

Synthesis and Characterization of Aliphatic Polyether Dendrons Based on Polystyrene Peripheries

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The synthesis of well-defined dendrons based on aliphatic polyether dendritic cores and glassy polystyrene peripheries is described. The synthetic route involves a combination of living anionic polymerization and a stepwise convergent method consisting of iterative Williamson etherification and hydroboration/oxidation reactions. On the basis of molecular weight, as characterized by gel permeation chromatography (GPC), the first generation dendron (**Generation-1**) shows a random coil conformation like a linear polystyrene, while higher generations (**Generation-2** and **3**) reveal globular forms in solution.

Key Words : Aliphatic polyether dendrons, Polymeric peripheries, Anionic polymerization, Convergent synthesis

Introduction

Variation of macromolecular chain architecture is a versatile tool to modify polymer properties. In particular, branched polymers have been studied as a counterpart of linear polymers to identify significantly distinct physical behavior.¹ As representative branched examples, star-shaped polymers² and dendrimers³ have well-defined chain structures with low molecular weight distributions, and therefore can be ideal models to study the correlation between chain architecture and physical properties. These two candidates, however, have been synthesized in different ways because of their architectural difference. Star-shaped polymers consist of polymeric chains at a single branching point, while dendrimers have regular small spacers and multiple branching points. In this regard, dendrimers can be classified as a different type of macromolecule from star-shaped polymers. Although cationic and radical mediated polymerizations have been adopted from time to time,⁴ synthesis of star-shaped polymers has mainly employed anionic polymerization methods for precise control of the polymeric chain.^{2,5} Due to the strong living nature of anionic methods, a variety of polymeric segments such as polystyrenes, polyisoprenes, poly(methyl methacrylate)s etc, have been integrated into the star architecture. On the other hand, dendrimers have been prepared stepwise using convergent or divergent routes, producing monodisperse tree-like architectures.³ Recently, several efforts have been made to combine the structural features of star-shaped polymers and dendrimers. In most cases, branched macromolecules have regular multi-branching points connected with polymeric chain spacers (not small spacers) by a combination of living polymerizations and dendrimer synthesis.⁶

Meanwhile, a polymeric architecture to compositionally compartmentalize polymeric chains and dendritic core has been rarely studied. To this end, we designed a series of dendrons which partition into an aliphatic polyether den-

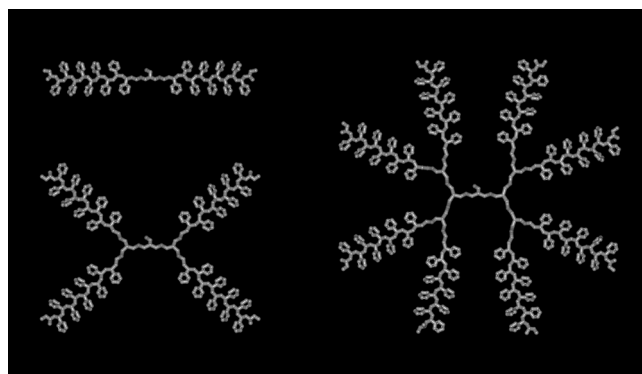


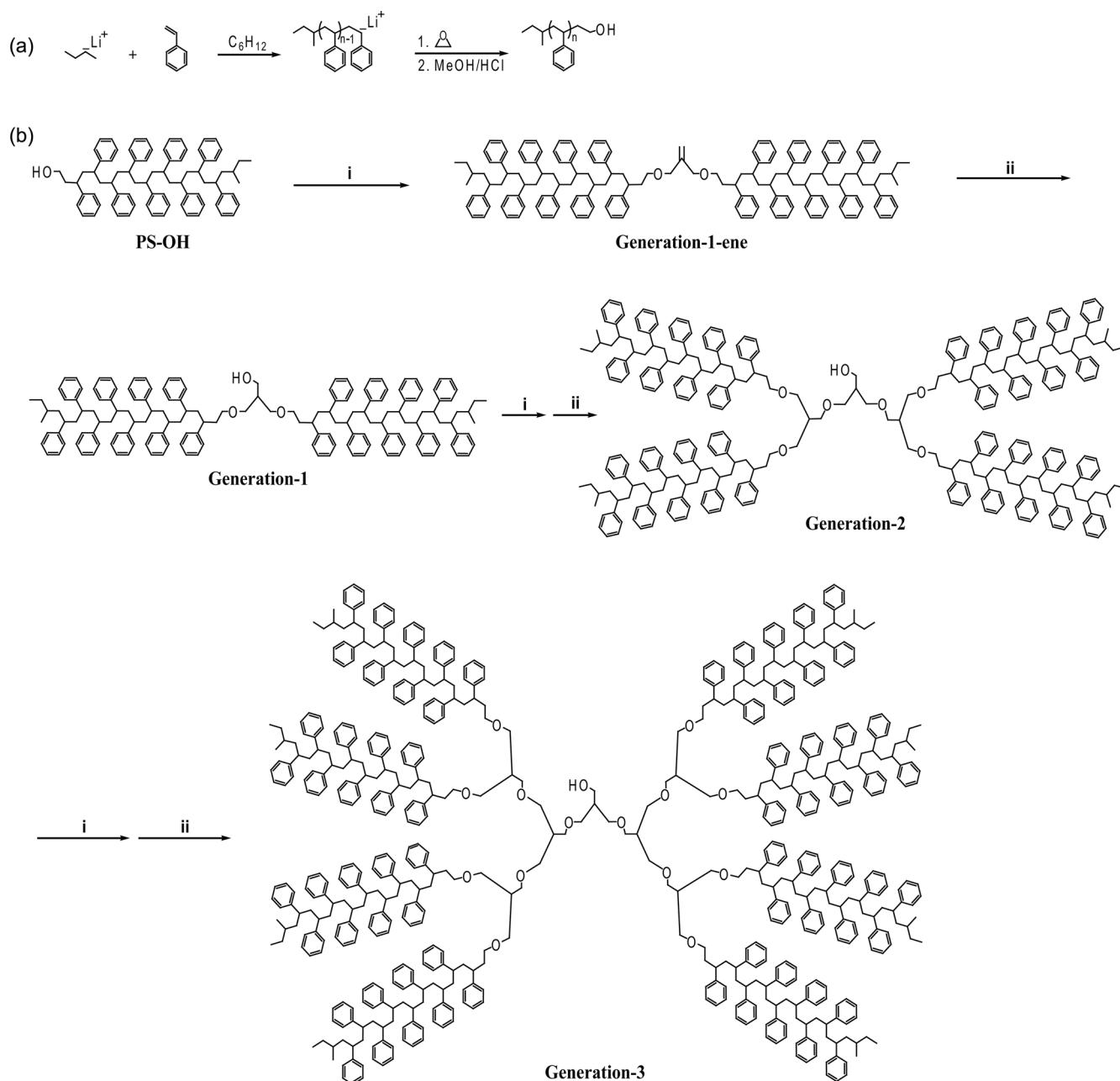
Figure 1. Dendritic structures from first to third generations. The peripheral groups consist of polystyrenes.

dritic core and polystyrene peripheries (Figure 1). In this paper, we report the synthesis of the dendrons and characterization of generation-dependent hydrodynamic conformational state as the solution property.

Experimental Section

Materials. *n*-Butyllithium (2.5 M solution in hexanes), *sec*-butyllithium (1.4 M solution in cyclohexane), methanolic HCl (1.25 M in methanol), and 9-BBN (0.5 M solution in tetrahydrofuran) were purchased from Sigma-Aldrich Chemical Co. 3-Chloro-2-chloromethyl-1-propene (methallyl dichloride, 96%) was purchased from Acros Organics Co. Styrene (Aldrich, $\geq 99\%$) was distilled from CaH_2 and then stored under a nitrogen atmosphere. Cyclohexane (from Burdick & Jackson Co.) was dried from deep red 1,1-diphenyl ethylene and butyllithium adduct. Ethylene oxide (Aldrich, 99.5 + %) was allowed to stand over butyllithium and was degassed several times before distillation into graduated ampoules.

Characterization. ^1H -NMR spectra were recorded from CDCl_3 solutions on Varian 200 and 250 MHz spectrometers.



Scheme 1. (a) Anionic polymerization of styrene to yield **PS-OH**, and (b) convergent dendron synthesis consisting of i) NaH, methallyl dichloride, ii) (1) 9-BBN, (2) $\text{H}_2\text{O}_2/\text{NaOH}$.

The purity of the products was checked by thin-layer chromatography (TLC; Merck, silica gel 60). IR absorption spectra were obtained from Perkinelmer Spectrum 100 FT-IR spectrometer. Gel permeation chromatography (GPC) measurements were carried out in THF and Waters R401 instrument equipped with Stragel HR 2, 3 and 4 columns at a flow rate of 1.0 mL/min. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) were performed on Perceptive Biosystems Voyager-DE STR Biospectrometry Workstation using a 2,5-dihydroxy benzoic acid (DHB) matrix.

Synthesis. The synthesis of the linear polystyrene (**PS-OH**) and dendrons (**Generation-n**: here, *n* designates generation number) is outlined in Scheme 1.

Synthesis of PS-OH. Styrene (120 g, 1.15 mol) was polymerized in cyclohexane (1.2 L) for 20 hours at room temperature, using *sec*-BuLi (144 mmol) as initiator. Then, freshly distilled ethylene oxide (12 mL) was added to the reaction vessel, then stirred for 2 hours. Subsequently degassed methanolic HCl (116 mL) was added for the termination of the chain end into a hydroxyl group. The solution was concentrated and dissolved with dichloromethane (2 L) then washed with deionized water (3×2 L), dried over MgSO_4 . The resulting compound was recovered by evaporation and drying under vacuum at 70 °C. ^1H NMR (200 MHz, CDCl_3) δ 7.38–6.36 (br, Ar-*H*), 3.30 (HOCH_2CH_2 -), 2.61–1.90 (br, *CH* of the polystyrene backbone; HOCH_2CH_2 -), 1.90–1.31 (br, CH_2 of the polystyrene backbone), 1.30–0.53

(br, $-\text{CH}(\text{phenyl})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_3$); TLC (eluent; Hexane/ $\text{CH}_2\text{Cl}_2 = 1:4$) R_f 0.46.

Synthesis of Generation-1-ene. PS-OH (135 g, 144 mmol), NaH (4.2 g, 173 mmol) and 3-chloro-2-chloromethyl-1-propene (9 g, 72 mmol) were dissolved in 600 mL of THF/DMF (3:1 volume ratio) solvent mixture. The mixture was heated at reflux for 48 hours under a N_2 atmosphere. After cooling to room temperature, the solution was concentrated and dissolved with dichloromethane (2 L), then washed with deionized water (2×2 L), dried over MgSO_4 . The resulting solid was purified by a column chromatography (from hexane: $\text{CH}_2\text{Cl}_2 = 3:2$ to 2:3, silica) to yield 74 g (53.3%) of a light yellow glassy solid. ^1H NMR (200 MHz, CDCl_3) δ 7.38–6.36 (br, Ar-H), 4.93 ($\text{CH}_2=\text{C}(\text{CH}_2\text{OCH}_2\text{CH}_2)_2$), 3.63 ($\text{CH}_2=\text{C}(\text{CH}_2\text{OCH}_2\text{CH}_2)_2$), 2.98 ($\text{CH}_2=\text{C}(\text{CH}_2\text{OCH}_2\text{CH}_2)_2$), 2.53–1.90 (br, CH of the polystyrene backbone; $\text{CH}_2=\text{C}(\text{CH}_2\text{OCH}_2\text{CH}_2)_2$), 1.90–1.31 (br, CH_2 of the polystyrene backbone), 1.30–0.53 (br, $-\text{CH}(\text{phenyl})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_3$); TLC (eluent; Hexane/ $\text{CH}_2\text{Cl}_2 = 2:3$) R_f 0.50.

Synthesis of Generation-1. Generation-1-ene (74 g, 38.4 mmol) was dissolved in 250 mL of 9-BBN solution (230 mL, 115 mmol). The reaction mixture was warmed at 50 °C and stirred for 20 hours, then cooled to 0 °C. The solution was carefully quenched with 60 mL of 3.0 M NaOH aqueous solution. After cooling again to 0 °C, and 60 mL of 30% H_2O_2 aqueous solution was carefully added. The mixture was concentrated and dissolved in dichloromethane (700 mL), then washed with deionized water (2×1 L), dried over MgSO_4 . The resulting solid was purified by a column chromatography (from hexane:ether = 7:3 to CHCl_3) to yield 45.6 g (61.3%) of a light yellow glassy solid. ^1H NMR (200 MHz, CDCl_3) δ 7.38–6.36 (br, Ar-H), 3.56 ($\text{HOCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}_2)_2$), 3.18 ($\text{HOCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}_2)_2$), 3.02 ($\text{HOCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}_2)_2$), 2.61–1.90 (br, CH of the polystyrene backbone and $\text{HOCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}_2)_2$), 1.90–1.31 (br, CH_2 of the polystyrene backbone), 1.31–0.58 (br, $-\text{CH}(\text{phenyl})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_3$); TLC (eluent; CH_2Cl_2) R_f 0.52.

Synthesis of Generation-2-ene. Generation-1 (45 g, 23.5 mmol), NaH (1.4 g, 31 mmol) and 3-chloro-2-chloromethyl-1-propene (1.59 g, 11.75 mmol) were dissolved in 146 mL of THF/DMF (3:1 volume ratio) solvent mixture. The mixture was heated at reflux for 38 hours under a N_2 atmosphere. After cooling to room temperature, the mixture was concentrated and dissolved with dichloromethane (500 mL) then washed with deionized water (2×500 mL), dried over MgSO_4 . The resulting solid was purified by a column chromatography (from hexane: $\text{CH}_2\text{Cl}_2 = 3:7$ to hexane:ether = 7:3) to yield 26.4 g (57.2%) of a light yellow glassy solid. ^1H NMR (200 MHz, CDCl_3) δ 7.38–6.36 (br, Ar-H), 4.99 ($\text{CH}_2=\text{C}(\text{CH}_2\text{OCH}_2\text{CH}_2)_2$), 3.70 ($\text{CH}_2=\text{C}(\text{CH}_2\text{OCH}_2\text{CH}_2)_2$), 3.34–2.75 (br, $\text{CH}_2=\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}_2)_2\text{-polystyrene})_2$), 2.53–1.90 (br, CH of the polystyrene backbone and $-\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}_2)_2\text{-polystyrene})_2$), 1.90–1.31 (br, CH_2 of the polystyrene backbone), 1.31–0.53 (br, $-\text{CH}(\text{phenyl})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_3$); TLC (eluent; Hexane/ether

= 3:2) R_f 0.76.

Synthesis of Generation-2. Generation-2-ene (21.8 g, 5.6 mmol, 1.0 equiv) was dissolved 66 mL of 9-BBN solution (66.5 mL, 33.3 mmol). The reaction mixture was warmed at 60 °C and stirred for 20 hours, then cooled to 0 °C. The solution was carefully quenched with 20 mL of 3.0 M NaOH aqueous solution. After cooling again to 0 °C, and 20 mL of 30% H_2O_2 aqueous solution was carefully added. The mixture was concentrated and dissolved in dichloromethane (200 mL), then washed with deionized water (2×200 mL), dried over MgSO_4 . The resulting solid was purified by a column chromatography (from CHCl_3 :ether = 9:1 to hexane:ether = 3:2) to yield 14.3 g (65.3%) of a light yellow glassy solid. ^1H NMR (200 MHz, CDCl_3) δ 7.38–6.36 (br, Ar-H), 3.56 ($\text{HOCH}_2\text{CH}-$), 3.34–2.75 (br, $\text{HOCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}_2)_2\text{-polystyrene})_2$), 2.53–1.90 (br, CH of the polystyrene backbone and $\text{HOCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}_2)_2\text{-polystyrene})_2$), 1.90–1.31 (br, CH_2 of the polystyrene backbone), 1.31–0.58 (br, $-\text{CH}(\text{phenyl})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_3$); TLC (hexane/ether 3:2) R_f 0.43.

Synthesis of Generation-3. Generation-2 (4.9 g, 1.24 mmol), NaH (0.27 g, 6.2 mmol) and 3-chloro-2-chloromethyl-1-propene (80.7 mg, 0.62 mmol) were dissolved in 14 mL of THF/DMF (3:1 volume ratio) solvent mixture. The mixture was heated at reflux for 35 hours under a N_2 atmosphere. After cooling to room temperature, the mixture was concentrated and dissolved with dichloromethane then washed with water once. The resulting solid was purified by a column chromatography (hexane:ether = 6:4) to remove unreacted **Generation-2**. However, a mono-substituted compound was not removed from **Generation-3-ene**. Thus, without further purification, a hydroboration/oxidation reaction was performed with the crude mixture under the same reaction condition as in the synthesis of **Generation-2**. The final purification was done by a column chromatography (hexane:ether = 7:3) to yield 1.82 g of a white glassy solid. ^1H NMR (200 MHz, CDCl_3) δ 7.38–6.36 (br, Ar-H), 3.56 ($\text{HOCH}_2\text{CH}-$), 3.34–2.75 (br, $-\text{CH}_2\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}_2)_2\text{-polystyrene})_2$), 2.53–1.90 (br, CH of the polystyrene backbone and $\text{HOCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}_2)_2\text{-polystyrene})_2$), 1.90–1.31 (br, CH_2 of the polystyrene backbone), 1.31–0.58 (br, $-\text{CH}(\text{phenyl})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_3$); TLC (eluent; hexane/ether = 3:2) R_f 0.54.

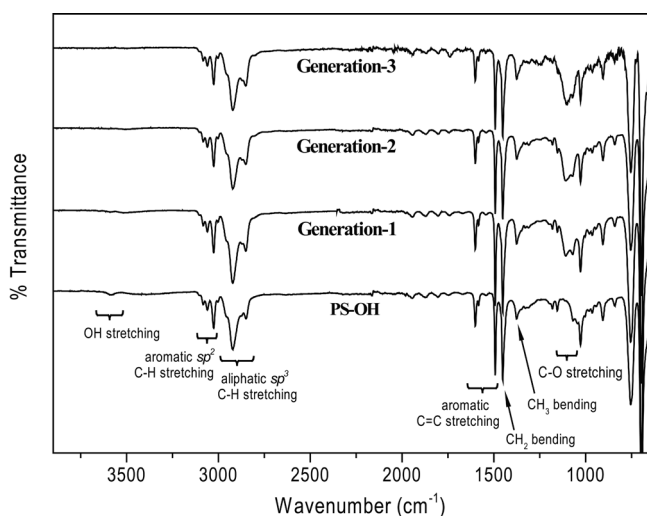
Results and Discussion

Synthesis. The present design of dendrons focused on the construction of an aliphatic polyether dendritic core surrounded by polystyrene peripheries (Scheme 1). For precise control of the molecular structure, we employed a combinational synthetic method consisting of anionic polymerization and a convergent synthesis. The living anionic polymerization of styrene was performed in the following steps. First, styrene was polymerized in cyclohexane with *sec*-butyllithium as initiator. After stirring at room temper-

Table 1. Characterization of **PS-OH** and dendrons (**Generation-n**)

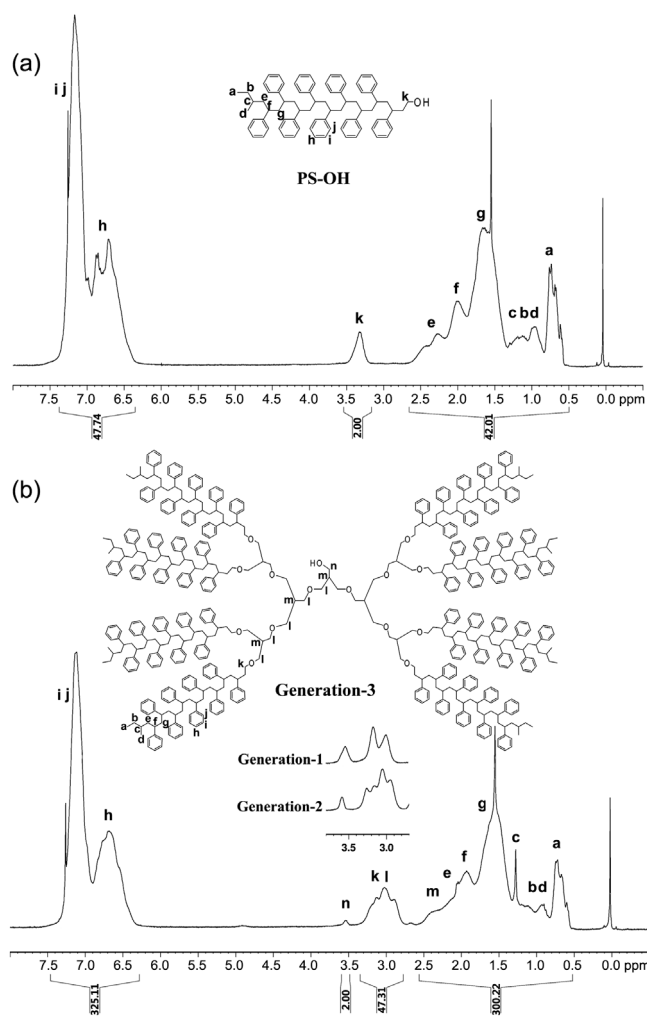
Compound	GPC ^a			MALDI-TOF MS	
	M _n ^{the} g/mol	M _n ^{GPC} g/mol	M _w /M _n	M _n ^{MAL} g/mol	M _w /M _n
PS-OH		1000	1.12		
Generation-1	2100 ^b	2000	1.05		
Generation-2	4200 ^b	3600	1.03	4000	1.03
Generation-3	8500 ^b	6000	1.03	8900	1.01

^aCalculated by polystyrene standard samples. ^bTheoretical number average molecular weight calculated based on the M_n^{GPC} of **PS-OH**.

**Figure 2.** FT-IR spectra of **PS-OH** and **Generation-n**.

ature, the living polystyrene end was further reacted with freshly distilled ethylene oxide. Although excess of ethylene oxide relative to polymer chains was added, a successive polymerization of ethylene oxide at the chain end did not occur, rather a single ethylene oxide unit was introduced at the chain end. It must be due to the reduction of oxyanion reactivity, resulting from the binding of sodium cation to terminal oxyanion in hydrophobic cyclohexane. A subsequent protonation with degassed methanolic HCl yielded a well-defined polystyrene with hydroxyl terminus (**PS-OH**). As assigned in Figure 2a, an IR spectrum of **PS-OH** displays typical absorption bands associated with the stretching and bending vibrational modes of the terminal hydroxyl, styryl aromatic and aliphatic backbone groups. Its ¹H-NMR spectrum shows the broad signals of the aromatic and aliphatic protons, and the chemical shift of two protons relative to the hydroxyl group at 3.35 ppm, consistent with the proposed molecular structure (Figure 3a). Furthermore, the estimated polydispersity (M_w/M_n) from GPC is 1.12 (Table 1). Considering the small molecular weight of **PS-OH** (1000 g/mol), the polydispersity reflects a narrow molecular weight distribution. Meanwhile, the molecular weight was determined by a GPC calibrated by monodisperse linear polystyrene standards, therefore the estimated molecular weight of M_n^{GPC} = 1000 g/mol can be considered nearly absolute (Table 1).

For the synthesis of the presented dendritic structure having polymeric **PS-OH** as polymeric peripheries, a

**Figure 3.** 250 MHz ¹H-NMR spectra of (a) **PS-OH**, and (b) **Generation-3**. In the inset of (b), the signals of the methylene proton next to the hydroxyl group of **Generation-1** and **2** are shown near 3.55 ppm.

convergent synthetic route consisting of a Williamson etherification and hydroboration/oxidation as growth and activation steps, respectively, was utilized.⁷ The growth step, the etherification of the hydroxyl terminus with methallyl dichloride, was implemented in a THF/DMF solvent mixture (3:1 volume ratio) in the presence of NaH as base. In this step, the addition of DMF in the major THF is for the facilitation of the etherification reaction, because the polar aprotic character of DMF assists the dissociation of deprotonated oxyanion and counter cation, enhancing the reaction rate. After the Williamson coupling, olefin compounds **Generation-1-ene** and **Generation-2-ene** were purified by silica column chromatography from appropriate solvent mixtures as eluents See Experimental Section. However, in purification of **Generation-3-ene**, we could not find a proper eluent to distinguish the product from a mono-substituted compound in thin-layer chromatography, thus proceeded to the next reaction without further purification.

In the activation step, the hydroboration reaction of olefin compounds with 9-BBN was performed above 50 °C in THF

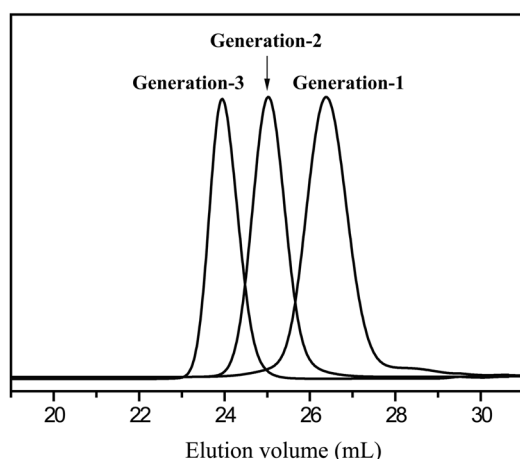


Figure 4. GPC traces of **Generation-n**.

for 20 hours. Subsequently, an oxidation reaction by insertion of NaOH/H₂O₂ was followed, resulting in the designed dendrons, *i.e.* **Generation-n**. The reason for using sterically hindered 9-BBN as the borane reagent is to eliminate undesired tertiary alcohol isomer; consequently the yield consisted only of the primary alcohol product. The purification of the dendrons was carried out by silica column chromatography See Experimental Section.

Characterization of **Generation-n** was done by IR, ¹H-NMR, GPC and MALDI-TOF MS techniques. FT-IR spectra of the compounds are presented in Figure 2b. In comparison with the IR data of **PS-OH**, the dendrons exhibit the absorption bands associated with C-O stretching vibrations near 1100 cm⁻¹, which become more intense with generation. On the other hand, OH stretching vibrational band is rarely observed in the dendron spectra. It is because the portion of hydroxyl group decreases on going from **PS-OH** to the dendrons. Meanwhile, the existence of terminal hydroxyl groups can be evidenced by NMR spectra. As shown in Figure 3b, we can observe the resonance near 3.55 ppm, corresponding to two methylene protons next to the hydroxyl group. In addition, its integration decreases in proportion to generation number, indicative of successful generation growth, See inset of Figure 3b. In Figure 4 and Table 1, all the dendrons show monomodal elugrams and narrow molecular weight distributions (M_w/M_n) of less than 1.05, indicative of high purity. MALDI-TOF MS experiments were conducted for **Generation-2** and **3**. In MALDI-TOF MS spectrum of **Generation-3**, each adjacent peak is separated by 104 a.m.u., consistent with the molecular weight of a styrene unit (Figure 5). Molecular weight analysis of the spectra affords number average molecular weights (M_n^{MAL}) of 4000 and 8900 g/mol for **Generation-2** and **3**, respectively, and polydispersity indexes (M_w/M_n) of less than 1.03 (Table 1).

Characterization of Solution Properties. Molecular weight measured by GPC is based upon hydrodynamic volume which is closely associated with chain conformational state in solution. Therefore, the utilization of GPC can provide elucidation of the conformational variation of

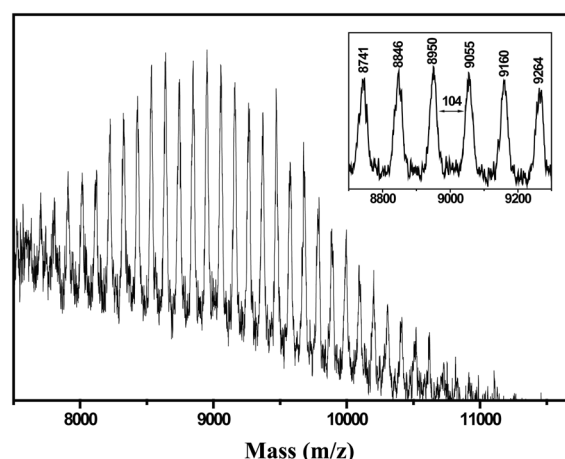


Figure 5. MALDI-TOF MS spectrum of **Generation-3**. The mass gap between two adjacent peaks in the inset corresponds to the molecular weight of a styrene unit.

the solution dependent upon chain architecture. The molecular weights (M_n^{GPC}) of the dendrons which represent the hydrodynamic states in the solution, were measured by the GPC method, as applied in **PS-OH**, and summarized in Table 1. In another column of the table, theoretical molecular weights (M_n^{the}) of the dendrons are also presented. These were calculated on the basis of the M_n^{GPC} of **PS-OH**, thus are assumed to be the absolute molecular weights, analogous to the molecular weights (M_n^{MAL}) determined by MALDI-TOF MS which provides realistic absolute molecular weights. By comparing M_n^{GPC} with M_n^{the} , we can describe the nature of dendron conformational state in the solution. From GPC data, the M_n^{GPC} of **Generation-1** was estimated to be 2000 g/mol. This is almost identical to its theoretical value, suggesting that the solution conformation of **Generation-1** mirrors linear polystyrenes, which have typical random coil conformations. In contrast, at higher generations **Generation-2** and **3**, the M_n^{GPC} values deviate from the corresponding theoretical ones. The M_n^{GPC} (3600 g/mol) of **Generation-2** was estimated to be 15% smaller than its M_n^{the} (4200 g/mol). Remarkably, the gap between the M_n^{GPC} (6000 g/mol) and the M_n^{the} (8500 g/mol) of **Generation-3** is further increased to approximately 30%. The molecular weight reduction in GPC indicate that the second and third generations adopt more compact globule-like states rather than random coils of linear polymers.⁸ As related to the similar property changes dependent upon dendron generation, in other dendrimer/dendron systems with small peripheral groups, the discontinuities have been observed at much higher generations.^{1,8,9} For example, hydrodynamic volume discontinuity happens between generation four and five in a poly(aryl ether) dendron system with small benzyl peripheral groups.¹ While in our dendron system with the polystyrene peripheries the transition occurs at the much earlier transition from first to second generation. Consequently, this result demonstrates that the length of peripheral chain as well as dendron generation plays a crucial role in determining the molecular shape in the solution.

Conclusions

A new series of dendrons from first to third generation (**Generation-n**) functionalized with polystyrene peripheries and aliphatic polyether dendritic cores have been synthesized in high purity by a combinational method consisting of living anionic polymerization and a Williamson etherification plus hydroboration/oxidation reactions. By determining the molecular weights in GPC and comparing them with the theoretical values, we were able to define the conformational state of each generation in the solution. **Generation-1** shows a random coil conformation like a linear polystyrene, while higher generations display globular conformations. Compared to other branched dendrons/dendrimers with small peripheral groups, the observed conformational transition happens at a much earlier generation stage. The result suggests that peripheral chain length as well as dendron generation significantly influences the solution conformation of dendritic molecules.

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