuum. The pure graft polymer (4.0 g, absolute $M_n = 430\,000$, $M_w/M_n = 1.01$, branching functionality $f_n = 336$) was isolated by precipitation fractionation from *n*-hexane/methanol, dried under high vacuum, and stored at −80 °C. The same conditions were used to obtain side chains with $M_n \approx 5000$ and 30 000 after 48 and 72 h of polymerization, respectively. The coupling reaction was allowed to proceed for 24 h in all cases.

Polymer Characterization. A size exclusion chromatography (SEC) system calibrated with linear polystyrene standards was routinely used to monitor the polymerization and coupling reactions as well as the sample fractionation procedure. The instrument, operated at room temperature, consisted of a Waters 510 HPLC pump, a 500 mm × 10 mm Jordi DVB linear Mixed-Bed column (molecular weight range 10^2-10^7), and a Waters 410 differential refractometer detector. THF at a flow rate of 1 mL/min served as eluent for the analysis.

The absolute number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the hybrid polymers and the polybutadiene side chains ($M_n \approx 30\,000$) were determined by SEC analysis using a Wyatt Dawn DSP-F MALLS (multiangle laser light scattering) detector operating at 632.8 nm. The SEC system consisted of a Waters 590 programmable HPLC pump coupled with Waters Ultrastyragel columns (10^4, 10^5, and 10^6 Å pore sizes) using THF at a flow rate of 1 mL/min. Polymer concentration measurements in the eluent were accomplished with a Waters 2410 DRI detector operating at 660 nm. Molecular weights were obtained from the MALLS and DRI signals, using the Astra Version 4.70.07 software package. The refractive index increment (d*n*/d*c*) values for the polybutadiene side chain samples and the hybrid polymers used in the MALLS analysis were determined in THF at 25 °C on a Brice-Phoenix differential refractometer equipped with a 632 nm band-pass interference filter.

^{1}H NMR spectroscopy served to monitor the hydrosilylation reaction, to confirm the structure of the carbosilane dendrimers synthesized, and to determine the absolute M_n of the polybutadiene side chains with $M_n \approx 1000$, 1500, and 5000. The microstructure of the polybutadiene chains was analyzed by the method of Tanaka et al.[17] All spectra were recorded on a Bruker-300 (300 MHz) instrument in $CDCl_3$ at a concentration of 5%.

Results and Discussion

Synthetic Strategy. Carbosilane dendrimers having 16, 32, or 64 vinyl functionalities were synthesized starting from a tetravinylsilane core, using cycles of hydrosilylation with dichloromethylsilane and nucleophilic displacement with vinylmagnesium chloride as described in the literature.[15] The corresponding chlorosilane coupling precursors with 32, 64, or 128 peripheral Si−Cl groups were obtained by hydrosilylation of the carbosilane dendrimers with dichloromethylsilane and coupled with short polybutadiene chains containing a high proportion of 1,2-units. These starlike graft polymer hybrids were again subjected to hydrosilylation to introduce a large number of chlorosilane moieties. The starlike substrates were finally reacted with 1,4-polybutadienyllithium chains of different molecular weights to generate series of high branching functionality dendrimer−arborescent polymer hybrids.

Synthesis of Carbosilane Dendrimers. The carbosilane dendritic substrates were synthesized as described previously,[15]

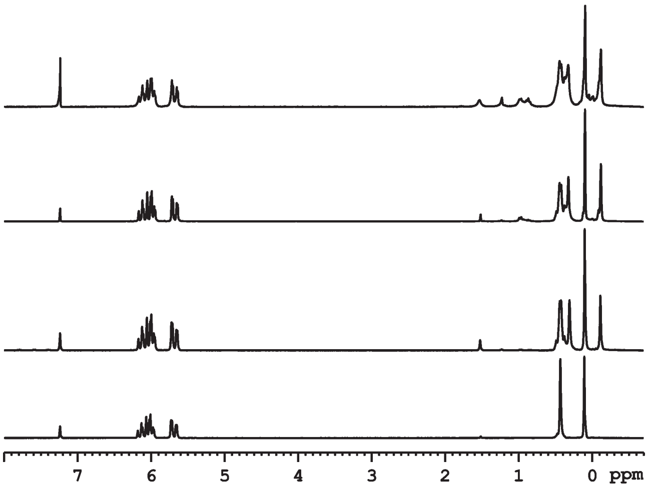


Figure 1. 300 MHz ^{1}H NMR spectra for the G1−G4 carbosilane dendrimers in CDCl$_3$ (from bottom to top).

but the procedures were adapted to the high-vacuum purification and polymerization techniques routinely used in our laboratory.[14] Another modification implemented was the use of commercially available vinylmagnesium chloride in replacement of vinylmagnesium bromide. It is noteworthy that while the reaction of the chlorosilane substrates with vinylmagnesium bromide was completed overnight,[15] much longer reaction times were required with vinylmagnesium chloride, as determined by NMR monitoring of the structure of the carbosilane dendrimer products. This is rather surprising, since the chloride form of Grignard reagents is generally more reactive than the bromide analogue.[18] It therefore appears that the reaction of chlorosilanes with vinylmagnesium chloride is much slower than with vinylmagnesium bromide, albeit impurities present in the commercial Grignard reagent used may also have contributed to the lower reactivity observed. Aside from the reactivity issue noted above, further discussion of the synthesis of the carbosilane dendrimers will be limited to a comparison of the results obtained in this work with those reported previously. The progress of the reaction and the formation of side products were monitored by ^{1}H NMR spectroscopy analysis. The ^{1}H NMR spectra obtained for the pure products, provided in Figure 1, are characteristic for the perfect carbosilane dendrimer structures, as incomplete reactions and structural defects destroy the symmetry of the spectra.[15]

For each generation three groups of proton resonances are present in the ^{1}H NMR spectra. Taking the carbosilane dendrimer of first generation (G1, 8-arm) as an example, the vinyl protons on the exterior of the molecules (δ 6.01 m, 4H and δ 5.71 m, 2H) are clearly distinguishable as well as the methyl protons attached to the silicon atoms (δ 0.11 s, 3H). The spectral pattern for the methylene groups (δ 0.43 m, 4H) is more complex and most sensitive to the presence of structural defects. The symmetry of these peaks is therefore a good indicator of the structural perfection and purity of the dendrimers.[15]

There are two types of methylene protons: one close to the central silicon core and the other one close to the vinyl groups. For the G2 (16-arm), G3 (32-arm), and G4 (64-arm) dendrimers the coupling patterns are very similar, except for the peaks becoming broader. The methylene proton resonances for these molecules appear in two groups, since the methylene units next to the vinyl groups (δ 0.43) are nonequivalent to the interior methylene protons (δ 0.31). There are also two single peaks for methyl groups in G2−G4 dendrimers. The one at δ 0.10 is for methyl groups next to the vinyl bonds, while the other at δ −0.10 is for the interior methyl groups. A singlet at δ 1.52 in all ^{1}H NMR spectra is due to traces of water, while the additional singlet at δ 1.24 and multiple peaks centered at δ 0.86 in the ^{1}H NMR spectrum of the G3 and G4 dendrimers correspond to traces of hexane in the products. The intensity of these peaks slowly decreases upon drying the samples under high vacuum, but they are still detectable even after drying for 1 week. Finally, it should be noted that while the spectra are quite similar, the relative integrated peak intensities change among the different generations. The NMR relative peak intensities obtained are compared in Table 1 with those previously reported[15] and with the theoretical values calculated based on structure. It is clear that the modified synthetic procedures are equivalent to the ones previously reported, as the measured intensities are very close to the calculated values for both methods.

Size exclusion chromatography (SEC) analysis was used to determine the apparent (polystyrene-equivalent) molecular weight and polydispersity index of the carbosilane dendrimers (Table 2). An increase in apparent molecular weight is observed over successive generation of the dendrimers, while a narrow molecular weight distribution is maintained ($M_w/M_n \leq 1.09$). The absolute M_n values determined with the MALLS detector are also reported in Table 2 for comparison, although these results are expected to be unreliable in view of the low molecular weight of the carbosilane dendrimers. In spite of this difficulty, the absolute M_n are in surprisingly good agreement with the theoretical (formula weight) values. The yields of purified vinylcarbosilane dendrimers, also reported in Table 2 for the G1−G4 substrates, are in good agreement (±3%) with those reported by Zhou and Roovers.[15] This again confirms the equivalence of the two synthetic procedures.

Synthesis of Starlike 1,2-Polybutadiene Hybrids. Three hybrids with target branching functionalities of 32, 64, and 128 arms were synthesized by a reported procedure[6,7] adapted to the high-vacuum purification and polymerization techniques used in our laboratory.[14] The synthetic procedure is summarized in Scheme 1, using the G2 carbosilane dendrimer substrate as an example. The nomenclature used for the star polymers identifies the number of sites on the dendrimer substrate and the molecular weight of the arms used in the synthesis; thus, CS32-*m*PBD1 refers to a polymer synthesized by coupling the carbosilane dendrimer with 32 Si−Cl sites with mixed microstructure polybutadiene arms with $M_n \approx 1000$. It should be noted that the 16-arm (G2) carbosilane dendrimer becomes precursor CS32 after hydrosilylation. Similarly, the G3 and G4 dendrimers become the CS64 and CS128 substrates, respectively.

The synthesis of the starlike polymers was achieved in THF. An excess of dichloromethylsilane was used in the hydrosilylation reaction to ensure complete hydrosilylation of the vinyl groups on the carbosilane dendrimers. This was achieved in 5 h at 50 °C for the G2 and G3 dendrimers and in 6 h for the G4 dendrimer, as evidenced by the complete disappearance of the vinyl signal at δ 5.70 and δ 6.01 in the ^{1}H NMR spectrum and the appearance of a new peak at δ 0.57 due to the $-SiCH_3(Cl)_2$ units (Figure 2b).

The microstructure of polybutadiene derived from organolithium initiators can vary depending on the reaction conditions:[19,20] A predominantly 1,4-microstructure is obtained in nonpolar (hydrocarbon) solvents, while THF (a more polar solvent) leads to a mixed microstructure with 1,4- and 1,2-butadiene units.[21−24] Accordingly, low molecular weight

Table 1. Integrated Intensities for the ^{1}H NMR Spectra of the Carbosilane Dendrimers

	structure ratios					integrated relative intensity				
generation	$CH_2{=}CH$		$CH_2{-}CH_2$	CH_3		$CH_2{=}CH$		$CH_2{-}CH_2$	CH_3	
G1 (8-arm)	2	1	2	1.5		2/2[a]	1/1	2/1.9	1.5/1.5	
G2 (16-arm)	2	1	3	1.5	0.76	2/2	1/1	2.9/2.9	1.5/1.5	0.76/0.73
G3 (32-arm)	2	1	3.5	1.5	1.1	2/2	1/1	3.5/3.6	1.6/1.5	1.2/1.2
G4 (64-arm)	2	1	3.8	1.5	1.3	2/2	1/1	3.8/3.7	1.8/1.5	1.4/1.3

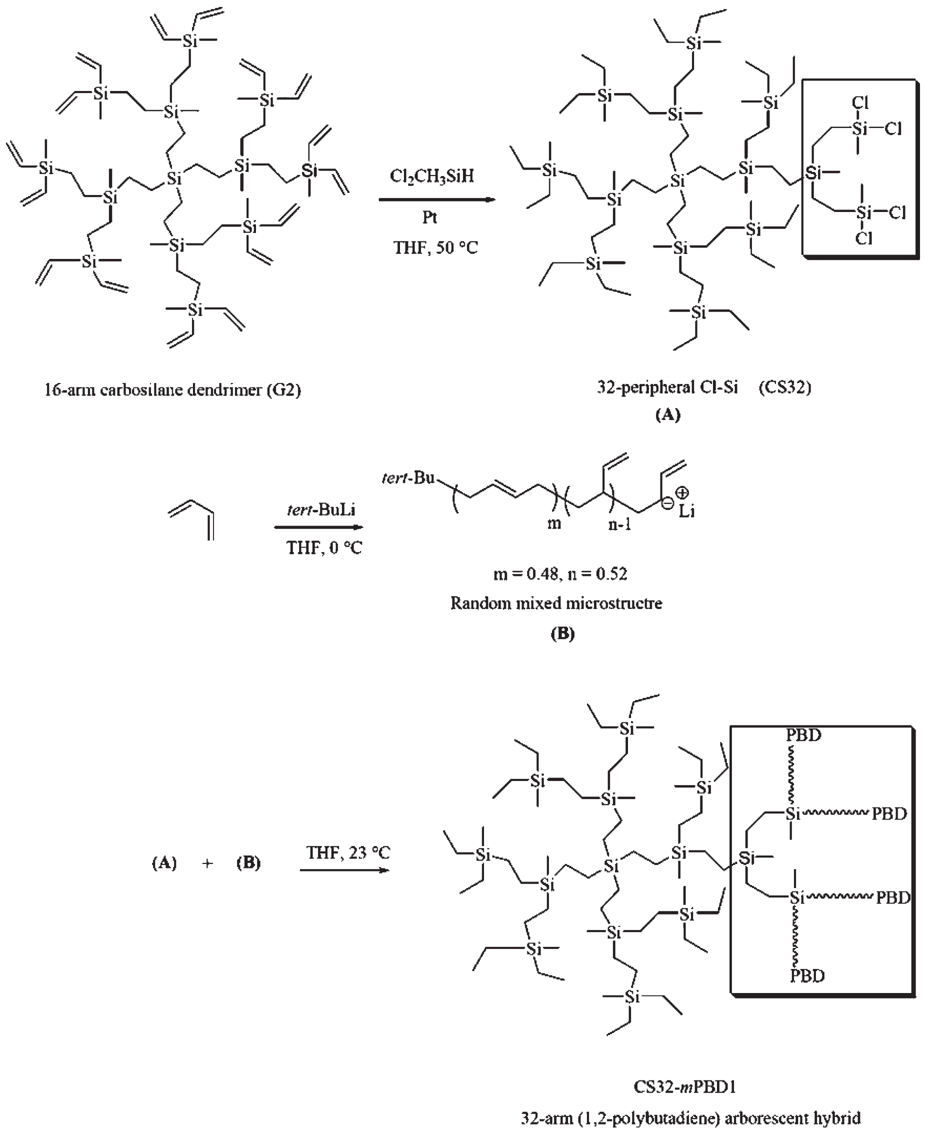
[a] The second number is the intensity reported by Zhou and Roovers.[15]

Table 2. Molecular Weight and Yield of Carbosilane Dendrimers

generation	formula	formula weight	functionality	M_n[a]	M_w/M_n[a]	M_n[b]	yield (%)
G1 (8-arm)	$C_{28}H_{52}Si_5$	528	8	730	1.05	505	52/55[c]
G2 (16-arm)	$C_{68}H_{132}Si_{13}$	1312	16	1400	1.06	1230	48/48
G3 (32-arm)	$C_{148}H_{292}Si_{29}$	2880	32	2300	1.05	2530	44/41
G4 (64-arm)	$C_{308}H_{612}Si_{61}$	6016	64	3900	1.09	5560	24/26

[a] Apparent values determined by SEC analysis based on linear PS standard calibration curve. [b] Absolute number-average molecular weight determined by SEC-MALLS analysis. [c] The second number is the yield reported by Zhou and Roovers.[15]

Scheme 1. Synthesis of 32-Arm 1,2-Polybutadiene Starlike Arborescent Hybrid



1,2-polybutadienyllithium was prepared in THF at 0 °C to produce compact starlike polymers. The ^{1}H NMR spectra in Figure 2 illustrate the reaction of the side chains with substrate CS32. The microstructure of the chains was determined from the relative peak areas of the two olefinic proton resonances at δ 5.32−5.76 (2H of the *cis*- and *trans*-1,4-microstructures) and at δ 4.90 (3H of the 1,2-microstructure) by the method of Tanaka et al.[17] This corresponds

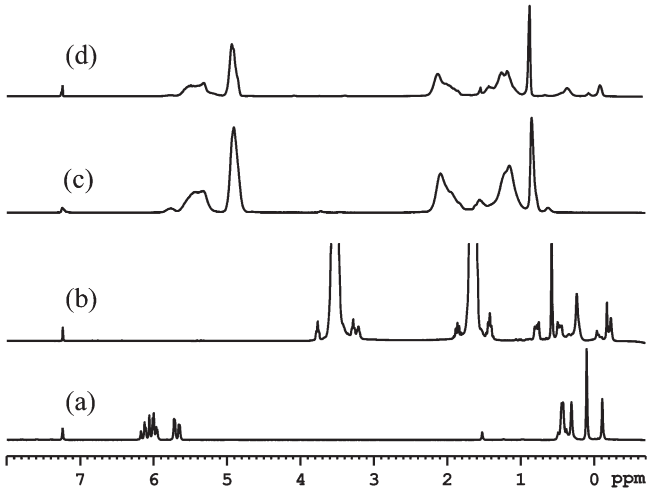


Figure 2. 300 MHz ^{1}H NMR spectra for the synthesis of sample CS32-*m*PBD1: (a) G2 carbosilane dendrimer before hydrosilylation, (b) hydrosilylated G2 dendrimer, (c) mixed microstructure polybutadiene side chains, and (d) fractionated starlike polymer.

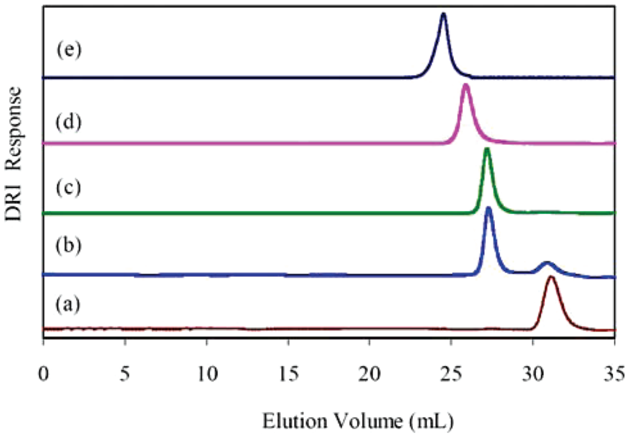


Figure 3. Synthesis of starlike 1,2-polybutadienes: SEC traces for (a) side chains, (b) crude grafting product, (c) fractionated sample CS32-*m*PBD1, (d) fractionated sample CS64-*m*PBD1, and (e) fractionated sample CS128-*m*PBD1.

to 1,4- (*cis*- and *trans*-isomers combined) and 1,2-units contents of 48 and 52%, respectively, for all samples.

The coupling reaction for substrate CS32 was carried out with a 20% excess of living ends with respect to the Si−Cl groups, whereas a 100% excess was used for CS64 and CS128. The extent of the coupling reaction was monitored by SEC analysis, from the increase in apparent molecular weight of the starlike polymer and the relative peak areas for the graft polymer and the side chains. The success of the coupling reaction is also evidenced by ^{1}H NMR analysis of the fractionated product (Figure 2d), by the appearance of a new peak at δ −0.11 for $-SiCH_3$ after displacement of the two Cl atoms. SEC analysis confirmed that the coupling reaction was essentially complete within 30 min for CS32, whereas for CS64 and CS128 it required 1 h. Since no further increases in molecular weight were observed after 24 h, this reaction time was used for all coupling reactions. This contrasts with the coupling times of 21 days to 8 weeks necessary in a previous study[6,7] where benzene served as solvent. The faster reactions are attributed to the higher polarity of the solvent used, since THF is known to decrease the extent of aggregation of living polymer chains and thus increase their reactivity.[25]

Size exclusion chromatography (SEC) characterization was performed for side-chain samples removed before the grafting reaction, the crude products, and the fractionated starlike polymers. A series of SEC curves are provided in Figure 3 to illustrate the synthesis of the starlike polymers. Using sample CS32-*m*PBD1 as an example, the 1,2-polybutadiene side chains have a relatively narrow MWD in spite of their low molecular weight (M_n = 540, M_w/M_n = 1.13, Figure 3a). Two peaks, corresponding to the starlike polymer and to the linear contaminant, are observed in the SEC trace for the crude product (Figure 3b). The leftmost peak corresponds to the graft polymer while the peak on right, with an elution volume identical to the side-chain sample removed before coupling, is mainly due to the 20% excess of side chains used in the coupling reaction. Complete removal of the linear chain contaminant by fractionation is confirmed in Figure 3c. The successful fractionation of samples CS64-*m*PBD1 and CS128-*m*PBD1 is likewise demonstrated in parts d and e of Figure 3, respectively.

Characterization data for the purified starlike polymers are provided in Table 3. The number-average branching functionality f_n was calculated from the equation

$$f_n = \frac{(M_n)_{star} - M_c}{(M_n)_{arm}} \qquad (1)$$

where $(M_n)_{star}$ represents the absolute number-average molecular weight of the graft polymer, $(M_n)_{arm}$ is the absolute number-average molecular weight of the side chains, and M_c is the mass of the core (coupling substrate) calculated from the equation

$$M_c = n(44) + (FW)_{CSD} \qquad (2)$$

where n is the number of arms, 44 is the formula weight of CH_3SiH, and $(FW)_{CSD}$ is the formula weight of the corresponding carbosilane dendrimer substrate reported in Table 2. The absolute polydispersity indices (M_w/M_n) for the starlike polymers determined by SEC-MALLS analysis (Table 3) demonstrate that narrow MWD were achieved. The branching functionalities in Table 3 are very close to the nominal functionalities for the CS32 and CS128 substrates and slightly lower for CS64. Since the deviation is relatively low even for CS64 (−8.8%), this could be due simply to cumulative errors in determining M_n for the starlike polymer and the side chains. The question of the coupling efficiency of carbosilane substrates of the type used in the current investigation and by Roovers et al.[7] was reexamined by Allgaier et al.[26] using MALDI-TOF analysis for the specific case of short polybutadiene side chains (M_n = 10^3). The authors concluded that even for these short side chains the experimental branching functionality attained was lower than the nominal value for substrates containing more than 16 coupling sites. Roovers et al. likewise reported branching functionality values slightly lower than the nominal values, but for significantly longer polybutadiene side chains (M_n = (6−70) × 10^3). The variance between the experimental branching functionalities reported in Table 3 and the nominal values is therefore in agreement with the earlier reports.

Synthesis of Arborescent 1,4-Polybutadiene Hybrids. Three series of dendrimer-arborescent polymer hybrids with 1,4-polybutadiene side chains were synthesized by coupling the hydrosilylated 1,2-polybutadiene star-like substrates with 1,4-polybutadienyllithium of different molecular weights ($M_n \approx$ 1500, 5000, 30 000) according to Scheme 2.

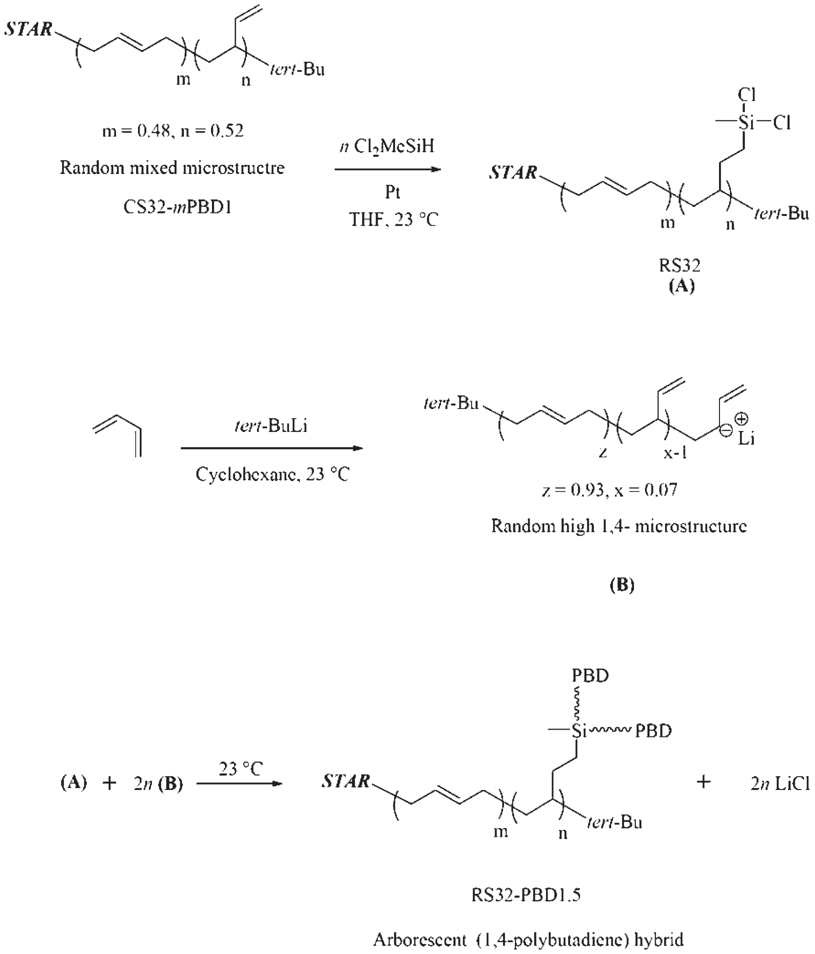
The sample nomenclature used to refer to the arborescent hybrids identifies the hydrosilylated starlike substrate serving in the reaction and the target molecular weight of the side

Table 3. Characteristics of Starlike Polybutadiene Hybrids

	side chains[c]				star polymer			
sample	M_n[a]	M_w/M_n[b]	DP	M_c[d]	d*n*/d*c*[e]	M_n[f]	M_w/M_n[f]	f_n[g]
CS32-*m*PBD1	540	1.13	10	2016	0.1121	1.9×10^4	1.02	31
CS64-*m*PBD1	1000	1.10	19	4288	0.1021	6.1×10^4	1.03	57
CS128-*m*PBD1	1200	1.10	21	8832	0.1122	1.6×10^5	1.16	126

[a] Determined from ^{1}H NMR analysis. [b] Apparent values from SEC analysis using a linear polystyrene standards calibration curve. [c] All side chains have 52% of 1,2- and 48% of 1,4-butadiene units. [d] From eq 2. [e] Refractive index increment in THF at 25 °C and 632 nm. [f] Absolute values from SEC-MALLS analysis. [g] Branching functionality determined using eq 1.

Scheme 2. Synthesis of 1,4-Polybutadiene Dendrimer−Arborescent Hybrid



chains. Thus, RS32-PBD1.5 refers to an arborescent hybrid synthesized by coupling the hydrosilylated starlike polybutadiene CS32-*m*PBD1 with 1,4-polybutadiene ($M_n \approx 1500$). It should be noted that samples CS64-*m*PBD1 and CS128-*m*PBD1 likewise become RS64 and RS128 upon hydrosilylation, respectively. The vinyl groups of the 1,2-butadiene units were easily converted to coupling sites by hydrosilylation with dichloromethylsilane in THF. Complete hydrosilylation of the vinyl groups was achieved in 24 h at 50 °C for substrate RS32, whereas it required 30 and 36 h for RS64 and RS128, respectively. This is evidenced by the ^{1}H NMR spectrum for RS32 (Figure 4b), confirming the complete disappearance of the vinyl resonance at δ 4.90 and the appearance of a new peak at δ 0.57 [$-SiCH_3(Cl)_2$]. The signals for the 1,4-units (δ 5.32−5.76) were unaffected, indicating that the internal double bonds of the polybutadiene chains were unreactive.

Polybutadienyllithium with a predominantly 1,4-microstructure serving as side chains was synthesized in cyclohexane at room temperature. The target $M_n \approx 1500$, 5000, and 30 000 were attained in 24, 48, and 72 h of polymerization time, respectively. The ^{1}H NMR spectrum shown in Figure 4c corresponds to the side chains used in the synthesis of sample RS32-PBD1.5. The microstructure, determined by the method of Tanaka et al.[17] described previously, corresponds to 93% of 1,4-units (*cis*- and *trans*-isomers combined) and 7% of 1,2-units. The microstructure analysis and characterization results for the side chains of all samples are summarized in Table 4.

The arborescent hybrids with a side chain $M_n \approx 1500$ were synthesized with a 50% excess of living chains vs Si−Cl groups, whereas for side chains with $M_n \approx 5000$ and 30 000 the living chains were in 75% and 100% excess, respectively. Since the concentration of living ends decreases for higher molecular weights, the larger excesses used ensured a reasonably fast coupling rate. Another reason for using an excess of living chains was to compensate for chain dimerization due to residual dichloromethylsilane in the reaction (vide infra).

The reaction of the coupling substrate is evidenced by the appearance in the ^{1}H NMR spectrum (Figure 4d) of a new peak at δ −0.11 [—$SiCH_3$] following the loss of the two Cl atoms. SEC monitoring of the reaction also confirmed that the coupling reaction for all arborescent hybrids was essentially complete within 24 h, as their molecular weight became constant.

Size exclusion chromatography (SEC) analysis was performed for the side chains, the crude products, and the fractionated arborescent hybrids. The chromatograms provided in Figure 5 as an example illustrate the synthesis of sample RS32-PBD1.5. The polybutadiene side chains are characterized by a relatively narrow MWD (M_n = 1200, M_w/M_n = 1.10; Figure 5a). As in the synthesis of the starlike substrates, the two peaks in the SEC curve for the crude grafting product (Figure 5b) correspond to the graft polymer (left) and to linear chain contaminant (right). Interestingly, the peak on the right has a molecular weight twice as large as the side chain sample removed before the coupling reaction (Figure 5a). This effect, also reported for the synthesis of 32-arm star polybutadiene from carbosilane substrates,[6] was attributed to coupling of the linear polymer with residual dichloromethylsilane from the hydrosilylation reaction contaminating the coupling precursor. The SEC traces in Figure 5c−e confirm the complete removal by fractionation of linear contaminant from samples RS32-PBD1.5, RS32-PBD5, and RS32-PBD30, respectively. SEC curves are also provided in Figures 6 and 7 to illustrate the synthesis of arborescent polybutadienes from substrates RS64 and RS128, respectively. Crude sample RS128-PBD1.5 has an extra peak between the linear precursor and the graft polymer (Figure 6b), again attributed to coupling of the linear polymer with dichloromethylsilane residues from the hydrosilylation reaction. The chromatograms of Figure 6c−e and Figure 7c−e likewise confirm the complete removal of linear contaminant by fractionation of the arborescent hybrid samples based on the RS64 and RS128 substrates, respectively.

Characterization data for the dendrimer−arborescent hybrids synthesized are provided in Table 4. The number-average branching functionality f_n was calculated according to the equation

$$f_n = \frac{(M_n)_{star} - M_c'}{(M_n)_{arm}} \tag{3}$$

where $(M_n)_{star}$ represents the absolute number-average molecular weight of the graft polymer (dendrimer−arborescent hybrid), $(M_n)_{arm}$ is the absolute number-average molecular weight of the side chains, and M_c' is the molecular weight of the core (substrate) calculated according to the equation

$$M_c' = (M_n)_{core} + \frac{(M_n)_{core} - M_c}{M_{BD}} \times 0.52 \times 44 \tag{4}$$

where $(M_n)_{core}$ represents the number-average molecular weight of the starlike polymer serving as substrate, M_c is the molecular weight of the dendrimer substrate used to

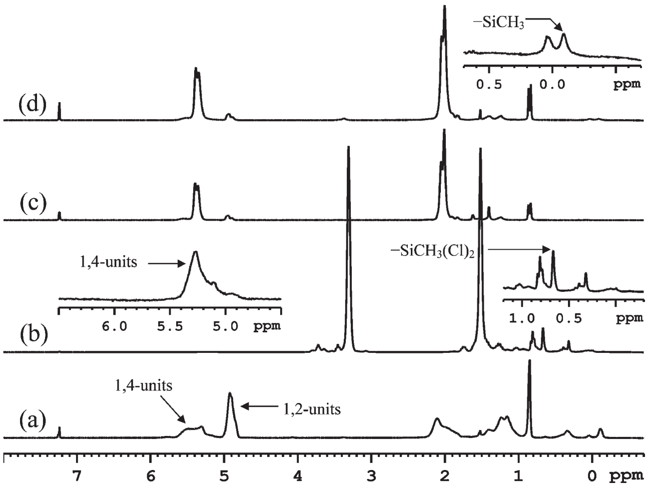


Figure 4. 300 MHz ^{1}H NMR spectra for the synthesis of sample RS32-PBD1.5: CS32-*m*PBD1 substrate (a) before and (b) after hydrosilylation, (c) 1,4-polybutadiene side chains, and (d) fractionated arborescent hybrid.

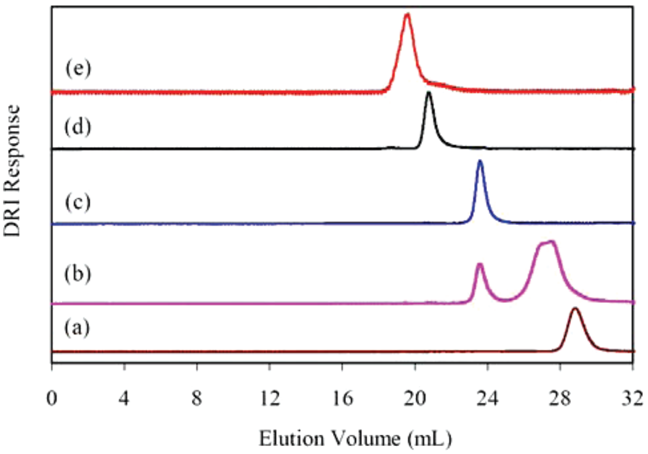


Figure 5. Synthesis of arborescent 1,4-polybutadiene hybrids from RS32 core: SEC traces for (a) side chains, (b) crude grafting product, and fractionated samples (c) RS32-PBD1.5, (d) RS32-PBD5, and (e) RS32-PBD30.

Table 4. Characteristics of 1,4-Polybutadiene Arborescent Hybrids

	side chains				hybrid polymers				
sample	M_n[a]	M_w/M_n[b]	1,4-units %[c]	M_c'[d]	d*n*/d*c*[e]	M_n[f]	M_w/M_n[f]	f_n[g]	coupling efficiency (%)[h]
RS32-PBD1.5	1200	1.10	93	26200	0.1200	4.3×10^5	1.01	336	99
RS32-PBD5	6500	1.11	94		0.1302	2.0×10^6	1.05	304	89
RS32-PBD30	26000[f]	1.08[f]	95		0.1364	3.7×10^6	1.03	141	41
RS64-PBD1.5	1270	1.11	94	85000	0.1269	1.5×10^6	1.07	1110	99
RS64-PBD5	4000	1.10	95		0.1300	3.8×10^6	1.03	929	83
RS64-PBD30	29900[f]	1.09[f]	96		0.1283	4.9×10^6	1.03	161	14
RS128-PBD1.5	1300	1.10	92	224000	0.1217	3.9×10^6	1.13	2830	95
RS128-PBD5	5800	1.13	95		0.1204	5.3×10^6	1.08	875	29
RS128-PBD30	23000[f]	1.06[f]	96		0.1229	8.6×10^6	1.14	364	12

[a] Absolute M_n from ^{1}H NMR analysis. [b] Apparent polydispersity from SEC analysis using a linear polystyrene standards calibration curve. [c] From ^{1}H NMR spectroscopy analysis. [d] Substrate M_n calculated from eq 4. [e] Refractive index increment in THF at 25 °C and 632 nm. [f] Absolute values determined from SEC-MALLS analysis. [g] Branching functionality calculated from eq 3. [h] Fraction of coupling sites on the substrate consumed.

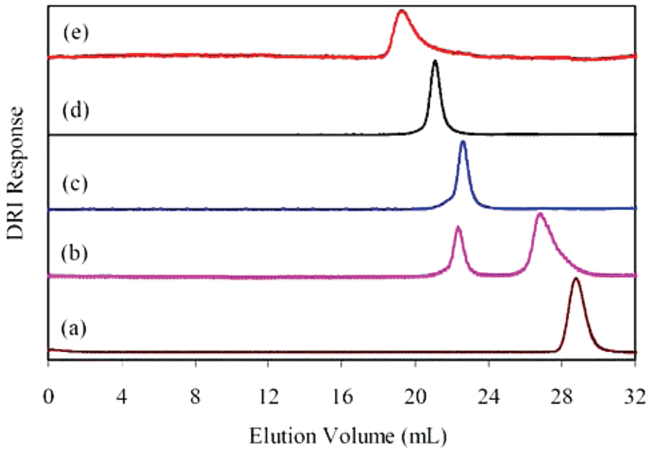


Figure 6. Synthesis of arborescent 1,4-polybutadiene hybrids from RS64 core: SEC traces for (a) side chains, (b) crude grafting product, and fractionated samples (c) RS64-PBD1.5, (d) RS64-PBD5, and (e) RS64-PBD30.

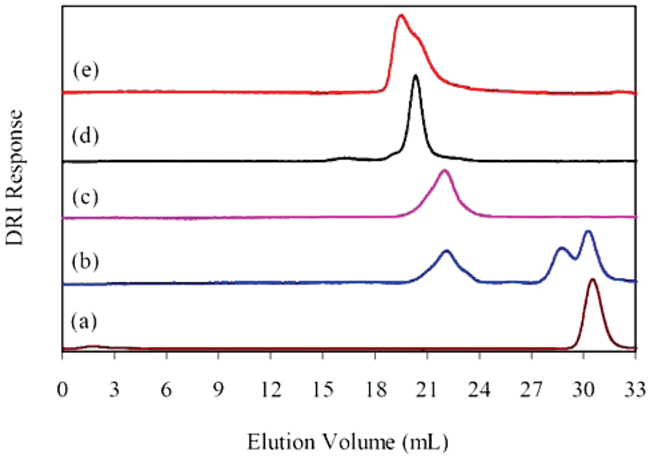


Figure 7. Synthesis of arborescent 1,4-polybutadiene hybrids from RS128 core: SEC traces for (a) side chains, (b) crude product, and fractionated samples (c) RS128-PBD1.5, (d) RS128-PBD5, and (e) RS128-PBD30.

synthesize the starlike polymer, 44 is the formula weight of the branching units (CH_3SiH), 0.52 is the mole fraction of 1,2-units in the starlike polymer, and M_{BD} is the molecular weight of the butadiene unit (54.04). The branching functionality f_n and M_c' are reported in Table 4 for all the samples. The f_n values range from 140 to 335 for the RS32 sample series, from 160 to 1110 for the RS64 series, and from 360 to 2830 for the RS128 series. The experimental branching functionalities are always lower than the number of coupling sites available on the substrates (column 9 in Table 4), the deviations being most significant for graft polymers with longer polybutadiene side chains. The extent of reaction under conditions using an excess of living ends (polybutadienyllithium:SiCl ratio > 1) is best quantified in terms of the coupling efficiency, defined as the fraction (percentage) of chlorosilane coupling sites consumed in the grafting reaction. This quantity was calculated as the ratio of the branching functionality f_n to the number of coupling sites C_s on the substrate, calculated according to the equation

$$C_s = \frac{(M_n)_{core} - (FW)_{DS}}{M_{BD}} \times 0.52 \times 2 \qquad (5)$$

where $(M_n)_{core}$ represents the number-average molecular weight of the starlike polymer used as substrate, $(FW)_{DS}$ represents the formula weight of the dendrimer substrate used for the synthesis of the starlike polymer, 0.52 is the mole fraction of 1,2-units in the arms of the starlike polymer, M_{BD} is the molecular weight of the butadiene unit (54.04), and the factor 2 accounts for the presence of two coupling sites per dichloromethylsilane unit added. The coupling efficiency decreases as the length of the polybutadiene side chains increases and likewise as the size of the substrate increases (column 10 in Table 4). This is consistent with previous findings in the synthesis of arborescent polymers.[11] The accessibility of the chlorosilane coupling sites should decrease due to steric crowding as side chains are added on the substrate. Another factor potentially limiting the yield of the grafting reaction is the consumption of the living polymer by dimerization after coupling with residual dichloromethylsilane as discussed earlier. When comparing SEC elution curves for the synthesis of dendrimer−arborescent hybrids with short ($M_n \approx 1500$) side chains, it is clear that chain dimerization dominated in some cases (Figures 5b and 6b): The peak for the linear contaminant has a molecular weight twice as large as the side chains, and only a shoulder corresponding to excess side chains is present in the crude product. In other cases, however, a significant portion of the living chains remained in the reaction for a significant time period (Figure 7b), as confirmed by gradual fading of the color over ca. 2 h after adding the substrate to the living chains. The extent of dimerization depends on the amount of residual dichloromethylsilane present after hydrosilylation of the starlike coupling substrates and is therefore highly variable. The situation depicted in Figure 7b, corresponding to a significant excess of living chains even after completion of the dimerization reaction, was actually observed in all cases except for samples RS32-PBD1.5 (Figure 5b) and RS64-PBD1.5 (Figure 6b). In the presence of excess living chains, increased steric crowding of the substrate as the reaction proceeds should decrease the rate of the coupling reaction. Chain termination (by the reaction of polybutadienyllithium with THF at room temperature) eventually dominates over coupling and ultimately consumes all the living chains. Since an excess of living chains was present in most reactions and the coupling efficiencies reported in Table 4 consistently decrease as the size of both the coupling substrate and the side chains increase, it appears that steric congestion (rather than chain dimerization) was the dominating factor controlling the coupling efficiency under the conditions used in the current investigation.

The absolute number-average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) of the arborescent polymers obtained as determined by SEC-MALLS analysis are provided in Table 4. A narrow MWD was achieved for all samples, with PDI < 1.08 except for the samples derived from substrate RS128. The molecular weight distribution of some hybrid polymers (particularly RS128-PBD30) appears almost bimodal. It is not clear whether the apparent bimodal MWD and comparatively higher PDI values obtained for the RS128 samples are linked to separation problems encountered in the SEC analysis of these very large molecules, to the higher PDI value of the corresponding starlike precursor (CS128-*m*PBD1, PDI = 1.16), or to side reactions. The graft polymers obtained nevertheless still have relatively narrow molecular weight distributions ($M_w/M_n \leq 1.14$).

Conclusions

A series of carbosilane dendritic macromolecules were synthesized from a tetravinylsilane core by hydrosilylation of the vinylsilane moieties with dichloromethylsilane and nucleophilic displacement of the chloride anions with vinylmagnesium chloride.

The ^{1}H NMR spectra and the narrow, symmetrical SEC peaks obtained are consistent with a perfect dendrimer structure. The carbosilane dendrimers, modified to contain 32, 64, or 128 peripheral Si−Cl sites, served as coupling substrates for low molecular weight 1,2-polybutadienyllithium. The 1,2-polybutadiene starlike hybrids also had narrow molecular weight distributions (PDI = 1.02−1.16). The starlike polymers were further hydrosilylated with dichloromethylsilane and used as coupling substrates for 1,4-polybutadienyllithium. Three series of dendrimer−arborescent hybrids were thus obtained containing 1,4-polybutadiene side chains with $M_n \approx 1500$, 5000, or 30 000. The arborescent hybrids had narrow molecular weight distributions, with PDI ≤ 1.08 for all but two samples. The arborescent hybrids have branching functionalities reaching 10 times higher than for star-branched polybutadiene synthesized previously. The branching functionalities obtained were nonetheless lower than the nominal (theoretical) values, the deviations being largest for graft polymers with longer side chains.

Interesting physical properties are expected for these polybutadiene arborescent hybrids due to their very high branching functionality and compact structure in combination with the very low entanglement molecular weight of the polybutadiene segments ($M_e = 1800$ for 1,4-polybutadiene). The detailed rheological characterization of these materials will be the subject of future work.

Acknowledgment. We thank Dr. Jacques Roovers for helpful suggestions and Prof. Neil McManus for providing access to the SEC-MALLS characterization equipment. The financial support of the Natural Science and Engineering Council of Canada (NSERC) is gratefully acknowledged.

References and Notes

(1) Roovers, J. *Macromolecules* **1991**, *24*, 5895–5896.

(2) Roovers, J.; Toporowski, P. M. *Macromolecules* **1987**, *20*, 2300–2306.

(3) Masuda, T.; Ohta, Y.; Onogi, S. *Macromolecules* **1986**, *19*, 2524–2532.

(4) (a) Khadir, A.; Gauthier, M. *Polym. Mater. Sci. Eng.* **1997**, *77*, 174–175. (b) Schmaljohann, D.; Pötschke, P.; Hässler, R.; Voit, B. I.; Froehling, P. E.; Mostert, B.; Loontjens, J. A. *Macromolecules* **1999**, *32*, 6333–6339. (c) Nunez, C. M.; Chiou, B.-S.; Andrady, A. L.; Khan, S. A. *Macromolecules* **2000**, *33*, 1720–1726.

(5) (a) Rempp, P.; Franta, E.; Herz, J.-E. *Adv. Polym. Sci.* **1988**, *86*, 145–173. (b) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Dekker: New York, 1996; Chapter 13. (c) Roovers, J.; Comanita, B. *Adv. Polym. Sci.* **1999**, *142*, 179–228.

(6) (a) Zhou, L.-L.; Hadjichristidis, N.; Toporowski, P. M.; Roovers, J. *Rubber Chem. Technol.* **1992**, *65*, 303–314. (b) Roovers, J.; Ding, J. In *Silicon-Containing Dendritic Polymers*; Dvornic, P. R., Owen, M. J., Eds.; Springer: Berlin, 2009; Chapter 3.

(7) Roovers, J.; Zhou, L.-L.; Toporowski, P. M.; van der Zwan, M.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1993**, *26*, 4324–4331.

(8) Roovers, J.; Toporowski, P.; Martin, J. *Macromolecules* **1989**, *22*, 1897–1903.

(9) Comanita, B.; Noren, B.; Roovers, J. *Macromolecules* **1999**, *32*, 1069–1072.

(10) Vasilenko, N. G.; Rebrov, E. A.; Muzafarov, A. M.; Esswein, B.; Striegel, B.; Möller, M. *Macromol. Chem. Phys.* **1998**, *199*, 889–895.

(11) Teertstra, S. J.; Gauthier, M. *Prog. Polym. Sci.* **2004**, *29*, 277–327.

(12) For examples of arborescent polymers constructed from elastomeric segments, see for example: (a) Yuan, Z.; Gauthier, M. *Macromolecules* **2005**, *38*, 4124–4132. (b) Zhang, H.; Li, Y.; Zhang, C.; Li, Z.; Li, X.; Wang, Y. *Macromolecules* **2009**, *42*, 5073–5079.

(13) Lipton, M. F.; Sorensen, C. M.; Sadler, A. C.; Shapiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155–158.

(14) Gauthier, M.; Tichagwa, L.; Downey, J. S.; Gao, S. *Macromolecules* **1996**, *29*, 519–527 and Supporting Information .

(15) Zhou, L.-L.; Roovers, J. *Macromolecules* **1993**, *26*, 963–968.

(16) Liu, W.-L.; Loveless, F. C. U.S. Patent 5,489,649, **1996**.

(17) Tanaka, Y.; Takeuchi, Y.; Kobayashi, M.; Tadokoro, H. *J. Polym. Sci., Part A-2: Polym. Phys.* **1971**, *9*, 43–57.

(18) Blomberg, C. In *Handbook of Grignard Reagents*; Silverman, G. S., Rakita, P. E., Eds.; Dekker: New York, 1996; p 254.

(19) Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1–90.

(20) Carella, J. M.; Graessley, W. W.; Fetters, L. J. *Macromolecules* **1984**, *17*, 2775–2786.

(21) Halasa, A. F.; Lohr, D. F.; Hall, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1357–1360.

(22) Uraneck, C. A. *J. Polym. Sci., Part A-1* **1971**, *9*, 2273–2281.

(23) Bywater, S.; Firat, Y.; Black, P. E. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 669–672.

(24) Hillmyer, M. A.; Bates, F. S. *Macromolecules* **1996**, *29*, 6994–7002.

(25) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Dekker: New York, 1996; p 164.

(26) Allgaier, J.; Martin, K.; Räder, H. J.; Müllen, K. *Macromolecules* **1999**, *32*, 3190–3194.