Nanostructured Dendrimer-Based Networks with Hydrophilic Polyamidoamine and Hydrophobic Organosilicon Domains

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ABSTRACT: Covalently cross-linked, three-dimensional nanodomained networks were prepared from radially layered poly(amidoamine−organosilicon) (PAMAMOS) copolymeric dendrimers containing hydrophilic polyamidoamine (PAMAM) interiors and reactive hydrophobic organosilicon (OS) exteriors. Two different types of curing chemistries were used, including (a) a sol−gel-type hydrolysis of alkoxysilyl-terminated dendrimers followed by a silanol condensation reaction and (b) irradiation or heat-induced, free-radical double-bond opening of vinylsilyl- or allylsilyl-terminated dendrimers, followed by free-radical coupling into carbosilane bridges. The first-mentioned process was investigated in more detail by monitoring the time-dependent weight loss, the glass transition temperatures (T_g), and the FT-IR spectroscopy of the resulting products. The effects of various coreagents, including acryloyldimethoxymethylsilane (DMOMS), tetraethoxysilane (TEOS) and α,ω-telechelic poly(dimethylsiloxane) disilanol (PDMS), on the structures and properties of the resulting networks, especially their T_g's, were examined. It was found that, by varying the type of the PAMAMOS dendrimer network precursor, the type and relative amount of the coreagent, and the set of curing conditions used, different films, sheets, and coatings can be obtained. These were characterized by contact angle measurements, AFM, SEM, EDS, XPS, SANS, and SAXS analyses. The results obtained revealed smoothness at the nanoscopic level and low surface energy of these network materials and confirmed uniform distribution of well-defined hydrophilic PAMAM domains within the hydrophobic OS matrixes. Most importantly, sizes and shapes of these nanoscopic domains can be controlled by the selection of dendrimer network precursors and by conditions applied to the network formation.

Introduction

During the past two decades, polymers with dendritic molecular architecture, particularly their most regular representatives, dendrimers, have attracted outstanding scientific attention because of their unprecedented structure, properties (including physical, chemical, and biological), and a variety of intriguing potential applications.[1a−q] Recently, we described a new family of radially layered copolymeric poly(amidoamine−organosilicon) (PAMAMOS) dendrimers that combine hydrophilic polyamidoamine (PAMAM) molecular interiors and hydrophobic organosilicon (OS) exteriors.[2,3] Among them, those with chemically inert end groups, such as trimethylsilyl or trimethylsiloxy units, were found to behave like covalently bonded inverted unimolecular micelles[4] and exhibit very interesting and useful surface activity,[5,6] while those with reactive functional end groups, such as vinylsilyl, allylsilyl, or alkoxysilyl, represent unique nanoscopic building blocks that open a variety of new synthetic avenues for preparation of more complex dendrimer-based structures,[7,8] including novel nanostructured materials, such as three-dimensional nanodomained networks.[9−12]

In general, dendrimer networks may be viewed as assemblies of covalently or noncovalently connected dendrimer building blocks (i.e., network precursors). They may be random (i.e., of uncontrolled *inter*-dendrimer connectivity) or ordered (i.e., of controlled *inter*dendrimer connectivity), depending on whether the precursor dendrimers were connected in an "unsystematic" way (e.g., by simple one-pot-type reactions) or in a "precisely juxtaposed" manner.[13] In either case, they represent the next level in the hierarchical order of nanoscale structural complexity of the organization of matter from single dendrimers and, therefore, the next step in the bottom-up construction of nanostructured materials, components, and ultimately objects.[14−17] However, although the importance of dendrimer-based networks has been realized and a variety of methods have been suggested for their construction,[13] no examples of such materials with controlled nanodomained structure have been reported. One of the reasons for this is the fact that, in a few of the attempts described,[18−20] only "homopolymeric" dendrimer precursors were used, providing no opportunity for the systematic control of spatial domain distribution. In contrast, we here describe dendrimer-based networks that are true compositionally nanodomained materials at the supramolecular level of structural organization due to the unique radially copolymeric nature of their PAMAMOS precursors.[2,9−12] These networks can be prepared by cross-linking of alkoxysilyl and/or vinylsilyl functionalized PAMAMOS dendrimers, and depending on the dendrimer selected, the composition of their OS domains may be varied from the siloxane to carbosilane, while the domain sizes and shapes may be predetermined by the choice of the reagents used in the preparation of precursor dendrimers. These sizes may vary from about 1 to about 13 nm for the hydrophilic PAMAM domains and between 1 and 5 nm for the hydrophobic (i.e., oleophilic) OS domains. As a result, a variety of new dendrimer-based materials that have well-organized three-dimensional nanostructures can be obtained, providing unique combinations of highly desirable physical and chemical properties and great promise for a variety of unprecedented applications in nanotechnology.

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Experimental Section

Materials. Polyamidoamine (PAMAM) dendrimers[1n] were obtained as methanol (MeOH) solutions from Dendritech, Inc., Midland, MI. For the synthesis of PAMAMOS−DMOMS and PAMAMOS−TMOS (for PAMAMOS dendrimer nomenclature see the beginning of the Results and Discussion section), these dendrimers were used without any further purification, while for the synthesis of PAMAMOS−DMVS they were first lyophilized under vacuum for 12−24 h depending on the amount required. (3-Acryloxypropyl)dimethoxymethylsilane (DMOMS), (3-acryloxypropyl)trimethoxysilane (TMOS), and chloromethyldimethylvinylsilane (DMVS) were obtained from Gelest and used without further purification. Tetraethoxysilane (TEOS), α,ω-telechelic poly(dimethylsiloxane) disilanol (PDMS), having declared weight-average molecular weight of 1000 (corresponding to an average degree of polymerization of about 12), 2,2′-azobis(isobutyronitrile) (AIBN), and benzoyl peroxide (BP) were obtained from Aldrich and used without further purification.

Synthesis. All PAMAMOS dendrimers were synthesized from amine-terminated PAMAMs. PAMAMOS−DMOMS, containing $-(CH_2)_2-C(O)O-(CH_2)_3-Si(CH_3)(OCH_3)_2$ end groups, and PAMAMOS−TMOS, containing $-(CH_2)_2-C(O)O-(CH_2)_3-Si(OCH_3)_3$ end groups, were prepared by Michael addition reaction of PAMAMs and silicon-containing acrylates, DMOMS and TMOS, respectively. PAMAMOS−DMVS dendrimers were prepared by haloalkylation of PAMAMs with commercial chloroalkylsilanes or iodoalkylsilanes made in situ. In all cases, the preparations followed our previously described procedures.[3]

Preparation of Networks from PAMAMOS−DMOMS Dendrimers. Films were cast from about 2 g of 20% PAMAMOS-[*x*,1]-DMOMS ($x = 0-5$) dendrimer solutions in MeOH in a plastic pan of 2.5 cm internal diameter. First, MeOH solvent was evaporated overnight at 25 °C under nitrogen, and then the solvent-free sample was cured at a selected temperature for a desired period of time in an oven that was open to atmosphere.

Preparation of Networks from Mixtures of PAMAMOS-[3,1]-DMOMS Dendrimers and DMOMS Acrylate. Films were cast from about 2 g of 20% PAMAMOS-[3,1]-DMOMS dendrimer solutions in MeOH containing 0, 10, 20, 30, 40, and 60 mol % excess DMOMS acrylate (relative to the amount of PAMAM NH groups used in the PAMAMOS synthesis) in a plastic pan of 2.5 cm internal diameter. Following an overnight evaporation of MeOH solvent under nitrogen at 25 °C, the solvent-free samples were cured with atmospheric moisture for 100 h at 60 °C. The DMOMS-free sample was obtained by ultrafiltration from a standard reaction mixture containing 20 mol % excess DMOMS acrylate. Ultrafiltration was performed in a 600 mL cell with three consecutive passes of respective MeOH/dendrimer solutions through a Millipore YM3 regenerated cellulose membrane having nominal cutoff molecular weight value of 3000. The sample with 10% excess DMOMS was prepared by adding the required amount of DMOMS acrylate to the DMOMS-free PAMAMOS−DMOMS solution, while samples with 30, 40, and 60% excess DMOMS acrylate were prepared by adding the required amounts of this reagent to the standard PAMAMOS−DMOMS solution containing 20 mol % excess DMOMS acrylate.

Preparation of Networks from Mixtures of PAMAMOS-[3,1]-DMOMS Dendrimers and Tetraethoxysilane (TEOS). Films were cast from about 2 g of 20% PAMAMOS-[3,1]-DMOMS dendrimer solutions in MeOH containing 10, 20, and 40 wt % of TEOS in a plastic pan of 2.5 cm internal diameter. Following an overnight evaporation of MeOH solvent under nitrogen at 25 °C, the solvent-free samples were cured with atmospheric moisture for 100 h at 60 °C.

Preparation of Networks from Mixtures of PAMAMOS-[3,1]-DMOMS Dendrimers and α,ω-Telechelic Poly(dimethylsiloxane) Disilanol (PDMS). Films were cast from about 2 g of 20% PAMAMOS-[3,1]-DMOMS dendrimer solutions in MeOH containing 10, 20, and 40 wt % of PDMS disilanol (having a weight-average molecular weight, M_w, of 1000, corresponding to an average degree of polymerization of about 12) in a plastic pan of 2.5 cm internal diameter. Following an overnight evaporation of MeOH solvent under nitrogen at 25 °C, the solvent-free samples were cured with atmospheric moisture for 100 h at 60 °C.

Preparation of Networks from PAMAMOS−TMOS Dendrimers. Films were cast from about 2 g of 20% PAMAMOS-[*x*,1]-TMOS ($x = 2$ and 5) dendrimer solutions in MeOH in a plastic pan of 2.5 cm internal diameter. Following an overnight evaporation of MeOH solvent under nitrogen at 25 °C, the solvent-free samples were cured with atmospheric moisture for 100 h at a selected temperature.

Preparation of Networks from PAMAMOS−DMVS Dendrimers. From PAMAMOS-[*x*,1]-DMVS ($x = 3$ and 4) dendrimers, networks were prepared by both UV and heat curing in the presence of free radical initiators, AIBN or BP. Films were cast from about 2 g of 20% PAMAMOS-[*x*,1]-DMVS dendrimer solutions in MeOH containing between 1 and 1.5 wt % of initiator (relative to the dendrimer amount) in a plastic pan of 2.5 cm internal diameter. Following an overnight evaporation of solvent under nitrogen at 25 °C, the solvent-free samples were cured for 100 h either with exposure to UV at 25 °C or without exposure to UV at 60 °C. PAMAMOS-[*x*,1]-DMVS dendrimers prepared by iodoalkylation of amine-terminated PAMAMs exhibited the ability to self-cure without added initiator.

Methods. For UV irradiation, a Spectroline UV pen, model 11SC-10P, operating at 254 nm was used. Glass temperatures (T_g) of the networks were measured by differential scanning calorimetry (DSC) using a Dupont Instruments model 912 unit. Measurements were performed between −80 and 80 °C, with about 10 mg samples at a heating rate of 10 °C/min. Infrared spectra were recorded on a Nicolet 20DXB FT-IR spectrophotometer to monitor the curing process. Samples were prepared by casting a PAMAMOS solution on a NaCl plate followed by solvent evaporation under nitrogen at 25 °C and curing under various conditions. Samples for atomic force microscopy (AFM) were prepared by casting the dendrimer solution on a mica support followed by curing under atmospheric conditions. The samples were examined using a tapping mode of imaging in a TopoMetrix 2000 Discoverer instrument under ambient conditions. Si probes having a spring constant of ca. 30 N/m were used at a resonance frequency of ca. 200−300 kHz. A 7 μm scanner calibrated by TopoMetrix was used. Contact angle data were collected using a VCA 2000 video contact angle system from Advanced Surface Technology, Inc. Dendrimer network surfaces were rinsed with MeOH and blown-dry with clean air before measurements were made. Quasi-equilibrium advancing contact angles were determined using the sessile drop technique, allowing a 30 s equilibration period before measurement. Distilled, deionized water, methylene iodide, and *n*-hexadecane were used as the contact angle test liquids. Average values from both sides of at least five drops on different positions on the surface were used in calculating surface energy from the Owens−Wendt geometric-mean approach.[21] Scanning electron microscopy (SEM) was carried out with the JEOL JSM-6100 instrument. Samples were coated with carbon prior to examination to prevent charging effects. A Noran Voyager III EDS system was used to collect energy dispersive spectroscopy (EDS) data. A Kratos Analytical AXIS 165 X-ray photoelectron spectroscopy (XPS) instrument equipped with a monochromatic Al Kα X-ray source was used to obtain XPS spectra. An electron source for surface charge compensation was employed, and data were collected in the normal angle mode (0° stage angle). This gives the maximum probe depth on the order of 8−10 nm. The SANS experiments were performed at the National Institute of Standards and Technology, and the procedure used is described elsewhere.[22]

Results and Discussion

Representative examples of radially layered PAMAMOS dendrimers with reactive end groups for network

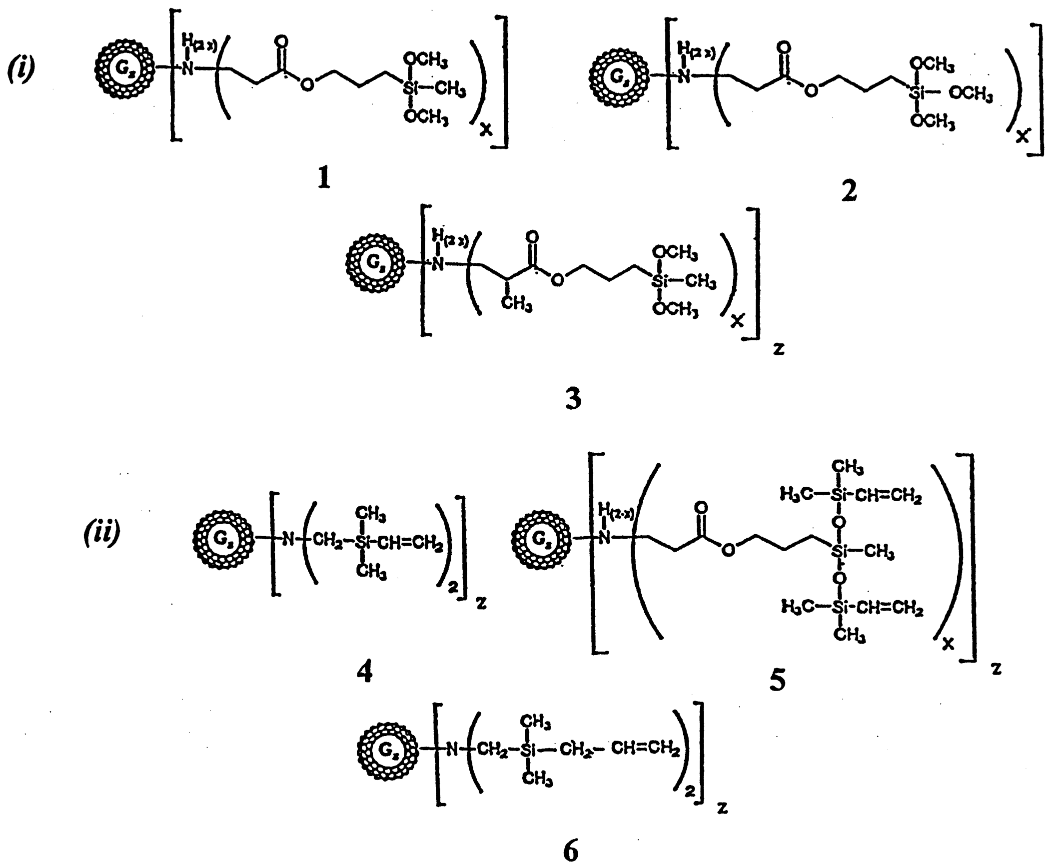


Figure 1. Representative examples of cross-linkable PAMAMOS dendrimers. Alkoxysilyl functionalized derivatives (i) are useful for silanol condensation reactions following the water hydrolysis, while those with unsaturated silyl functionalities (ii) can be cross-linked with free radical initiators.

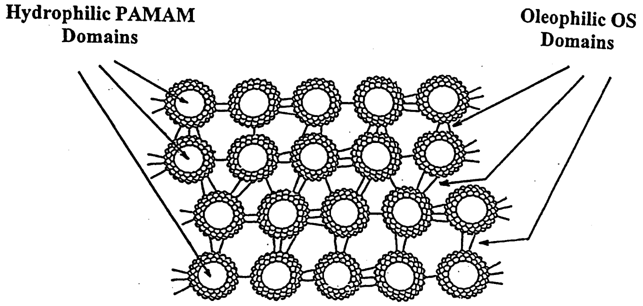
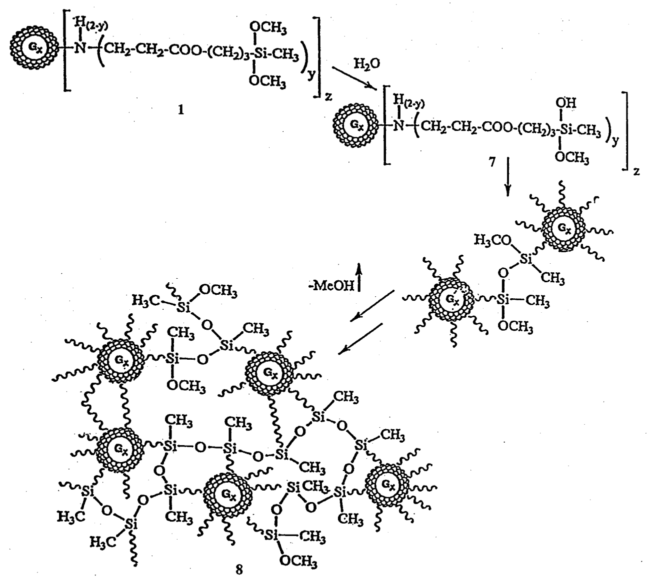


Figure 2. Schematic illustration of a cross section of idealized PAMAMOS dendrimer-based networks. Rounded contours represent spheroidal hydrophilic/nucleophilic polyamidoamine (PAMAM) domains that may range in increments of about 1 nm between 1 and 15 nm in diameter, while connecting lines depict intermeshed organosilicon (OS) domains that may range from about 1 to 5 nm.

Scheme 1



formation are shown in Figure 1. These dendrimers may be prepared from amine-terminated PAMAM precursors either by Michael addition to silicon-containing acrylates (dendrimers **1**−**3** and **5**) or by haloalkylation with chloro- or iodoalkylsilanes (dendrimers **4** and **6**) following procedures described in our previous report.[3] The nomenclature used in this figure and throughout this paper utilizes the generic abbreviation PAMAMOS-[*x*,*y*]-XYZ, where *x* denotes the generation of the PAMAM precursor from which the respective PAMAMOS dendrimer was prepared, *y* defines the number of OS branch cell layers in the PAMAMOS dendrimer exterior, and XYZ specifies the type of PAMAMOS end groups. Thus, DMOMS refers to dimethoxymethylsilyl, $-Si(CH_3)(OCH_3)_2$, end groups, TMOS to trimethoxysilyl, $-Si(OCH_3)_3$, end groups, and DMVS to dimethylvinylsilyl, $-Si(CH_3)_2(CH{=}CH_2)$, end units.

Depending on the nature of the reactive end groups, PAMAMOS dendrimers may be cross-linked with or without addition of curing agents, catalysts, or coreagents to form three-dimensional, covalently bonded, nanostructured networks containing well-defined hydrophilic PAMAM and hydrophobic OS domains, as schematically represented in Figure 2. The sizes of these domains and the properties of the resulting networks depend on a

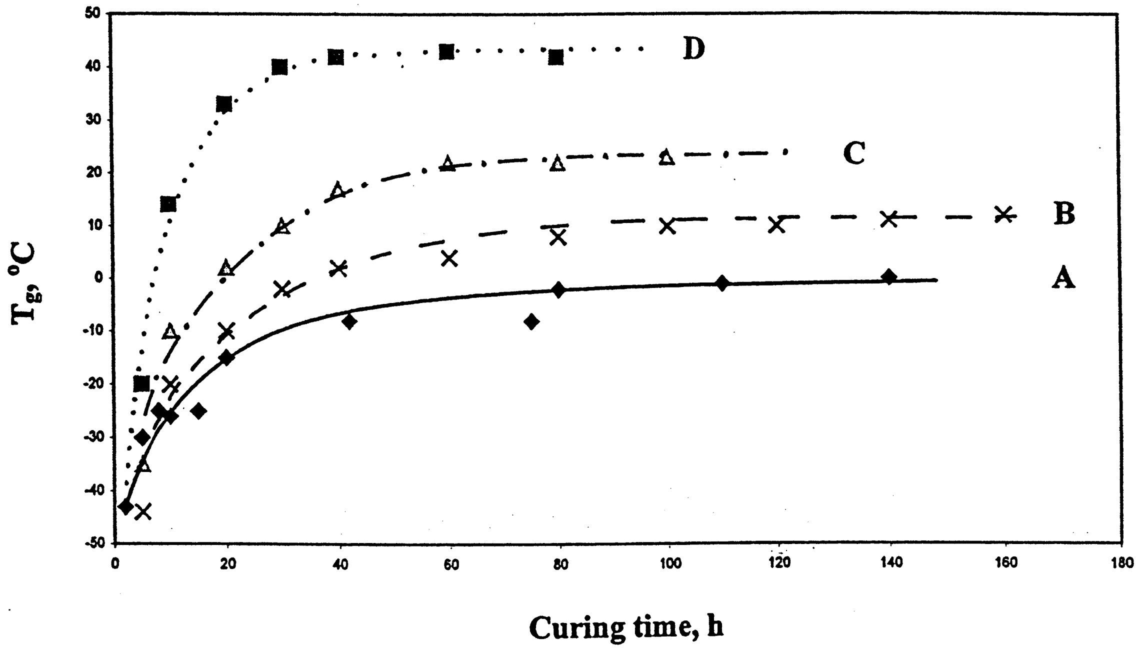


Figure 3. Dependence of T_g's of PAMAMOS-[3,1]-DMOMS networks on the extent of curing (i.e., the cross-linking reaction time). Curing was in air at (a) 25, (b) 60, (c) 80, and (d) 100 °C. Data are from the second DSC scan at a heating rate of 10 °C/min.

number of different compositional, structural, and processing factors, including the type of organosilicon reagent and the generation of PAMAM dendrimer used in the PAMAMOS synthesis; the number of OS branch cell layers in the PAMAMOS dendrimer network precursor; the type and the relative amount of cross-linking agent, catalyst, coreagent, and any additive used in the network formation; the reaction conditions employed in the curing process, etc. Clearly, a wide variety of different networks with correspondingly different properties can be produced by appropriate selection of these parameters.

Networks from Methoxysilyl Functionalized PAMAMOS Dendrimers. Cross-linking chemistry for the formation of nanodomained networks from methoxysilyl functionalized PAMAMOS dendrimers, such as **1**−**3** of Figure 1, is a sol−gel process[23,24] illustrated in Scheme 1.

The preparation involves casting from a solution of precursor dendrimer in an appropriate solvent, such as MeOH, wherein the solvent is first evaporated at 25 °C and then the dendrimer is exposed to moisture under selected reaction conditions for a desired period of time. During the process, the network formation proceeds through two consecutive reaction steps: (a) a water hydrolysis of methoxysilyl dendrimer end groups to the corresponding silanols and (b) a condensation of these silanol intermediates to form siloxane bridges. The second step is self-catalyzed by the basic PAMAM interior of the PAMAMOS network precursor, and the process is easily accomplished either by direct exposure of PAMAMOS dendrimer to atmospheric moisture or by controlled addition of water, either in the form of vapor (for example, in a controlled humidity chamber) or as liquid.[2,9−12,25] However, while participation of water is absolutely necessary for the reaction to occur, the required amounts are only very small. For example, while solvent-free PAMAMOS-[3,1]-DMOMS stored under nitrogen at 25 °C typically remains sticky and completely soluble in MeOH even after 1 month, when exposed to atmospheric moisture at 25 °C, this same dendrimer forms insoluble, self-supporting films after only 5 days. This is consistent with the chain character of the curing process where water used in the hydrolysis of methoxysilyl groups is regenerated in the silanol condensation reaction. As a result, much smaller than stoichiometric amounts of water are needed for complete curing.

A number of methods have been used for monitoring the progress of this process, including recording of the time-dependent weight loss of the cross-linking samples, increase of T_g of the resulting networks, and FT-IR analysis of the cross-linking samples. Of these, the time-dependent weight loss of a curing sample after initial evaporation of the solvent medium is caused by the liberation of MeOH byproduct from the cross-linking reaction (see Scheme 1), while the increase in T_g of the forming network results from the increase in its cross-link density. Consequently, while the former reflects the kinetics of the formation of silanol intermediates **7** from methoxysilyl PAMAMOS precursor **1**, the latter results from the establishment of *inter*dendrimer siloxane bonds **8**. Unfortunately, although the weight-loss method appears appealingly easy to perform, in reality it becomes inapplicable beyond a certain stage of curing when changes in sample weight become too small to measure. For example, when about 1 g sample of PAMAMOS-[3,1]-DMOMS dendrimer was cured with atmospheric moisture at 25 °C, this detection limit was reached after only 5 days of curing, although under these conditions the cross-linking reaction continues for several months as evidenced by the continuous increase in the resulting network T_g, as shown in Figure 3a.

Figure 3 shows the effect of curing time and temperature on T_g's of networks prepared by cross-linking PAMAMOS-[3,1]-DMOMS dendrimers with atmospheric moisture. It can be seen from this figure that both the curing rate and the corresponding T_g's increased with curing temperature. The higher T_g's correspond to the higher cross-linking densities of the resulting networks, consistent with the observed increase in their mechanical strength and decrease in flexibility.

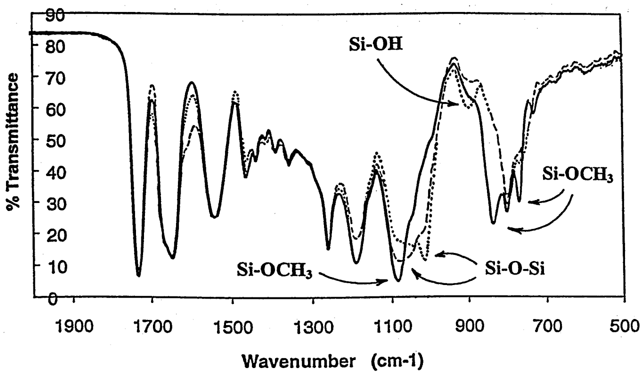


Figure 4. FTIR monitoring of the course of network formation from PAMAMOS-[3,1]-DMOMS dendrimer precursor. (a) Solid line: solvent free dendrimer 1 of Scheme 1. (b) Dotted line: partially cured sample 7 of Scheme 1. (c) Dashed line: fully cured network 8 of Scheme 1.

Table 1. T_g's of PAMAMOS-[*x*,1] Dendrimer Networks, Their PAMAMOS-[*x*,1]-DMOMS Precursors, and the Corresponding PAMAM Dendrimers

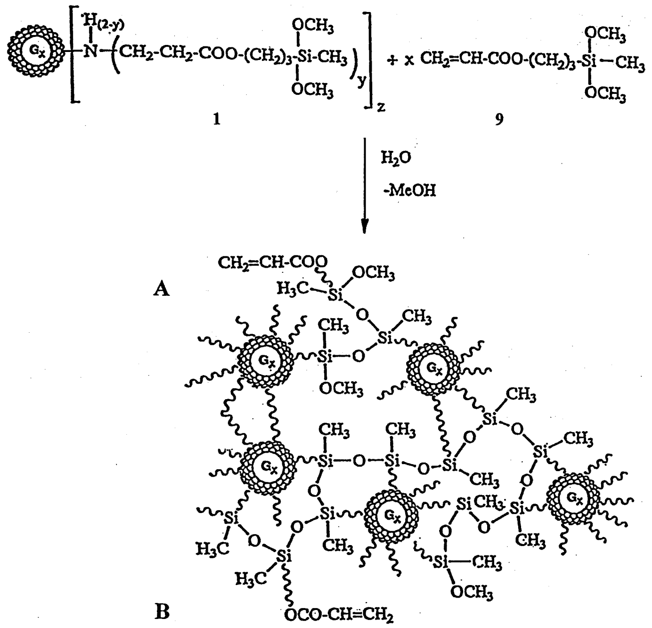
generation, *x*	PAMAM dendrimer, T_g (°C)	PAMAMOS-[*x*,1]-DMOMS dendrimer, T_g (°C)	PAMAMOS-[*x*,1] network, T_g (°C)[a]
0	−11	−57	−1
1	−3	−52	3
2	0	−48	6
3	11	−46	10
4	14	−41	11
5	14	−38	13

[a] All samples were cured 100 h at 60 °C.

The upper limit for the curing temperature of PAMAMOS dendrimer networks is predetermined by the thermooxidative stability of their PAMAM interiors, and it corresponds to about 140 °C for longer (i.e., more than 1 h) exposure times.[3,4] In principle, efficient curing can be achieved between about 60 and 100 °C, and stable T_g products may be obtained within several days of reaction time.[2,11] For example, when PAMAMOS-[3,1]-DMOMS was cured at 100 °C, the T_g plateau of curve d in Figure 3 was reached after about 30 h, indicating that cross-linking was essentially complete. At 80 °C, this required about 60 h of curing time, while at 60°C, as many as 100 h was needed.

As shown in Figure 4, monitoring of the PAMAMOS-[3,1]-DMOMS cross-linking reaction by FT-IR spectroscopy confirmed the chemistry presented in Scheme 1. In a typical experiment, a thin film of the dendrimer precursor **1** was cast on a NaCl plate, and after 30 h of solvent evaporation in N_2 atmosphere at 25 °C, spectrum a of Figure 4 was obtained. It showed strong absorptions at 1090, 840, and 760 cm^{-1}, corresponding to $Si-OCH_3$ stretching and bending. Following this, the sample was exposed to curing by atmospheric moisture, first at 60 °C for 30 h and then at 100 °C for another 30 h. After the first heating phase, the obtained spectrum (b in Figure 4) clearly indicated partial cross-linking by the appearance of the absorption band at 900 cm^{-1}, corresponding to the stretching vibrations of Si−OH groups formed by hydrolysis of the starting $Si-OCH_3$ dendrimer end groups (see structure **7** of Scheme 1). After the second heating stage, however, this Si−OH absorption disappeared, and the fully cured sample (structure **8** of Scheme 1) showed only absorption bands at 1050 and 1000 cm^{-1}, corresponding to Si−O−Si stretching (spectrum c of Figure 4). Expectedly, absorptions at 1275 and 800 cm^{-1}, which are attributed to $Si-CH_3$ stretching and bending, respectively, did not change during the course of the curing process.

Scheme 2



Effect of Domain Size on the T_g of Networks from PAMAMOS-[*x*,1]-DMOMS Dendrimers. The effect of the relative size of the hydrophilic PAMAM domains on the T_g's of PAMAMOS dendrimer networks was examined for a series of samples prepared from PAMAMOS-[*x*,1]-DMOMS precursors having *x* values ranging from 0 to 5. All samples were cured by exposure to atmospheric moisture for 100 h at 60 °C, and the results obtained are listed in Table 1.

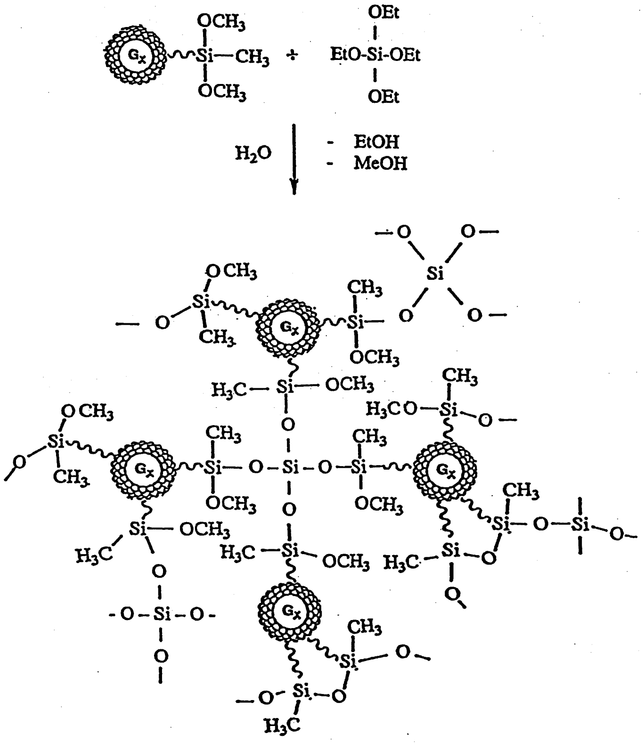
It can be seen from this table that replacement of primary NH_2 PAMAM end groups with extended $-(CH_2)_2-C(O)O-(CH_2)_3-Si(CH_3)(OCH_3)_2$ OS units caused a significant decrease in the resulting PAMAMOS dendrimer T_g's which ranged from 46 °C for [0,1] derivative to as much as 57 °C for a generation [3,1] dendrimer. This trend clearly reflects the "flexibilizing" character of OS units, probably resulting both from their $(CH_2)_x$ segments and the outermost Si−O bonds. Furthermore, it can also be seen from this table that, similar to the behavior of both PAMAM and uncured PAMAMOS−DMOMS dendrimers, the T_g's of the corresponding PAMAMOS dendrimer networks also increased with increasing size of their PAMAM domains (i.e., with increasing generation of the PAMAM dendrimer used for the preparation of the respective PAMAMOS network precursor). However, this increase was clearly less for networks than for both dendrimer families, so that while the T_g of PAMAMOS-[0,1] network was −1 °C (compared to −57 °C for its PAMAMOS-[0,1]-DMOMS precursor and −11 °C for the PAMAM from which the former was prepared), the T_g of the [5,1] network was 13 °C (compared to −38 °C for its PAMAMOS precursor and 14 °C for the corresponding generation 5 PAMAM dendrimer). In fact, the T_g's of PAMAMOS networks were higher than the T_g's of the corresponding PAMAMs for all generations lower than 3 and became equal to or slightly lower than those for generation 3 and higher. This indicates that T_g's of these dendrimer networks were strongly dependent on both PAMAM and OS domains, but while the former

Table 2. Effect of DMOMS Acrylate on the T_g's of PAMAMOS-[3,1]-DMOMS Networks[a]

sample	DMOMS content (mol %)[b]	network T_g (°C)
1	0	18
2	10	15
3	20	10
4	30	0
5	40	−13
6	60	−22

[a] All samples were cured at 60 °C for 100 h. [b] Excess amounts relative to the number of end groups in idealized dendrimer structure.

Scheme 3



dictated the overall trend of the dependence, the latter (the size of which remained constant throughout the examined PAMAMOS-[*x*,1] series) caused the lessening of the T_g increase that results from the increasing size (i.e., generation) of the PAMAM domains.

Interestingly, in all cases, T_g's of the networks were significantly higher than the T_g's of the corresponding non-cross-linked dendrimer precursors. This is somewhat surprising, since it is well-known that highly flexible siloxane, Si−O−Si, bonds usually decrease T_g's of the copolymers in which they are incorporated, and in this particular case, these bonds are formed only upon network formation (compare structures **7** and **8** of Scheme 1).[26] Therefore, this behavior seems to be dominated by reduced segmental mobility resulting from the cross-linking of precursor dendrimers into the covalently (i.e., permanently) bonded three-dimensional network, rather than by the effect of their intrinsic chemical composition.

Effect of the Composition of Cross-Linking Reaction Mixture on the T_g of Networks from PAMAMOS-[*x*,1]-DMOMS Dendrimers. Expectedly, composition of the cross-linking reaction mixture and thus the fine structure (i.e., composition) of the resulting network exerts significant influence on the properties of the latter. This study was particularly focused on the effects of coreagents, such as nondendrimer bound (i.e., unreacted) DMOMS acrylate, tetraethoxysilane (TEOS), and α,ω-telechelic poly(dimethylsiloxane) disilanols (PDMS).

a. Effect of DMOMS Acrylate. The effect of the presence of non-dendrimer bound DMOMS acrylate (**9** in Scheme 2) in a PAMAMOS−DMOMS dendrimer cross-linking reaction mixture on the properties of the resulting networks was very important because, as described in the preceding section, our typical network preparation procedure utilized reaction mixtures obtained directly from the synthesis of the PAMAMOS−DMOMS precursor without any subsequent work-up, dendrimer isolation, or purification. Since typical PAMAMOS−DMOMS synthesis involves up to about a 20 mol % excess of DMOMS acrylate over the stoichiometrically required quantity,[3,27] unreacted DMOMS acrylate is always present in such cross-linking systems, and its methoxysilyl groups are expected to participate in the cross-linking reaction together with their dendrimer counterparts.

As shown in Scheme 2, DMOMS acrylate may be incorporated into the cross-linking PAMAMOS dendrimer network forming dangling acrylate, $-C(O)-CH{=}CH_2$, end groups (A or B in Scheme 2), which not only provide potentially useful reactive sites for further chemical utilization but also act as structural defects (i.e., imperfections) in ideal network connectivity and exert influence on the T_g's of the resulting products. Therefore, to evaluate the magnitude of this effect on network T_g's, a series of PAMAMOS-[3,1]-DMOMS networks were prepared from reaction mixtures containing 10, 20, 30, 40, and 60 mol % excess of DMOMS acrylate relative to the number of end groups in idealized dendrimer structure (i.e., idealized number of PAMAM NH groups used in the PAMAMOS synthesis). The samples were cured with atmospheric moisture for 100 h at 60 °C, and their resulting T_g's are listed in Table 2. The DMOMS-free sample of this series was prepared by ultrafiltration of a standard PAMAMOS-[3,1]-DMOMS reaction mixture containing 20 mol % excess of DMOMS acrylate. The sample with 10 mol % excess DMOMS acrylate was prepared by adding the required amount of DMOMS acrylate to the DMOMS-free sample, while samples with 30, 40, and 60% excess DMOMS acrylate were prepared by adding the required amounts of the reagent to the standard sample containing 20 mol % excess DMOMS acrylate.

It can be seen from this table that an increase in the content of DMOMS acrylate in PAMAMOS−DMOMS cross-linking reaction mixture resulted in a decrease in the T_g's of the resulting networks, indicating increased mobility of network segments due to the presence of acrylate dangling end groups. This is consistent with the acrylate groups remaining unreactive under the cross-linking conditions, rendering DMOMS effectively difunctional and able to either incorporate into the network as a mono-connected chain end (A of Scheme 2 if only one of its methoxysilyl groups undergoes reaction) or act as a linear spacer between two adjacent dendrimers (B of Scheme 2 if both methoxysilyl groups undergo reaction). In either case, incorporation of DMOMS into the PAMAMOS network reduces overall cross-linking density and hence lowers the resulting T_g. Note, however, that in the 60 mol % excess DMOMS sample incorporation of DMOMS was incomplete, and a fraction remained dispersed within the network

Scheme 4

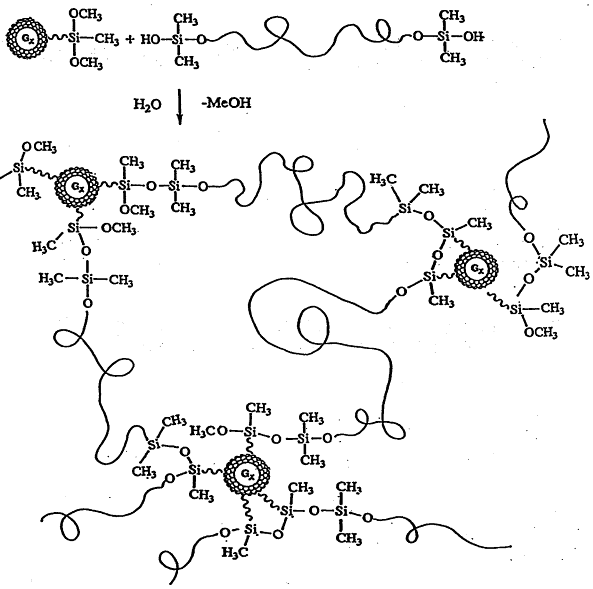


Table 3. T_g's of Networks Prepared from PAMAMOS−TMOS Dendrimers[a]

	T_g, °C		
dendrimer precursor	curing at 25 °C	curing at 60 °C	curing at 80 °C
PAMAMOS-[2,1]-TMOS	27	42	51
PAMAMOS-[5,1]-TMOS	34	48	55

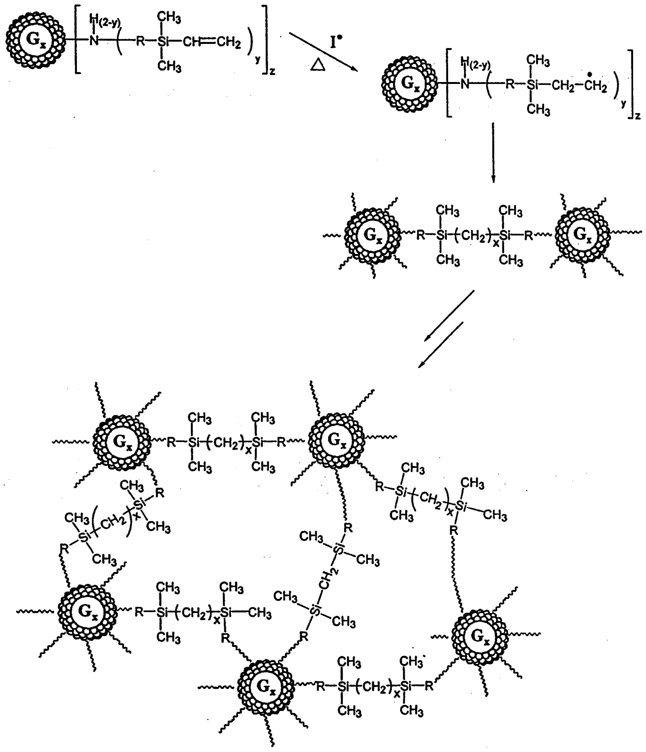
[a] All samples were cured for 100 h.

matrix as a liquid plasticizer. Consequently, the T_g of this sample was probably lower than it would have been if covalent bonding was complete and partial phase separation did not occur.

b. Effect of Tetraethoxysilane (TEOS). To evaluate the ability of small molecular weight multifunctional cross-linking agents to increase the cross-link density of PAMAMOS dendrimer networks, a series of samples were prepared from mixtures containing 10, 20, and 40 wt % of TEOS in PAMAMOS-[3,1]-DMOMS. As in other cases, curing of these samples was also performed with atmospheric moisture for 100 h at 60 °C, to yield networks having T_g's of 25, 32, and 33 °C, respectively. Compared to the T_g of 10 °C characteristic for the base PAMAMOS-[3,1] network prepared without TEOS, these values showed an increase in T_g's which leveled off between about 20 and 40 wt % TEOS. These results are consistent with the expected increase in the degree of network cross-linking resulting from the chemistry of TEOS incorporation shown in Scheme 3.

c. Effect of α,ω-Telechelic Poly(dimethylsiloxane) Disilanol (PDMS). To contrast the effect of TEOS and examine the ability of long-chain *inter*dendrimer connectors to reduce the cross-linking density and increase the overall network flexibility, a series of samples were prepared from mixtures containing 10, 20, and 40 wt % of α,ω-telechelic PDMS disilanol (having a M_w of 1000, corresponding to an average degree of polymerization of about 12) in the standard PAMAMOS-[3,1]-DMOMS dendrimer. Curing of these samples was performed as usual with atmospheric moisture for 100 h at 60 °C. Unexpectedly, microphase separation of an oily phase was observed in networks obtained from reaction mixtures containing 20 and 40 wt % PDMS, but the T_g values for the products were expectedly lower than that of the corresponding network without PDMS, equaling −15, −20, and −22 °C. Apparently, the compatibility limit of the two components was achieved at approximately 20 wt % PDMS, and further increase in its content did not affect the network T_g. A schematic representation of the structure of this type of network is shown in Scheme 4.

Scheme 5



Networks from PAMAMOS-[*x*,1]-TMOS Dendrimers. To further examine the effect of cross-link density on the T_g's of PAMAMOS dendrimer networks, a series of samples were prepared from PAMAMOS-[*x*,1]-TMOS precursors (**2** of Figure 1) having three methoxy groups at every terminal silicon atom and values of *x* equal to 2 and 5. Table 3 shows T_g's of the networks obtained from these PAMAMOS-[2,1]-TMOS and PAMAMOS-[5,1]-TMOS dendrimers by exposure to atmospheric moisture for 100 h at 25, 60, and 80 °C. Expectedly, these T_g's were higher than those of the corresponding DMOMS derivatives (compare with values of Table 1), but interestingly, the generational effect (i.e., the T_g difference between the corresponding samples of the DMOMS and TMOS series) appears to be the same.

It was also observed that, under comparable reaction conditions, the cross-linking of PAMAMOS−TMOS networks was considerably faster than that of the corresponding PAMAMOS-[*x*,1]-DMOMS derivatives. For example, formation of a network from PAMAMOS-[2,1]-TMOS at 25 °C was completed (as judged by the leveling off of its T_g value) in only 4 days instead of several months that is typically needed for the similarly complete cross-linking of its PAMAMOS-[2,1]-DMOMS homologue.

Networks from Vinylsilyl Functionalized PAMAMOS-[*x*,1]-DMVS Dendrimers. An alternative synthetic approach to PAMAMOS dendrimer networks involves cross-linking precursors having unsaturated end groups, such as vinyl or allyl, shown as structures **4**−**6** of Figure 1. This may be accomplished by a variety

Table 4. T_g's of Networks Prepared from PAMAMOS-[*x*,1]-DMVS Dendrimers[a]

sample	dendrimer preparation method[b]	% DMVS end groups	curing initiation[c]	curing temp, °C	T_g (°C) of dendrimer precursors	T_g (°C) of the resulting networks
[3,1]	chloroalkylation	67	UV/AIBN	25	14	18
[3,1]	chloroalkylation	67	heat/BP	60	14	20
[3,1]	iodoalkylation	81	UV/AIBN	25	15	20
[3,1]	iodoalkylation	81	heat	60	15	20
[3,1]	iodoalkylation	81	heat/BP	60	15	22
[4,1]	chloroalkylation	62	UV/AIBN	25	15	18
[4,1]	chloroalkylation	62	heat/BP	60	15	21
[4,1]	iodoalkylation	75	UV/AIBN	25	17	18
[4,1]	iodoalkylation	75	heat	60	17	20
[4,1]	iodoalkylation	75	heat/BP	60	17	24

[a] All samples were cured for 100 h under the selected conditions. [b] See ref 3 for details. [c] AIBN = azobis(isobutyronitrile); BP = benzoyl peroxide.

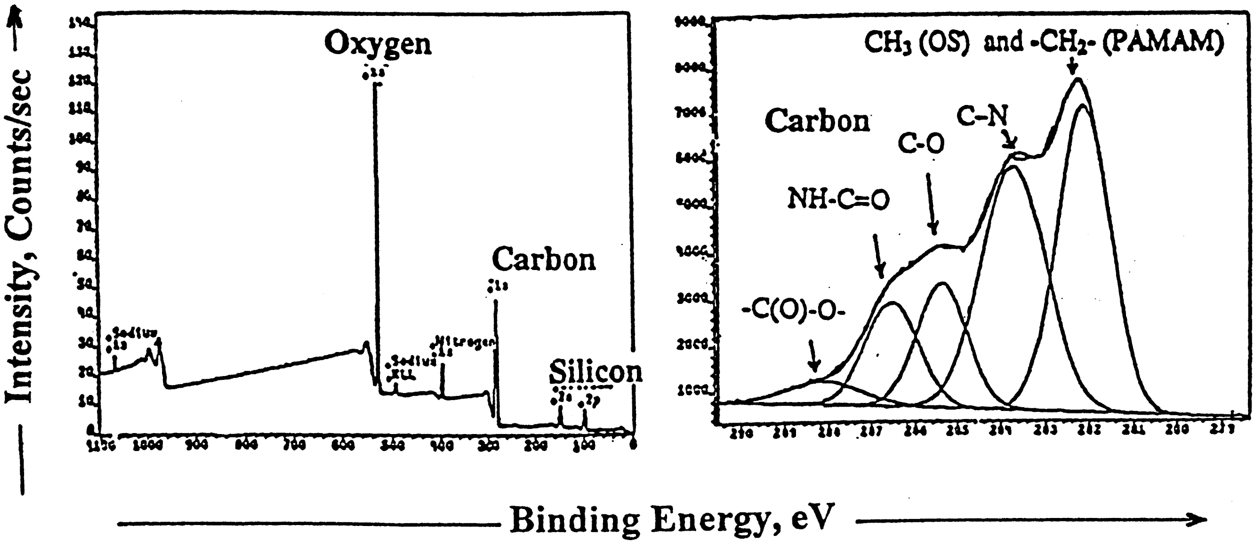


Figure 5. XPS spectra of networks from PAMAMOS-[4,1]-DMOMS dendrimer precursors.

of different procedures, including heating with a free radical initiator illustrated in Scheme 5. The resulting networks contain carbosilyl (Si$-$C$_x$-Si) *inter*dendrimer linkages instead of the siloxane (Si$-$O$-$Si) bridges that are formed on curing of PAMAMOS$-$DMOMS and PAMAMOS$-$TMOS dendrimers as discussed in the preceding sections.

Networks from PAMAMOS-[*x*,1]-DMVS dendrimers (structure **4** of Figure 1; $x = 3$ and 4) were prepared by exposure to both UV irradiation and heat with or without free radical initiators. Of the latter, 2,2′-azobis(isobutyronitrile) (AIBN) and benzoyl peroxide (BP) were used, and the heating was at temperatures between 60 and 100 °C. Additionally, PAMAMOS-[*x*,1]-DMVS dendrimers prepared by iodoalkylation of amine-terminated PAMAMs[3,27] could also be cured by heating at 60 °C without any added initiator. This was probably due to the presence of either I_2 or HI left over from the dendrimer synthesis, since they are both effective cationic polymerization initiators for vinyl-group-containing monomers. Indeed, elemental analysis of several PAMAMOS$-$DMVS dendrimer samples confirmed the presence of trace amounts of iodine even after careful purification by repeated ultrafiltration.

Table 4 lists T_g's of various networks obtained from PAMAMOS-[*x*,1]-DMVS dendrimers by these cross-linking procedures. It can be seen from these data that, irrespective of the cross-linking method applied, all networks prepared from the same precursor showed practically identical T_g's, indicating satisfactory reproducibility of the experimental techniques used. Second, in contrast to the behavior of PAMAMOS$-$DMOMS networks where T_g's substantially increased with respect to the T_g's of uncured dendrimer precursors (see Table 1), the T_g's of networks prepared from PAMAMOS$-$DMVS dendrimers had values very similar to those of their dendrimer precursors, ranging from 18 to 24 °C. Third, the values of T_g's of these networks were about 10 °C higher than the corresponding values of their PAMAMOS$-$DMOMS-derived counterparts. Evidently, this results from the more pronounced flexibility of the siloxane (Si$-$O$-$Si) *inter*dendrimer linkages relative to that of the carbosilane (Si$-$C$_x$$-$Si) bonds.[27,28] Finally, similar to the situation with the DMOMS networks, there was no significant difference between the T_g's of the [3,1] and [4,1] networks in this network series either.

Other Physical Properties of PAMAMOS Dendrimer Networks. Quasi-equilibrium advancing contact angle measurements on the surfaces of PAMAMOS$-$DMOMS networks gave for water, methylene iodide, and *n*-hexadecane the values of 109$-$112°, 70$-$76°, and 30$-$32°, respectively. Using the Owens$-$Wendt geometric mean approach,[21] these results translate to a solid surface energy of 21$-$24 mN/m, which is within the range of values usually found for all-methyl surfaces such as those of PDMS (22.8 mN/m) or paraffin wax (25.4 mN/m).[2] This implies that PAMAMOS dendrimer network surfaces are dominated by the low surface energy methyl groups from Si$-$CH$_3$ units, although the X-ray photoelectron spectroscopy (XPS) also revealed the presence of oxygen together with carbon and silicon

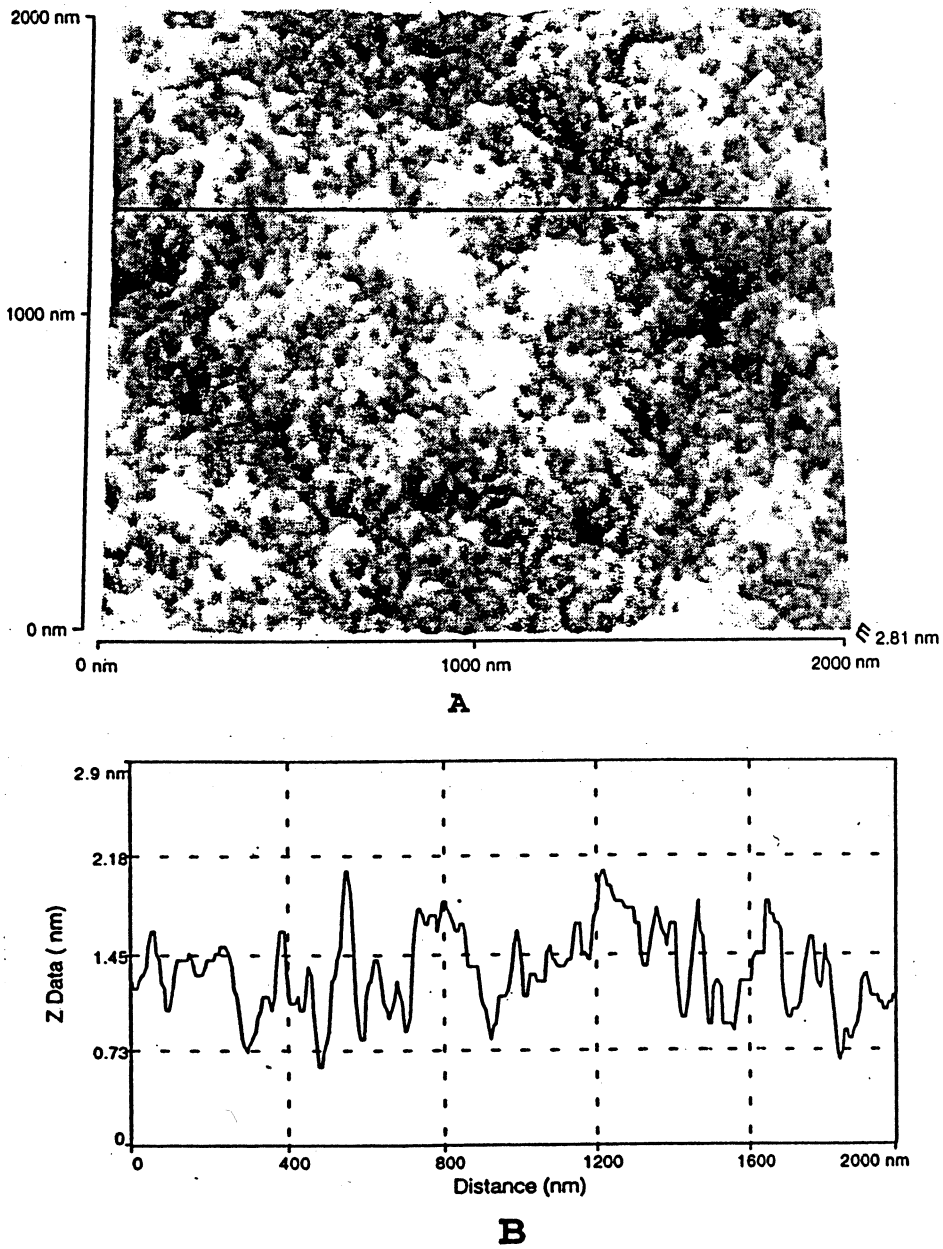


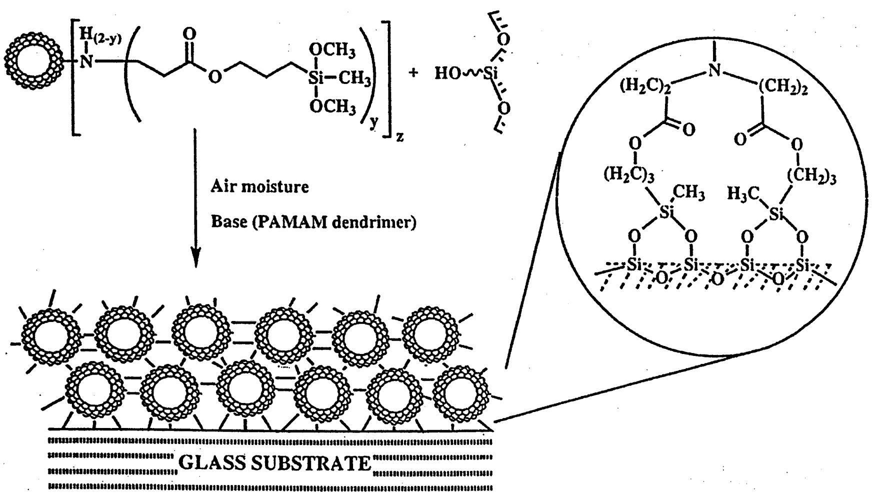
Figure 6. (A) Tapping mode atomic force microscopy image of a network from PAMAMOS-[4,1]-DMOMS dendrimer precursor prepared by spin-casting PAMAMOS solution on a mica support followed by curing under atmospheric condition. (B) The height profile associated with the arbitrary line drawn on the image.

in the surface region. In fact, the C 1s XPS spectrum (see Figure 5) showed five different carbon states corresponding to Si$-$CH$_3$ end groups and CH$_2$ units from both PAMAM and OS domains (at 285 eV), C$-$N and N(H)$-$C(O) groups from PAMAM domains (at 286 and 289 eV, respectively), and C$-$O and C(O)O groups from OS regions (at 287 and 290 eV, respectively). Hence, it appears that although the Si$-$CH$_3$ groups may be dominating wetting properties of PAMAMOS dendrimer networks, other units from both OS and PAMAM domains also contribute to this XPS spectrum. This is expected since the XPS data were collected in the normal angle mode that probes a depth on the order of 8$-$10 nm whereas the contact angle data are most sensitive to the outermost monolayer composition.

That the outermost surface layer seems to be dominated by methyl groups implies that any roughness derived from the dendritic structure is of too small a scale to affect the measured contact angles. In fact, smoothness of these surfaces on a nanometer scale was confirmed by atomic force microscopy (AFM) which showed (see Figure 6) that PAMAMOS networks prepared by casting on the mica support and subsequent curing under atmospheric conditions had a maximum roughness of less than 1.5 nm.

The same PAMAMOS dendrimer networks were also examined by scanning electron microscopy (SEM), which showed fairly featureless, uniform cross-sectional organization[2] consistent with nanoscopic sizes of both of their PAMAM and OS structural domains. More information about this fine structure, however, was obtained from small-angle neutron scattering (SANS).[22] Typical data are shown in Figure 7 for an example of a network prepared from PAMAMOS-[4,1]-DMOMS dendrimer according to Scheme 1. The characteristic spacing was calculated from the peak position as $D = 2\pi/q_{\max}$, resulting in a core-to-core spacing of the neighboring PAMAM domains of about 3.7 nm ($q_{\max} = 0.17$ Å^{-1}).

Scheme 6



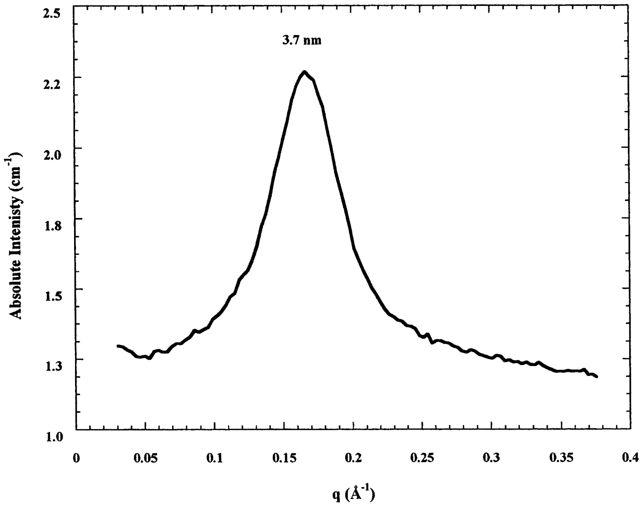


Figure 7. Small-angle neutron scattering from a PAMAMOS-[4,1]-DMOMS network after soaking in D_2O.[22]

This value is in very good agreement with 3.9 and 5 nm, which had been independently determined for the diameter of un-cross-linked generation 4 PAMAM dendrimers by SANS and dilute solution viscometry, respectively.[29]

Hence, the SANS data clearly confirm that PAMAMOS dendrimer networks are, indeed, well-organized three-dimensional nanostructures having core-to-core spacings correlating well with the diameters of the dendrimer precursors used. This also indicates that dendrimer precursors retain their shapes and sizes on incorporation into such networks and that diameters of the spheroidal PAMAM network domains (see Figure 2) are predetermined by the selection of PAMAM dendrimer generation used for the PAMAMOS synthesis. A small-angle X-ray scattering (SAXS) measurement was also performed to further verify the core-to-core spacing on the same sample giving as a result $q_{\max}$ of 0.18 Å^{-1}.[22]

PAMAMOS Network Coatings. In addition to being able to cross-link into self-supporting films, these cross-linkable PAMAMOS dendrimers can also yield excellent coatings on a wide variety of different substrates. Among these, of particular interest are substrates that contain reactive surface groups (such as Si−OH units of various glasses, silicas, or silicon wafers) with which alkoxysilane functionalized dendrimers (**1**−**3** of Figure 1) or their silanol-terminated intermediates (**7** in Scheme 1) can form covalent bonds during the cross-linking reaction as shown in Scheme 6.

In cases where substrates do not show chemical reactivity toward the network coatings, but contain charged surface units, secondary bonds can establish with specific network domains, resulting in the formation of coatings that tenaciously stick to the substrate surface but may still be removed by applying adequate mechanical action. Using either or both of these methods, a variety of substrates including glasses, metals, plastics, textiles, paper, graphite, wood, etc., were successfully coated, resulting in materials with surface properties that are characteristic of the self-supporting PAMAMOS nanodomained networks described in the preceding sections.

Conclusions

Alkoxy and vinyl functionalized poly(amidoamine−organosilicon) (PAMAMOS) dendrimers[2,3] can be conveniently cross-linked into well-organized three-dimensional, covalently bonded networks comprising intermeshed hydrophilic and hydrophobic (i.e., oleophilic) nanoscopic domains of well-defined shapes and sizes. These networks are optically clear, colorless, highly transparent nanostructured materials that show smoothness at the nanoscopic level and low surface energy and exhibit useful mechanical properties. Their T_g's are structurally dependent and may be predetermined by selecting appropriate dendrimer precursor and/or cross-linking chemistry. Some of the key compositional and architectural parameters that influence these T_g's include the generation of PAMAM dendrimer and the type of organosilicon reagent used in the synthesis of PAMAMOS dendrimer network precursor; the type and molecular density of the PAMAMOS dendrimer end groups; the type of cross-linking chemistry, initiator, catalyst, and reaction conditions applied; and the type and relative amount of the cross-linking coreagents and any additives used.

These PAMAMOS networks represent a rare example of dendrimer-based materials described to date. They can be produced in the form of self-supporting films, sheets, or coatings on a variety of different substrates. The unique copolymeric composition of their PAMAMOS dendrimer precursors provides uniform distribution of constitutive PAMAM and OS network domains. Because the precursor dendrimers retain their shapes and sizes upon incorporation into the covalently bonded networks, the sizes of the resulting network domains may be predetermined (with precision of about ±1 nm) by appropriate selection of the dendrimer precursor used (i.e., its type and generation).

In addition to the properties described herein, these PAMAMOS dendrimer-based networks also exhibit well-known nucleophilicity of their PAMAM domains which, in turn, provides for pronounced affinity to complex inorganic, organic, and/or organometallic electrophiles.[2,10,12,30] This opens up exciting opportunities for utilization of these networks as nanotemplates for organizing nanoparticles of metals, metal oxides, metal sulfides, metal selenides, as well as organic dyes, drugs, catalysts, indicators, etc., into unprecedented nanostructured materials, including various nanocomplexes and organic−inorganic nanocomposites. These unique new materials offer great promise for application in a variety of challenging areas such as optics, electronics, photonics, medicine, sensors, new types of protective and functional coatings, semipermeable and catalytic membranes, environmental protection, absorbents, etc.

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