Macromolecules **1998,** *31,* 8644−8646

Communications to the Editor

Carbosilazane Dendrimers—Synthesis and Preliminary Characterization Studies

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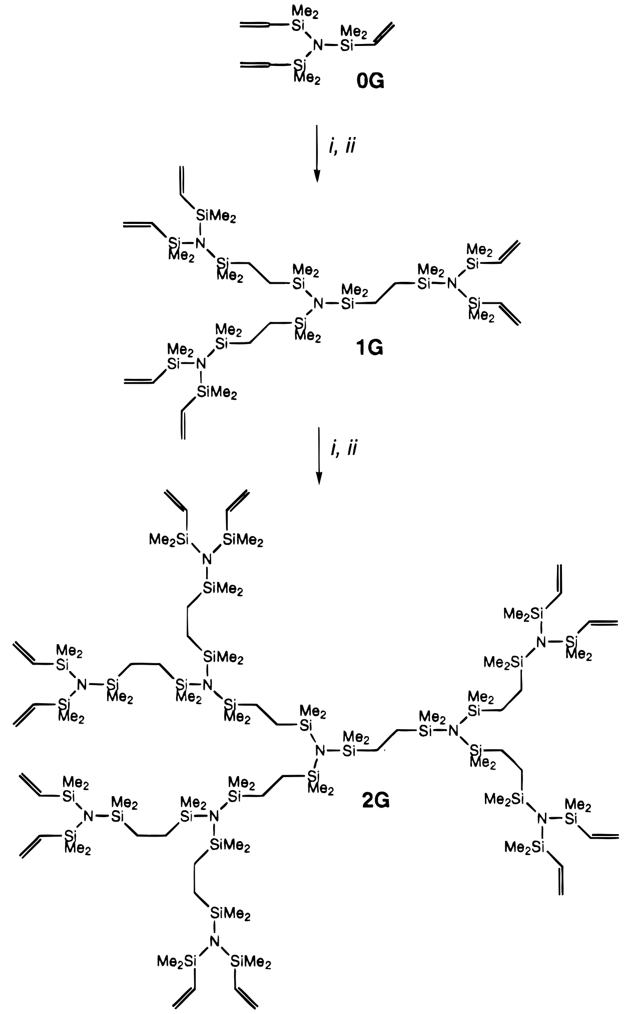
Received June 5, 1998
Revised Manuscript Received October 5, 1998

Recent years have seen a rapid growth in the discovery and application of new dendrimers.[1] Among the many types of dendrimers that have been synthesized are the organosilicon dendrimers.[2] These dendrimers typically possess low glass transition temperatures and relatively low viscosities. Furthermore, the availability and versatility of many synthetic reactions in organosilicon chemistry enable the facile synthesis of a variety of these dendrimers. As a result, the synthesis, characterization, and application of dendritic poly(carbosilanes), poly(carbosiloxanes), poly(silanes), and poly(siloxanes) have been reported in the literature.[2]

The synthesis of organosilicon dendrimers containing Si−N−Si linkages along the branches has not yet been reported. Such poly(carbosilazane) dendrimers would be of interest for several reasons: (1) the known planarity of $N(Si)_x$ centers ($x \geq 2$)[3] could induce unique structural geometries in the dendrimers, (2) the Lewis basicity of nitrogen may enable binding of electron-deficient moieties in the dendrimer interiors, and (3) the relative sensitivity of Si−N bonds could provide a pathway for facile degradation. These features would set poly(carbosilazane) dendrimers apart from the other reported organosilicon dendrimers. In this report, we describe our initial work on the synthesis and characterization of new poly(carbosilazane) dendrimers.

For the synthesis of these dendrimers, we chose a divergent approach starting from tris(dimethylvinylsilyl)amine (**0G**) as the core molecule. This compound was prepared in 76% isolated yield from the reaction of lithium bis(dimethylvinylsilyl)amide (LDMVSA) with chlorodimethylvinylsilane in THF.[4] Dendrimer layers were then added by alternating hydrosilylation[5] and nucleophilic substitution[6] reactions (Scheme 1). With this synthetic approach, each nitrogen atom serves as a branch point and is bonded to three silicon atoms. The hydrosilylation steps required a 3-day reaction period but yielded the products in quantitative yield. After the resulting chlorosilyl-terminated intermediates were reacted with LDMVSA, dendrimers **1G**[7] and **2G**[8] were obtained in 88% and 87% yields, respectively. To date, our efforts to add another layer to **2G** have been unsuccessful. We have successfully achieved the complete hydrosilylation of **2G** with chlorodimethylsilane but reactions of this intermediate with LDMVSA, sodium bis(dimethylvinylsilyl)amide, or LDMVSA/TMEDA in hexane resulted in incompletely substituted products in all cases, as indicated by ^1H NMR spectroscopy.

Scheme 1. Preparation of 0G, 1G, and 2G[a]



[a] Reagents and conditions: (*i*) excess HMe_2SiCl, Pt catalyst (Karstedt's catalyst), THF (see ref 5); (*ii*) lithium bis(dimethylvinylsilyl)amide (LDMVSA), THF, −78 °C (see ref 6).

Compounds **1G** and **2G** were completely characterized using IR and NMR spectroscopy and elemental analysis. As an example, the 400 MHz ^1H NMR spectrum of **2G** is shown in Figure 1, which also illustrates the product purity. In addition to these data, molecular weight data were obtained for both **1G** and **2G**. Molecular weight values obtained for **1G** (999) and **2G** (2289) using vapor pressure osmometry[9] were very close to the theoretical molecular weight values (**1G**, 1000; **2G**, 2462). In addition, preliminary MALDI-TOF mass spectroscopy data[10] confirmed the ideal structures of **1G** and **2G**. Differential scanning calorimetry was also used to

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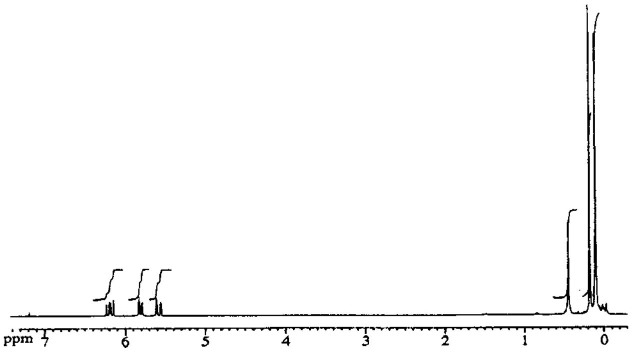

Figure 1. ^{1}H NMR spectrum of **2G**.

characterize these products. Compound **2G** had a glass transition temperature of −53 °C; no glass transition was observed for **1G** to temperatures as low as −100 °C.

An examination of the dendrimers' general reactivities constituted the next part of our investigation. Compounds **0G**, **1G**, and **2G** are quite stable to air and water, and can be kept for long periods in a normal room atmosphere. Hydrolytic stability of these species is not surprising, considering that tris(trialkylsilyl)amines have been reported to be relatively unreactive toward water.[11] However, we observed different degrees of stability toward protic acids, in particular hydrochloric acid. On treatment of **2G** with an anhydrous ethereal solution of HCl followed by removal of volatiles in vacuo, no changes were observed in the ^{1}H NMR spectrum of **2G**. The molar ratios of HCl/**2G** we utilized in separate experiments were 1/1 and 10/1. To examine the possibility that the HCl was being removed during the vacuum treatment, we treated the residue from the 10/1 (HCl/**2G**) experiment with water. This resulted in an exothermic degradation reaction taking place, accompanied by the formation of small amounts of ammonium chloride and unidentified compounds of low molecular weight. On increasing the HCl/**2G** ratio to 40/1 and subsequently adding water, a 78% recovery of ammonium chloride was achieved.

While it was apparent that the HCl in these experiments remained in the dendrimer phase even during the vacuum treatment, it was of interest to us to determine the nature of the interactions between the HCl and the dendrimer. ^{14}N NMR experiments proved to be inconclusive, as the signals from these dendrimers were extremely weak. IR spectroscopy, however, suggested that some H−N interaction exists. IR spectra of the residues from HCl/**2G** ratios of 0/1 (untreated **2G**), 1/1, and 10/1 are shown in Figure 2. These spectra were taken before any water was added to the samples. On treatment of **2G** with 1 equiv of HCl (Figure 2b), a new peak at 3145 cm^{-1} appears in the spectrum. On increasing the amount of HCl added to **2G** (Figure 2c), the intensity and broadness of the peak increases, suggesting that this peak is indicative of a N−H interaction. This is not surprising, considering that this type of interaction has been observed in the reaction between monomeric silylamines and protic acids.[12]

In conclusion, new poly(carbosilazane) dendrimers have been prepared via repetitive hydrosilylation and nucleophilic substitution steps. These molecules represent a new class of organosilicon dendrimers. Dendrimers higher than second generation are not accessible at this point, possibly due to steric congestion. Although the dendrimers are stable to water and to anhydrous hydrogen chloride solutions, they degrade rapidly and exothermically in aqueous hydrochloric acid solutions. These results suggest that controlled degradation of these dendrimers is attainable. This possibility and additional characterization studies are the focus of future investigations in our laboratory.

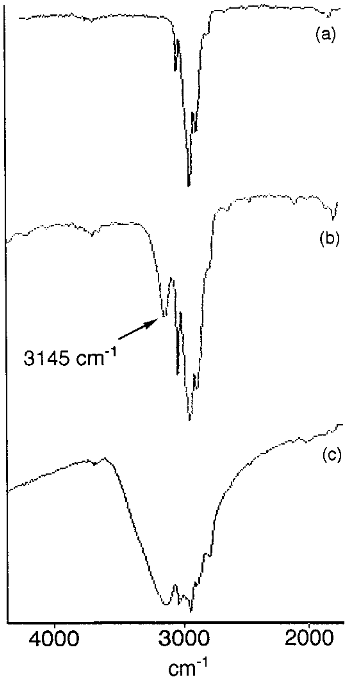

Figure 2. IR spectra of **2G** (a) before treatment with HCl, (b) treated with 1 equiv of HCl, and (c) treated with 10 equiv of HCl.

Acknowledgment. The authors are grateful to Southern Methodist University and the Petroleum Research Fund (administered by the American Chemical Society) for financial support of this research.

References and Notes

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(4) Procedure: A 100-mL round-bottomed flask equipped with a stir bar was charged with 1,3-divinyltetramethyldisilazane (5.0 g, 0.027 mol, Gelest) and 50 mL of THF. The flask was placed in an ice water bath, and *n*-BuLi (10.8 mL of a 2.5 M hexane solution, 0.027 mol) was injected via syringe. After 1 h of stirring, vinyldimethylchlorosilane (4.0 g, 0.033 mol) was added. The mixture was stirred overnight at room temperature. Saturated aqueous NaCl solution was then added, and the aqueous layer was extracted with ether. The organic layer was dried over anhydrous magnesium sulfate and all volatiles were removed using a rotary evaporator. The residual viscous oil was distilled at reduced pressure to yield **0G** as a waxy solid (76% yield, bp 85 °C/0.1 mmHg, mp 55 °C). ^{1}H NMR (CDCl$_3$): δ 0.23 (s, 18H, SiCH_3), 5.67 (dd, 3H, $^2J = 3.6$ Hz, $^3J = 20$ Hz, C=CHH), 5.87 (dd, 3H, $^2J = 3.6$ Hz, $^3J = 15$ Hz, C=CHH), 6.25 (dd, 3H, $^3J = 15$ Hz, $^3J = 20$ Hz, CH=CH$_2$). Anal. Calcd for C$_{12}$H$_{27}$NSi$_3$: C, 53.34; H, 10.10; N, 5.19. Found: C, 53.42; H, 10.40; N, 5.27.

(5) General hydrosilylation procedure: **0G** or **1G** is dissolved in THF at the ratio of approximately (4 mL of THF)/(1 g of **0G** or **1G**). Two to three drops of platinum catalyst solution (Karstedt's catalyst in xylene) are added to the solution and the solution is stirred for 15 min. Dimethylchlorosilane (approximately 1.5 molar equiv relative to the number of

double bonds) is then added to the flask, and the resulting solution is stirred under nitrogen at room temperature for 3 days. All volatiles are then removed under reduced pressure, and the corresponding hydrosilylated product is obtained as a thick yellow oil. These compounds were used in the subsequent nucleophilic substitution step without further purification.

(6) General nucleophilic substitution procedure: *n*-BuLi (2.5 M in hexane) is added to a 25% molar excess of 1,3-divinyltetramethyldisilazane in THF (0.6 mM solution) cooled in an ice bath. After stirring for 10 min, this solution is added to an ice-cooled solution of the hydrosilylated product dissolved in THF (4 mL of THF/mmol of hydrosilylated product). The lithiated divinyltetramethyldisilazane should be used in 25% molar excess relative to the number of Si−Cl bonds. The reaction mixture is stirred cold for 4 h, after which the ice bath is removed and the mixture is stirred overnight at room temperature. At this point, the reaction mixture is poured into ice-cold water. The aqueous layer is extracted with ether and the combined organic layers are washed with water and saturated aqueous NaCl solution. After the solution is dried over anhydrous magnesium sulfate, most volatiles are removed using a rotary evaporator and the residue is heated at 80 °C under vacuum (0.025 mmHg) to give **1G** or **2G** as thick yellow oils.

(7) **1G**: yield = 88%. ^{1}H NMR ($CDCl_3$): δ 0.15 (br s, 36H, NSi(CH_3)CH_2CH_2−), 0.23 (s, 36H, NSi(CH_3)CH═CH_2), 0.50 (s, 12H, CH_2CH_2), 5.63 (dd, 6H, ^2J = 3.6 Hz, ^3J = 20 Hz, CH═CH*H*), 5.86 (dd, 6H, ^2J = 3.6 Hz, ^3J = 15 Hz, CH═CH*H*), 6.24 (dd, 6H, ^3J = 15 Hz, ^3J = 20 Hz, C*H*═CH_2). Anal. Calcd for $C_{42}H_{102}N_4Si_{12}$: C, 50.43; H, 10.28; N, 5.60. Found: C, 50.23; H, 10.46; N, 5.54.

(8) **2G**: yield = 87%. ^{1}H NMR ($CDCl_3$): δ 0.15 (s, 108H, NSi(CH_3)CH_2CH_2−), 0.22 (s, 72H, NSi(CH_3)CH═CH_2), 0.49 (s, 36H, CH_2CH_2), 5.63 (dd, 12H, ^2J = 3.6 Hz, ^3J = 20 Hz, CH═CH*H*), 5.86 (dd, 12H, ^2J = 3.6 Hz, ^3J = 15 Hz, CH═CH*H*), 6.24 (dd, 12H, ^3J = 15 Hz, ^3J = 20 Hz, C*H*═CH_2). Anal. Calcd for $C_{102}H_{252}N_{10}Si_{30}$: C, 49.76; H, 10.32; N, 5.69. Found: C, 49.66; H, 10.47; N, 5.49.

(9) Wescan Model 233 molecular weight apparatus; chloroform was used as solvent.

(10) The authors thank Dr. Petar Dvornic of Michigan Molecular Institute for his assistance in obtaining these data. Complete MALDI-TOF mass spectroscopy results and details will be included in a future full paper.

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MA9808934