Crown-Ether End-Capped Carbosiloxane Dendrimers

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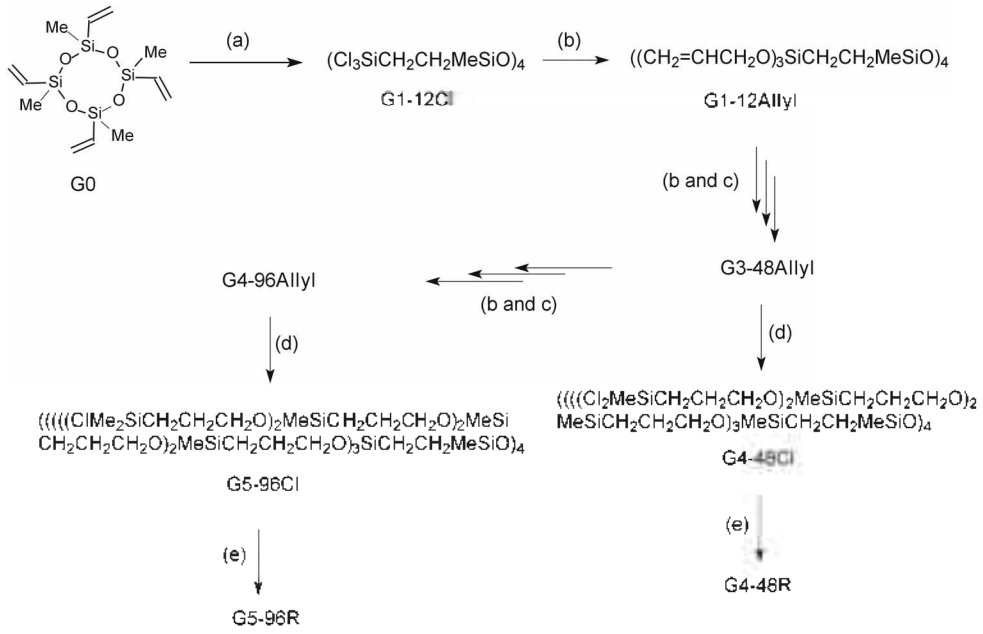
Dendrimers are perfect and unified macromolecules with regular and highly branched architectures that are obtained from an iterative procedure.[1] Due to their chemical and physical properties, dendrimers are used for many fields in material science.[2] The end-functionalized dendritic macromolecules with specific groups were studied by many researchers who used the electro-active groups or molecular recognition groups that could find applications as components in sensors and electro-devices etc.[3] Especially, crown-ether end-capped dendrimer and polymer could possibly be used as the high ion selective sensor.[2e] In our previous paper, we described the preparation of allyloxy and propagyloxy group functionalized carbosiloxane dendrimers, based on siloxane tetramer $(MeSiOCH=CH_2)_4$ as a core molecule and methylallyloxy groups as generating units.[4] For the purpose of extending of applicability, we have shifted our attention to the preparation of crown-ether end-capped dendrimers.[5]

The parent dendrimers, constructed with Si-Cl bonds on the fourth and fifth generations, were prepared by the use of catalytic hydrosilation with allyloxy groups on the dendrimers and $H\text{-}SiMe_2Cl$.[5] The reaction of the 4th (G4-48Cl) and 5th (G5-96Cl) generations of the parent dendrimers with crown-ether (2-(hydroxymethyl)-12-crown-4 and 2-(hydroxymethyl)-15-crown-5) in the presence of TMEDA produced crown-ether end-capped dendrimers with a very high yield (Scheme 1). The Si-O-C bonds on the outmost periphery are very stable against air and moisture. Therefore, after alcoholysis with 2-(hydroxymethyl)-12-crown-4 and 2-(hydroxymethyl)-15-crown-5, the handling of the prepared dendrimers in the atmosphere is possible. The successful addition of crown-ether to parent dendrimers can be easily detected by the characteristic shift of the dimethylsilyl group in the ^{13}C NMR spectra. A shift of the ^{13}C NMR signals ranges from 3.50 ppm for the dimethylsilyl groups of the parent dendrimers (**G4-48Cl** and **G5-96Cl**) to 0.99 ppm in the case of **G4-48Crown-4** or to -2.22 ppm in the case of **G5-96Crown-4**. Both dendrimers can be observed in oxo-ether groups on crown-ether ring at 62.6, 70.2, 70.5, 70.6, 70.9 and 71.4 ppm. The **G4-48Crown-5** and **G5-96Crown-5** revealed the same evidence at -2.18 ppm for both dendritic dimethylsilyl groups and oxo-ether groups at 62.6, 70.3, 70.5, 70.7, 71.0, and 71.1 (Figure 1). The **G4-48Crown-4**, **G5-96Crown-4**, **G4-48Crown-5** and **G5-96Crown-5** could be prepared in 55, 66, 53 and 60% yield after flash



(a) Hydrosilation with $HSiCl_3$, Pt/C, toluene, reflux (b) Alcoholysis with $CH_2=CHCH_2OH$, TMEDA, RT ~ 50 °C, toluene
(c) Hydrosilation with $HSiMeCl_2$ (d) Hydrosilation on the terminal groups with $HSiMe_2Cl$
(e)Termination with crown ether; R = 2-Methoxy-12-crown-4 and 2-Methoxy-15-crown-5, excess TMEDA, RT, toluene.

Scheme 1. Overview of reaction route of crown-ether end capped dendrimers.

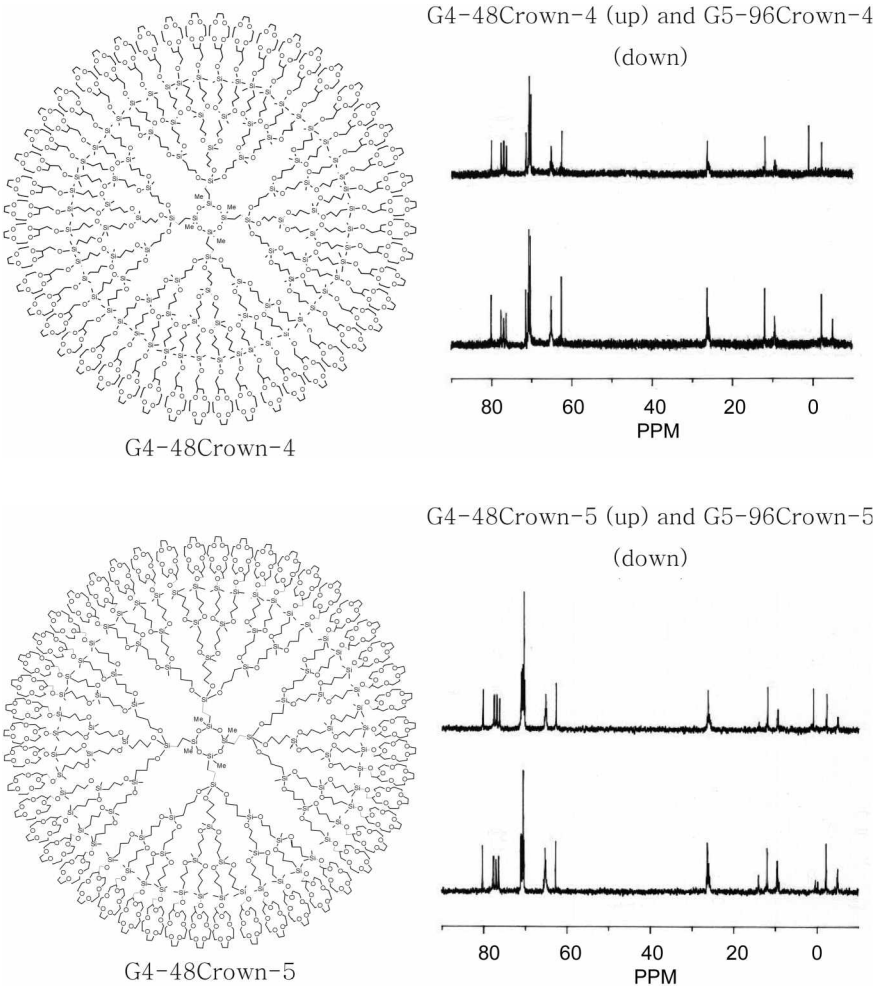


Figure 1. ^{13}C NMR spectra of crown ether end-capped dendrimers.

chromatography, respectively. The isolation of pure dendrimers from the reaction mixture was progressed under flash chromatography with chloroform as well as mixed eluents such as chloroform, THF (9 : 1) and silica gel columns. The identification of the end-capped dendrimers was done by the NMR, GPC as well as elemental analysis. The crown ether end-capped dendrimers could not provide MALDI-TOF-MS signals. The polydispersity index (PDI) values on gel permeation chromatography (GPC) remained almost unchanged in going from the fourth to the fifth generation (1.03-1.04). Therefore, the end-capped dendritic macromolecules with fourth and fifth generations were grossly estimated to structural perfection.

Experimental Section

All reactions were carried out under dried N_2 atmosphere. NMR spectra were recorded on a Bruker AC-200 Spectrometer. Size exclusion chromatography was performed in THF at 25 °C with a Waters 515 HPLC pump together with a Waters 2410 Refractive Index Detector. Three 7.8 × 30 cm columns (Ultrastyragel) were connected in series, calibrated with narrow molecular weight polystyrene standard. Low generational dendrimers (**G1-G4**) were prepared according to previous works.[4]

G4-48Crown-4 (Mw: 19,538). A mixture of 2-(hydroxymethyl)-12-crown-4 (0.43 g, 2.10 mmol dissolved in 25 mL of THF) and 0.24 g of TMEDA was slowly added to G4-48Cl (0.47 g, 0.04 mmol) in 50 mL of toluene. After the addition was finished, the reaction mixture was warmed up to 50 °C for 1 h. Amine salt was filtered off, leaving 0.85 g of a light yellow solid. This was chromatographed on a silica gel with chloroform. Yield: 0.56 g (0.014 mmol, 55%) of a colorless gel. ^1H NMR (ppm, $CDCl_3$): δ = 0.04 (s, 120H, SiMe, G0-G3), 0.09 (s, 288H, SiMe, G4) 0.47-0.76, 1.49-1.83 (m, 352H, CH_2, G0-G3), 3.40-3.90 (m, 984H, OCH_2, G1-G3 and crown ether). ^{13}C NMR (ppm, $CDCl_3$): δ = -2.25 (SiMe, G0-G3), 0.99 (SiMe, G4), 9.38 (CH_2, G0), 11.87, 26.24 (CH_2, G3), 9.38, 26.24 (CH_2, G1-G2), 65.20 (OCH_2, G1-G3), 80.06 (OCH_2, G4), 62.67, 70.26, 70.54, 70.64, 70.79, 71.45 (OCH_2 and crown-ether). GPC: PDI (M_w/M_n), 1.05 (5082/4853); Rt, 16.05 min. Anal. calcd. for $C_{828}H_{1744}Si_{92}O_{328}$: C, 50.89; H, 9.02%. Found: C, 49.38; H, 9.36%.

G5-96Crown-4 (Mw: 39,892). The same procedure as that for **G4-48Crown-4** was used in the reaction of 0.60 g

(0.026 mmol) of G5-96Cl, 0.54 g (2.63 mmol) of 2-(hydroxymethyl)-12-crown-4 and 0.58 g (4.92 mmol) of TMEDA. The product was chromatographed on a silica gel with chloroform and a mixed eluent ($CHCl_3$: THF = 9 : 1). Yield: 0.36 g (0.016 mmol, 66%) of a colorless gel. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.09 (s, 264H, SiMe, G0-G4), 0.43-0.77, 1.45-1.75 (m, 736H, CH_2, G0-G4), 3.40-3.94 (m, 1992H, OCH_2, G1-G4 and crown-ether). ^{13}C NMR (ppm, $CDCl_3$): δ = -4.99 (SiMe, G0-G4), -2.22 (SiMe, G5), 9.46 (CH_2, G0), 11.92, 26.26 (CH_2, G4), 9.40, 25.99 (CH_2, G1-G3), 65.18 (OCH_2, G1-G4), 80.11 (OCH_2, G5), 62.54, 70.30, 70.61, 70.67, 70.86, 71.47 (OCH_2, crown-ether). GPC: PDI (M_w/M_n), 1.05 (6036/5766): Rt, 15.88 min. Anal. calcd. for $C_{1692}H_{3567}Si_{188}O_{664}$: C, 51.02; H, 9.05%. Found: C, 49.99; H, 8.76%.

G4-48Crown-5 (Mw: 21,651). The same procedure as that for **G4-48Crown-4** was used in the reaction of 0.28 g (0.026 mmol) of G4-48Cl, 0.33 g (1.30 mmol) of 2-(hydroxymethyl)-15-crown-5 and 0.15 g (1.30 mmol) of TMEDA. The product was chromatographed on a silica gel with chloroform and a mixed eluent ($CHCl_3$: THF = 9 : 1). Yield: 0.41 g (0.021 mmol, 53%) of a colorless gel. ^{1}H NMR (ppm, $CDCl_3$): δ = 0.09 (s, 408H, SiMe, G0-G4), 0.45-0.73, 1.43-1.73 (m, 352H, CH_2, G0-G3), 3.50-3.88 (m, 1176H, OCH_2, G1-G3 and crown ether). ^{13}C NMR (ppm, $CDCl_3$): δ = -4.31 (SiMe, G0-G3), -2.18 (SiMe, G4), 9.00 (CH_2, G0), 9.54, 26.05 (CH_2, G1, G2), 12.88, 26.32 (CH_2, G3), 65.24 (OCH_2, G1-G3), 80.24 (OCH_2, G4), 62.68, 70.31, 70.54, 70.70, 74.90, 71.00, 71.12 (OCH_2, crown-ether). GPC: PDI (M_w/M_n), 1.03 (5733/5580): Rt, 15.98 min. Anal. calcd. for $C_{924}H_{1936}Si_{92}O_{376}$: C, 51.25; H, 9.03%. Found: C, 50.13; H, 9.25%.

G5-96Crown-5 (Mw, 44,059). The same procedure as that for **G4-48Crown-4** was used in the reaction of 0.23 g (0.01 mmol) of G5-96Cl, 0.32 g (1.28 mmol) of 2-(hydroxymethyl)-15-crown-5 and 0.15 g (1.30 mmol) of TMEDA. The product was chromatographed on a silica gel with chloroform and a mixed eluent ($CHCl_3$: THF = 9 : 1). Yield: 0.25 g (0.006 mmol, 60%) of a colorless gel. ^{1}H NMR (ppm, $CDCl_3$): δ = 0.09 (s, 264H, SiMe, G0-G4), 0.16 (s, 576H, SiMe, G5), 0.39-0.72, 1.41-1.76 (m, 736H, CH_2, G0-G4), 3.52-3.84 (m, 2376H, OCH_2, G1-G4 and crown-ether). ^{13}C NMR (ppm, $CDCl_3$): δ = -4.97 (SiMe, G0-G4), -2.18 (SiMe, G5), 9.00 (CH_2, G0), 11.48, 26.29 (CH_2, G4), 9.48, 26.26 (CH_2, G1-G3), 65.24 (OCH_2, G1-G5), 80.24 (OCH_2, G5), 62.68, 70.31, 70.54, 70.70, 70.90, 71.00, 71.12 (OCH_2, crown-ether). GPC: PDI (M_w/M_n), 1.06 (7739/7311): Rt, 15.55 min. Anal. calcd. for ($C_{1884}H_{3952}Si_{188}O_{760}$): C, 51.36; H, 9.06%. Found: C, 49.38; H, 8.43%.

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