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Studies on the synthesis and thermal properties of alkoxysilane-terminated organosilicone dendrimers

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Silicone core dendrimers bearing terminal dialkoxy and trialkoxy silane groups were prepared in a three-step synthesis. Initially, the Si–H terminated multifunctional silicone dendrimer, i.e. tetrakis(dimethylsiloxy)silane, was prepared by the reaction of tetraethoxysilane and dimethylethoxysilane. Tetrakis(dimethylsiloxy)silane on reaction with allylglycidylether in the presence of Speier's catalyst under pressure (100 psi) yielded epoxy-terminated dendrimer in very high yield (95%). The epoxy-terminated dendrimer was reacted with aminopropylalkoxysilanes to yield the next-generation dendrimer bearing dialkoxy and trialkoxy silane groups. The dendrimers were characterized by the usual physico-chemical techniques, i.e. elemental analysis, FT-IR, ^{1}H, ^{13}C and ^{29}Si NMR. Thermal studies (Thermogravimetric analysis and Thermomechanical analysis) of the alkoxy terminated dendrimers and its cured products were also carried out.

Keywords: silicone; Speier's catalyst; dendrimer; tetraethoxysilane

Introduction

The design and architecture of any macromolecule and polymer depends on the requirement of the properties and end use application of the material. With the realization of the fact that the branching of the polymer chain and functional group mainly determines the properties of the materials, several hyper-branched[1–5] and dendritic polymers[1,6–10] have been prepared. For the synthesis of these building blocks, in general, classical organic and organometallic synthetic methods are used.[1] The synthesis of dendrimers requires multiple steps, so obtaining high-purity materials is difficult, yet few reports are available to synthesize very high purity and quantitative yields of the dendrimers up to the third generation.[11] Despite, the several high tech. applications of dendrimers like chemical sensors,[12,13] catalysts,[14] molecular devices[15,16] and chemo-delivery in biology,[17] these new classes of materials have failed to make any commercial impact. Moreover, as compared with organic hyperbranched polymers and dendrimers, inorganic hyperbranched polymers and dendrimers have been less studied.

Most of the building blocks of dendrimers are prepared using widely studied class of reactions like hydrosilylation, Grignard reactions, dehydrocoupling, alcoholysis and alkenylation reactions, either by divergent or convergent method.[1,18–27] The first silicon-containing dendrimer was reported by Aziz Muzafarov *et al*. in 1989,[28] and the first commercially available silicon-containing dendrimer was PAMAMOS.[29] Since then, several such dendrimers have been reported in the literature.[1,10,11,18–27] A number of applications of organosilicone dendrimers based on the terminal functional groups and polysiloxycarbosilane core have also been enumerated in the literature.[1,10,30,31] Globular geometries, internal void spaces and high number of chain ends of the dendrimers make them more soluble in solvent systems, having lesser bulk viscosity as compared with equivalent molecular weight linear polymers, which make silicon dendrimers potential substrates for crosslinking reagents.[1,10,30,32] Hence they are used as coating materials and resin matrices for FRP composites.

As we have continued interest in the synthesis of multifunctional organosilanes,[33–37] it has been considered worthwhile to synthesize and characterize dendrimers bearing a silicone core and exterior hydrolysable alkoxysilane functionalities. As alkoxysilane groups are susceptible to moisture and hydroxyl groups present on metal and glass surfaces, these dendrimers may act as very good coating and coupling reagents for the preparation of FRPs, RTVs and HTVs.

Experimental

Chemicals

Benzene (LR grade, Ranbaxy) and hexane (LR grade, E. Merck) were purified and dried before use, as reported.[38] Dimethylethoxysilane (95%, Acros), tetraethoxysilane (98%, E. Merck) and allylglycidylether (99%, Aldrich) were used after distillation. 3-Aminopropyldiethoxymethylsilane (97%, Lancaster), dibutyltin dilaurate (Technical grade, Fluka), 3-aminopropyltriethoxysilane (96%, Fluka) and silica gel (60–120 mesh LR grade, SD Fine Chemicals) were used as such.

Equipment and Analytical Measurements

Perkin Elmer FT-IR Spectrometer RX1 was used to record IR spectra using KBr pellets, Bruker Avance 400 MHz NMR spectrometer was used for NMR studies using deutrated chloroform as solvent

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and TMS as external reference. Vario EL III CHNOS elemental analyzer was used for elemental analysis. Thermal properties were measured using a Hi-Res TGA 2950 thermogravimetric analyzer (TA Instruments, USA) and a TMA 2940 thermomechanical analyzer at a heating rate of 10 °C/min under a N_2 atmosphere.

Typical Procedure and Product Characterization

Synthesis of tetrakis(dimethylsiloxy)silane dendrimer

A solution of tetraethoxysilane (TEOS; 12.48 g, 0.06 mol) and dimethylethoxysilane (31.20 g, 0.30 mol) in benzene (200 ml) was taken in a dropping funnel, added slowly in a beaker containing water (500 ml) and magnetic stirrer and further stirred for 2 h at 38–40 °C. Afterwards the organic layer was separated using a separating funnel in the presence of brine solution. The solution was distilled on a water bath to remove benzene. The tetrakis(dimethylsiloxy)silane (G_0A) dendrimer ($C_8H_{28}O_4Si_5$) was distilled as colorless liquid, yield 13.50 g, 69%, b.p. 190–192 °C (lit. b.p. 190 °C[39]). IR (cm^{-1}) 1080 (–SiOSi–), 2131 (–SiH); ^{1}H NMR ($CDCl_3$) δ (ppm), 0.22 (d, 24H, $-Si-C\underline{H}_3$), 4.74 (m, 4H, $-Si-\underline{H}$); ^{13}C NMR ($CDCl_3$) δ (ppm) 0.2 ($-Si-\underline{C}H_3$); ^{29}Si NMR ($CDCl_3$) δ (ppm) −108 [$\underline{Si}(OSi)_4$], 8.5 [$Si(O\underline{Si})H(CH_3)_2$]; elemental analysis (%) C 29.23, H 8.56, O 19.48, Si 42.74 (calcd 29.21, 8.58, 19.47, 42.73 respectively).

Synthesis of G_0B dendrimer

A solution of G_0A dendrimer (9.84 g, 0.03 mol), allylglycidylether (17.1 g, 0.15 mol) and Speier's catalyst[40] (0.03 mol%) was taken in a pressure reactor (100 psi) under argon. The reaction mixture was stirred (750 rpm) at 100 °C for 3 h and allowed to cool to room temperature. The excess amount of allylglycidylether was removed under vacuum (3 torr, 40 °C) leaving behind the colorless liquid. The colorless liquid was column chromatographed on silica using hexane as eluting agent. The hexane solution was distilled on a water bath leaving behind a colorless liquid which was identified as G_0B dendrimer ($C_{32}H_{68}O_{12}Si_5$), yield 22.25 g, 95%. IR (cm^{-1}) 913 (epoxy ring, asy), 1080 (–SiOSi–), 3050 (epoxy ring, sym); ^{1}H NMR ($CDCl_3$) δ (ppm,) 0.07 (s, 24H, $-Si-C\underline{H}_3$), 0.54 (t, 8H, $-Si-C\underline{H}_2-$), 1.82 (m, 8H, $-CH_2-C\underline{H}_2-CH_2-$), 2.59 (t, 4H, epoxy ring, $-C\underline{H}_2-$, *trans*), 2.77 (t, 4H, epoxy ring, $-C\underline{H}_2-$, *cis*), 3.13 (m, 4H, epoxy ring, $-C\underline{H}-$), 3.37 (t, 4H, $-O-C\underline{H}_2-$epoxy ring, *cis*), 3.71 (t, 4H, $-O-C\underline{H}_2-$epoxy ring, trans), 4.01 (t, 8H, $-CH_2-C\underline{H}_2-O-$); ^{13}C NMR (ppm, $CDCl_3$): $\delta = 0.1$ ($-Si-\underline{C}H_3$), 14.1 ($Si-\underline{C}H_2-$), 23.5 ($-CH_2-\underline{C}H_2-CH_2-$), 44.6 (epoxy ring, $-\underline{C}H_2-$), 50.9 (epoxy ring, $-\underline{C}H-$), 70.9 ($-O-\underline{C}H_2-$epoxy ring), 74.5 ($-CH_2-\underline{C}H_2-O-$). ^{29}Si NMR ($CDCl_3$) δ (ppm) −108 [$\underline{Si}(OSi)_4$], 7.2 [$Si(O\underline{Si})(CH_3)_2CH_2$]; elemental analysis (%) C 48.91, H 8.72, O 24.48 Si 17.90 (calcd 48.92, 8.73, 24.46, 17.89 respectively).

Synthesis of G_1 dendrimers

G_0B dendrimer (7.84 g, 0.01 mol) and 3-aminopropyldiethoxymethylsilane (3-APDES; 7.64 g, 0.04 mol) were taken into a three-necked flask and stirred for 5 h at 38–40 °C under inert atmosphere to afford dendrimer G_1A ($C_{64}H_{152}O_{20}Si_9N_4$) in quantitative yield. The progress of the reaction was monitored using FT-IR. IR (cm^{-1}) 1090 (–SiOSi–), 3364 (–NH), 3472 (–C–OH); ^{1}H NMR ($CDCl_3$) δ (ppm) 0.07 [s, 24H, $-Si-(C\underline{H}_3)_2$], 0.13 (s, 12H, $-Si-C\underline{H}_3$), 0.55 [t, 8H, $-Si(CH_3)_2-C\underline{H}_2-$], 1.08 (m, 4H, $-CH_2-N\underline{H}-CH_2-$), 0.64 (t, 8H, $-Si-C\underline{H}_2-$), 1.57 (t, 24H, $-O-CH_2-C\underline{H}_3$), 1.82 (m, 16H, $-CH_2-C\underline{H}_2-CH_2-$), 2.57 (m, 8H, $-NH-C\underline{H}_2-CH_2-$) 2.61 (t, 8H, $-CHOH-C\underline{H}_2-NH-$), 3.15 (m, 4H, $-C\underline{H}OH-$), 3.21 (d, 4H, $-CHO\underline{H}-$), 3.42 (d, 8H, $-O-C\underline{H}_2-CHOH-$), 3.75 (q, 16H, $-O-C\underline{H}_2-CH_3$), 4.03 (t, 8H, $-CH_2-C\underline{H}_2-O-$); ^{13}C NMR ($CDCl_3$) δ (ppm) 0.1 [$-Si-(\underline{C}H_3)_2$, $-Si(OCH_2CH_3)_2-\underline{C}H_3$)], 10.5 ($-Si-\underline{C}H_2-$), 14.1 ($-Si-\underline{C}H_2-$), 18.0 ($-CH_2-\underline{C}H_3$), 23.5 ($-CH_2-\underline{C}H_2-CH_2-$), 44.1 ($-CHOH-\underline{C}H_2-NH-$), 52.1 ($-NH\underline{C}H_2CH_2-$), 59.1 ($-O-\underline{C}H_2-$), 63.4 ($-\underline{C}HOH-$), 70.1 ($-O\underline{C}H_2-CHOH-$), 74.5 ($-CH_2-\underline{C}H_2-O-$); ^{29}Si NMR ($CDCl_3$) δ (ppm) −108 [$\underline{Si}(OSi)_4$], −17 [$\underline{Si}CH_3(OEt)_2CH_2$], 7.1 [$Si(O\underline{Si})(CH_3)_2CH_2$]; elemental analysis (%) C 49.54, H 9.86, O 20.65, Si 16.32, N 3.59 (calcd 49.55, 9.88, 20.64, 16.31, 3.61 respectively).

Similarly, G_1B was synthesized by the reaction of G_0B dendrimer (7.84 g, 0.01 mol) and 3-aminopropyltriethoxysilane (3-APTES; 8.84 g, 0.04 mol). The yield of the product (G_1B dendrimer, $C_{68}H_{160}O_{24}Si_9N_4$) was quantitative. IR (cm^{-1}) 1092 (–SiOSi–), 3361 (–NH), 3475 (–C–OH); ^{1}H NMR ($CDCl_3$) δ (ppm) 0.07 [s, 24H, $-Si-(CH_3)_2$], 0.56 [t, 8H, $-Si(CH_3)_2-C\underline{H}_2$], 1.07 (m, 4H, $CH_2-N\underline{H}-CH_2$), 0.64 (t, 8H, $-Si-C\underline{H}_2$), 1.59 (t, 36H, $-O-CH_2C\underline{H}_3$), 1.81 (m, 16H, $CH_2-C\underline{H}_2-CH_2$), 2.56 (m, 8H, $-NH-C\underline{H}_2-CH_2$) 2.62 (t, 8H, $-CHOH-C\underline{H}_2-NH$), 3.15 (m, 4H, $-C\underline{H}OH$), 3.20 (d, 4H, $-CHO\underline{H}$), 3.41(d, 8H, $-O-C\underline{H}_2-CHOH-$), 3.75 (q, 24H, $-O-C\underline{H}_2-CH_3$), 4.01 (m, 8H, $-CH_2-C\underline{H}_2-O-$); ^{13}C NMR ($CDCl_3$) δ (ppm) 0.1 ($-Si-\underline{C}H_3$), 10.4 ($-Si-\underline{C}H_2$), 14.1 ($-Si-\underline{C}H_2$), 18.1 ($-\underline{C}H_2-CH_3$), 23.6 ($-CH_2-\underline{C}H_2-CH_2$), 44.1 ($-CHOH-\underline{C}H_2-NH-$), 52.1 ($-NH-\underline{C}H_2-CH_2-$), 59.0 ($-O-\underline{C}H_2$), 63.5 ($-\underline{C}HOH$), 70.1 ($-O\underline{C}H_2-CHOH-$), 74.6 ($-CH_2-\underline{C}H_2-O-$); ^{29}Si NMR ($CDCl_3$) δ (ppm) −108 [$\underline{Si}(OSi)_4$], −40 [$\underline{Si}(OEt)_3CH_2$], 7.1 [$Si(O\underline{Si})(CH_3)_2CH_2$]; elemental analysis (%) C 48.87, H 9.64, O 22.98, Si 15.14, N 3.34 (calcd 48.86, 9.66, 22.99, 15.13, 3.35 respectively).

Curing of G_1 dendrimers

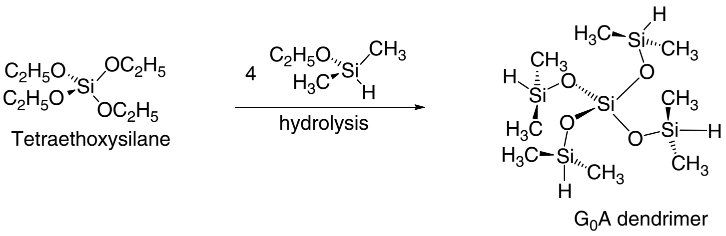
(i) Curing of G_1A dendrimer using TEOS in presence of dibutyltin dilaurate (DBTDL): G_1A dendrimer (1.55 g, 0.001 mol), TEOS (0.42 g, 0.002 mol) and DBTDL (15 mol% of TEOS) as catalyst were properly mixed and poured into a mold. The mixture was left exposed to air for 24 h followed by sequential heating at 40 °C for 1 h, 50 °C for 1 h and finally at 60 °C for 3 h. A sheet of cured material was obtained (CD_1). Similarly, G_1B dendrimer was processed to afford cured dendrimer (CD_3).

(ii) Curing of G_1A dendrimer using (DBTDL): G_1A dendrimer (1.55 g, 0.001 mol) and DBTDL (15 mol% of TEOS) were properly mixed and poured into a mold. The mixture was left exposed to air for 24 h followed by sequential heating at 40 °C for 1 h, 50 °C for 1 h and finally at 60 °C for 3 h. A sheet of cured material was obtained (CD_2). Similarly, G_1B dendrimer was processed to afford cured dendrimer (CD_4).

Results and Discussion

For the preparation of high-performance FRP composite and other thermally stable structural material, such resin matrix and curing agents are required which give high char yield and highly cross-linked structures, so that better mechanical and thermo-oxidative stable properties can be achieved. Organosilicones have been used extensively as resin matrices, coupling agents, cross-linking agents and reactive diluents for organic resins to tailor the properties of composites, but such studies with dendrimers are very limited. Therefore, we have prepared dendrimers and studied their curing behavior and thermal properties as potential future materials for composites and other cross-linked structures.

Although the tetrakis(dimethylsiloxy)silane (G_0A dendrimer) has been prepared by the reaction of $(LiO)_4Si$ and



Scheme 1. Synthesis of tetrakis(dimethylsiloxy)silane (G_0A) dendrimer.

chlorodimethylsilane[39] and also by the reaction of tetramethyldisiloxane, isopropanol and tetraethoxysilane,[41] we tested an alternative route to prepare it by the reaction of tetraethoxysilane and dimethyethoxysilane in one pot, which gave 69% yield (Scheme 1). The other byproducts formed were identified as 1,1,3,3-tetramethyldisiloxane (3.65g, 19%), b.p. 71–72 °C (lit. b.p. 72–73 °C), along with highly viscous silicones and silica.

The G_0B dendrimer was also synthesized by the reaction of G_0A dendrimer and allylglycidylether under high temperature and pressure in very high yield (95%) and in a much shorter time (3 h) as compared with the earlier reported method.[6,42,43] The G_0B dendrimer was reacted with 3-aminopropylalkoxysilanes under inert atmosphere at 38–40 °C for 5 h to afford alkoxy group-terminated G_1 dendrimer (Scheme 2).

When the G_1 dendrimer was reacted with TEOS in the presence of DBTDL, it yielded a high char yield resin matrix (Scheme 3). The G_1 dendrimer also crosslinked intermolecularly in the presence of DBTDL, but the char yield of the cured materials was lower compared with previous ones. In such cases, curing occurs through hydrolysis of alkoxy groups followed by condensation of hydroxyl groups.[44]

IR Studies

FT-IR spectra of dendrimers were studied in the range 400–4000 cm^{-1} using KBr pellets. The G_0A dendrimer showed the presence of $\nu_{Si-O-Si}$ absorption at 1080 cm^{-1} and ν_{Si-H} at 2131 cm^{-1}. The ν_{Si-CH3} absorption was not characteristic as both the reactants showed the same absorption for ν_{Si-CH3} groups. Thus, it may be tentatively concluded that G_0A dendrimer formed.

The FT-IR spectra of G_0B dendrimer showed the appearance of characteristic absorption peaks of oxirane ring at 913 and 3054 cm^{-1} and disappearance of ν_{Si-H} peak at 2131 cm^{-1}, which was very prominent in the G_0A dendrimer. The olefinic bond of allylglycidylether at 1649 cm^{-1} also disappeared in the product. Therefore, it may be inferred that the hydrosilylation reaction of G_0A and allylglycidylether took place.

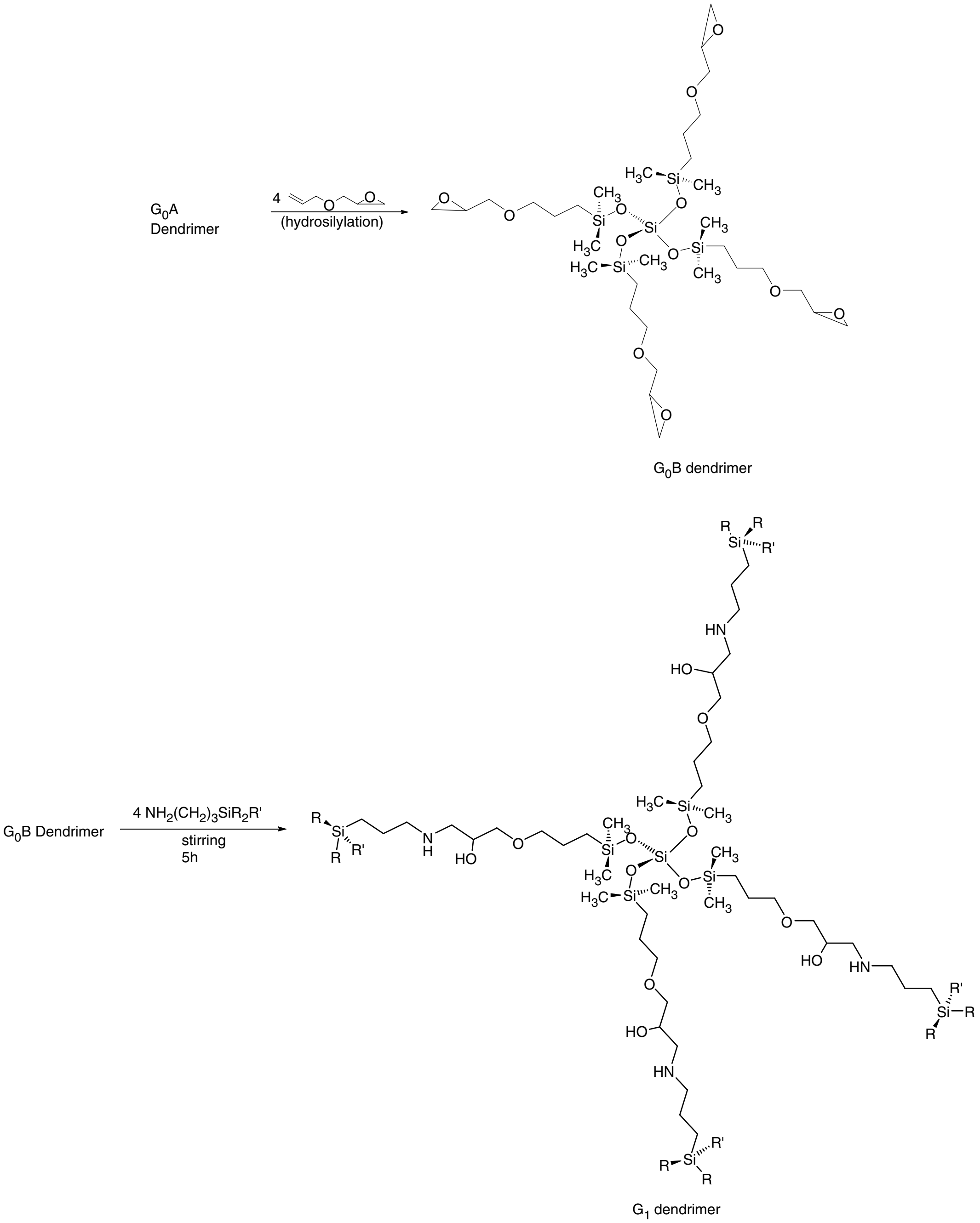
In the reaction product of G_0B and 3-aminopropylalkoxysilanes, the oxirane ring absorption peaks at 913 and 3054 cm^{-1} disappeared and secondary –OH peaks apperared at ~3475 cm^{-1}. The ν_{NH2} absorption peaks at ~3420 cm^{-1} disappeared and a broad peak appeared at ~3361 cm^{-1}, which may be due to overlapping of ν_{OH} and ν_{NH} peaks. Therefore, it may be concluded that epoxy group reacted smoothly with 3-aminopropylalkoxysilanes and G_1 dendrimers formed.

NMR Studies

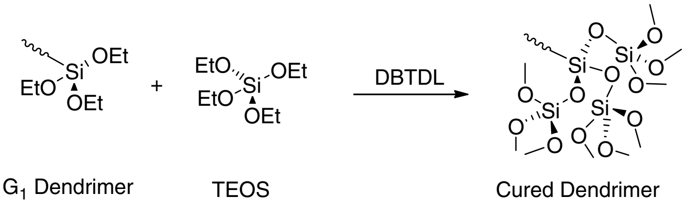
^1H NMR spectra of G_0A dendrimer showed multiplet for δ SiH at 4.74 ppm due to coupling with $SiCH_3$ protons and doublet for δ $SiCH_3$ at 0.22 ppm due to coupling with protons of SiH group. In the product δ CH_2CH_3 protons of ethoxy group, which were present in tetraethoxysilane and dimethylethoxysilane, did not appear. ^{13}C NMR gave only one peak at δ 0.2 ppm, which may be assigned to δ CH_3. ^{29}Si NMR showed two peaks at δ −108 and δ 8.5 ppm. The peak at higher field may be assigned to structural species Q^4 $[Si(OSi)_4]$ and corresponds to a silicon atom attached to four silicon species via oxygen bridges.[44,45] Similarly, the peak at lower field may be assigned to structural species M^1 $[Si(OSi)H(CH_3)_2]$ and corresponds to a silicon atom attached to one silicon atom via an oxygen bridge.[44,45] Therefore, it may be concluded that the G_0A dendrimer synthesized successfully.

The progress of the hydrosilylation reaction of G_0A dendrimer and allylglycidylether was monitored with the disappearance of δ SiH proton at 4.74 ppm and δ $H_2C{=}CH_2$ at ~5–6 ppm. ^1H NMR of G_0B dendrimer showed characteristic signals for an oxirane ring at δ 2.59 ppm (CH_2, *trans*), 2.77 ppm (CH_2, *cis*) and 3.13 ppm (CH). The δ $SiCH_3$ appeared as a singlet at 0.07 ppm whereas δ $SiCH_2$ appeared as a triplet at 1.17 ppm due to coupling with protons of the nearby $-CH_2$ group. The signals of δ $-CH_2$ of the $Si-CH_2-CH_2-CH_2-$ group appeared as a multiplet at 1.82 ppm, which may be assigned to the coupling of protons of the $-CH_2$ group with the protons present on either side carbon atom, δ CH_2, which joins the ether linkage to the oxirane ring appearing at 3.37 ppm (*cis*) and 3.71 ppm (*trans*), both appearing as triplets due to coupling with the proton present on the same carbon atom as well as protons attached to the next carbon atom of the oxirane ring. The δ CH_2 of the CH_2-CH_2-O- group appeared at 4.01 ppm as a triplet, which showed coupling with the protons of the next CH_2 group. ^{13}C NMR spectra showed that the signals for δ $SiCH_3$ appeared at 0.1 ppm, for δ $SiCH_2$ at 14.1 ppm, δ $-CH_2$ of the $Si-CH_2-CH_2-CH_2-$ group appeared at 23.5 and 74.5 ppm, δ $SiCH_2$ of the oxirane ring at 44.6 ppm, δ CH_2 of the $O-CH_2-$oxirane ring at 70.9 and δ CH of the epoxy ring at 50.9. ^{29}Si NMR spectra showed the two peaks at δ −108 ppm and δ 7.2 ppm for Q^4 species $[Si(OSi)_4]$ and M^1 species $[Si(OSi)(CH_3)_2CH_2]$, respectively, and there was hardly any change with the G_0A. Therefore, it may be concluded that the G_0B dendrimer was synthesized successfully.

The formation of dendrimer G_1A and G_1B was also confirmed by NMR spectra. ^1H NMR spectra of dendrimer G_1A and G_1B showed a peak at ~3.21 ppm as a doublet for protons of the hydroxyl group and at 1.08 ppm as a multiplet for the amine group proton; splitting of peaks occurred due to the coupling with the nearby protons. The peak for δ OCH_2 and δ CH_2CH_3 of the ethoxy group appeared at 3.75 ppm as quartet due to the coupling with $-CH_3$ group protons and at 1.57 ppm as a triplet due to the coupling with $-OCH_2$ protons. The spectra also showed additional peaks at 0.13 for $Si-CH_3$ in the case of 3-aminopropyldiethoxymethylsilane. ^{13}C NMR spectra of dendrimer G_1A and G_1B showed peaks for δ CHOH at 63.4 ppm. The peak for δ OCH_2 appeared at 59.0 ppm and for δ CH_2CH_3 at 18.1 ppm. ^{29}Si NMR spectra of dendrimer G_1A and G_1B showed peaks at −108 ppm for Q^4 species $[Si(OSi)_4]$ and 7.1 ppm



Scheme 2. Synthesis of G$_1$ dendrimers, where for G$_1$A, R = OCH$_2$CH$_3$, R' = CH$_3$ and for G$_1$B, R = R' = OCH$_2$CH$_3$.



Scheme 3. Synthesis of cured dendrimers.

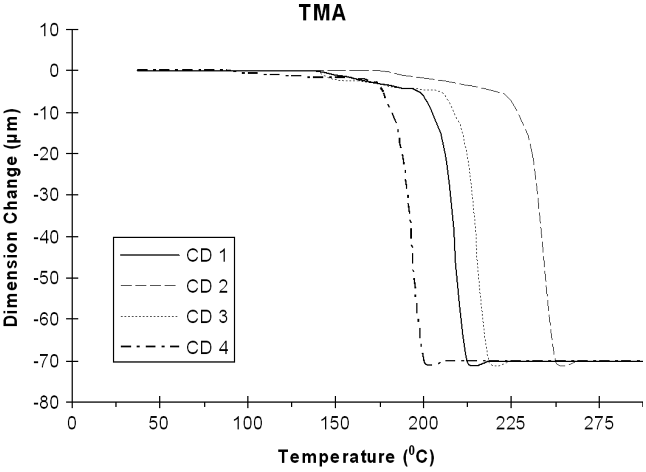


Figure 1. Thermomechanical analysis of cured dendrimers.

Table 1. Thermal analysis data for G_1 and cured dendrimers

Cured dendrimers	T_g (°C)	T_d (°C)	T_d (°C)	Char yield (%) (800 °C)
G_1A	–	344	–	25
G_1B	–	350	–	27
CD_1	212	359	472	42
CD_2	236	352	466	40
CD_3	173	317	441	32
CD_4	216	360	452	35

T_g, glass transition temperature; T_d, crest temperature of first stage degradation; T_d, crest temperature of second stage degradation.

for M^1 species $[Si(OSi)(CH_3)_2CH_2]$. The peaks for T structural species $[Si(OEt)_3CH_2]$ appeared at δ −40 ppm and for D structural species $[SiCH_3(OEt)_2CH_2]$ at δ −17 ppm.

Thermal Analysis

TMA and TGA methods were carried out for the thermal property studies of the cured and uncured dendrimers. Figure 1 shows the TMA curves of all the cured dendrimers. All the TMA curves indicated a single transition, giving the idea that there is uniform cross-linking. Comparative study of different cured materials showed that CD_2 had the highest glass transition temperature (T_g) and CD_3 had lowest T_g. The variation in T_g data of different cured dendrimers can be explained by the fact that T_g increases with high cross-linking density. Among all the cured dendrimers, CD_2 had the highest T_g due to high cross-linking density as the more peripheral cross linking sites were available in the dendritic reactant used for its synthesis.

The TGA data (Table 1) showed that the degradation of uncured dendrimers occurred in one step with the crest temperature of ~344 °C, whereas in case of cured dendrimers, it occurred in two steps. The first step degradation started at ~340 °C with the crest temperature at ~355 °C, indicating mainly the decomposition of ether linkage; simultaneously other groups attached remotely to the silicon atom also decomposed. The second stage of degradation with a crest temperature of ~466 °C corresponded to the decomposition of groups nearer to the silicon atom. It is obvious from the results that both cured as well as uncured dendrimers are high temperature-resistant materials.

From the data it also appears that the char yield increased as the silicon content increased in the materials. The char yields of uncured dendrimers were comparatively lower than that of cured dendrimers but were quite good (Table 1). The char yield of virgin dendrimer cured with the DBTDL was lower as compared to dendrimers when cured with TEOS in the presence of DBTDL. The char yield of the cured dendrimers in general was very high and ranged between 32 and 42% (Fig. 2).

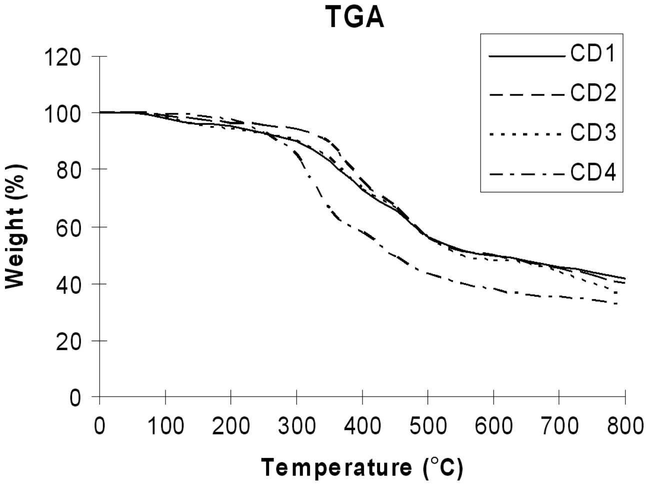


Figure 2. Thermogravimetric analysis of cured dendrimers.

Conclusions

The G_0A and G_0B dendrimers were synthesized in high yield via a new alternative method. G_1 dendrimers gave high char yield, so may be used as resin matrices for composites and also for RTVs and HTVs. All the materials were characterized by FT-IR, NMR (^1H, ^{13}C and ^{29}Si) and elemental analysis.

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