Organic−Inorganic Polyamidoamine (PAMAM) Dendrimer−Polyhedral Oligosilsesquioxane (POSS) Nanohybrids

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ABSTRACT: A series of novel core−shell organic−inorganic hybrid materials having polyamidoamine (PAMAM) dendrimer cores and polyhedral oligosilsesquioxane (POSS) shells were prepared. Compositional variety of these hybrids was achieved by varying the dendrimer generation and POSS content. Structures were confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR, IR, and MALDI−TOF mass spectrometry where trihydroxyacetophenone monohydrate (TAM) was used as a matrix. Structure−property relationships across a range of dendrimer generations and POSS contents were studied. Glass transition temperatures varied with the degree of dendrimer end group substitution and generation, while melting temperatures were largely unaffected by degree of end group substitution. Solubility characteristics were directly related to POSS content and were practically independent of dendrimer generation. Best quality transparent films were obtained when a quarter of the dendrimer amino end groups were reacted with POSS, which corresponded to an approximately one-to-one dendrimer to POSS mass ratio. Cross-linkable variants of film-forming hybrids were synthesized by reacting a portion of the PAMAM amino end groups with 3-acrylopropyldimethoxymethylsilane (DMOMS). These hybrids yielded transparent, robust films by moisture cure in ambient air.

Introduction

One of the prime goals of nanotechnology today is finding new ways for controlled bottom-up syntheses of nanostructured, functional materials. For this purpose, libraries of precisely defined, reactive, nanoscopic building blocks are needed, and it is, therefore, not surprising that their synthesis, characterization, and utilization have attracted significant research interest. However, only a limited number of such building blocks have been successfully made. These include fullerenes,[1] various polyhedral oligosilsesquioxanes (POSS),[2] carbon nanotubes,[3] dendrimers,[4−6] and their less regular polydispersed relatives, hyperbranched polymers.[7] Of these, although precise in structure, fullerenes and POSS are limited to discrete sizes within a narrow size range between 0.5 and 1.5 nm, carbon nanotubes and hyperbranched polymers are generally characterized with rather broad size distributions, and only dendrimers offer a series of discrete homologous species having identical chemical composition while spanning the entire lower nanoscopic size domain from 1 to 10 nm in regular increments of approximately 1 nm from one member of the series to the next. Hence, it is almost self-evident why dendrimers have attracted such scientific interest over the past couple of decades,[4−6] and it is not surprising that many of the most important studies have reported using these highly versatile species to construct new tailor-made, complex nanostructures. Examples of such nanostructures include various multiarm star polymers,[8] the so-called tectodendrimers,[9,10] nanodomained dendrimer-based networks,[11,12] and soluble[13,14] or insoluble[15] organic−inorganic nanocomposites.

Here, we report on the first example of yet another type of nanostructure in which two of the abovementioned basic building blocks of present day nanotechnlogy, namely, dendrimers and POSS, are combined together to create more complex organic−inorganic macromolecular hybrids. In these hybrids, dendrimers serve as the core species and POSS cages are covalently attached to their outer molecular surface. In this way, particularly at higher degrees of dendrimer substitution with POSS cages, a series of new POSS-like nanoconstructs are obtained, the sizes of which depend on the generation of dendrimer used to build them. As a consequence, the resulting "macro-POSS" products not only combine characteristic properties of both POSS and selected dendrimers but also open to POSS chemistry a completely new realm of previously unattainable sizes that may extend up to 10−15 nm in diameter.

Historically, several hybrid dendrimer−POSS compounds have already been reported. For example, carbosilane dendrimers were prepared from Si_8O_{12} silsesquioxane cores using consecutive hydrosilylation and alkenylation steps[16,17] followed by surface functionalization with ferrocenyl redox units.[18] In another example, phosphine-containing carbosilane dendrimers based on POSS cores were used as ligands in hydroformylation[19,20] and hydrocarbonylation[21] of alkenes catalyzed by rhodium compounds. Photo- and redox-active metallodendrimers were prepared by attaching terpyridine-functionalized polyether dendrons to a POSS core and reacting the resulting dendrimers with ruthenium(II) species.[22,23] Silsesquioxane cores were also used to grow liquid crystal[24,25] as well as polyamidoamine (PAMAM)-like dendrimers[26] from them. Notably, in all these cases, POSS cages were used as the core units,[27] from which dendrons were either grown divergently or to which they were appended convergently. Here, we report on the inverted concept where silsesquioxane

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cages are attached to the surface of a dendrimer core in an attempt to create macro-POSS-like particles that will, at higher degrees of dendrimer substitution, look like POSS from the outside and thus interact with surrounding environments in a manner similar to the way that their smaller "mono-POSS" relatives are well-known to interact.

In another respect, these dendrimer−POSS hybrids may also be considered as related to radially layered copolymeric poly(amidoamine−organosilicon) (PAMAMOS) dendrimers reported earlier.[28] The latter are generally prepared by functionalization of amine-terminated polyamidoamine (PAMAM) dendrimers with organosilicon acrylates or methacrylates via Michael addition reactions or by various haloalkylation approaches. The surface properties of PAMAMOS dendrimers with inert organosilicon end groups, such as trialkylsilyl, were studied,[29−31] and the use of their reactive derivatives as building blocks for more complex materials with supramolecular structural organization at the nanolevel was also reported.[6,12,32−34] Honeycomb-like, covalently cross-linked, nanodomained PAMAMOS dendrimer-based networks were prepared by curing alkoxysilyl-terminated dendrimers in sol−gel-type hydrolysis reactions or by curing vinylsilyl- or allylsilyl-terminated derivatives with various free radical initiators,[11] and their corresponding nanocomposites with a variety of different metals were also described.[15] Similarly, the dendrimer−POSS hybrids reported here are envisioned to be able to yield well-defined cross-linked networks containing nanodomains of PAMAM and POSS compositions and also to open up additional potential areas of application that are not accessible to dendrimers alone.

Some of these areas may include (a) the preparation of a homologous series of nanoparticles, the mechanical properties of which may be tuned by varying the chemical composition of dendrimers while their sizes may be controlled at will by varying the dendrimer generation, (b) the preparation of novel nanocomposites with metals encapsulated within the dendrimer cores, and (c) the development of new approaches to ultralow dielectric thin films for advanced microelectronics. New approaches to nanoporosity based on these systems or other similar hybrids would be of particular interest since they may avoid the porogen agglomeration and porogen matrix phase separation problems encountered with the so-called templating technique where a "sacrificial" (for example, dendrimer) component is first added to and then thermally removed from a two-component system in an attempt to create well-defined voids in the remaining matrix.[35−38]

Experimental Section

Materials. Diagnostic grade PAMAM dendrimers in methanol (MeOH) were obtained from Dendritech Inc., Midland, MI, while isocyanatopropyldimethylsilylisobutyl-POSS and isocyanatopropyldimethylsilylheptacyclohexyl-POSS were obtained from Hybrid Plastics Inc., Fountain Valley, CA.[39] All materials were used without further purification.

General Procedures. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Varian Unity 300 MHz NMR spectrometer equipped with a 5 mm multinuclei probe. Solvent signals were used as internal standards, and chemical shifts are reported relative to tetramethylsilane (TMS). IR spectra were recorded on a Nicolet 20DXB FTIR spectrometer. Samples were prepared for IR analysis by solution casting onto KBr disks. MALDI−TOF mass spectra were recorded using a Vision 2000 mass spectrometer from Thermobioanalysis. Samples were prepared by dissolving materials of interest in THF at 10 mg/mL and then mixing the solutions in a ratio of 1:10 with a 10 mg/mL solution of the 2,4,6-trihydroxyacetophenone monohydrate (TAM) matrix material. The mixtures were spotted on the MALDI−TOF MS source target and allowed to air-dry prior to analysis. DSC measurements were performed on a DuPont Instruments model 912 unit at a scanning rate of 10 °C/min. TGA measurements were performed on a DuPont Instruments model 951 unit in air. In the TGA measurements, a temperature range from 25 to 800 °C was scanned at 10 °C/min. In solubility tests, 10 mg samples were mixed with 1 mL of solvent at room temperature. Soluble samples gave clear solutions instantaneously while insoluble samples gave either cloudy solutions or precipitates which persisted with time.

Preparation of PAMAM−POSS Hybrids from Generation 2 (G2) PAMAM Dendrimer Precursors. G2 PAMAM−(POSS-*i*-Bu$_7$)$_{16}$ (1): Isocyanatopropyldimethylsilylisobutyl-POSS (0.587 g, 0.602 mmol, 16 equiv) and 0.461 g of a 26.58% w/w MeOH solution of G2 PAMAM having NH_2 end groups (0.123 g of dendrimer, 0.038 mmol, 1 equiv) were stirred in 10 mL of chloroform at room temperature for 24 h in a one-necked round-bottomed flask equipped with a Teflon-coated magnetic stirrer bar and nitrogen inlet. Upon evaporation of the volatile components under vacuum, a white solid was obtained in quantitative yield. ^{1}H NMR (1:1 v/v $CDCl_3$−CD_3OD): δ (ppm) 0.13 (s; Si*CH*$_3$), 0.59−0.64 (m; Si*CH*$_2$), 0.95−0.97 (d; CH*CH*$_3$), 1.13−1.24 (m; *CH*$_2$CH$_2$NHCONH), 1.79−1.93 (m; *CH*(CH$_3$)$_2$), 2.36 (m; PAMAM dendrimer protons), 2.59 (m; PAMAM dendrimer protons), 2.70−2.82 (m; PAMAM dendrimer protons), 2.75−2.80 (t; *CH*$_2$NHCONH), 3.23−3.31 (m; PAMAM dendrimer protons), 4.76 (s; PAMAM dendrimer protons). ^{13}C NMR (1:1 v/v $CDCl_3$−CD_3OD): δ (ppm) 0.0 (Si*CH*$_3$), 15.4 (Si*CH*$_2$), 21.8, 23.3, 24.9 (*i*-Bu carbons and SiCH$_2$*CH*$_2$), 33.2 (*CH*$_2$NHCONH), 36.9−52.6 (PAMAM dendrimer carbons), 159.1 (NH*C*ONH), 172.7, 173.2 (PAMAM dendrimer *C*ONH groups). ^{29}Si NMR (1:1 v/v $CDCl_3$−CD_3OD): δ (ppm) 12.8 (O*Si*(CH$_3$)$_2$CH$_2$), −65.5 and −66.3 (O$_3$*Si*CH). MALDI−TOF MS (TAM matrix): *m*/*z* 18 718 (calcd 18 852) minor peak on high mass side of 8−16 POSS per dendrimer distribution. TGA (10 °C/min, air): onset of mass loss at 232 °C, 71% mass loss at 800 °C. DSC (10 °C/min, nitrogen): 178 °C (T_m). Soluble: chloroform, 1:1 v/v chloroform−MeOH, THF, toluene. Insoluble: MeOH, acetone, NMP (1-methyl-2-pyrrolidinone).

G2 PAMAM−(POSS-*i*-Bu$_7$)$_{12}$ (2): A procedure described for the preparation of hybrid **1** was used with appropriately adjusted relative quantities of reagents: isocyanatopropyldimethylsilylisobutyl-POSS (0.202 g, 0.208 mmol, 12 equiv) and 0.212 g of a 26.58% w/w MeOH solution of G2 PAMAM having NH_2 end groups (0.056 g of dendrimer, 0.017 mmol, 1 equiv). The product was obtained in quantitative yield and ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR data were identical to those of hybrid **1**. MALDI−TOF MS (TAM matrix): *m*/*z* 14 829 (calcd 14 952) minor peak on high mass side of 7−12 POSS per dendrimer distribution. TGA (10 °C/min, air): onset of mass loss at 200 °C, 68% mass loss at 800 °C. DSC (10 °C/min, nitrogen): 166 °C (T_m). Soluble: chloroform, toluene, THF. Insoluble: MeOH, toluene, acetone, NMP. The material formed a white flaky film on a glass substrate when coated from chloroform solution (0.25 g in 3 mL) and dried in air at room temperature.

G2 PAMAM−(POSS-*i*-Bu$_7$)$_8$ (3): A procedure described for the preparation of hybrid **1** was used with appropriately adjusted relative quantities of reagents: isocyanatopropyldimethylsilylisobutyl-POSS (0.216 g, 0.221 mmol, 8 equiv) and 0.339 g of a 26.58% w/w MeOH solution of G2 PAMAM having NH_2 end groups (0.090 g of dendrimer, 0.028 mmol, 1 equiv). The product was obtained in quantitative yield and ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR data were identical to those of hybrid **1**. MALDI−TOF MS (TAM matrix): *m*/*z* 11 054 (calcd 11 053) major peak at center of 4−12 POSS per dendrimer distribution. TGA (10 °C/min, air): onset of mass loss at 154 °C, 81% mass loss at 800 °C. DSC (10 °C/min, nitrogen): 169 °C (T_m). Soluble: chloroform, 1:1 v/v chloroform−MeOH, THF. Insoluble: MeOH, toluene, acetone, NMP. The material formed a white flaky film on a glass substrate when coated from

chloroform solution (0.25 g in 3 mL) and dried in air at room temperature.

G2 PAMAM−(POSS-*i*-Bu$_7$)$_4$ (4): A procedure described for the preparation of hybrid **1** was used with appropriately adjusted relative quantities of reagent: isocyanatopropyldimethylsilylisobutyl-POSS (0.140 g, 0.144 mmol, 4 equiv) and 0.441 g of a 26.58% w/w MeOH solution of G2 PAMAM having NH_2 end groups (0.117 g of dendrimer, 0.036 mmol, 1 equiv). The product was obtained in quantitative yield and ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR data were identical to those of hybrid **1**. MALDI−TOF MS (TAM matrix): *m*/*z* 7164 (calcd 7155) major peak at center of 2−6 POSS per dendrimer distribution. TGA (10 °C/min, air): onset of mass loss at 178 °C, 94% mass loss at 800 °C. DSC (10 °C/min, nitrogen): 134 °C (T_m). Soluble: chloroform. Insoluble: MeOH, toluene, THF, acetone, NMP. The material formed a transparent film on a glass substrate when coated from chloroform solution (0.25 g in 3 mL) and dried in air at room temperature.

G2 PAMAM−(POSS-*i*-Bu$_7$)$_2$ (5): A procedure described for the preparation of hybrid **1** was used with appropriately adjusted relative quantities of reagents: isocyanatopropyldimethylsilylisobutyl-POSS (0.109 g, 0.112 mmol, 2 equiv) and 0.683 g of a 26.58% w/w MeOH solution of G2 PAMAM having NH_2 end groups (0.182 g of dendrimer, 0.056 mmol, 1 equiv). The product was obtained in quantitative yield and ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR data were identical to those of hybrid **1**. MALDI−TOF MS (TAM matrix): *m*/*z* 5396 (calcd 5205) major peak at center of 0−4 POSS per dendrimer distribution. TGA (10 °C/min, air): onset of mass loss at 200 °C, 95% mass loss at 800 °C. DSC (10 °C/min, nitrogen): 3 °C (T_g), 125 °C (crystallization), 170 °C (T_m). Soluble: 9:1 v/v chloroform−MeOH. Insoluble: chloroform, MeOH, toluene, THF, acetone, NMP. The material formed a soft cloudy film on a glass substrate when coated from chloroform−methanol solution (0.25 g in 3 mL) and dried in air at room temperature.

G2 PAMAM−(POSS-*i*-Bu$_7$) (6): A procedure described for the preparation of hybrid **1** was used with appropriately adjusted relative quantities of reagents: isocyanatopropyldimethylsilylisobutyl-POSS (0.041 g, 0.042 mmol, 1 equiv) and 0.509 g of a 26.58% w/w MeOH solution of G2 PAMAM having NH_2 end groups (0.135 g of dendrimer, 0.042 mmol, 1 equiv). The product was obtained in quantitative yield and ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR data were identical to those of hybrid **1**. MALDI−TOF MS (TAM matrix): *m*/*z* 4243 (calcd 4231) major peak at center of 0−2 POSS per dendrimer distribution. TGA (10 °C min^{-1}, air): onset of mass loss at 200 °C, 91% mass loss at 800 °C. DSC (10 °C/min, nitrogen): 9 °C (T_g). Soluble: MeOH, 9:1 v/v chloroform−MeOH. Insoluble: chloroform, toluene, THF, acetone, NMP. The material formed a soft cloudy film on a glass substrate when coated from chloroform−methanol solution (0.25 g in 3 mL) and dried in air at room temperature.

Attempted Preparation of G2 PAMAM−(POSS-cyclohexyl$_7$)$_{16}$ (7): Isocyanatopropyldimethylsilylcyclohexyl-POSS (0.224 g, 0.193 mmol, 16 equiv) and 0.148 g of a 26.58% w/w MeOH solution of G2 PAMAM having NH_2 end groups (0.039 g of dendrimer, 0.012 mmol, 1 equiv) was stirred in 10 mL of chloroform at room temperature for 24 h in a one-necked round-bottomed flask equipped with a Teflon-coated magnetic stirrer bar and nitrogen inlet. Upon evaporation of volatile components under vacuum, a white solid was obtained. ^{1}H NMR (1:1 v/v $CDCl_3$−CD_3OD): δ (ppm) 0.13 (s; SiCH_3), 0.58−0.64 (m; SiCH_2), 0.74 (m; SiCH-cyclohexyl), 1.14−1.30 (m; CH_2-CH_2NHCONH and cyclohexyl-CH_2), 1.63−1.79 (m; cyclohexyl-CH_2), 2.36 (m; PAMAM dendrimer protons), 2.59 (m; PAMAM dendrimer protons), 2.70−2.82 (m; PAMAM dendrimer protons), 2.75−2.80 (t; CH_2NHCONH), 3.23−3.31 (m; PAMAM dendrimer protons), 4.76 (s; PAMAM dendrimer protons). ^{13}C NMR (1:1 v/v $CDCl_3$−CD_3OD): δ (ppm) 0.0 (SiCH_3), 15.3 (SiCH_2), 23.4 (cyclohexyl *C*), 24.4 ($CH_2CH_2CH_2$NH) 26.8 (cyclohexyl *C*), 27.1 (cyclohexyl *C*), 27.7 (cyclohexyl *C*), 34.6 (CH_2-NHCONH), 36.9−52.6 (PAMAM dendrimer carbons), 160.0 (NH*C*ONH), 173.0, 173.5 (PAMAM dendrimer *C*ONH groups). ^{29}Si NMR (1:1 v/v $CDCl_3$−CD_3OD): δ (ppm) −79.0 and −79.4 (O_3SiCH). MALDI−TOF MS (TAM matrix): *m*/*z* 18 266 (calcd 18 297) corresponding to 13 POSS per dendrimer at the center of an 11−14 POSS per dendrimer distribution. TGA (10 °C/min^{-1}, air): onset of mass loss at 233 °C, 57% mass loss at 800 °C. DSC (10 °C/min, air): 171 °C (T_m). Soluble: chloroform, 2:1 v/v chloroform−MeOH, THF. Insoluble: MeOH, toluene, acetone, NMP.

Preparation of PAMAM−POSS Hybrids from Generation 3 (G3) PAMAM Dendrimer Precursors. G3 PAMAM−(POSS-*i*-Bu$_7$)$_{32}$ (8): Isocyanatopropyldimethylsilylisobutyl-POSS (0.147 g, 0.151 mmol, 32 equiv) and 0.109 g of a 29.95% w/w MeOH solution of G3 PAMAM having NH_2 end groups (32.6 mg of dendrimer, 4.76 μmol, 1 equiv) was stirred in 10 mL of chloroform at room temperature for 24 h in a one-necked round-bottomed flask equipped with a Teflon-coated magnetic stirrer bar and nitrogen inlet. Upon evaporation of volatile components under vacuum, a white solid was obtained in quantitative yield. ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR data were identical to those of hybrid **1**. MALDI−TOF MS (TAM matrix): *m*/*z* 26 655 (calcd 26 403) major peak corresponding to 20 POSS groups per dendrimer at the center of 18−32 POSS per dendrimer distribution. TGA (10 °C/min, air): onset of mass loss at 220 °C, 70% mass loss at 800 °C. DSC (10 °C/min, air): 155 °C (T_m). Soluble: chloroform, toluene, THF. Insoluble: MeOH, acetone, NMP.

Attempted Preparation of G3 PAMAM−(POSS-*i*-Bu$_7$)$_{32}$ from OH-Functionalized G3 PAMAM Dendrimer Precursor: Isocyanatopropyldimethylsilylisobutyl-POSS (0.321 g, 0.329 mmol, 32 equiv) and 0.237 g of a 30.11% w/w MeOH solution of G3 PAMAM having OH end groups (71.4 mg of dendrimer, 10.28 μmol, 1 equiv) was stirred in 10 mL of chloroform at room temperature for 24 h in a one-necked round-bottomed flask equipped with a Teflon-coated magnetic stirrer bar and nitrogen inlet. Volatile components were evaporated under vacuum to give a white solid residue with a mass which corresponded to a cyclic POSS dimer side product (**9**). MALDI−TOF MS (TAM matrix): *m*/*z* 1938 (calcd 1949). In an attempt to verify the proposed structure of **9**, 0.044 g of isocyanatopropyldimethylsilylisobutyl-POSS (45.14 μmol) was stirred in 5 mL of chloroform at room temperature for 7 days in a one-necked round-bottomed flask equipped with a Teflon-coated magnetic stirrer bar and nitrogen inlet. Chloroform was evaporated to give a white solid residue containing a mixture of cyclic POSS dimer (**9**) and trimer. MALDI−TOF MS (TAM matrix): *m*/*z* 1933 (calcd 1949 for the dimer) and 2899 (calcd 2924 for the trimer).

Preparation of PAMAM−POSS Hybrids from Generation 4 (G4) PAMAM Dendrimer Precursors. G4 PAMAM−(POSS-*i*-Bu$_7$)$_{64}$ (10): Isocyanatopropyldimethylsilylisobutyl-POSS (0.336 g, 0.344 mmol, 64 equiv) and 0.304 g of a 25.16% w/w MeOH solution of G4 PAMAM having NH_2 end groups (76.5 mg of dendrimer, 5.381 μmol, 1 equiv) was stirred in 10 mL of chloroform at room temperature for 24 h in a one-necked round-bottomed flask equipped with a Teflon-coated magnetic stirrer bar and nitrogen inlet. Upon evaporation of volatile components under vacuum, a white solid was obtained in quantitative yield. ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR were identical to those of hybrid **1**. MALDI−TOF MS (TAM matrix): *m*/*z* 60 000 (calcd 60 028) major peak corresponding to 47 POSS groups per dendrimer at the center of 31−64 POSS per dendrimer distribution. TGA (10 °C/min, air): onset of mass loss at 199 °C, 62% mass loss at 800 °C. DSC (10 °C/min, air): 148 °C (T_m). Soluble: chloroform, THF, toluene. Insoluble: MeOH, acetone, NMP.

G4 PAMAM−(POSS-*i*-Bu$_7$)$_{32}$ (11): A procedure described for the preparation of hybrid **10** was used with appropriately adjusted relative quantities of reagents: isocyanatopropyldimethylsilylisobutyl-POSS (0.213 g, 0.218 mmol, 32 equiv) and 0.385 g of a 25.16% w/w MeOH solution of G4 PAMAM having NH_2 end groups (96.9 mg of dendrimer, 6.814 μmol, 1 equiv). The product was obtained in quantitative yield, and ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR data were identical to those of hybrid **1**. MALDI−TOF MS (TAM matrix): *m*/*z* 42 070 (calcd 42 482) major peak corresponding to 29 POSS groups per dendrimer at the center of 21−36 POSS per dendrimer distribution. TGA (10 °C/min, air): onset of mass loss at 221 °C, 79% mass loss

at 800 °C. DSC (10 °C/min, nitrogen): 26 °C (T_g) 148 °C (T_m). Soluble: chloroform, THF, toluene. Insoluble: MeOH, acetone, NMP.

Preparation of PAMAM−POSS Hybrids from Generation 5 (G5) PAMAM Dendrimer Precursors. Attempted Preparation of G5 PAMAM−(POSS-*i*-Bu$_7$)$_{128}$ (12): Isocyanatopropyldimethylsilylisobutyl-POSS (0.224 g, 0.230 mmol, 128 equiv) and 0.241 g of a 21.52% w/w MeOH solution of G5 PAMAM having NH_2 end groups (51.9 mg of dendrimer, 1.799 μmol, 1 equiv) was stirred in 10 mL of chloroform at room temperature for 24 h in a one-necked round-bottomed flask equipped with a Teflon-coated magnetic stirrer bar and nitrogen inlet. Upon evaporation of volatile components under vacuum, a white solid was obtained in quantitative yield. ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR data were identical to those of hybrid **1**. MALDI−TOF MS (TAM matrix): no spectrum obtained. TGA (10 °C/min, air): onset of mass loss at 216 °C, 84% mass loss at 800 °C. DSC (10 °C/min, nitrogen): 133 °C (T_m). Soluble: chloroform, THF. Insoluble: MeOH, toluene, acetone, NMP.

Attempted Preparation of G5 PAMAM−(POSS-*i*-Bu$_7$)$_{64}$ (13): A procedure described for the preparation of hybrid **12** was used with appropriately adjusted relative quantities of reagents: isocyanatopropyldimethylsilylisobutyl-POSS (0.198 g, 0.204 mmol, 64 equiv) and 0.426 g of a 21.52% w/w MeOH solution of G5 PAMAM having NH_2 end groups (91.7 mg of dendrimer, 3.18 μmol, 1 equiv). The product was obtained in quantitative yield, and ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR data were identical to those of hybrid **1**. MALDI−TOF MS (TAM matrix): *m*/*z* 62 158 (calcd 61 964) peaks poorly resolved but composition corresponds to 34 POSS groups per dendrimer at the center of a 22−53 POSS per dendrimer distribution. TGA (10 °C/min, air): onset of mass loss at 208 °C, 79% mass loss at 800 °C. DSC (10 °C/min, nitrogen): 146 °C (T_m). Soluble: chloroform, 1:1 v/v chloroform−MeOH, THF. Insoluble: MeOH, toluene, acetone, NMP. The material formed a white flaky film on a glass substrate when coated from chloroform solution (0.25 g in 3 mL) and dried in air at room temperature.

Attempted Preparation of G5 PAMAM−(POSS-*i*-Bu$_7$)$_{32}$ (14): A procedure described for the preparation of hybrid **12** was used with appropriately adjusted relative quantities of reagents: isocyanatopropyldimethylsilylisobutyl-POSS (0.056 g, 0.057 mmol, 32 equiv) and 0.240 g of a 21.52% w/w MeOH solution of G5 PAMAM having NH_2 end groups (51.6 mg of dendrimer, 1.792 μmol, 1 equiv). The product was obtained in quantitative yield, and ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR data were identical to those of hybrid **1**. MALDI−TOF MS (TAM matrix): *m*/*z* 45 377 (calcd 45 398) peaks poorly resolved but composition corresponds to 17 POSS groups per dendrimer at the center of a 6−29 POSS per dendrimer distribution. TGA (10 °C/min, air): onset of mass loss at 186 °C, 88% mass loss at 800 °C. DSC (10 °C/min, nitrogen): 30 °C (T_g). Soluble: chloroform. Insoluble: MeOH, toluene, THF, acetone, NMP. The material formed a transparent film on a glass substrate when coated from chloroform solution (0.25 g in 3 mL) and dried in air at room temperature.

Synthesis of Cross-Linkable G2 DMOMS Series. Attempted Preparation of G2 PAMAM−(POSS-*i*-Bu$_7$)$_4$-(SiCH$_3$(OCH$_3$)$_2$)$_{12}$ (15) in Chloroform: Isocyanatopropyldimethylsilylisobutyl-POSS (0.193 g, 0.198 mmol, 4 equiv) and 0.607 g of a 26.58% w/w MeOH solution of G2 PAMAM having NH_2 end groups (0.161 g of dendrimer, 0.050 mmol, 1 equiv) was stirred in 10 mL of chloroform at room temperature for 24 h in a one-necked round-bottomed flask equipped with a Teflon-coated magnetic stirrer bar and nitrogen inlet. Following this step, 0.130 g of 3-acryloxypropyldimethoxymethylsilane (DMOMS, 0.595 mmol, 12 equiv) was added, and stirring was continued for 7 days. The resulting solution was stored in a refrigerator, and samples were removed for analysis. The yield for the DMOMS addition step was calculated from NMR integrals and indicated that the obtained degree of substitution was 33% (i.e., an average of 4 Si(OCH$_3$)$_2$ groups per dendrimer). ^{1}H NMR ($CDCl_3$): δ (ppm) 0.11 (s; SiCH_3), 0.13 (s; Si(CH_3)$_2$), 0.59−0.69 (m; SiCH_2), 0.94−0.96 (CHCH_3), 1.50 (m; CH_2CH_2NH), 1.70−1.89 (2m; CH(CH_3)$_2$ and $CH_2CH_2SiCH_3$), 2.35, 2.51, 2.74 (3m; PAMAM dendrimer protons), 2.88 (t; NHCH_2CH_2COO), 3.12 (m; CH_2NH), 3.28 (m; PAMAM dendrimer protons), 3.52 (s; OCH_3), 4.04 (t; NHCH$_2$-CH$_2$COOCH_2 reacted DMOMS), 4.13 (t; CH$_2$=CHCOOCH_2 unreacted DMOMS), 5.79−5.83, 6.07−6.17, 6.37−6.43 (3m; CH_2=CH and CH$_2$=CH of unreacted DMOMS). ^{29}Si NMR ($CDCl_3$): δ (ppm) 1.3 (CH_2SiCH_3(OCH_3)$_2$), 14.4 (OSi(CH_3)$_2$-CH_2), −65 and −64 (O_3SiCH). IR: ν (cm^{-1}) 3289, 3074 (PAMAM NH), 2956 (*i*-Bu), 2874 (*i*-Bu), 2830 (CH_2 DMOMS), 1727 (C=O unreacted DMOMS) 1461 (*i*-Bu), 1405 (*i*-Bu), 1379 (*i*-Bu), 1361 (*i*-Bu), 1327 (*i*-Bu), 1280 (CH$_2$=CH unreacted DMOMS), 1254 (POSS SiCH), 1228 (POSS SiCH), 1110 (POSS SiOSi), 840 (POSS SiOSi).

Preparation of G2 PAMAM−(POSS-*i*-Bu$_7$)$_4$(SiCH$_3$-(OCH$_3$)$_2$)$_{12}$ (15) in MeOH: The reaction described above for hybrid **14** was repeated except that chloroform was removed in vacuo after the first step and the second DMOMS addition step was carried out in 10 mL of MeOH. The resulting solution was stored in a refrigerator, and samples were removed for analysis. The yield for the DMOMS addition step was calculated from NMR integrals and indicated that the obtained degree of substitution was 70% (i.e., an average number of 8 Si(OCH$_3$)$_2$ groups per dendrimer). ^{1}H NMR and ^{29}Si NMR data were identical to those obtained above. The material formed a robust, transparent film on a glass substrate when coated from chloroform solution (0.25 g in 3 mL) and cured in air at 115 °C for 1 h. TGA (10 °C/min, air): onset of mass loss at 188 °C, 79% mass loss at 800 °C.

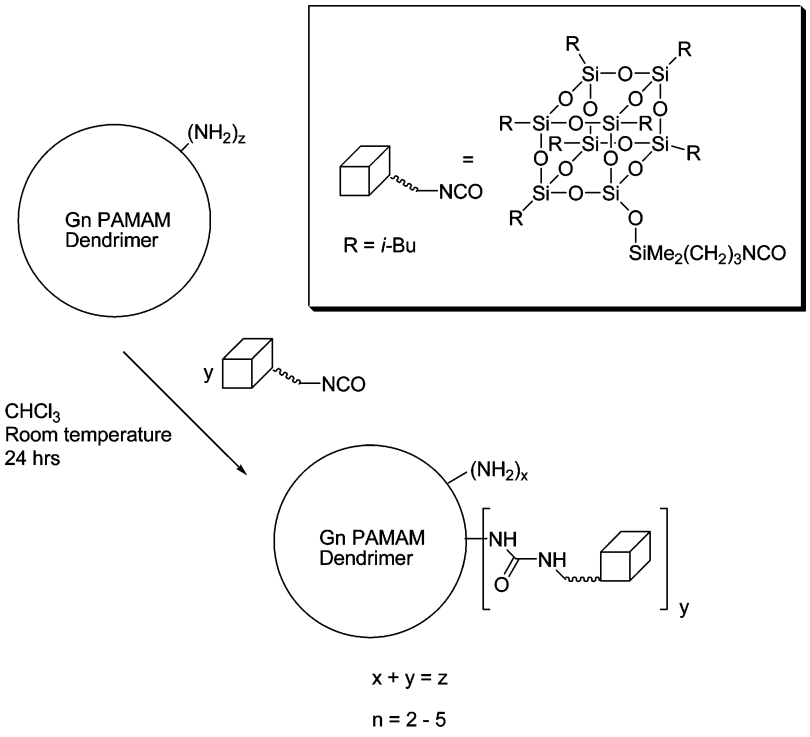
Attempted Preparation of G2 PAMAM−(POSS-*i*-Bu$_7$)$_{12}$-(SiCH$_3$(OCH$_3$)$_2$)$_4$ (16): The MeOH procedure described above for hybrid **15** was repeated with appropriate quantities of reagents: isocyanatopropyldimethylsilylisobutyl-POSS (0.226 g, 0.232 mmol, 12 equiv), 0.237 g of a 26.58% w/w MeOH solution of G2 PAMAM having NH_2 end groups (0.063 g of dendrimer, 0.019 mmol, 1 equiv), and 0.017 g of 3-acryloxypropyldimethoxymethylsilane (DMOMS, 0.077 mmol, 4 equiv). The yield for the DMOMS addition step was calculated from NMR integrals and indicated that the obtained degree of substitution was 27% (i.e., an average number of 1 Si(OCH$_3$)$_2$ group per dendrimer). ^{1}H NMR and ^{29}Si NMR data were identical to those of hybrid **15** above. The material formed a white flaky film on a glass substrate when coated from chloroform solution (0.25 g in 3 mL) and cured in air at 115 °C for 1 h.

Results and Discussion

Synthesis of PAMAM Dendrimer−POSS Hybrids. A series of PAMAM dendrimer−POSS hybrids were synthesized by reacting the amine-functionalized PAMAM dendrimers of generation 2 through 5 (having 16, 32, 64, and 128 amino end groups, respectively) with isocyanato-functionalized isobutyl-POSS. All of the reactions were performed under identical conditions in chloroform at room temperature (see Scheme 1 and Table 1). For each target hybrid G*n* PAMAM-(NH$_2$)$_x$-(POSS-*i*-Bu$_7$)$_y$, 1 equiv of G*n* PAMAM-(NH$_2$)$_{x+y}$ and y equivalents of isocyanato-functionalized isobutyl-POSS were used. The percent of dendrimer end group substitution in such hybrids is given by $100[y/x + y]$, based on ideal structure of the starting dendrimer. In reality, however, imperfections always occur during the dendrimer synthesis (e.g., loops or missing arms), resulting in the presence of nonideal dendrimer molecules.

It was found that this approach always led to a mixture of homologous reaction products having a distribution of numbers of POSS cages attached to dendrimer cores. Nevertheless, the relative content of POSS cages per dendrimer−POSS covalent hybrid could be controlled within these mixtures by adjusting the relative proportion of the POSS to dendrimer reagents used. Reactions gave quantitative yields under rela-

Scheme 1



G2 series (z=16), Hybrid **1** (y=16), **2** (y=12), **3** (y=8), **4** (y=4), **5** (y=2), **6** (y=1)
G3 series (z=32), Hybrid **8** (y=32)
G4 series (z=64), Hybrid **10** (y=64), **11** (y=32)
G5 series (z=128), Hybrid **13** (y=34), **14** (y=17)

Table 1. POSS Content of PAMAM Dendrimer−POSS Hybrids as a Function of Dendrimer Generation G*n* and Degree of End-Group Substitution

	degree of end-group substitution, %						
dendrimer generation	0	6.25	12.5	25	50	75	100
G2	0	**6**, 23%[a]	**5**, 37%	**4**, 54%	**3**, 71%	**2**, 78%	**1**, 83%
G3	0						**8**, 82%
G4	0				**11**, 68%		**10**, 81%
G5	0		**14**, 35%	**13**, 51%			

[a] POSS content is defined as the wt % of POSS reagent in the total molecular mass of the hybrid.

tively mild conditions, and products were easily isolated by solvent evaporation. The chemical structures of the products obtained were characterized by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI−TOF MS), ^{1}H, ^{13}C, and ^{29}Si nuclear magnetic resonance (NMR), and infrared spectroscopy (IR), while their physical properties were evaluated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and solubility tests.

MALDI−TOF mass spectrometry turned out to be the most useful tool for the characterization of these dendrimer−POSS hybrids. Well-resolved mass spectra were obtained from samples dissolved in anhydrous tetrahydrofuran (THF) with trihydroxyacetophenone monohydrate (TAM) as the matrix. The spectra always showed a distribution of PAMAM-$(NH_2)_x$(NHCONH$(CH_2)_3$Si$(CH_3)_2$O−POSS-*i*-$Bu_7)_y$ species, where y is the number of POSS groups per dendrimer core and x is the number of unreacted NH_2 groups, such that $x + y = z$ where z is the number of NH_2 end groups in the ideal dendrimer of a given generation. The mass peaks in these distributions were evenly spaced, with separations between them corresponding to the mass of one POSS substituent group (i.e., CONH$(CH_2)_3$Si$(CH_3)_2$O−POSS-*i*-Bu_7). For medium to low values of y (i.e., the degree of NH_2 substitution), such as 50% and below, the mass peaks corresponding to the target structures appeared in the center of the distribution (see Figure 1). For higher degrees of substitution, such as 75% and above, the mass peaks corresponding to the target structures were usually less prominent and appeared on the high mass side of the distributions. This effect is probably due to a greater steric hindrance at higher degrees of dendrimer substitution.

For a given dendrimer generation, spectral resolution was quite acceptable even at high POSS content (see Figure 1). In contrast, for a constant degree of substitution, spectral resolution improved with decreasing dendrimer generation and decreasing overall molecular mass of the hybrid product (see Figure 2). As a consequence, separate peaks were easily distinguished in the G2 products but not in the G3, G4, and G5 derivatives. Dithranol and dihydroxybenzoic acid (DHB) matrices, as well as increasing water content in either the solvent or the matrix, gave inferior mass spectral resolutions. More details about these MALDI−TOF MS studies will be reported in a separate publication.

All PAMAM−POSS hybrids prepared in this work were also characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. In the ^{1}H NMR spectra, the resonances

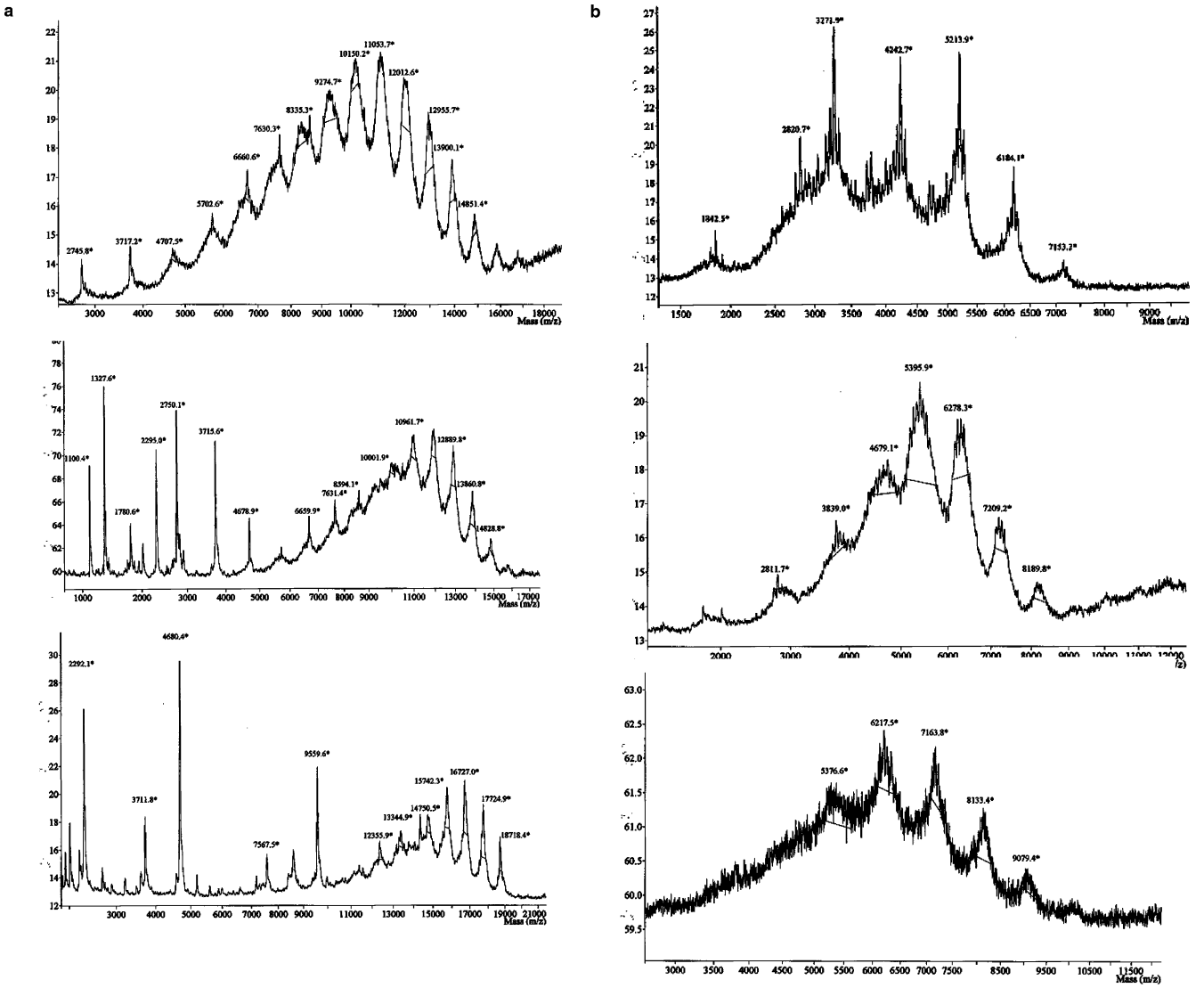


Figure 1. (a) MALDI−TOF MS for G2 PAMAM(POSS-*i*-Bu$_7$)$_x$. Top to bottom: G2 PAMAM(POSS-*i*-Bu$_7$)$_8$ (**3**), G2 PAMAM(POSS-*i*-Bu$_7$)$_{12}$ (**2**), and G2 PAMAM(POSS-*i*-Bu$_7$)$_{16}$ (**1**). (b) MALDI−TOF MS for G2 PAMAM(POSS-*i*-Bu$_7$)$_x$. Top to bottom: G2 PAMAM-(POSS-*i*-Bu$_7$) (**6**), G2 PAMAM(POSS-*i*-Bu$_7$)$_2$ (**5**), and G2 PAMAM(POSS-*i*-Bu$_7$)$_4$ (**4**).

at 3.1 ppm (*CH*$_2$NCO) and 1.4 ppm (*CH*$_2$CH$_2$NCO), characteristic of isocyanato-functionalized POSS reagents, disappeared as the NCO groups were converted into urea linking units, and the corresponding *CH*$_2$-NHCONH triplet appeared at 2.75 ppm. Proton NMR resonance integration was consistent with reagent stoichiometries and with MALDI−TOF spectra results. Chemical shifts were unaffected by the dendrimer generation or the extent of POSS substitution. The PAMAM resonances became typically less well resolved with increasing dendrimer generation, a well-known effect. The loss of PAMAM resolution, however, did not affect the resolution of the peaks of the POSS groups. In the ^{13}C NMR spectra, the isocyanate resonance at 46 ppm (*CH*$_2$NCO) disappeared and two urea resonances appeared at 33.2 ppm (*CH*$_2$NHCONH) and 159.1 ppm (NH*C*ONH). The ^{29}Si NMR spectra showed that POSS cages remained intact upon addition to the dendrimer cores (two CH$_2$*Si*O$_3$ resonances around −65 ppm). Only a slight change took place in the chemical shift of the O*Si*(CH$_3$)$_2$CH$_2$ groups, reflecting the conversion of isocyanate (10.8 ppm) to urea (12.8 ppm) four bonds away from this silicon nucleus.

IR spectroscopy was of limited use in the characterization of these products. While the disappearance of the isocyanate band at 2267 cm^{-1} clearly showed that the starting POSS reagent had been consumed, the urea bands expected for the products at 3340 cm^{-1} (NH), 1585 and 1535 cm^{-1} (CNH), and 1626 cm^{-1} (NHCONH)[40] were obscured by the presence of PAMAM bands at 3281 cm^{-1} (NH), 3074 cm^{-1} (CNH overtone), 1553 and 1638 cm^{-1} (NHCO), respectively.

An attempt was also made to use hydroxyl-functionalized PAMAMs in a reaction with isocyanato-functionalized POSS to prepare the corresponding POSS hybrids. MALDI−TOF MS results showed, however, a very small degree of dendrimer substitution (i.e., only 1−3 POSS groups per G3 dendrimer; see Figure 3). In this case, the isocyanate POSS molecules interreacted in pairs to give the corresponding POSS dimer **9** (see Scheme 2). This result is consistent with the lower nucleophilicity of hydroxyl-terminated PAMAMs compared to their amino-functionalized derivatives, which leads to a very slow isocyanate−hydroxyl addition reaction relative to isocyanate dimerization.[41] Accordingly, in a control experiment where only isocyanato-

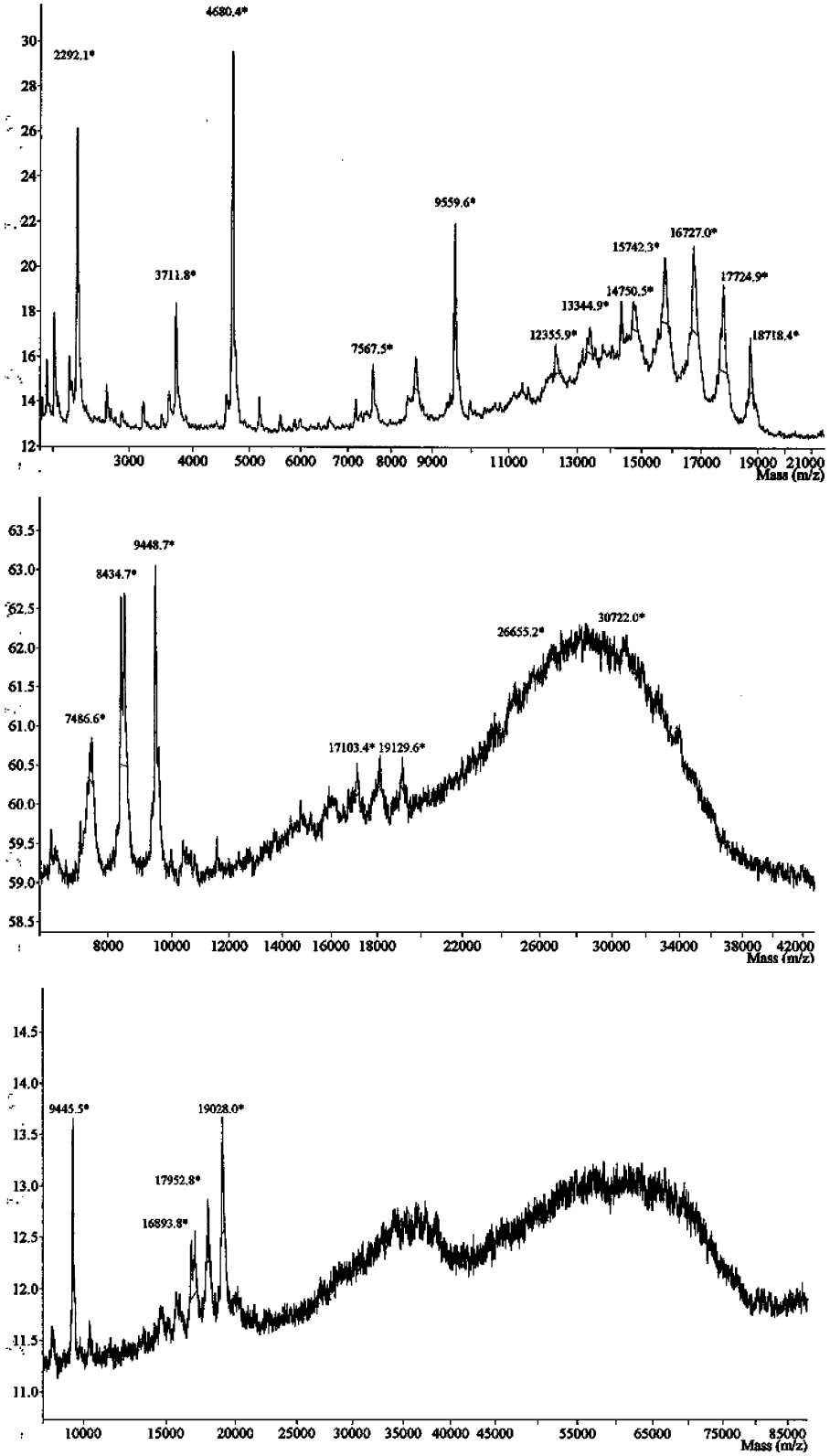


Figure 2. MALDI−TOF MS for various generations of PAMAM dendrimer at 100% POSS substitution. From top to bottom: G2 PAMAM(POSS-*i*-Bu$_7$)$_{16}$ (**1**), G3 PAMAM(POSS-*i*-Bu$_7$)$_{32}$ (**8**), and G4 PAMAM(POSS-*i*-Bu$_7$)$_{64}$ (**10**).

propyldimethylsilylisobutyl-POSS was stirred in chloroform at room temperature for several days, MALDI−TOF spectra showed the formation of the same POSS dimer species **9**, and related POSS trimer species.

For dendrimer−POSS hybrids prepared from G2 through G4 dendrimers the molecular masses obtained by MALDI−TOF MS agreed well with the targeted values. However, in the case of the G5 series, the mass spectra obtained suggested that only about 50% of the targeted degree of substitution was attainable. For example, when the synthesis of the 50% substituted hybrid (i.e., 64 out of 128 groups) was attempted, the 25% substituted derivative (i.e., 32 out of 128 groups) was obtained. Similarly, when synthesis of the 25%

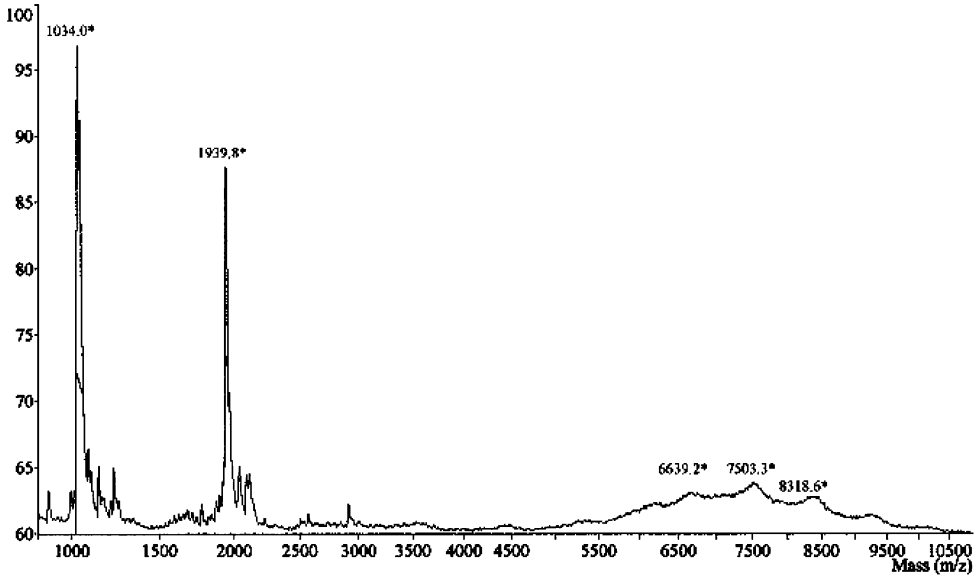
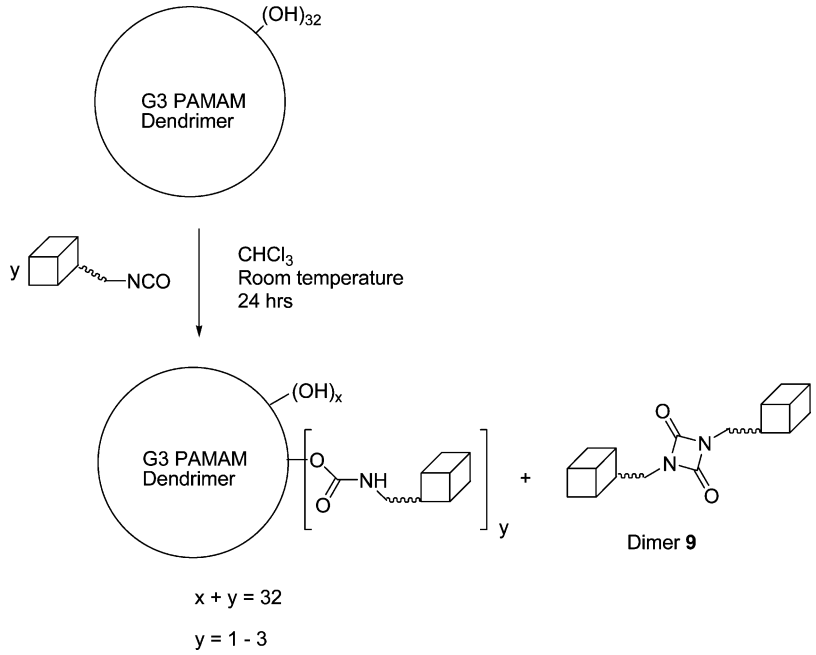


Figure 3. MALDI−TOF MS of the product from attempted substitution of hydroxyl-terminated G3-PAMAM dendrimers.

Scheme 2



substituted hybrid (i.e., 32 out of 128 groups) was attempted, the 12.5% substituted derivative (i.e., 16 out of 128 groups) resulted.

We do not have a plausible explanation for this behavior based on these data alone. However, it is possible that an incoming POSS reagent approaching an unreacted dendrimer amino group adjacent to an already attached POSS group on a higher generation dendrimer would face a greater steric hindrance and a higher energy barrier than it would in corresponding situations with lower generation dendrimers. This would result in a slower rate of dendrimer−POSS reaction relative to the competing POSS dimerization and, consequently, the formation of the POSS dimer in greater quantities. Indeed, the mass signals associated with POSS dimer and trimer structures were observed in the low mass regions of G5 hybrid MALDI−TOF spectra. Because of this, in the following text these hybrids are discussed in terms of their actual degrees of dendrimer substitution, i.e., as obtained from MALDI−TOF MS data, rather than by their originally targeted values.

Solubility. The solubility characteristics of the PAMAM dendrimer−POSS hybrids obtained are summarized in Table 2. Solubilities were found to be heavily dependent on the relative degree of dendrimer substitution and the type of organic groups attached to the POSS cages. For example, while PAMAM dendrimers are highly soluble in MeOH and NMP, their corresponding isobutyl-POSS hybrids showed reduced solubility in MeOH with increasing POSS content (i.e., increased alkyl character of the hybrid outer surface), becoming completely insoluble between 6.25% and 12.5% dendrimer substitution. Even more drastically, the attachment of a single POSS group to the dendrimer core (e.g., as in compound **6**) rendered the hybrid insoluble in NMP. Conversely, in solvents where the POSS starting reagents showed good solubility, such as

Table 2. Solubility of PAMAM Dendrimer−POSS Hybrids in Various Solvents at Room Temperature[a−c]

	POSS content[d]							
compound	0	6.25	12.5	25	50	75	100	
	PAMAM dendrimer (G2)	**6** (G2)	**5** (G2) **14** (G5)	**4** (G2) **13** (G5)	**3** (G2) **11** (G4)	**2** (G2)	**1** (G2) **8** (G3) **10** (G4)	POSS reagent
$CHCl_3$	−	−(G2)	−(G2) +(G5)	+(G2) +(G5)	+(G2) +(G4)	+(G2)	+(G2) +(G3) +(G4)	+
9:1 (v/v) $CHCl_3$−MeOH	−	+(G2)	+(G2)	+(G2) +(G5)	+(G2)	+(G2)	+(G2)	+
1:1 (v/v) $CHCl_3$−MeOH	−				+(G2)		+(G2)	+
MeOH	+	+(G2)	−(G2) −(G5)	−(G2) −(G5)	−(G2) −(G4)	−(G2)	−(G2) −(G3) −(G4)	−
THF	−	−(G2)	−(G2) −(G5)	−(G2) +(G5)	+(G2) +(G4)	+(G2)	+(G2) +(G3) +(G4)	+
toluene	−	−(G2)	−(G2) −(G5)	−(G2) −(G5)	−(G2) +(G4)	+(G2)	+(G2) +(G3) +(G4)	+
acetone	−	−(G2)	−(G2) −(G5)	−(G2) −(G5)	−(G2) −(G4)	−(G2)	−(G2) −(G3) −(G4)	−
NMP	+	−(G2)	−(G2) −(G5)	−(G2) −(G5)	−(G2) −(G4)	−(G2)	−(G2) −(G3) −(G4)	−

[a] (+): Instantaneous clear solution for 10 mg of sample per mL of solvent at room temperature. [b] (−): Visible precipitate for 10 mg of sample per mL of solvent at room temperature which persists. [c] G*n* in parentheses refers to the generation of the dendrimer core. Bold numbers identify individual hybrids described in the Experimental Section. [d] % of dendrimer end-group substitution.

chloroform, toluene, and THF, the increase in POSS content in the hybrid resulted in the corresponding increase in the solubility of the hybrids in these solvents. Thus, although PAMAMs are insoluble in toluene and THF, good solubility of the hybrids in toluene was achieved when the degree of substitution was 50−75% and in THF when the degree of substitution was 25%−50%.

In contrast to the degree of substitution, the solubility of the hybrids was observed to be rather independent of dendrimer generation, although at a constant degree of substitution the lower generations appeared to have inferior solubility in chloroform, THF, and toluene. This effect is probably due to the more open structure of the lower generation dendrimers, which have their PAMAM interiors more exposed to interactions with the surrounding media.

Purity of PAMAM Dendrimer−POSS Hybrids. The MALDI−TOF MS results show that reacting the stoichiometrical quantity of POSS reagent with amine-terminated dendrimers gives products with a distribution of species in which the target structure is generally represented by the major peak, and ^1H and ^{13}C NMR and IR results show that all of the starting isocyanato-POSS reagent is consumed. However, when hydroxyl-functionalized PAMAM dendrimer was used, the isocyanato-POSS reagent predominately reacted with itself to form a dimer **9** (Scheme 2), and the MALDI−TOF mass spectra of other hybrids contained low mass peaks (Figures 1 and 2). Hence, the possibility that POSS dimer may also have been present in the other hybrids was evaluated by ultrafiltering hybrid **6** in MeOH using a cellulose ultrafiltration membrane with a molecular mass cutoff of 3000 (since the target mass of compound **6** is 4231 and the mass of dimer **9** is 1949). However, on removal of MeOH from the low mass filtrate, a few milligrams of oil was isolated which NMR showed to contain neither POSS nor PAMAM, nor POSS dimer.

Table 3. Mass Loss of Generation 2 Hybrids as a Function of Their Composition

POSS content[a]	100	75	50	25	12.5	6.25
hybrid number[b]	**1**	**2**	**3**	**4**	**5**	**6**
total mass loss (%) at 800 °C	71	68	81	94	95	91
initial hybrid SiO content (%)	39	37	33	26	18	11
initial hybrid organic content (%)	61	63	67	74	82	89

[a] % of dendrimer end-group substitution. [b] Bold numbers identify individual hybrids described in the Experimental Section.

The high mass fraction was recharacterized, and the NMR, MALDI−TOF MS, and solubility results were found to be identical to the original sample **6** before ultrafiltration, confirming that purification of these products was not necessary.

Thermal Stability. Thermal stability of dendrimer−POSS hybrids was evaluated by TGA in air. There was no obvious correlation between the onset temperature of mass loss and POSS content. At 100% and at 12.5% substitution the onset temperature increased with decreasing PAMAM dendrimer generation, reaching the maximum of about 230 °C for the G2 derivative. At 50% and at 25% substitution the onset temperature decreased with decreasing PAMAM dendrimer generation. Table 3 lists the observed values for total mass loss and initial SiO and organic contents for the G2 series of hybrids. Figure 4 shows the TGA traces for 100% POSS-substituted vs parent G2 PAMAM dendrimers.

It can be seen from these data that, for all examined hybrids, the observed mass loss was greater than the initial organic content and that this difference was greatest for the middle members of the series. The residues remaining at the end of degradation were pale gray to white, indicating a predominantly inorganic composition. These observations imply that some silicon−oxygen-containing volatiles were lost together with the organic matter during the thermooxidative degradation process. Similar behavior was also previously observed for methylsilyl-substituted PAMAMOS dendrimers.[29]

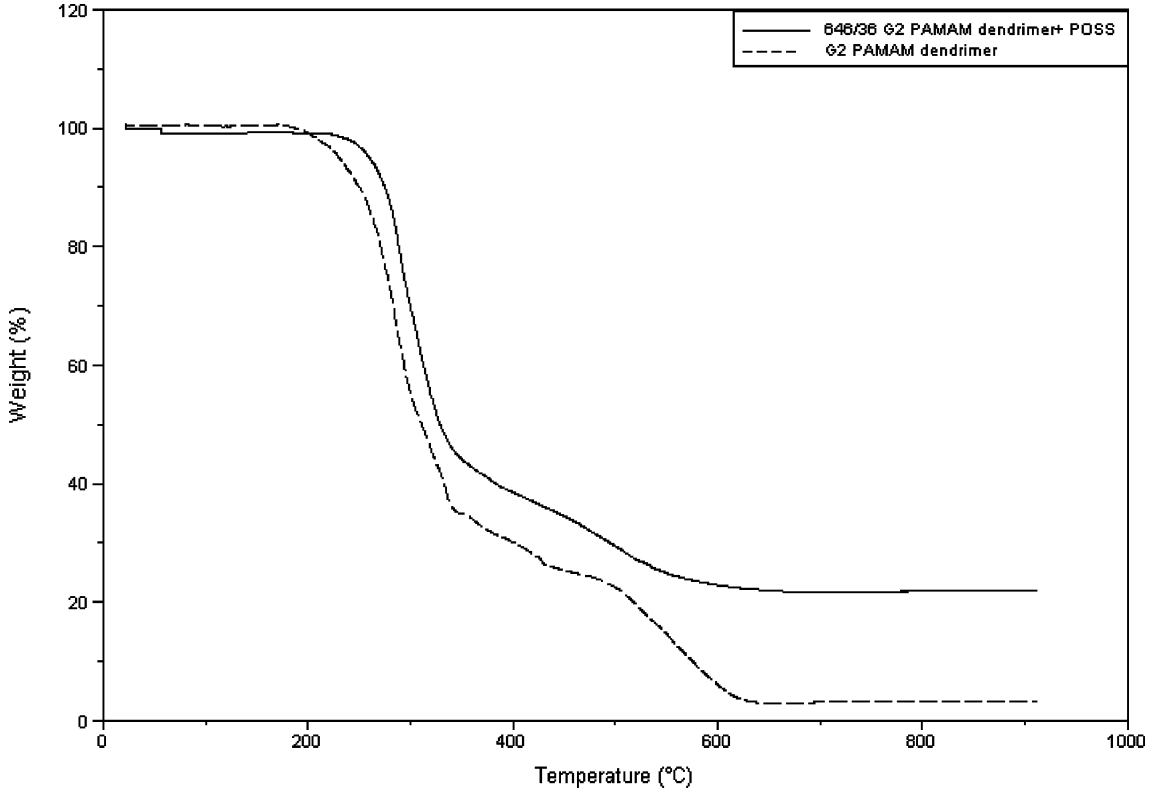


Figure 4. TGA thermograms of parent G2 PAMAM dendrimer (dashed line) and its G2 PAMAM (POSS-*i*-Bu$_7$)$_{16}$ **1** (i.e., 100% substitution) hybrid (solid line).

Table 4. Glass Transition and Melting Temperatures of PAMAM Dendrimer−POSS Hybrids and Parent Dendrimers

POSS content[a]	G2	G3	G4	G5
0	T_g = 0 °C	T_g = 11 °C	T_g = 14 °C	T_g = 14 °C
6.25	T_g = 9 °C			
12.5	T_g = 3 °C			T_g = 30 °C
	T_m = 170 °C			T_m = 160 °C
25	T_m = 134 °C			T_m = 146 °C
50	T_m = 169 °C		T_g = 26 °C	
			T_m = 148 °C	
75	T_m = 166 °C			
100	T_m = 178 °C	T_m = 155 °C	T_m = 148 °C	

[a] % of dendrimer end-group substitution.

Thermal Transitions. While dendrimer−POSS hybrids in which less than 50% of the dendrimer end groups were substituted with POSS cages clearly showed glass transition temperatures by DSC, their higher substituted homologues did not. At 12.5% substitution, the glass transition temperature increased with increasing dendrimer generation, consistent with the trend seen for the unsubstituted parent PAMAM dendrimers (see Table 4). Glass transition temperatures of hybrids were observed to be higher than those of the corresponding PAMAM dendrimers.

Melting temperatures were observed for all hybrids with a degree of POSS substitution of 12.5% and above (see Table 4 and Figure 5), but at any given generation they were largely unaffected by the value of this degree. They generally appeared to decrease with increasing dendrimer generation with the exception of 25% substituted hybrids **4** and **13**.

Influence of POSS Alkyl Groups on Properties. To examine the effect of the type of POSS alkyl groups on the properties of the resulting hybrids, a G2 hybrid

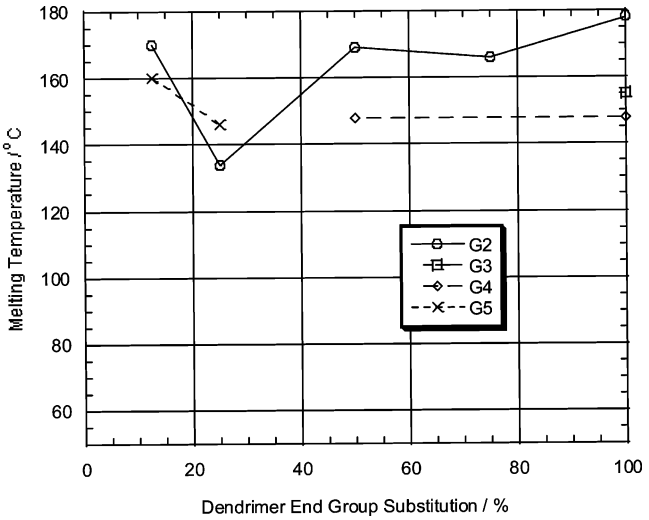


Figure 5. Melting temperatures of PAMAM dendrimer−POSS hybrids for indicated dendrimer generations and at various POSS contents.

(**7**) was prepared from isocyanatopropyldimethylsilyl-cyclohexyl-POSS and compared with its isobutyl derivative (see Table 5). Although the cyclohexyl-POSS target structure was complete substitution of all 16 dendrimer amino groups, in contrast to the isobutyl-POSS case, no mass signal corresponding to the structure containing 16 cyclohexyl-POSS cages could be seen in the MALDI−TOF spectrum of the obtained product. Instead, the highest *m*/*z* value signal observed was that corresponding to 14 POSS groups. The cyclohexyl-POSS hybrid also yielded a lower overall degree of substitution than its isobutyl derivative (i.e., an 11−14 distribution vs an 8−16 distribution). This result is consistent with the expected steric hindrance caused by the bulkier cyclohexyl groups in contrast to the isobutyl ones.

Table 5. Structures and Properties of Cyclohexyl and Isobutyl-Substituted Generation 2 PAMAM Dendrimer−POSS Hybrids at 100% End-Group Conversion

target structure	G2 PAMAM-(POSS−Cyclohexyl$_7$)$_{16}$ **7**	G2 PAMAM-(POSS-*i*-Bu$_7$)$_{16}$ **1**
POSS content (wt %)	85	83
MALDI TOF MS	11−14 signal distribution	8−16 signal distribution
	18266 (13 peak)[a]	18815 (16 peak)[a]
	18297 (calcd for **13** POSS substitution)	18852 (calcd)[b]
DSC	T_m = 171 °C	T_m = 178 °C
(10 °C/min in N_2)		
TGA	onset at 233 °C	onset at 232 °C
(10 °C/min in air)	57% mass loss at 800 °C	71% mass loss at 800 °C
	dark gray residue	white residue
theoretical composition[b] (wt %)	34% SiO	39% SiO
	66% organic	61% organic
solubility[c]	chloroform	chloroform
	2:1 (v/v) chloroform−MeOH	1:1 v/v chloroform−MeOH
	THF	THF
		toluene
nonsolvents	MeOH	MeOH
	1:1 (v/v) chloroform−MeOH	acetone
	toluene	NMP
	acetone	
	NMP	

[a] Numbers in parentheses correspond to the numbers of POSS units attached to the dendrimer core. [b] Calculated for complete substitution assuming ideal dendrimer structure. [c] 10 mg of sample mixed with 1 mL of solvent at room temperature. Soluble samples gave clear solutions and insoluble samples gave precipitates.

Table 6. Quality of Hybrid Films as a Function of POSS Content[a]

POSS content[b]	6.25	12.5	25	50	75
hybrid number[c]	**6**	**5**	**4**	**3**	**2**
film quality	soft	soft	firm	flaky	flaky
film appearance	cloudy	cloudy	transparent	opaque	opaque

[a] Generation 2 hybrids were used in all cases. [b] % of dendrimer end-group substitution. [c] Bold numbers identify individual hybrids described in the Experimental Section.

Table 7. Quality of Films from PAMAM−POSS−DMOMS Hybrids

precursor composition	G2 PAMAM−(POSS-*i*-Bu$_7$)$_4$−(DMOMS)$_{12}$	G2 PAMAM−(POSS-*i*-Bu$_7$)$_{12}$−(DMOMS)$_4$
hybrid no.	**15**	**16**
film quality	robust	flaky
film appearance	transparent	opaque

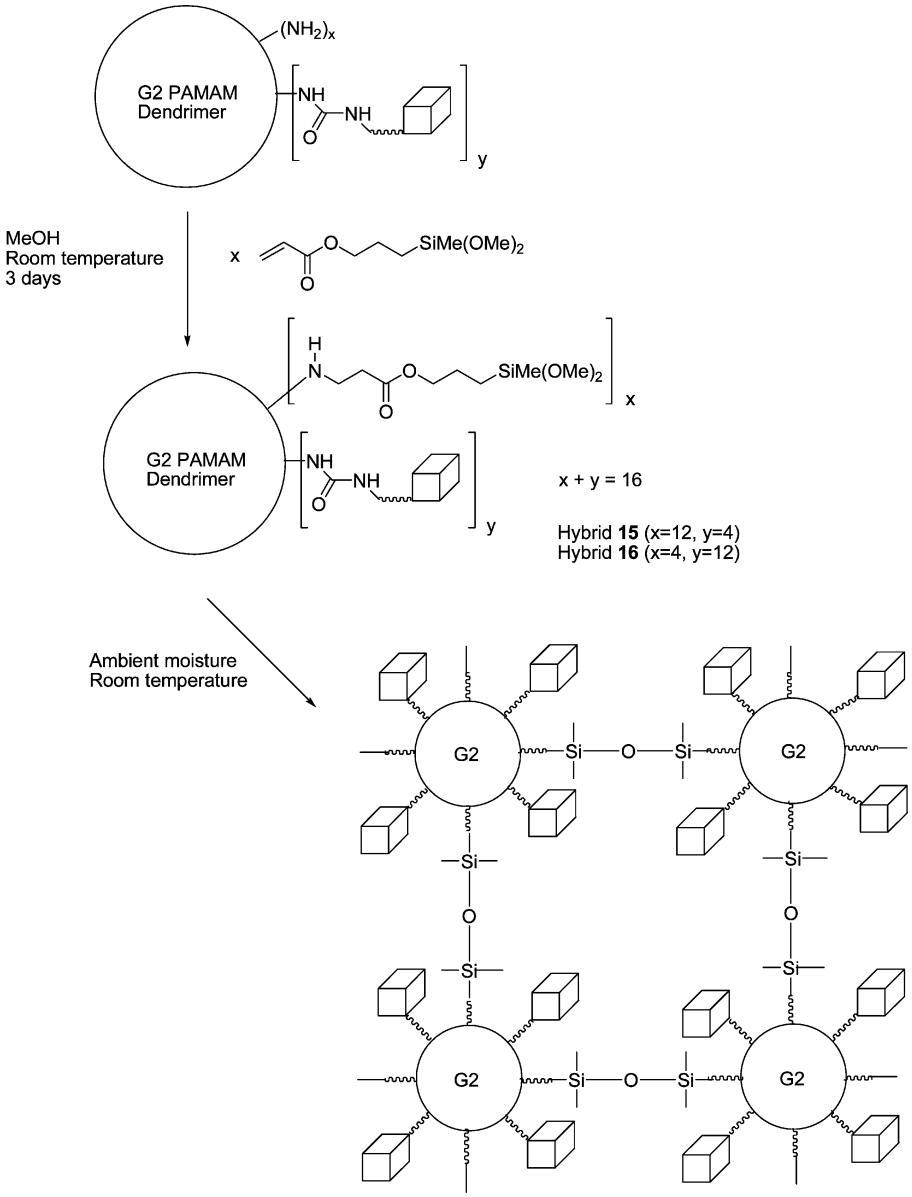
The DSC-determined melting temperatures for these two materials were similar. Results from TGA runs in air showed that the total mass loss from the cyclohexyl hybrid (**7**) at 800 °C was less than its initial organic content. This result is opposite to that of the total mass loss of the isobutyl derivative (**1**) which was greater than its initial organic content. The remaining organic content in the residue from the cyclohexyl hybrid (**7**) was apparent from its dark gray color, whereas the residue from the isobutyl hybrid (**1**) was completely white, suggesting that only silica remained. The solubility characteristics of these two hybrids were similar except that toluene was found to be a good solvent for the *i*-Bu-POSS hybrid but a nonsolvent for the cyclohexyl-POSS hybrid.

Film Formation. Initial attempts to prepare films of G2 PAMAM dendrimer−POSS hybrids were made by casting onto glass slides from chloroform solutions (see Table 6). For the hybrids with lower POSS content it was necessary to add one drop of methanol into 3 mL of casting solution in order to enhance solubility. The results obtained were not satisfactory. Films obtained from hybrids with higher POSS contents were opaque and flaky, with poor adhesion to the substrate, while those obtained from hybrids with lower POSS contents were soft and cloudy. The optimum composition for good transparent film formation appeared to be at 25% substitution, which corresponds to a composition having approximately 50/50 wt % ratio of dendrimer and POSS components.

Synthesis of Cross-Linkable PAMAM Dendrimer−POSS Hybrids by Incorporation of Methoxysilyl End Groups and Film Formation. We have recently reported on high quality transparent nanodomained films from radially layered polyamidoamine−organosilicon (PAMAMOS) dendrimers having alkoxysilyl end groups for cross-linking.[11,28b] The formation of cross-linked networks from these dendrimers involves hydrolysis of alkoxysilyl groups to silanols in the presence of atmospheric or added moisture, followed by silanol condensation into interdendrimer siloxane bridges.[11,28b,42] Hence, in an attempt to introduce good film-forming properties to the PAMAM dendrimer−POSS hybrids of this study, cross-linkable dimethoxymethylsilane derivatives (Table 7) were synthesized using a two-step process shown in Scheme 3.

In the first step of this process, PAMAM dendrimer−POSS hybrids were prepared in the usual manner at room temperature in chloroform (see Scheme 1), following which the purposely left unreacted amino groups were reacted in a Michael addition with 3-acryloxypropyldimethoxymethylsilane (DMOMS). It was expected that as in the case of PAMAMOS[11] this reaction would lead to the attachment of one or two $-SiCH_3(OCH_3)_2$ groups per primary NH_2 unit, depending on the relative amount of DMOMS reagent used. In the initial attempt to prepare compound **15**, targeted to have 12 $-SiCH_3(OCH_3)_2$ groups, cholorform was used as the reaction solvent and DMOMS addition was performed without isolation of the PAMAM dendrimer−POSS intermediate. However, since ^{1}H NMR showed that the yield of DMOMS addition was only 33% even after 7 days at room temperature, the procedure was modified and chloroform was replaced with methanol following the removal of the former in vacuo after the POSS addition step. This raised the DMOMS addition reaction yield to 70%, indicating that methanol is not only a good solvent for such systems, but that it may also act as a reaction catalyst as previously suggested.[28a]

Scheme 3



The products obtained were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR and IR. The ^{13}C NMR spectra were highly complex, particularly in the 30−60 ppm region, and could not be fully assigned. Nevertheless, it was possible to determine that a single $-SiCH_3(OCH_3)_2$ group was generally attached to a single NH_2 end group as indicated by the presence of the signal at 34.75 ppm for $NHCH_2\mathit{CH}_2COO(CH_2)_3Si$ groups rather than the signal at 32.37 ppm for $N[CH_2\mathit{CH}_2COO(CH_2)_3Si]_2$ units. Interestingly, this was in clear contrast to double addition reaction products, usually observed for the closely related PAMAMOS dendrimers.[28] In the IR spectra, unreacted and reacted acrylate groups could be distinguished by the carbonyl stretch bands at 1727 and 1735−1740 cm^{-1}, respectively.

Films from hybrids **15** and **16** were cast onto glass slides from chloroform solutions (see Table 7) and cured in air for 1 h at 115 °C. As with the non-$SiCH_3(OCH_3)_2$-containing films (compare Tables 6 and 7), the 75% POSS-containing hybrid **16** gave a flaky white cure while the 25% POSS-containing derivative **15** gave a robust (scratch-resistant) and transparent film. A qualitative comparison of the physical properties of the 25% POSS-containing films showed that samples from hybrid **15** were hard and scratch-resistant whereas the corresponding samples obtained from hybrid **4** having no cross-linkable $SiCH_3(OCH_3)_2$ groups were softer and easier to scratch. A TGA experiment carried out on film **15** gave a white residue with a total mass loss of 79% at 800 °C, suggesting that all organic content (the theoretical organic content of this hybrid was 76%) had been lost and only silica remained.

It should be noted that some excess of unreacted DMOMS was present in the film-forming solution, as was also the case for the previously described PAMAMOS dendrimers.[11] As a consequence, its $SiOCH_3$ groups took part in the cure chemistry by reacting with $SiOCH_3$ groups on the hybrids or on other DMOMS molecules, resulting in a complex network. The effect of this factor on the properties of the obtained films will be the subject of another study.

Conclusions

A series of organic−inorganic, polyamidoamine (PAMAM) dendrimer−polyhedral oligosilsesquioxane

(POSS) core−shell hybrids were prepared from different dendrimer generations and with various POSS contents. Notably, these hybrids represent the first dendrimer−POSS nanoconstructs where dendrimers are the core component.

The solubility characteristics of these hybrids were dependent on the degree of dendrimer−POSS substitution, so that the higher the degree of substitution, the more POSS-like behavior they showed, and vice versa. Even when the PAMAM core contributed to more than two-thirds of the hybrid molecular weight (e.g., at as low as 12.5% NH_2 dendrimer end groups substitution with POSS cages), the resulting hybrids showed typical POSS-like behavior by being soluble in $CHCl_3$, in which PAMAMs are not soluble, while being insoluble in MeOH and NMP, which are good solvents for PAMAM dendrimers. This clearly indicates that POSS cages are predominantly located at the outer surfaces of these hybrids and provide the principal mode of their interaction with the surrounding environments.

While hybrids with lower POSS content (i.e., below 50% dendrimer end group substitution) showed "PAMAM-like" glass transition temperatures, indicating segmental mobility inside the dendrimer cores, their higher substituted derivatives did not. The lack of a clearly resolved glass transition temperature was either caused by the crowding of dendrimer surfaces with closely packed POSS cages and the consequent stiffening of the dendrimer interior segments, or it was due to the "dilution" of PAMAM-like character in the heavily POSS-dominated hybrids. Accordingly, the higher POSS-containing hybrids also showed melting temperatures that are generally not found in dendrimers and that, therefore, indicate ordering of the POSS cages in either intra- or intermolecular crystalline domains. Contributing further support to the view that the latter was an exclusively POSS-associated property, these melting temperatures were largely independent of the degree of dendrimer core substitution.

As expected, the hybrids' thermal degradation behavior was dominated by their less-stable PAMAM component. In fact, their volatilization, coupled with almost complete loss of organic content, also carried away a small but finite fraction of the original silica component. Since PAMAM degradation proceeds at significantly lower temperatures than that of the POSS cages, it is conceivable that by controlling heating conditions it should be possible to design a thermal treatment procedure that will produce closed nanoporous silica structures starting from these hybrids. In principle, such procedures would be highly desirable because the covalent nature of these hybrids would eliminate the usual agglomeration and phase separation problems generally associated with the more common physically mixed two-component systems.

The controlled introduction of alkoxysilyl functional groups into these dendrimer−POSS core−shell hybrids enables their convenient cross-linking into 3D nanodomained films or coatings. Coupled with the above-described degradation behavior this further emphasizes the potential applications of these hybrids for the preparation of precise nanoporous structures. Other application possibilities include metal-encapsulated nanocomposites (for which PAMAM and PAMAMOS dendrimers are already very well-known) and a variety of tailor-made, 1−10 nm diameter, POSS-like filler particles, the mechanical properties of which would depend on the chemical composition and generation of the dendrimers used.

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