Synthesis of Novel Carbosilane Dendritic Macromolecules†

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ABSTRACT: A series of carbosilane dendritic macromolecules grown from four directions of a tetrahedral central core has been synthesized and characterized. In the synthesis tetravinylsilane is used as the central core molecule and dichloromethylsilane as the propagation unit. Two reactions are involved in the synthesis of each generation: hydrosilylation of vinylsilane with dichloromethylsilane and nucleophilic replacement of silicon chloride by vinylmagnesium bromide. The reaction conditions for hydrosilylation must be well controlled. After purification by chromatography on silica gel pure products for each generation are obtained. The ^1H and ^{13}C NMR spectra are consistent with the proposed structures. The molecular weights of the resulting carbosilane dendrimers have been determined by vapor pressure osmometry or light scattering. Their experimental values are in very good agreement with the theoretical values. The dilute solution properties of these dendrimers are different from linear polymers.

Introduction

Polymers of geometric beauty have been of great interest in polymer chemistry. These molecules, by their distinct three-dimensional structures, are supreme challenges to synthetic chemists. They offer new and unique physical and chemical properties; they provide new models for basic and theoretical studies; and they are expected to lead to new applications.

Starburst dendrimers are highly ordered, hyperbranched oligomeric and polymeric molecules formed by multiplicative growth from a central core containing more than one functional group. The concept of the three-dimensional growth was initially introduced by Flory and by Zimm and Stockmayer.[1] While early work on hyperbranched molecules was carried out more than 30 years ago, it was not until the mid-1980's that Tomalia's and Newkome's groups reported independently their successful syntheses of "starburst" dendrimers and "arborol" structures.[2,3] Since then, new syntheses of dendrimers of different structures have been completed.[4] There are two different approaches to the synthesis of dendrimers. The first is the controlled step-growth propagation. This approach starts with the selection of a multifunctional initiator core molecule. The multibranched dendrimers are formed by a stepwise geometric growth of the branches. For example, Tomalia's synthesis starts with ammonia as the initiator core. Michael addition of ammonia to methyl acrylate, followed by amidation with ethylenediamine, yields the zero generation compound. These two reactions are repeated for each generation. The second approach was developed by Hawker and Frechet and by Miller and Neenan.[5,6] In this approach the dendritic fragments are prepared by starting from what will become the periphery of the molecule and progressing inward. After several generations of growth, the resulting dendritic wedges can be coupled to a polyfunctional core to form the final hyperbranched macromolecules.

Dendrimers based upon siloxane chemistry have been introduced recently by Rebrov's, Masamune's, and Kakimoto's groups.[7-9] The advantage of using silicon chemistry to synthesize dendrimers is that the electrophilic silicon (Si^+) can be easily accessed by nucleophilic species.

In this report we describe the synthesis of dendritic macromolecules based upon carbosilane unit structures. These dendrimers are hyperbranched dendrimers growing in four directions from a tetrahedral core. These molecules are truly three dimensional symmetric dendrimers. Using these dendrimers as the coupling core molecules we have successfully synthesized well-defined 32- and 64-arm star polymers.[10,11]

Results and Discussion

Synthesis of Carbosilane Dendritic Macromolecules. In the controlled step growth approach, there should be two basic units for the constructuion of dendrimers: the initial core and the propagation unit. The initial core contains more than two functional groups, which are represented by A in Scheme I. These functional groups are used for the branch growth; e.g., if the initial core contains three functional groups the final dendrimers will be built up from three dendritic branches. Initial cores can be simple compounds such as ammonia, and trichloromethylsilane, or multifunctional oligomers. The propagation unit always has two different functional groups, depicted in Scheme I as B and C. It is not only required that both functions B and C are stable to each other but also that function C does not react with function A. Function C can be either a new functional group or a protected functional A. In the first step each function A of the initial core reacts with B of the propagation unit to form a symmetric growth compound with 2 or more times the number of functions C. Then each function C is converted to A in order to form the first generation. The resulting first generation is used as a new core and the reactions of the first generation are repeated to yield the second generation. The third and fourth generations are made in the same manner. It should be noted that all reactions involved in each growth step should be quantitative and without side reactions, since incomplete reactions or side reactions will cause structural defects and/or coupling between dendrimers. It is also obvious that the purity of each generation is very important for the subsequent growth of starburst dendrimers.

In our synthesis of carbosilane dendrimers, tetravinylsilane was chosen as the initial core molecule and dichloromethylsilane was used as the propagation unit. This selection was made on the basis of the simplicity of the structures and the clean hydrosilylation reaction. The hydrosilylation of vinylsilanes with dichloromethylsilane has been used previously for the synthesis of coupling agents for star polymers.[12-14]

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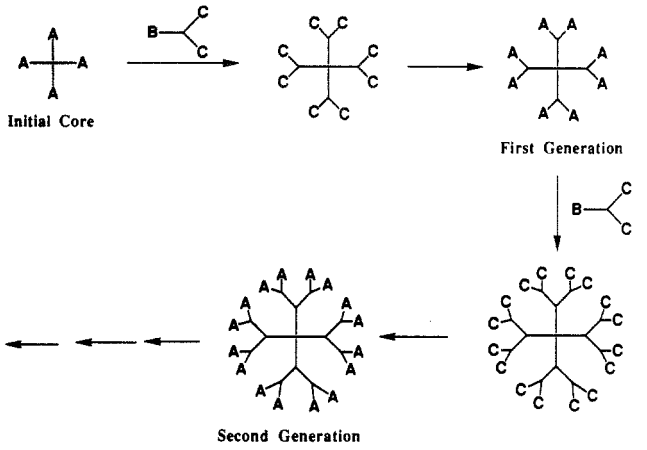
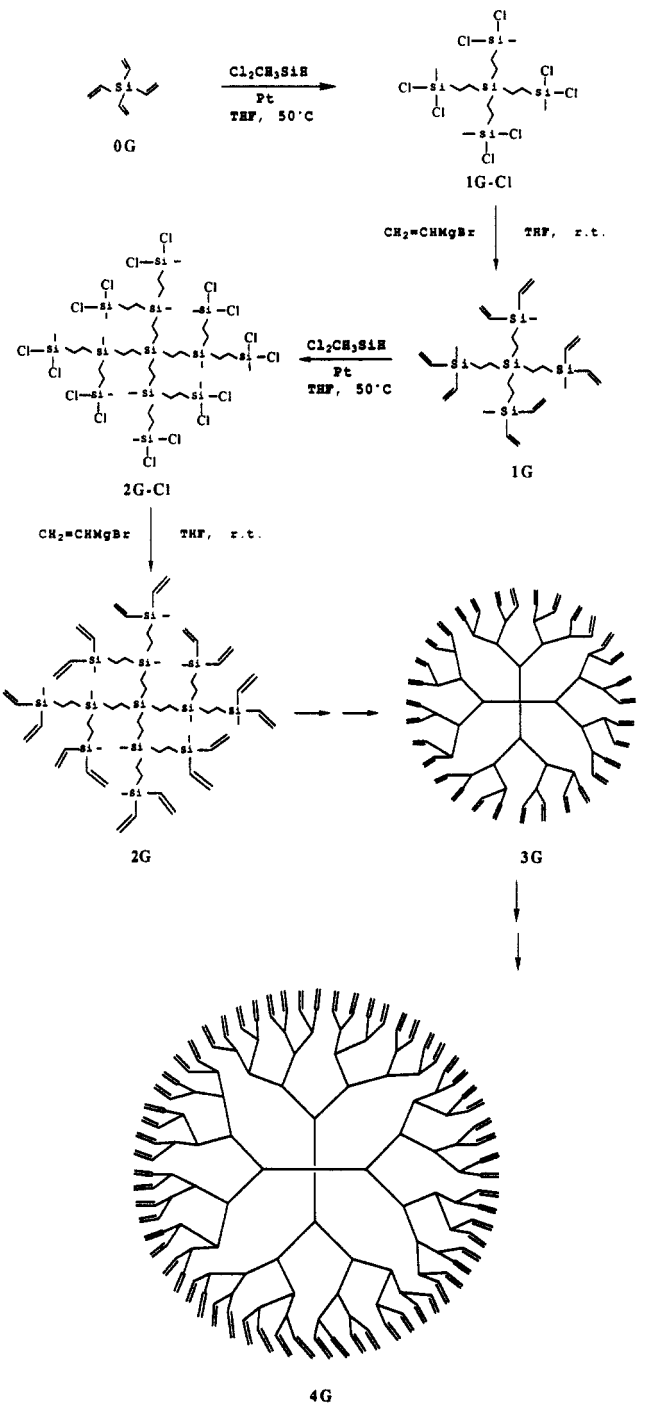
Scheme I



Scheme II



The synthesis as shown in Scheme II started with the Pt-catalyzed hydrosilylation of the vinyl groups of tetravinylsilane with dichloromethylsilane. All the silicon chloride groups were then replaced by vinyl magnesium bromide to give the first generation with eight vinyl groups connected to four silicon atoms.

The hydrosilylation reaction, an addition reaction of a Si–H group to an carbon–carbon unsaturated bond, found its first application as early as 1957.[15] It has proved to be a very convenient method for forming silicon–carbon bonds. The advantages of using this reaction in the dendrimer synthesis are its high yields and minimal side reactions, provided a good system is selected and the reaction conditions are well controlled. The direct hydrosilylation of tetravinylsilane with dichloromethylsilane is carried out in THF at 50 °C under nitrogen with platinum divinyltetramethyldisiloxane complex in xylene (Petrarch PC 072) as the catalyst. Both dichloromethylsilane and anhydrous THF are distilled immediately before use. Excess dichloromethylsilane is used to enhance completion of the reaction. Following an induction period, the reaction becomes exothermic. It is essential to have the reactions go exothermic to get quantitatively complete reactions; otherwise, much longer reaction times are needed and side reactions occur. During the reaction, expecially in the exothermic period, temperature control is very important to prevent side reactions. Observed by other groups, the possible side reactions include α-addition of hydrosilylation, dehydrogenation, and methyl silylation.[16,17] It has been observed that fewer side products are formed in THF relative to benzene. This is probably due to the lower boiling point of THF than benzene and, hence, the lower reaction temperature. The degree of completion of the reaction and the formation of side products are monitored by NMR. Very symmetric spectra of the products are obtained. Incomplete reactions and structural defects would destroy the symmetry in the spectra. The hydrosilylation of the first generation (1G), the second generation (2G), and the third generation (3G) are carried out by similar procedures.

The conversion of silicon chloride to vinyl groups is performed by reacting the hydrosilylation product with vinylmagnesium bromide in THF. After the hydrosilylation the excess dichloromethylsilane and solvent are removed under vacuum. The isolated product is redissolved in anhydrous THF. This solution is then slowly added to a freshly made vinylmagnesium bromide/THF solution at room temperature. The reaction mixture is stirred at room temperature for 1–4 days, depending on the generation. (It should be mentioned that we found the quality of commercial vinylmagnesium bromide solution to be very unreliable. This led to several failed reactions.) After the remaining reagents are removed by adding water and extracting with a large quantity of hexane, the final products contain about 10% impurities which are usually higher molecular weight compounds. These higher molecular weight impurities are believed to be introduced in the coupling reactions with vinylmagnesium bromide.

Each generation is purified by chromatography on a silica gel column. Fractional precipitation and reprecipitation in different solvents was attempted without success. Even the fourth generation product cannot be obtained as a precipitate in methanol, despite its hydrophobicity. Later we found that this is because of the low T_g's of these dendrimers; the T_g's of 2G, 3G, and 4G are around −20 °C. The first and second generation products are purified by flash chromatography on regular silica gel columns eluted with a solution of 0.8% (by volume) ethyl acetate in hexane.

Table I
Molecular Information of the Carbosilane Dendrimers

generation	formula	functionality	M_{calc}	M
1G	$C_{28}H_{52}Si_5$	8	528	508[a]
2G	$C_{68}H_{132}Si_{13}$	16	1312	1160[a]
3G	$C_{148}H_{292}Si_{29}$	32	2880	2870[b]
4G	$C_{308}H_{612}Si_{61}$	64	6016	5760[c]

[a] Vapor pressure osmometry in toluene at 50 °C. [b] Light scattering in *n*-hexane at 35 °C, $dn/dc = 0.165_3$ at $\lambda_0 = 633$ nm. [c] Light scattering in *n*-hexane at 35 °C, $dn/dc = 0.1590$ at $\lambda_0 = 633$ nm.

The isolated yields were 55% and 48% for 1G and 2G, respectively. It should be noted that since these compounds are different from low molecular weight organic compounds, there are some losses on the silica gel column during the purification. For the third and fourth generation dendrimers, because of their large sizes, the regular silica gel columns were not effective. After many trials, the best method of purification was found to be a small column containing about 3 cm of silica gel. The elution solutions contained 4 and 10 drops of ethyl acetate in 400 mL of hexane, for the third and fourth generation products, respectively. The isolated yields were 41% for 3G and 26% for 4G. All the final products show a single spot on TLC plates developed by hexane–ethyl acetate mixtures. All these pure products are either oily or very viscous liquids. They are soluble in most organic solvents. When kept in a refrigerator, the pure 2G, 3G, and 4G products crystallize, but they melt at room temperature. The detailed study of their thermodynamic properties is still in progress. The molecular characterization of each generation is summarized in Table I.

^{1}H and ^{13}C NMR Spectroscopy. As mentioned above, in each step of the synthesis only perfect growth and pure products give simple, symmetric, and well-defined NMR spectra. For each generation there are three types of hydrogens and carbons. The exterior vinyl protons and carbons are quite easily distinguished in both the proton and carbon NMR spectra. The methyl groups which are attached to silicons are also easily recognized in the spectra. Only the methylene groups give a more complex spectrum, but it is not difficult to distinguish them in the proton and carbon spectra. If there are some structural defects in the dendrimers, the methylenes will give very complicated spectra, so their symmetry in the spectra is a good indicator of the perfection and purity of these products.

As seen in Figure 1, the ^{1}H spectrum of 1G shows vinyl protons at δ 6.13, 6.00, and 5.70. The methylene protons give multiple peaks at δ 0.44. There are two types of methylenes; one is close to the center silicon and the other one is close to the vinyl groups, so they split each other to give multiple peaks. The methyl groups give a single peak at δ 0.12. For 2G, 3G, and 4G, the pattern of these vinyl protons does not change. The only difference is that these peaks become broader as the molecular weight becomes larger. The methylene protons of 2G, 3G, and 4G appear in two groups in the spectra since the position of the methylene groups which are next to the vinyl groups from are different from the position of the interior methylene groups. The methylene protons which are next to the vinyl groups give multiple peaks at the same position, as observed in 1G. The interior protons give a single peak at δ 0.33. (It actually is not a single peak, but the coupling constant is very small.) There are also two single peaks for the 2G's, 3G's, and 4G's methyl groups; the one at δ 0.12 is for methyl groups next to the vinyl groups, and the other at δ −0.12 is for the interior methyl groups. (A high-resolution spectrum shows that this peak for 3G can be decomposed into two peaks at δ −0.10 and −0.11 with a 4:1 ratio. This indicates that the methyl groups near the central core are further upfield.) It should be noted that all the spectra are quite similar, but the ratio of the different peaks changes from generation to generation. The NMR peak ratios and their structure ratios are shown in Table II. The experimental ratios of all these products are very close to their theoretical ratios.

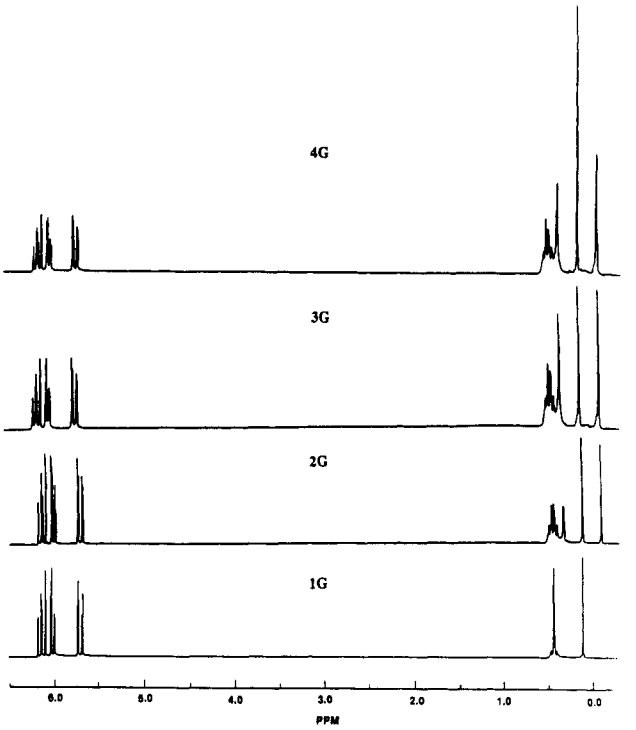


Figure 1. ^{1}H NMR spectra of the carbosilane dendrimers.

The ^{13}C NMR spectra of all the generations are also quite similar, as seen in Figure 2. The two vinyl carbons are found at δ 136.86 and 132.86. The methyl carbons which are close to the vinyl groups are at δ −5.91 for 1G, at δ −5.82 for 2G, at δ −5.80 for 3G, and at δ −5.77 for 4G. The interior methyl carbons are found at δ −6.58 for 2G, at δ −6.49 for 3G, and at δ −6.43 for 4G. The methylene carbons are more complicated. For 1G, the carbons which connect to the central silicon are at δ 2.53, and the carbons which are close to the vinyl groups are at δ 6.02. For 2G, the exterior methylene carbons are found at δ 6.10 for the carbons connecting to the exterior silicon and at δ 4.40 for the carbons connecting to the interior silicon; the interior methylene carbons are found at δ 4.71 for the carbons connecting to the interior silicon and at δ 2.55 for the carbons connecting to the central silicon. For 3G and 4G, the exterior carbons are shown at δ 6.07 and 4.38, all the other carbons except the ones connecting to the central silicon are seen as a broad peak at δ 4.70. As the dendrimer grows bigger, the concentration of the four carbons which connect to the central silicon becomes lower, and the intensity of the peak at δ 2.40 for these carbons decreases form 2G to 4G.

Molecular Weight Determination. The molecular weights of each generation are determined by vapor pressure osmometry and laser light scattering. All the results are summarized in Table I. As seen in Table I, the experimental molecular weights are very comparable to their calculated numbers, within the experimental errors.

Intrinsic Viscosity. The intrinsic viscosity is a important characteristic of polymeric molecules. Since the dendrimers are more compact than linear polymers, the viscosity of dendrimers is expected to be lower than that of linear polymers. The viscosity measurements were

Table II
Integration Ratio of the ^1H NMR Spectra of the Dendrimers

	structure ratio					spectra ratio				
generation	CH_2=CH		CH_2—CH_2	CH_3		CH_2=CH		CH_2—CH_2	CH_3	
1G	2	1	2	1.5		2	1	1.9	1.5	
2G	2	1	3	1.5	0.75	2	1	2.9	1.5	0.73
3G	2	1	3.5	1.5	1.1	2	1	3.6	1.5	1.2
4G	2	1	3.8	1.5	1.3	2	1	3.7	1.5	1.3

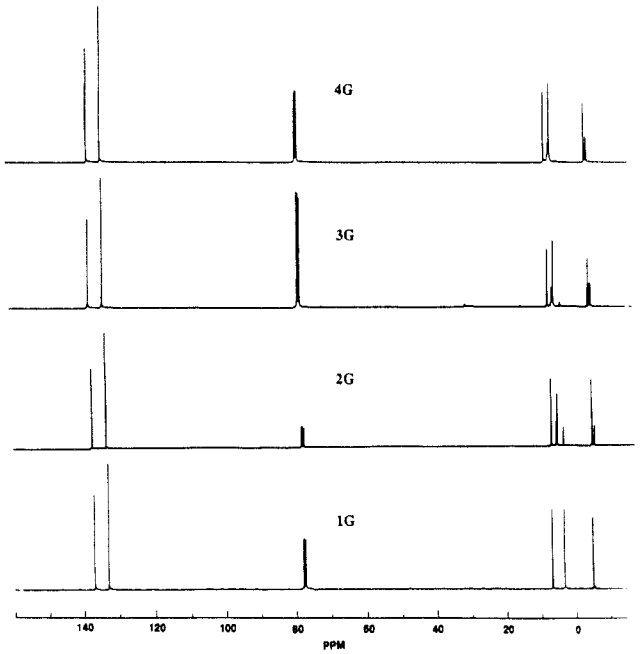


Figure 2. ^{13}C NMR spectra of the carbosilane dendrimers.

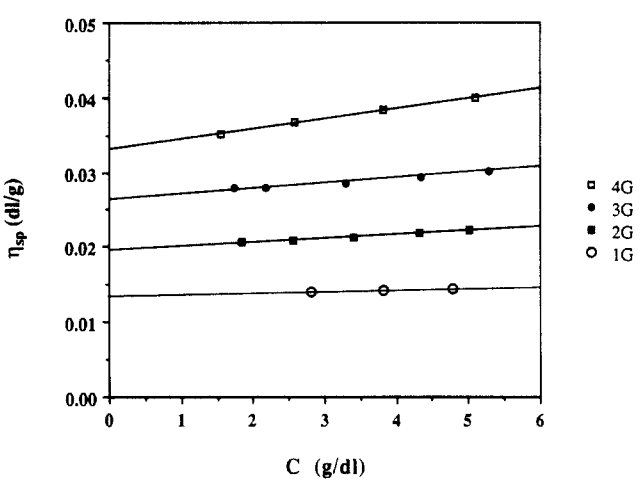


Figure 3. Relationship of reduced viscosity η_{sp}/c and concentration c.

Table III
Intrinsic Viscosity Values and Hydrodynamic Radius

generation	$[\eta]$ (dL/g)	R_v (Å)
1G	0.0133	4.80
2G	0.0196	7.42
3G	0.0264	10.64
4G	0.0338	14.77

carried out in cyclohexane at 25 °C. Since these dendrimers are quite soluble in many organic solvents, the selection of solvent for the measurement is probably not crucial. Figure 3 shows the viscosity of each generation as a function of concentration in cyclohexane. The intrinsic viscosities of these dendrimers are summarized in Table III. The double logarithmic plot of intrinsic viscosity against molecular weight is shown in Figure 4.

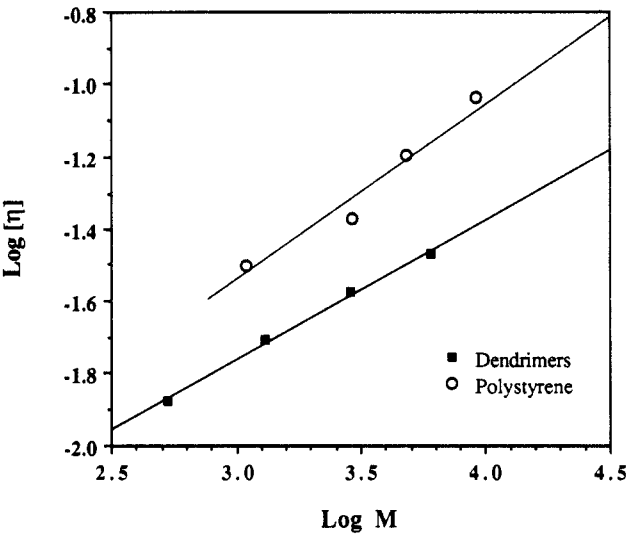


Figure 4. Relationship of log[η] and log M of the dendrimers and polystyrene.

The relationship for polystyrene is also shown. The value of a in $[\eta] = KM^a$, calculated from the straight line, is 0.4; which is smaller than that of most linear polymers. From the intrinsic viscosity the equivalent hydrodynamic radius of the dendrimer molecules, also shown in Table III, can be calculated according to $R_v = (3[\eta]M/10\pi N_A)^{1/3}$ where N_A is Avogadro's number. Since these molecules are nearly spherical, it is expected that their hydrodynamic radii are close to their molecular sphere radii.

It can be seen from Table III that R_v is almost a linear function of the generation number of the dendrimer. Similar behavior was recently found also by Mourey et al.[18] who give a complete comparison of R_v and $[\eta]$ data with recent theories for dendrimers.[19,20] Our results are in agreement with the data for low molecular weight dendrimers below the maximum in $[\eta]$. In this range dendrimers have a fractal dimension slightly over 2.

Size Exclusion Chromatography. Size exclusion chromatography (SEC) is a convenient method for checking the molecular weights and molecular weight distributions of polymers. It should be realized that the elution volume depends on the hydrodynamic volume of the sample.

The SEC diagram of each generation is shown in Figure 5. Tetravinylsilane (0G) is also shown for comparison. As seen in Figure 5, the broadness of the peak of each generation is the same as that of a single organic compound. This suggests that axial dispersion of all these compounds is quite similar during their residence time in the columns. Furthermore, it shows that there are no gross structural imperfections in the dendrimers.

The relationship between the elution volume and the hydrodynamic volume, $[\eta]M$, is shown in Figure 6 and compared to that for linear polystyrene standards. Only 4G seems to fit the universal calibration. For 3G, 2G, and 1G the deviations from the polystyrene line increase as the molecular weight decreases. In the high molecular weight range, the spherical dendrimers are compared to

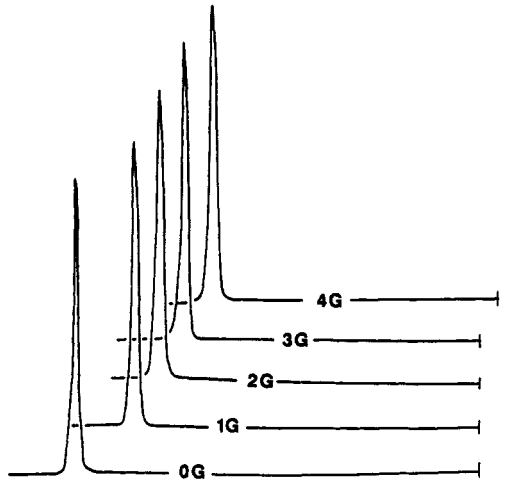


Figure 5. SEC diagrams of each generation of the carbosilane dendrimers.

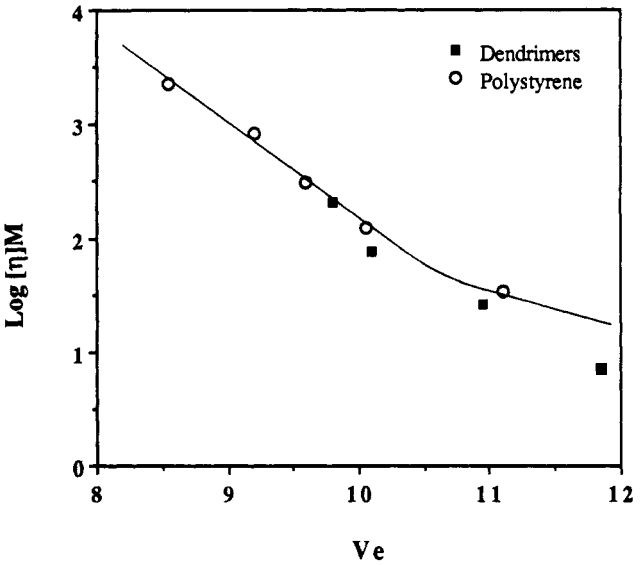


Figure 6. Relationship of (log $[\eta]$) M and GPC retention volume V_e of polystyrene and the dendrimers.

random-coil polystyrene chains. However, at low molecular weights linear polystyrenes are better described as wormlike molecules.[21] Their behavior in SEC is quite different from that of the spherical dendrimers.

For this reason, the molecular weight distribution of the dendrimers cannot be computed by means of the universal calibration curve that is based on linear polystyrene standards. Moreover, since the dendrimers are branched polymers, the branching parameter has also to be included. The molecular weight distribution of branched polymers cannot be obtained from the universal calibration alone. An additional measurement, either the molecular weight or the intrinsic viscosity, over the elution peak is rquired.[22]

Conclusion

We have shown the successful synthesis of a series of carbosilane dendritic macromolecules. In the synthesis, tetravinylsilane was used as the initial core molecule. Two important reactions are involved in the synthesis: hydrosilylation and nucleophilic displacement of chloride by vinylmagnesium bromide. The reaction conditions of hydrosilylation must be well controlled to obtain quantitative yields of products. These dendrimers have been characterized by NMR spectra and GPC. Their viscosity properties have been shown to be different from linear polymers.

Experimental Section

General Information. Tetrahydrofuran was dried over calcium hydride for at least 2 days and distilled right before usage. Tetravinylsilane was purchased from Aldrich Chemical Co. and used without further purification. Dichloromethylsilane was stored in a vacuum system and distilled before usage. Platinum divinyltetramethyldisiloxane complex in xylene was purchased from Petrarch Chemical Co. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker IBM AM400 spectrometer.

Vinyl Magnesium Bromide. Vinylmagnesium bromide was made in anhydrous THF by reacting magnesium metal coil with vinyl bromide (1.1 mol equiv to Mg) at room temperature. During the reaction the vinyl bromide in THF was added dropwise into the flask containing magnesium and a small amount of vinyl bromide in THF at a speed to keep the reaction system gently refluxing under nitrogen.

First Generation Carbosilane Dendrimer (1G). Into a 100-mL flask was added 2.7 g (20 mmol) of tetravinylsilane, 10.1 g (88 mmol) of dichloromethylsilane, 40 mL of anhydrous THF, and 4 drops (about 75 μL) of platinum divinyltetramethyldisiloxane complex in xylene. The reaction system was heated to about 50 °C by a heating mantle. The heating mantle was removed (sometimes a cooling bath was needed) as soon as the reaction solution started to reflux (exothermic reaction). The temperature was controlled to let the exothermic reaction go smoothly. After the exothermic period, the heating mantle was replaced to keep the temperature at 50 °C for 4 h. After cooling to room temperature, the reaction flask was connected to a vacuum system. The excess dichloromethylsilane and all THF were removed, and 40 mL of fresh anhydrous THF was transferred to the flask through the vacuum system. Then this solution was dropwisely added into freshly made vinylmagnesium bromide (192 mmol) in 120 mL of THF. The mixture was stirred at room temperature overnight. Then about 200 mL of hexane was added, and the mixture was washed with 200 mL of water three times and with saturated NaCl solution twice. The organic solution was dried over anhydrous $MgSO_4$. After the solvent was removed through evaporation, the 11-g residue was purified by flash chromatography on a silica gel column eluted with a solution of 0.8% of ethyl acetate in hexane to give 5.5 g of pure oily product 1G in a 55% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.13 (m, 2 H), 6.01 (m, 2 H), 5.70 (m, 2 H), 0.45 (m, 4 H), 0.12 (s, 3 H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 136.86, 132.88, 6.02, 2.53, -5.91.

Second Generation Carbosilane Dendrimer (2G). Into a 100-mL flask was added 2.6 g (5 mmol) of 1G, 5.1 g (44 mmol) of dichloromethylsilane, 40 mL of anhydrous THF, and 4 drops (about 75 μL) of platinum divinyltetramethyldisiloxane complex in xylene. The reaction system was heated to about 50 °C by a heating mantle. The heating mantle was removed (sometimes a cooling bath was needed) as soon as the reaction solution started to reflux (exothermic reaction). The temperature was controlled to let the exothermic reaction go smoothly. After the exothermic period, the heating mantle was replaced to keep the temperature at 50 °C for 4 h. After cooling to room temperature, the reaction flask was connected to a vacuum system. The excess dichloromethylsilane and all THF were removed, and 40 mL of fresh anhydrous THF was transferred to the flask through the vacuum system. Then this solution was added dropwise into freshly made vinylmagnesium bromide (96 mmol) in 60 mL of THF. The mixture was stirred at room temperature overnight. Then about 200 mL of hexane was added, and the mixture was washed with 200 mL of water three times and with saturated NaCl solution twice. The organic solution was dried over anhydrous $MgSO_4$. After the solvent was removed through evaporation, the 6.8-g residue was purified by flash chromatography on a silica gel column eluted with a solution of 0.8% of ethyl acetate in hexane to give 3.1 g of pure oily product of 2G in a 48% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.13 (m, 4 H), 6.01 (m, 4 H), 5.70 (m, 4 H), 0.45 (m, 8 H), 0.33 (m, 4 H), 0.12 (s, 6 H), -0.09 (s, 3 H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 136.86, 132.87, 6.10, 4.72, 4.40, 2.55, -5.82, -6.58.

Third Generation Carbosilane Dendrimer (3G). Into a 100-mL flask was added 1.9 g (1.4 mmol) of 2G, 3.2 g (28 mmol) of dichloromethylsilane, 30 mL of anhydrous THF, and 3 drops (about 50 μL) of platinum divinyltetramethyldisiloxane complex in xylene. The reaction system was heated to about 50 °C by a heating mantle. The heating mantle was removed as soon as the reaction solution started to reflux (exothermic reaction). The temperature was controlled to let the exothermic reaction go smoothly. After the exothermic period, the heating mantle was replaced to keep the temperature at 50 °C for 4 h. After cooling to room temperature, the reaction flask was connected to a vacuum system. The excess dichloromethylsilane and all THF were removed, and 30 mL of fresh anhydrous THF was transferred to the flask through the vacuum system. Then this solution was added dropwise into freshly made vinylmagnesium bromide (67 mmol) in 40 mL of THF. The mixture was stirred at room temperature overnight. Then about 200 mL of hexane was added, and the mixture was washed with 200 mL water three times and with saturated NaCl solution twice. The organic solution was dried over anhydrous $MgSO_4$. After the solvent was removed through evaporation, the 3.9-g residue was purified by chromatography on 3-cm silica gel columns eluted with a solution of 4 drips of ethyl acetate in 400 mL of hexane to give 1.7 g of pure viscous liquid product 3G in a 41% yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.11 (m, 8 H), 5.98 (m, 8 H), 5.68 (m, 8 H), 0.44 (m, 16 H), 0.32 (m, 12 H), 0.10 (s, 12 H), −0.12 (s, 9 H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 136.84, 132.86, 6.06, 4.71, 4.36, 2.37, −5.80, −6.49.

Fourth Generation Carbosilane Dendrimer. Into a 100-mL flask was added 1.3 g (0.5 mmol) of 3G, 2.5 g (22 mmol) of dichloromethylsilane, 30 mL of anhydrous THF, and 3 drops (about 50 μL) of platinum divinyltetramethyldisiloxane complex in xylene. The reaction system was heated to about 50 °C by a heating mantle. The heating mantle was removed as soon as the reaction solution started to reflux (exothermic reaction). The temperature was controlled to let the exothermic reaction go smoothly. After the exothermic period, the heating mantle was replaced to keep the temperature at 50 °C for 4 h. After cooling to room temperature, the reaction flask was connected to a vacuum system. The excess dichloromethylsilane and all THF were removed, and 30 mL of fresh anhydrous THF was transferred to the flask through the vacuum system. Then this solution was added dropwise into freshly made vinylmagnesium bromide (48 mmol) in 40 mL of THF. The mixture was stirred at room temperature overnight. Then about 200 mL of hexane was added, and the mixture was washed with 200 mL water three times and with saturated NaCl solution twice. The organic solution was dried over anhydrous $MgSO_4$. After the solvent was removed through evaporation, the 2.6-g residue was purified by chromatography on a 3-cm silica gel column eluted with a solution of 8 drops of ethyl acetate in 400 mL of hexane to give 0.7 g of viscous liquid product of 4G in a 26% yield. ^1H NMR ($CDCl_3$, 400 MHz); δ 6.11 (m, 16 H), 5.98 (m, 16 H), 5.68 (m, 16 H), 0.44 (m, 32 H), 0.32 (m, 28 H), 0.10 (s, 24 H), −0.12 (s, 21 H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 136.81, 132.89, 6.07, 4.69, 4.37, 2.44, −5.77, −6.42.

Gel Permeation Chromatography. Gel permeation chromatography was performed on a Waters system with three μ Styragel columns (100-, 500-, and 1000-Å nominal pore size) at 35 °C. THF at 1 mL/min is the eluent. A differential refractometer and UV spectrometer at 254 nm are used as detectors.

Intrinsic Viscosities. Intrinsic viscosities were measured in cyclohexane at 25 °C in a Cannon-Ubbelohde viscometer with a Hewlett-Packard automatic timer. Solvent flow times were around 183 s. Measurements were made on concentrations obtained by dilution in the viscometer.

Light Scattering. Light scattering was made on a Brookhaven system in the Zimm mode. Four concentrations in *n*-hexane at 35 °C are measured at a 90° angle with λ_0 = 633-nm He–Ne light. The Rayleigh ratio of toluene is 14×10^{-6} cm^{-1}. The refractive index was determined on the same solutions with a Price Phoenix differential refractometer.

Vapor Pressure Osmometry. Vapor pressure osmometry was performed with a Wescan in toluene at 50 °C. The instrument was calibrated with sucrose octaacetate.

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