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Preparation and Characterization of Novel Carbosilane Dendrimers Carrying Mesogens

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A series of new carbosilane dendrimers carrying cyanobiphenyl derivatives was prepared starting from the tertiary core molecule, triallylphenylsilane. The phase transition of the dendrimers depends on the dendrimer generation, and the spacer lengths were investigated by using differential scanning calorimetry (DSC) and an optical polarizing microscope. All of the dendrimers prepared exhibited smectic A phases. The phase behavior on the phase-transition pattern of the DSC curve and the texture appearances of G2-mesogen(5) carrying twenty-seven mesogens were observed to be similar to that of the reported G2 dendrimer prepared starting from the quarternary core molecule, tetraallylsilane, carrying thirty-six mesogens.[4]

Recently, dendrimers have been paid much attention as well-defined macromolecules with a regular, three-dimensional structure. A homogeneous polyfunctionality is one of the striking characteristics of dendrimers.[2] Interest has been concentrated on introducing functional moieties, such as transition metals,[3] liquid crystals,[4] and sugar derivatives,[5] as well as the synthesis of the dendrimer with a higher generation.[6] The reported dendrimers have been classified into several categories according to the atoms or molecules, which consist of branch-points, such as carbon, nitrogen, silicon, germanium, and benzyne derivatives. We considered that the carbosilane dendrimer is one of the best choices for preparing a precisely designed dendrimer-skeleton carrying mesogens, because it is flexible enough to form a liquid-crystalline phase. Also it is easy to choose the number of branches at each generation from one to three, and the chain length between the terminal silicon and the mesogen. Furthermore, the carbosilane dendrimer is soluble in a common solvent, such as tetrahydrofuran (THF), chloroform and ethyl acetate, even though the molecular weight of the dendrimer is huge, being over thousands. In this paper we wish to report on the preparation and characterization of new carbosilane dendrimers carrying mesogens.[1]

Results and Discussion

Preparation of New Dendrimers. The successful preparation of a carbosilane dendrimer bearing mesogens, starting from the quarternary core molecule, has already been reported.[4] This paper also describes the difficulties for a complete transformation of the functional hydroxyl groups to mesogens due to the crowded surface of the dendrimer.[4a]

A series of new dendrimers, starting from the tertiary core molecule, triallylphenylsilane, were designed (G*n*-mesogen(*m*) (n = 0, 1, 2, and 3; m = 4, 5, 6, and 7) (Fig. 1). We expected that the use of the tertiary core molecule would decrease the difficulties in preparing completely substituted liquid-crystalline dendrimers, and the phenyl substituent on the core molecule might take part as another type of function.

Triallylphenylsilane was treated with trichlorosilane in the presence of a catalytic amount of chloloplatinic acid, and then with an excess amount of allylmagnesium bromide to yield tris[3-(triallylsilyl)propyl]phenylsilane (G1). The higher generation dendrimers (G1, G2, G3, and G4) were prepared by repeated hydrosilylation/Grignard reaction (Scheme 1).

The yields decreased according to the generation growth, since the higher was the generation, the more did the steric hindrance of the dendrimer surface increase. The dendrimers G2 and G3 were purified by using silica-gel chromatography (Hexane : Ethyl acetate = 98 : 2). The purification of G4, however, was unsuccessful under similar conditions of silica-gel chromatography, because G4 eluted quickly from the silica-gel column, although the R_f value on the thin-layer chromatography of G4 showed 0.2—0.3 (Hexane : Ethyl acetate = 98 : 2), which was close to that of G2 and G3. It is supposed that G4 forms a virtually spherical structure, and that the exclusive mechanism works for G4 rather than the affinity one in column chromatography. It may be one

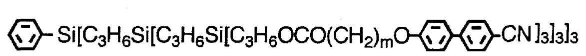
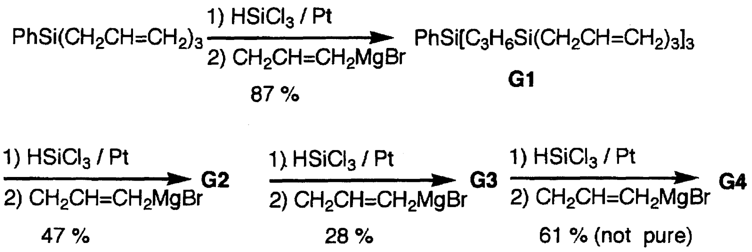


Fig. 1. G2-mesogen(*m*) (m = 4, 5, 6, and 7).

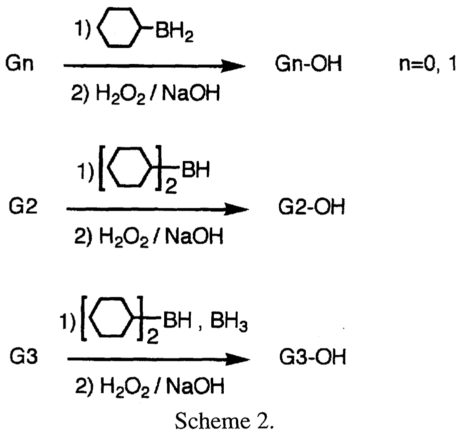


Scheme 1.

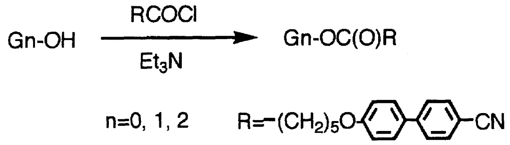
proof that the dendrimer over G4 approximates more closely to a spherical form.

Hydroboration reactions of the dendrimers were performed to give hydroxyl derivatives (G0-, G1-, G2-, G3-, and G4-OH) in 88, 97, 90, 91, and 10% yield, respectively (Scheme 2). Cyclohexylborane, prepared in situ by mixing an equimolar amount of borane and cyclohexene in tetrahydrofuran (THF) at 0 °C, was used for the hydroboration of G0 and G1, and dicyclohexylborane was used for the higher generation dendrimers over G2 in order to avoid any precipitation of the bridged organoborane polymers during the hydroboration reactions. Since dicyclohexylborane was too bulky to accomplish hydroboration for G3 and G4, another 0.2 molar equivalents of the diborane solution in THF were required to complete the hydroboration reactions. However, G4-OH was obtained only in low yield, perhaps due to an increased number of functions (243) and an enormous steric hindrance. G2-OH was purified by reprecipitation from a mixture of THF and chloroform. G2-, G3-, and G4-OH were also purified by reprecipitation ($MeOH/CHCl_3$). Completion of the hydroboration reactions was confirmed by the disappearance of olefinic signals in the ^{1}H NMR spectra.

The Effects of Dendrimer Generation. The polyol derivatives, G*n*-OH ($n = 0, 1, 2$), were treated with an acid chloride derivative of a mesogenic molecule, 6-(4′-cyanobiphenyl-4-yloxy)hexanoic acid, in the presence of triethylamine to afford the corresponding dendrimers carrying mesogen moieties (Scheme 3), G*n*-mesogen(5) ($n = 0, 1, 2$). The yields of G0-, G1-, and G2-mesogen were 50, 52, and 67%, respectively. That the preparation of the completely substituted G3-mesogen(5) was unsuccessful, may have been due to the bigger steric hindrance of the G3 dendrimer. The structures of the G*n*-mesogens ($n = 0, 1, 2$) were confirmed by the NMR spectra.



Scheme 2.



Scheme 3.

Characterizations of G*n*-mesogens(5) ($n = 0, 1, 2$) were performed using differential scanning calorimetry (DSC) and an optical polarizing microscope. The DSC charts for the carbosilane dendrimer derivatives (G0-, G1, and G2-mesogen(5)), are shown in Fig. 2. All of the G*n*-mesogens exhibit enantiotropic liquid-crystalline phases, and a slight hysteresis was found in the DSC profiles (Table 1). Higher clearing points were observed according to the propagation of dendrimer generation, although the melting points (glass transition point) showed little difference. G2-mesogen(5) shows a wider range of the liquid-crystalline phase, from 15 to 115 °C, than that of G1- and G0-mesogen (G1-mesogen, 14—72 °C; G0-mesogen, 7—44 °C), and a sharp isotropic curve upon heating. These data may show that the mesogens on the surface of G2 are able to form a more concentrated liquid-crystalline layer than the mesogens in the corresponding

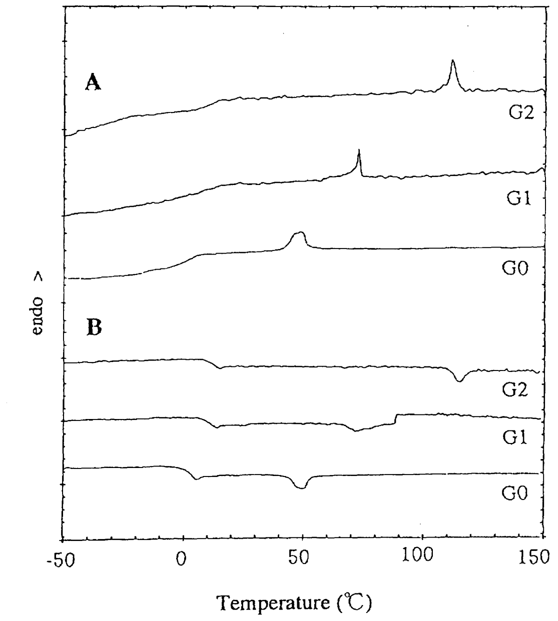


Fig. 2. The DSC traces of G*n*-mesogen(5) ($n = 0, 1, 2$), **A**; cooling, **B**; 2nd heating.

Table 1. Thermal Behavior of G*n*-mesogen(5) (n = 0, 1, 2)[a)]

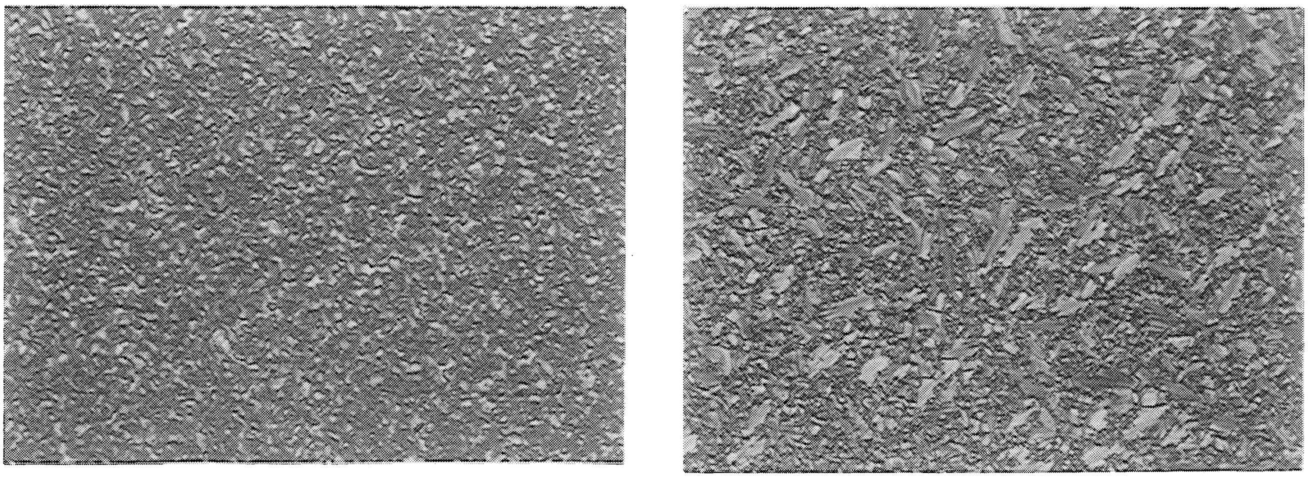
G$_n$-mesogen	Phase behavior/°C	
n	Cooling	Second heating
0	I 43 S_A 4 G	G 7 S_A 44 I
1	I 73 S_A 11 G	G 14 S_A 72 I
2	I 111 S_A 11 G	G 15 S_A 115 I

a) I; isotropic, G; Glass transition temperature, S_A; smectic A.

G0 and G1. Also the difficulties encountered in preparing G2-, and G3-mesogen(5) described above support these inferences. The transition enthalpies of G0-, G1-, and G2-mesogen(5) are 3.7, 6.3, and 38.4 kJ mol^{-1}, which correspond to 1.2, 0.7, and 1.4 kJ mol^{-1} per mesogenic unit, respectively. These values have similar magnitudes to that of the G2 dendrimer prepared by using tetrachlorosilane as a core molecule.[4a] Pictures of the polarizing microscope analyses for G*n*-mesogen(5) (n = 0, 1, and 2) are shown in Fig. 3. The liquid crystal-phases exhibited a focal conic fan texture, typical of smectic A phases. It was found that greater generations of the dendrimers showed bigger domain sizes in the pictures.

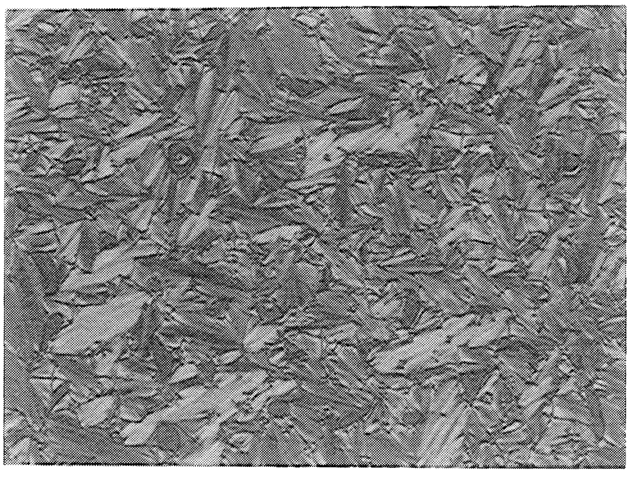
The Effects of the Spacer Length of Dendrimer. In order to investigate the effects of the spacer length between the terminal oxygen and the mesogens, G2-mesogens having different numbers of methylene spacers, from four to seven, were prepared. G2-mesogen was used for the study because it showed the clearest phase-transition curve among the investigated G*n*-mesogens as described above. G2-OH was treated with acid chloride derivatives of mesogens: 4-(4′-cyanobiphenyl-4-yloxy) butanoic-, 6-(4′-cyanobiphenyl-4-yloxy)hexanoic-, and 7-(4′-cyanobiphenyl-4-yloxy)heptanoic acid, in the presence of triethylamine to give G2-mesogen(4), (6), and (7) in 18, 27, and 20% yield, respectively (Scheme 4).

All of the dendrimers prepared here also exhibited a focal conic fan texture, typical of smectic A phases. No significant differences in the isotropic temperature dependence on



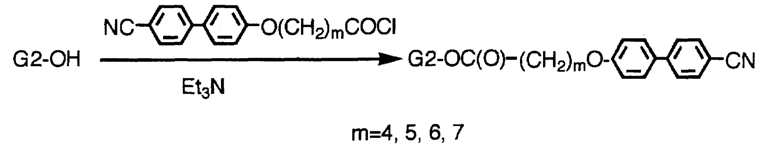
(a) G0-mesogen(5) at 42 ℃

(b) G1-mesogen(5) at 40 ℃



(c) G2-mesogen(5) at 105 ℃

Fig. 3. Optical polarizing photomicrographs.



Scheme 4.

the spacer length (*m* = 4, 5, 6, and 7) were observed in the DSC analyses (Fig. 4 and Table 2). Clear odd-even effects according to the spacer length (*m* = 4, 5, 6, and 7) were not found with regard to the clearing points. However, polarizing microscope analyses showed that the texture of the G2-mesogen bearing a spacer length of five has a similar feature to that of seven, and that of four has a similar one to that of six. The transition enthalpy of G2-mesogen(4), (6), and (7) is 0.7, 1.4, and 1.3 kJ mol^{-1} per mesogen, respectively.

Conclusions

All of the carbosilane dendrimers carrying mesogens prepared here showed smectic A phases. The phase behavior on the DSC and optical polarizing microscope analyses of G2-mesogen(5), which carried twenty-seven mesogens, was observed to be similar to that of the reported G2-mesogen-(4) prepared from the quarternary core molecule carrying thirty-six mesogens.[4a] It is noted that the use of the tertiary core is sufficient for preparing liquid-crystalline carbosilane dendrimers.

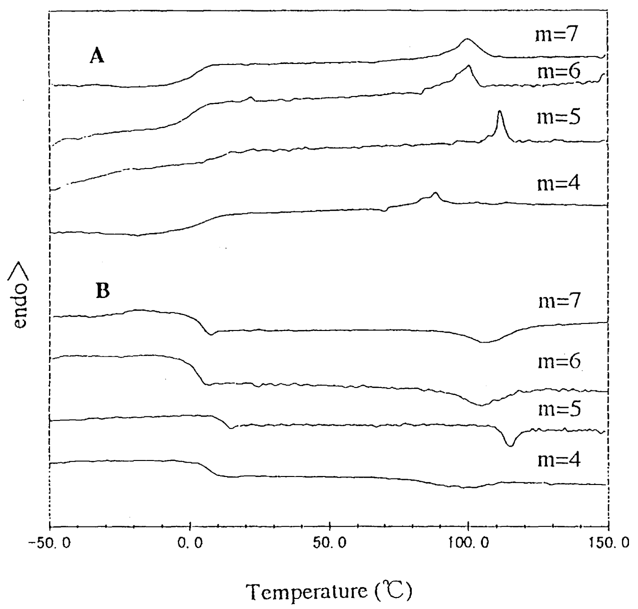


Fig. 4. The DSC traces of G2-mesogen(*m*) (*m* = 4, 5, 6, 7), **A**; cooling, **B**; 2nd heating.

Table 2. Thermal Behavior of G2-mesogen(*m*) (*m* = 4, 5, 6, 7)[a)]

G2-mesogen(*m*)	Phase behavior/°C	
m	Cooling	Second heating
4	I 88 S_A 8 G	G 12 S_A 100 I
5	I 111 S_A 10 G	G 15 S_A 115 I
6	I 102 S_A 5 G	G 8 S_A 105 I
7	I 102 S_A 5 G	G 9 S_A 107 I

a) I; isotropic, G; Glass transition temperature, S_A; smectic A.

Experimental

The NMR spectra were recorded on a Bruker AR400 (400 MHz) and a Gemini 200 (200 MHz) spectrometer in $CDCl_3$ using TMS as the internal standard, unless otherwise stated. Phase sequences were observed using a Nikon OPTIPHOT2-POL polarizing microscope equipped with a Mettler FP-90/FP-82HT thermal-control system. The phase-transition temperatures were determined using a MAC Science DSC-3100 differential scanning calorimeter. All of the reaction was carried out under a dry argon atmosphere, and the solvents used were dried over sodium and distilled just before use.

Preparation of G1. A solution of trichlorosilane (25.0 g, 185 mmol) in THF (10 ml) was added to a solution of triallylphenylsilane (9.4 g, 41 mmol) in THF (10 ml), with a small amount of Speier catalyst at 0 °C. The mixture was stirred at room temperature for 24 h, then refluxed for 2 h. Excess trichlorosilane was evaporated. A part of the residue (5.0 g correspond to 7.9 mmol of the hydrosilylation product) was dissolved in THF (10 ml). To the solution, a Grignard regent prepared from 3-bromo-1-propene (25.8 g, 213 mmol) and Mg (5.2 g, 213 g-atom) in Et_2O (160 ml) was added with external cooling. The mixture was refluxed for 24 h with stirring. Aqueous HCl (1 M, 100 ml, 1 M = 1 mol dm^{-3}) was added to the reaction mixture. The mixture was extracted with Et_2O (10 ml×3). The combined extracts were dried (Na_2SO_4). The solvent was evaporated in vacuo, and the residue was column-chromatographed on silica-gel (Hexane) to give G1 in 4.7 g (87%) yield. ^{1}H NMR ($CDCl_3$) δ = 0.6—0.7 (m, 6H, $SiCCCH_2$ (G0)), 0.8—0.9 (m, 6H, $SiCH_2$ (G0)), 1.3—1.4 (m, 6H, $SiCCH_2$ (G0)), 1.55 (d, *J* = 8.0 Hz, 18H, $SiCH_2$ (G1)), 4.8—4.9 (m, 18H, $=CH_2$), 5.7—5.8 (m, 9H, CH=), 7.3—7.5 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$) δ = 16.4 ($PhSiCCCH_2$), 17.0 ($PhSiCH_2$), 17.9 ($PhSiCCH_2$), 19.6 ($SiCH_2$ (G1)), 113.5 ($=CH_2$), 133.9 (CH=), 127.6, 127.7, 128.7, 134.3 (Ar). Found: C, 73.48; H, 10.15%. Calcd for $Si_4C_{42}H_{68}$: C, 73.61; H, 10.00%.

Preparation of G2, G3, and G4. Higher generation of dendrimers (G2, G3, and G4) were prepared in a similar manner to that descried above.

G2: Yield 47%. ^{1}H NMR ($CDCl_3$) δ = 0.5—0.6 (m, 24H, $SiCCCH_2$ (G0), $SiCH_2$ (G1)), 0.6—0.7 (m, 18H, $SiCCCH_2$ (G1)), 0.8—0.9 (m, 6H, $SiCH_2$ (G0)), 1.3—1.4 (m, 24H, $SiCCH_2$ (G0), $SiCCH_2$ (G1)), 1.57 (d, *J* = 8.1 Hz, 54H, $SiCH_2$ (G2)), 4.8—4.9 (m, 54H, $=CH_2$), 5.7—5.8 (m, 27H, CH=), 7.3—7.5 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$) δ = 16.6 ($SiCH_2$ (G1)), 17.4 ($SiCCCH_2$ (G1)), 17.70 ($SiCH_2$ (G0)), 17.72 ($SiCCCH_2$ (G0)), 18.2 ($SiCCH_2$ (G1)), 18.5 ($SiCCH_2$ (G0)), 19.7 ($SiCH_2$ (G2)), 113.5 ($=CH_2$), 133.4 (=CH), 122.7, 128.7, 133.9, 137.6 (Ar). Found: C, 71.80; H, 10.45%. Calcd for $Si_{13}C_{123}H_{212}$: C, 71.85; H, 10.39%.

G3: Yield 27.6%. ^{1}H NMR ($CDCl_3$) δ = 0.5—0.7 (m, 96H, $SiCCCH_2$ (G0), $SiCH_2$ (G1), $SiCCCH_2$ (G1), $SiCH_2$ (G2)), 0.6—0.7 (m, 54H, $SiCCCH_2$ (G2)), 0.8—0.9 (m, 6H, $SiCH_2$ (G0)), 1.2—1.4 (m, 78H, $SiCCH_2$ (G0), $SiCCH_2$ (G1), $SiCCH_2$ (G2)), 1.57 (d, *J* = 8.0 Hz, 162H, $SiCH_2$ (G3)), 4.8—4.9 (m, 162H, $=CH_2$), 5.7—5.8 (m, 54H, CH=), 7.3—7.5 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$) δ =

16.7 (SiCH$_2$ (G2)), 17.5 (SiCCCH$_2$ (G2)), 17.8 (SiCCCH$_2$ (G1)), 18.2 (SiCCCH$_2$ (G0)), 18.22 (SiCH$_2$ (G1)), 18.4 (SiCH$_2$ (G3)), 18.6 (SiCCH$_2$ (G1)), 19.5 (SiCH$_2$ (G0)), 19.7 (SiCCH$_2$ (G2)), 19.9 (SiCH$_2$ (G0)), 113.6 (=CH$_2$), 133.2 (=CH), 127—138 (Ar). Found: C, 71.47; H, 10.76%. Calcd for $\mathrm{Si_{121}C_{1095}H_{1940}}$: C, 71.07; H, 10.57%.

G4 (not pure): ^{1}H NMR (CDCl$_3$) δ = 0.5—0.7 (m, 474H, SiCCCH$_2$ (G0), SiCH$_2$ (G1), SiCCCH$_2$ (G1), SiCH$_2$ (G2), SiCCCH$_2$ (G2), SiCH$_2$ (G3), SiCCCH$_2$ (G3)), 0.8—0.9 (m, 6H, SiCH$_2$ (G0)), 1.2—1.6 (m, 240H, SiCCH$_2$ (G0), SiCCH$_2$ (G1), SiCCH$_2$ (G2), SiCCH$_2$ (G3)), 1.55 (d, J = 8.1 Hz, 486H, SiCH$_2$ (G4)), 4.8—4.9 (m, 162H, =CH$_2$), 5.7—5.8 (m, 243H, CH=), 7.3—7.5 (m, 5H, Ar); ^{13}C NMR (CDCl$_3$) δ = 16.9—19.9 (SiCH$_2$ (G0), SiCCH$_2$ (G0), SiCCCH$_2$ (G0), SiCH$_2$ (G1), SiCCH$_2$ (G1), SiCCCH$_2$ (G1), SiCH$_2$ (G2), SiCCH$_2$ (G2), SiCCCH$_2$ (G2), SiCH$_2$ (G3), SiCCH$_2$ (G3), SiCCCH$_2$ (G3)), 19.7 (SiCH$_2$ (G4)), 113.9 (=CH$_2$), 134.0 (=CH), 127—138 (Ar).

Preparation of G1-OH. A solution of G1 (0.20 g, 0.29 mmol) in THF (1 ml) was added to a solution of cyclohexylborane, which was prepared from a borane: THF complex in THF (1.96 ml of 1 M solution in THF) and cyclohexene (0.16 g, 1.96 mmol) in THF (1 ml) at 0 °C. After stirring at room temperature for 3 h, methanol (0.3 ml) was added to the reaction mixture. Aqueous sodium hydroxide (3.48 ml of 3 M solution) and hydrogen peroxide (1.42 ml of 30% aqueous solution) was added to the reaction mixture at 0 °C, subsequently. The reaction mixture was stirred at 60 °C for 1 h. After the usual workup, the residue was purified by reprecipitaion from chloroform to give G1-OH in 0.24 g (97%) yield. ^{1}H NMR (DMSO-d_6) δ = 0.4—0.5 (m, 18H, SiCH$_2$ (G1)), 0.5—0.6 (m, 6H, SiCCCH$_2$ (G0)), 0.8—0.9 (m, 6H, SiCH$_2$ (G0)), 1.3—1.4 (m, 24H, SiCCH$_2$ (G0), SiCCH$_2$ (G1)), 3.29 (q, J = 5.6 Hz, 18H, CH$_2$O), 4.3—4.4 (broad s, 9H, OH), 7.3—7.5 (m, 5H, Ar); ^{13}C NMR (DMSO-d_6) δ = 8.1 (SiCH$_2$ (G1)), 17.06 (SiCH$_2$ (G0)), 17.1 (SiCCCH$_2$ (G0)), 18.3 (SiCCH$_2$ (G0)), 27.2 (SiCCH$_2$ (G1), 64.2 (SiCCCH$_2$ (G1)), 127.9, 128.9, 133.9, 137.5 (Ar).

G2-OH: Hydroboration of G2 was performed in the similar manner to that described above, besides the use of dicyclohexylborane instead of cyclohexylborane. Yield 90%. ^{1}H NMR (DMSO-d_6) δ = 0.39—0.43 (m, 54H, SiCH$_2$ (G2)), 0.43—0.55 (m, 42H, SiCCCH$_2$ (G0), SiCH$_2$ (G1), SiCCCH$_2$ (G1)), 0.7—0.8 (m, 6H, SiCH$_2$ (G0)), 1.2—1.3 (m, 24H, SiCCH$_2$ (G0), SiCCH$_2$ (G1)), 1.3—1.4 (m, 54H, SiCCH$_2$ (G2)), 3.31 (q, J = 5.8 Hz, 54H, CH$_2$O), 4.43 (t, J = 5.3 Hz, 27H, OH), 7.3—7.4 (m, 5H, Ar); ^{13}C NMR (DMSO-d_6) δ = 7.2 (SiCH$_2$ (G2)), 16.0—17.0 (SiCH$_2$ (G0), SiCCH$_2$ (G0), SiCCCH$_2$ (G0)), 16.42 (SiCH$_2$ (G1)), 16.45 (SiCCCH$_2$ (G1)), 17.4 (SiCCH$_2$ (G1)), 26.3 (SiCCH$_2$ (G2), 63.4 (CH$_2$O), 126—133 (Ar).

G3-OH: Hydroboration of G3 was performed in a similar manner to that described above, besides the use of dicyclohexylborane instead of cyclohexylborane and the addition of a small amount of borane to the reaction mixture to complete the hydroboration. Yield 91%. ^{1}H NMR (DMSO-d_6) δ = 0.4—0.6 (m, 312H, SiCCCH$_2$ (G0), SiCH$_2$ (G1), SiCCCH$_2$ (G1), SiCH$_2$ (G2), SiCCCH$_2$ (G2), SiCH$_2$ (G3)), 0.7—0.8 (m, 6H, SiCH$_2$ (G0)), 1.1—1.4 (m, 240H, SiCCH$_2$ (G0), SiCCH$_2$ (G1), SiCCH$_2$ (G2), SiCCH$_2$ (G3)), 3.34 (broad s, CH$_2$O), 4.13 ((broad s, 81H, OH), 7.2—7.4 (Ar); ^{13}C NMR (DMSO-d_6) δ = 8.1 (SiCH$_2$ (G3)), 17.0—19.0 (SiCH$_2$ (G0), SiCCH$_2$ (G0), SiCCCH$_2$ (G0), SiCH$_2$ (G1), SiCCH$_2$ (G1), SiCCCH$_2$ (G1)), 17.4 (SiCH$_2$ (G2)), 17.4 (SiCCCH$_2$ (G2)), 18.4 (SiCCH$_2$ (G2)), 27.2 (SiCCH$_2$ (G3), 64.3 (CH$_2$O), 126—133 (Ar).

Preparation of G0-mesogen(5). A solution of 6-(4′-cyanobiphenyl-4-yloxy)hexanoyl chloride (0.27 g, 0.81 mmol) in THF (2 ml) was added to a solution of G0 (50 mg, 0.18 mmol) in THF (3 ml) at 0 °C. The mixture was stirred at 50 °C for 3 d. After the usual workup, the residue was column-chromatographed on silica-gel (dichloromethane : ethyl acetate = 98 : 2) to give G0-mesogen-(5) in 0.12 g (59%) yield. ^{1}H NMR (CDCl$_3$) δ = 0.8—0.9 (m, 6H, SiCH$_2$), 1.5—1.6 (m, 12H, SiCCH$_2$, C(=O)CCCH$_2$), 1.7—1.8 (m, 6H, C(=O)CCH$_2$), 2.34 (t, J = 7.5 Hz, 6H, C(=O)CH$_2$), 3.99 (t, 6.3 Hz, 6H, OCH$_2$), 4.03 (t, 6.8 Hz, 6H, SiCCCH$_2$O), 6.9—7.8 (29H, Ar); ^{13}C NMR (CDCl$_3$) δ = 8.1 (SiCH$_2$), 23.0 (SiCCH$_2$), 24.6 (C(=O)CCCH$_2$), 25.6 (C(=O)CCH$_2$), 28.9 (CH$_2$CO), 34.1 (C(=O)CH$_2$), 66.6 (SiCCCH$_2$), 67.7 (CH$_2$O), 110 (CN), 114.8—159.6 (Ar), 173.5 (C=O). Found: C, 75.02; H, 6.79; N, 3.58%. Calcd for $\mathrm{Si_1C_{72}H_{77}N_3O_9}$: C, 74.78; H, 6.71; N, 3.63%.

G1-mesogen(5): Preparation of G1-mesogen(5) was performed in a similar manner to that described above. Yield 52%. ^{1}H NMR (CDCl$_3$) δ = 0.4—0.5 (m, 18H, SiCH$_2$ (G1)), 0.6—0.7 (m, 6H, SiCCCH$_2$ (G0)), 0.8—0.9 (m, 6H, SiCH$_2$ (G0)), 1.2—1.4 (m, 6H, SiCCH$_2$ (G0)), 1.4—1.6 (m, 36H, SiCCH$_2$ (G1), CH$_2$CO), 1.6—1.7 (m, 18H, C(=O)CCH$_2$), 1.8—1.9 (m, 18H, C(=O)CCCH$_2$), 2.33 (t, J = 7.5 Hz, 18H, C(=O)CH$_2$), 4.0—4.1 (t, J = 6.8 Hz, 18H, OCH$_2$), 4.0—4.1 (t, J = 7.0 Hz, 18H, SiCCCH$_2$ (G1)), 6.9—7.7 (77H, Ar); ^{13}C NMR (CDCl$_3$) δ = 7.9 (SiCH$_2$ (G1)), 16.9 (SiCCCH$_2$ (G0)), 17.4 (SiCH$_2$ (G0)), 18.3 (SiCCH$_2$ (G0)), 22.9 (SiCCH$_2$ (G1)), 24.6 (C(=O)CCH$_2$), 25.6 (C(=O)CCCH$_2$), 28.8 (C(=O)CCCCH$_2$), 34.0 (C(=O)CH$_2$), 67.4 (CH$_2$O), 68.2 (SiCCCH$_2$ (G1)), 110 (CN), 114.8—158.6 (Ar), 173.4 (C=O). Found: C, 73.51; H, 6.72; N, 3.70%. Calcd for $\mathrm{Si_4C_{213}H_{239}N_9O_{27}}$: C, 73.74; H, 6.94; N, 3.63%.

G2-mesogen(5): Preparation of G2-mesogen(5) was performed in a similar manner to that described above. Yield 67%. ^{1}H NMR (CDCl$_3$) δ = 0.5—0.7 (m, 96H, SiCCCH$_2$ (G0), SiCH$_2$ (G1), SiCCCH$_2$ (G1), SiCH$_2$ (G2)), 0.8—0.9 (m, 6H, SiCH$_2$ (G0)), 1.2—1.3 (m, 24H, SiCCH$_2$ (G0), SiCCH$_2$ (G1)), 1.4—1.5 (m, 54H, C(=O)CCCH$_2$), 1.5—1.6 (m, 54H, SiCCH$_2$ (G2)), 1.6—1.7 (m, 54H, C(=O)CCH$_2$), 1.7—1.8 (m, 54H, CH$_2$CO), 2.31 (t, J = 7.2 Hz, 54H, C(=O)CH$_2$), 3.92 (t, J = 6.5 Hz, 54H, CH$_2$O), 3.99 (t, J = 6.7 Hz, SiCCCH$_2$ (G2)), (221H, Ar); ^{13}C NMR (CDCl$_3$) δ = 7.9 (SiCH$_2$ (G2)), 14.1—18.4 (SiCH$_2$ (G0), SiCCH$_2$ (G0), SiCCCH$_2$ (G0), SiCH$_2$ (G1), SiCCH$_2$ (G1), SiCCCH$_2$ (G1)), 23.1 (SiCCH$_2$ (G2), 24.7 (C(=O)CCH$_2$), 25.7 (C(=O)CCCH$_2$), 28.9 (C(=O)CCCH$_2$), 34.0 (C(=O)CH$_2$), 66.7 (CH$_2$O), 67.6 (SiCCCH$_2$ (G2)), 110.1 (CN), 113.3—159.5 (Ar), 173.3 (C=O). Found: C, 73.10; H, 6.92; N, 3.42%. Calcd for $\mathrm{Si_{13}C_{636}H_{725}N_{27}O_{81}}$: C, 73.39; H, 7.02; N, 3.63%.

Preparation of G2-mesogen(*m*) (*m* = 4, 6, and 7). Preparations of G2-mesogens bearing a different number of methylene number were carried out in a similar manner to that described above using the corresponding acid chloride mesogen derivatives.

G2-mesogen(4): Yield 18%. ^{1}H NMR (CDCl$_3$) δ = 0.5—0.7 (m, 96H, SiCCCH$_2$ (G0), SiCH$_2$ (G1), SiCCCH$_2$ (G1), SiCH$_2$ (G2)), 0.8—0.9 (m, 6H, SiCH$_2$ (G0)), 1.2—1.3 (m, 24H, SiCCH$_2$ (G0), SiCCH$_2$ (G1)), 1.5—1.7 (m, 54H, SiCCH$_2$ (G2)), 1.7—1.9 (m, 108H, C(=O)CCH$_2$, C(=O)CCCH$_2$), 2.35 (t, J = 7.2 Hz, 54H, C(=O)CH$_2$), 3.89 (t, J = 5.6 Hz, 54H, OCH$_2$), 3.99 (t, J = 6.8 Hz, 54H, SiCCCH$_2$ (G2)), 6.9—7.7 (221H, Ar); ^{13}C NMR (CDCl$_3$) δ = 7.9 (SiCH$_2$ (G2)), 14.1—15.5 (SiCH$_2$ (G0), SiCCH$_2$ (G0), SiCCCH$_2$ (G0)), 17.5, 17.6, 18.5 (SiCH$_2$ (G1), SiCCH$_2$ (G1), SiCCCH$_2$ (G1)), 21.6 (C(=O)CCH$_2$), 23.2 (SiCCH$_2$ (G2)), 28.5 (C(=O)CCCH$_2$), 33.8 (C(=O)CH$_2$), 66.7 (CH$_2$O), 67.4 (SiCCCH$_2$ (G2)), 110.2 (CN), 113.4—159.4 (Ar), 173.3 (C=O). Found: C, 73.10; H, 6.70; N, 3.56%. Calcd for $\mathrm{Si_{13}C_{609}H_{671}N_{27}O_{81}}$: C, 72.93; H, 6.74; N, 3.77%.

G2-mesogen(6): Yield 27%. ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 0.5—0.7 (m, 96H, $\mathrm{SiCCCH_2}$ (G0), $\mathrm{SiCH_2}$ (G1), $\mathrm{SiCCCH_2}$ (G1), $\mathrm{SiCH_2}$ (G2)), 0.8—0.9 (m, 6H, $\mathrm{SiCH_2}$ (G0)), 1.2—1.3 (m, 24H, $\mathrm{SiCCH_2}$ (G0), $\mathrm{SiCCH_2}$ (G1)), 1.3—1.4 (m, 54H, $\mathrm{C(=O)CCCH_2}$), 1.4—1.5 (m, 54H, $\mathrm{C(=O)CCCCH_2}$), 1.5—1.7 (m, 108H, $\mathrm{SiCCH_2}$ (G2), $\mathrm{C(=O)CCH_2}$), 1.7—1.8 (m, 54H, $\mathrm{CH_2CO}$), 2.29 (t, J = 7.2 Hz, 54H, $\mathrm{C(=O)CH_2}$), 3.93 (t, J = 6.4 Hz, 54H, $\mathrm{CH_2O}$), 3.98 (t, J = 6.6 Hz, 54H, $\mathrm{SiCCCH_2}$ (G2)), (221H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$) δ = 7.9 ($\mathrm{SiCH_2}$ (G2)), 14.1—18.4 ($\mathrm{SiCH_2}$ (G0), $\mathrm{SiCCH_2}$ (G0), $\mathrm{SiCCCH_2}$ (G0), $\mathrm{SiCH_2}$ (G1), $\mathrm{SiCCH_2}$ (G1), $\mathrm{SiCCCH_2}$ (G1)), 23.1 ($\mathrm{SiCCH_2}$ (G2)), 24.8 ($\mathrm{C(=O)CCCH_2}$), 25.8 ($\mathrm{C(=O)CCCCH_2}$), 29.0, 29.1 ($\mathrm{C(=O)CCH_2}$, $\mathrm{C(=O)CCCCCH_2}$), 34.1 ($\mathrm{C(=O)CH_2}$), 66.6 ($\mathrm{CH_2O}$), 67.8 ($\mathrm{SiCCCH_2}$ (G2)), 110.1 (CN), 113.3—159.5 (Ar), 173.4 (C=O). Found: C, 7.359; H, 7.41; N, 3.66%. Calcd for $\mathrm{Si_{13}C_{663}H_{779}N_{27}O_{81}}$: C, 73.82; H, 7.28; N, 3.51%.

G2-mesogen(7): Yield 20%. ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 0.5—0.7 (m, 96H, $\mathrm{SiCCCH_2}$ (G0), $\mathrm{SiCH_2}$ (G1), $\mathrm{SiCCCH_2}$ (G1), $\mathrm{SiCH_2}$ (G2)), 0.8—0.9 (m, 6H, $\mathrm{SiCH_2}$ (G0)), 1.2—1.3 (m, 24H, $\mathrm{SiCCH_2}$ (G0), $\mathrm{SiCCH_2}$ (G1)), 1.3—1.4 (m, 108H, $\mathrm{C(=O)CCCH_2CH_2}$), 1.4—1.5 (m, 54H, $\mathrm{CH_2CCO}$), 1.6—1.7 (m, 108H, $\mathrm{C(=O)CCH_2}$, $\mathrm{SiCCH_2}$ (G2)), 1.7—1.8 (m, 54H, $\mathrm{CH_2CO}$), 2.29 (t, J = 7.2 Hz, 54H, $\mathrm{C(=O)CH_2}$), 3.93 (t, J = 6.4 Hz, 54H, $\mathrm{CH_2O}$), 3.98 (t, J = 6.6 Hz, 54H, $\mathrm{SiCCCH_2}$ (G2)), (221H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$) δ = 7.9 ($\mathrm{SiCH_2}$ (G2)), 14.1—18.4 ($\mathrm{SiCH_2}$ (G0), $\mathrm{SiCCH_2}$ (G0), $\mathrm{SiCCCH_2}$ (G0), $\mathrm{SiCH_2}$ (G1), $\mathrm{SiCCH_2}$ (G1), $\mathrm{SiCCCH_2}$ (G1)), 23.1 ($\mathrm{SiCCH_2}$ (G2), 24.9 ($\mathrm{C(=O)CCCH_2}$), 25.9 ($\mathrm{C(=O)CCCCH_2}$), 29.0, 29.1, 29.1 ($\mathrm{C(=O)CCH_2}$, $\mathrm{C(=O)CCCCCH_2}$, $\mathrm{C(=O)CCCCCCH_2}$), 34.1 ($\mathrm{C(=O)CH_2}$), 66.6 ($\mathrm{CH_2O}$), 67.9 ($\mathrm{SiCCCH_2}$ (G2)), 110.1 (CN), 113.3—159.5 (Ar), 173.4 (C=O). Found: C, 73.99; H, 7.69; N, 3.52%. Calcd for $\mathrm{Si_{13}C_{690}H_{833}N_{27}O_{81}}$: C, 74.22; H, 7.52; N, 3.39%.

References

1 Preliminary report was published. D. Terunuma, T. Kato, R. Nishio, K. Matsuoka, H. Kuzuhara, Y. Aoki, and H. Nohira, *Chem. Lett.*, **1998**, 59.

2 Recent reviews: a) G. R. Newkome, "Advances in Dendritic Macromolecules," JAI, Greenwich, CT, Vol. 1 (1994), and 2 (1995). b) D. A. Tomalia and H. D. Duest, in "Topics in Current Chemistry," ed by E. Weber, Vol. 165, 193 (1993). c) J. Issberner, R. Moors, and F. Vögtle , *Angrew. Chem., Int. Ed. Engl.*, **33**, 2413 (1994). d) J. M. J. Fréchet, *Science*, **263**, 1710 (1994). e) N. Ardorin and D. Astruc, *Bull. Soc. Chim. Fr.*, **132**, 875 (1995).

3 a) J. W. J. Knapen, A. W. Van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijkens, D. Grove, and G. van Koten, *Nature*, **372**, 659 (1994). b) D. Seyferth, T. Kugita, A. Rheingold, and G. P. A. Yap, *Organometallics*, **14**, 5362 (1995). c) I. Cuadrado, M. Moràn, C. M. Casado, B. Alonso, F. Lobete, B. Garcia, M. Ibisate, and J. Losada, *Organometallics*, **15**, 5278 (1996).

4 a) K. Lorenz, D. Hölter, B. Stühn, R. Mülhaupt, and H. Frey, *Adv. Mater.*, **8**, 414 (1996). b) H. Frey, R. Mülhaupt, K. Lorenz, and U. Rapp, *Polym. Mater. Sci. Eng.*, **73**, 127 (1995). c) S. A. Ponomarenko, E. A. Rebrov, A. Y. Bobrovsky, N. I. Boiko, A. M. Muzafarov, and V. P. Shibaev, *Liq. Cryst.*, **21**, 1 (1996). d) K. Lorenz, H. Frey, B. Stühn, and R. Mülhaupt, *Macromolecules*, **30**, 6860 (1997). e) K. Lorenz, D. Hölter, H. Frey, and B. Stühn, *Polym. Mater. Sci. Eng.*, **77**, 168 (1997). f) E. V. Getmanova, T. B. Chenskaya, O. B. Gorbatsevich, E. A. Rebrov, N. G. Vasilenko, and A. M. Murzafarov, *React. Funct. Polym.*, **33**, 289 (1997). g) S. W. Shane and D. Seyferth, *J. Am. Chem. Soc.*, **120**, 3604 (1998).

5 a) K. Aoi, K. Itoh, and M. Okada, *Macromolecules*, **28**, 5391 (1995). b) D. Zanini, W. K. C. Park, S. J. Meunier, Q. Wu, S. Aravind, B. Kratzer, and R. Roy, *Polym. Mater. Sci. Eng.*, **73**, 82 (1995).

6 a) D. Seyferth, D. Y. Son, A. L. Rheingold, and R. L. Ostrander, *Organometallics*, **13**, 2682 (1994). b) A. W. van der Made and P. W. N. M. van Leeuwen, *J. Chem. Soc., Chem. Commun.*, **1992**, 1400. c) C. Kim and E. Park, *Bull. Korean Chem. Soc.*, **17**, 419 (1996). d) C. Kim and E. Park, *Bull. Korean Chem. Soc.*, **17**, 592 (1996). e) C. Kim and K. An, *Bull. Korean Chem. Soc.*, **18**, 164 (1997).