Preparation of New Carbosilane Dendrimers Carrying Mesogenic Groups

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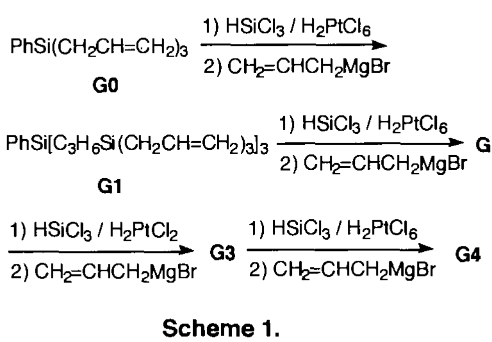
A series of new carbosilane dendrimers was prepared by repeating a combination of hydrosilation and allylation on a core molecule, triallylphenylsilane. Subsequent hydroboration and oxidation of the dendrimers gave the polyol derivatives, which were treated with a mesogenic molecule, 6-(4-cyanobiphenyl-4'-oxy)hexanoyl chloride, to give new carbosilane dendrimers carrying mesogenic groups. It was found that the all carbosilane dendrimers exhibited liquid crystal phases. The effects of the dendrimer generations on the ranges of liquid crystal temperatures were investigated.

Recently, dendrimers have attracted much attention as a well-defined macromolecules with a regular, three-dimensional, tree-like structure.[1] The interests have been focused on an introduction of functional moieties such as transition metals,[2] mesogenic groups [3] and sugar derivatives,[4] as well as synthesis of the higher generation dendrimers.[5]

We have been interested in the preparation of functionalized carbosilane dendrimers, since they have potentials for wide varieties of functions. In this paper, we wish to describe the preparation and characterization of new carbosilane dendrimers carrying mesogenic groups.

Triallylphenylsilane (G0) was chosen as a core molecule because it was expected that the phenyl substituent on silicon is useful for introduction of another type of function.

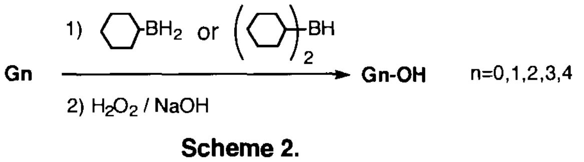
Hydrosilation and subsequent allylation reaction of G0 were carried out repeatedly to give a new series of carbosilane dendrimers, G1, G2, G3, and G4 in 80, 45, 13, and 8% yield, respectively, based on the starting G0 (Scheme 1). The each dendrimers were purified by column chromatography (hexane-ethyl acetate mixture), and their structures were elucidated by proton nmr spectra and elemental analyses.[6] Attempts to prepare dendrimer G5 were unsuccessful probably because it would have too much crowded surface.



$$\underset{\mathbf{G0}}{\mathrm{PhSi(CH_2CH{=}CH_2)_3}} \xrightarrow[\text{2) } \mathrm{CH_2{=}CHCH_2MgBr}]{\text{1) } \mathrm{HSiCl_3 / H_2PtCl_6}} \underset{\mathbf{G1}}{\mathrm{PhSi[C_3H_6Si(CH_2CH{=}CH_2)_3]_3}} \xrightarrow[\text{2) } \mathrm{CH_2{=}CHCH_2MgBr}]{\text{1) } \mathrm{HSiCl_3 / H_2PtCl_6}} \mathbf{G2} \xrightarrow[\text{2) } \mathrm{CH_2{=}CHCH_2MgBr}]{\text{1) } \mathrm{HSiCl_3 / H_2PtCl_2}} \mathbf{G3} \xrightarrow[\text{2) } \mathrm{CH_2{=}CHCH_2MgBr}]{\text{1) } \mathrm{HSiCl_3 / H_2PtCl_6}} \mathbf{G4}$$

Scheme 1.

In order to introduce mesogen moiety, conversion of the olefines of G1, G2, G3 and G4 including core molecule G0, into the hydroxy derivatives were carried out through hydroboration and oxidation reaction giving polyol derivatives, Gn-OH (n=0, 1, 2, 3, 4) (Scheme 2). Cyclohexylborane was used for G0 and G1, and dicyclohexylborane was used for higher generation than G2, to avoid precipitation of the produced organoboran polymers. Since dicyclohexylborane was too bulky to accomplish the hydroboration of G3 and G4, another 0.2 molar equivalents of diborane solution in tetrahydrofuran (THF) were required to complete the hydroboration. The structures of the polyol derivatives were confirmed by nmr spectra.[7] The polyols Gn-OH (n=0, 1, 2, and 3) were soluble in alcohols, such as methanol and ethanol, but not in water. Only G4-OH was soluble in water.



Scheme 2.

Then the polyol derivatives, Gn-OH (n=0, 1, 2), were treated with an acid chloride derivative of a mesogenic molecule, 6-(4-cyanobiphenyl-4'-oxy)hexanoic acid, in the presence of pyridine to afford corresponding dendrimers having mesogen moiety, Gn-mesogen (n = 0, 1, 2) (Figure 1). The yields of G0-, G1- and G2-mesogen were 50, 52, and 67%, respectively. The complete conversion from hydroxy groups to mesogenetic esters were confirmed by the down field shift of the triplet corresponding to the methylene group adjacent to the hydroxy oxygen, from 3.30 ppm to 4.00 ppm in their nmr spectra.[7, 8] It took 3 days to complete the esterification. Unfortunately, the complete esterification of G3 and G4 was failed.

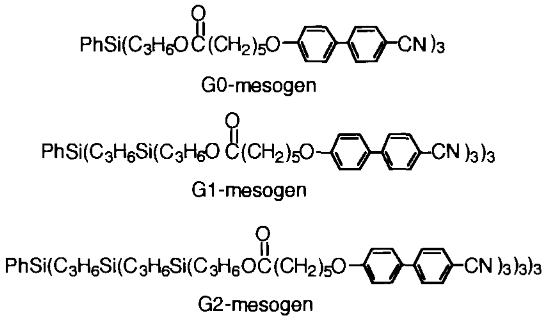


Figure 1.

The unique characteristics of the carbosilane dendrimer supported liquid crystal compared with a polymer supported liquid crystals, are its mono-dispersiveness and high solubility in solvents. Indeed, it was easily soluble in ordinal organic solvents such as ether, ethyl acetate, although the dendrimer G2-mesogen has 27 mesogens in a molecule and the molecular weight is so high as 10409. So, it was possible to purify Gn-mesogen (n=0, 1, 2) by using silica-gel chromatography.

Characterization of the Gn-mesogen (n=0, 1, 2) were performed using differential scanning calorimetry (DSC) and optical polarizing microscope. All the dendrimers prepared here showed enantiotropic liquid crystal phases (Figure 2), in spite of ethyl ester derivative of the mesogen did not exhibit any liquid

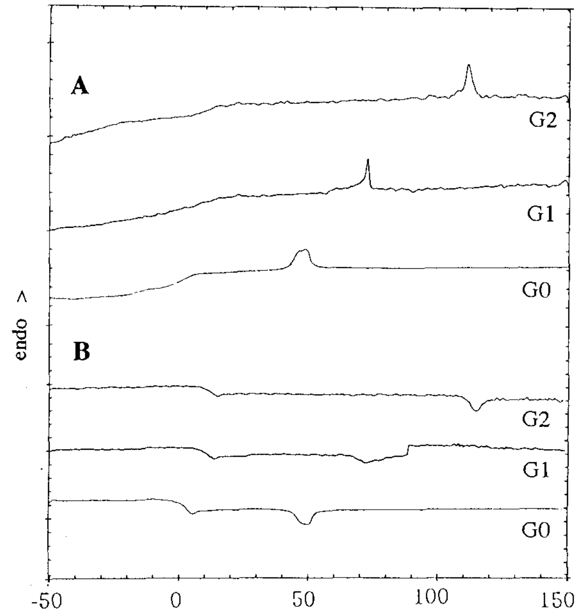


Figure 2. The DSC traces of Gn-mesogen (n=0, 1, 2), A; cooling, B; 2nd heating.

Table 1. Thermal behavior of Gn-mesogen (n=0-2)[a]

Gn-mesogen n	Phase behavior/℃								
	Cooling				Second heating				
0	I	43	Sm	r.t.	S	7	Sm	44	I
1	I	73	Sm	r.t.	S	14	Sm	72	I
2	I	111	Sm	r.t.	S	15	Sm	115	I

[a] I; isotropic, S; solid, Sm; smectic, r.t.; room temperature.

crystal phases (mp 45 ℃). The liquid crystal phases exhibited a focal conic fan texture, typical of smectic A phases. The glass transition points (Tg) of G0-, G1-, and G2-mesogen are in a narrow region from 7 ℃ to 15 ℃, however, the clearing point increases with growth of the dendrimer generations (Table 1). It is clear that the dendrimer generations in this dendrimer systems gave strong effects on the liquid crystallinities.

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6 The representative proton nmr of G2 is described. ^{1}H-NMR (CDCl$_3$, 400MHz): δ 0.49-0.57 (m, 24H, SiCCCH$_2$ (G0), SiCH$_2$ (G1)), 0.63 (t, J = 10.6 Hz, 18H, SiCCCH$_2$ (G1)), 0.83 (t, J = 10.7 Hz, 6H, SiCH$_2$(G0)), 1.26-1.35 (m, 24H, SiCCH$_2$ (G0), SiCCH$_2$ (G1)), 4.85-4.90 (m, 54H, SiCCCH$_2$ (G2)), 5.72-5.82 (m, 27H, SiCCH=), 7.32-7.42 (m, 5H, Ph). Found: C, 71.80; H, 10.45%. Calcd for $Si_{13}C_{123}H_{212}$: C,71.85; H, 10.39%.

7 The representative proton nmr of G2-OH is described. ^{1}H-NMR (DMSO-d$_6$, 400MHz): δ 0.41 (t, J = 8.4 Hz, 54H, SiCH$_2$ (G2)), 0.43-0.55 (m, 42H, SiCCCH$_2$ (G0), SiCH$_2$ (G1), SiCCCH$_2$ (G1)), 0.72-0.79 (m, 6H, SiCH$_2$ (G0)), 1.19-1.27 (m, 24H, SiCCH$_2$ (G0), SiCCH$_2$ (G1)), 1.34-1.39 (m, 54H, SiCCH$_2$ (G2)), 3.30 (t, J = 6.1Hz, 54H, CH$_2$O (G2)), 4.42 (s, 27H, OH), 7.28-7.34 (m, 5H, Ph).

8 The representative proton nmr of G2-mesogen is described. ^{1}H-NMR (CDCl$_3$, 400MHz): δ 0.53-0.62 (m, 60H, SiCCCH$_2$ (G0), SiCH$_2$ (G2), SiCCCH$_2$ (G1), SiCH$_2$ (G2)), 0.83-0.89 (m, 6H, SiCH$_2$ (G0)), 1.20-1.33 (m, 24H, SiCCH$_2$ (G0), SiCCH$_2$ (G1)), 1.48-1.51 (m, 54H, CH$_2$CO), 1.57-1.72 (m, 108H, SiCCH$_2$ (G2), OCCH$_2$), 1.75-1.83 (m, 54H, OCCCH$_2$), 2.23-2.34 (m, 54H, C(O)CH$_2$), 3.92 (t, J = 6.4Hz, 54H, CCH$_2$O), 4.00 (t, J = 6.8 Hz, 54H, SiCCCH$_2$ (G2)), 6.89-7.63 (m, 221H, Ar).