

## 실옥산테트라머를 이용한 나뭇가지꼴 실란거대분자의 제조와 정지반응

金貞均\* · 朴恩美

동아대학교 자연과학대학 화학과  
(1998. 2. 3 접수)

### Preparation and Termination of Carbosilane Dendrimer Based on Siloxane Tetramer

Chungkyun Kim\* and Eunmi Park

Department of Chemistry, Dong-A University, Pusan 604-714

(Received February 3, 1998)

**요약.** Siloxane tetramer( $\text{Me}(\text{CH}_2=\text{CH})\text{SiO}$ )<sub>4</sub>를 중심분자로 한 나뭇가지꼴 거대분자(제1세대~제4세대)를 allylmagnesium bromide와 dichloromethylsilane를 이용한 alkenylation과 hydrosilation 반응을 통해 제조하였다. Dichlorosilyl기를 가진 G4세대와 *p*-bromophenol, *p*-phenylphenol, lithium phenylethynylide 등과의 반응에서 특정기능을 가지는 G4P-BP(Mw: 16,300), G4P-PP(16,121), G4P-PA(11,764) 등이 합성되었다. 새롭게 형성된 나뭇가지꼴 거대분자는 NMR, UV, MALDI mass의 분석에 의해 균일한 구조를 가지고 있음이 확인 되었다.

**ABSTRACT.** Dendritic macromolecules of the first to fourth generation were synthesized, using alkenylation and hydrosilation cycles with allylmagnesium bromide and dichloromethylsilane as building blocks and siloxane tetramer ( $\text{Me}(\text{CH}_2=\text{CH})\text{SiO}$ )<sub>4</sub> as core molecule. By the reaction of the dichloromethylsilyl-capped generation (G4P) with *p*-bromophenol, *p*-phenylphenol and lithium phenylethynylide, dendrimers with specific functions (G4P-BP (Mw: 16,300), G4P-PP (16,121), and G4P-PA (11,764)) have been produced. Analysis of new dendrimers by NMR, UV and MALDI mass spectrometry suggests that they are pure and unified.

### INTRODUCTION

Dendritic macromolecules have received considerable attention as a new class material.<sup>1,2</sup> The interest is due to their highly branched structure, which may result in a variety of new and improved property.<sup>3</sup> Currently, the development of this area is shifting from the preparation of even larger molecules to that of dendrimers with useful supramolecular phenomena.<sup>4</sup> The use of dendrimers includes many purposes which as nanoscale compounds, agents for delivering drugs, chemical sensors and liquid crystals.<sup>9,11,14</sup> The first preparation of carbosilane dendrimers introduced by van der Made *et al.* was performed by repetitive alkenylation-hydrosilation cycles.<sup>6</sup> Roovers and Seyferth described the synthesis of carbosilane dendrimers via repetitive addition of chlorosilane to

alkene in G<sub>n</sub>-type dendrimers, while admitting nucleophilic substitution with vinylmagnesium bromide of the terminal chlorosilyl groups.<sup>7,8</sup> To date, most of the synthetic methods for silicon containing dendrimers have been demonstrated by repeating units possessing many functions such as vinyl,<sup>7,9</sup> allyl,<sup>6,10</sup> and polyol<sup>5</sup> groups. As an extension of a part of our previous paper,<sup>1</sup> we now report some detailed result on the reactions of dichlorosilyl-capped carbosilane dendrimers (G4P with 64 Si-Cl bonds) with allylmagnesium bromide, *p*-bromophenol, *p*-phenylphenol and lithium phenylacetylde. The reaction of them produces the dendrimers with specific functions, such as allyl, bromophenoxy, *p*-phenylphenoxy and phenylacetyl groups (Mw: 7,913 (G4), 16,300 (G4P-BP), 16,121 (G4P-PP), and 11,764 (G4P-PA)) on their

periphery. The identification of the terminated molecules can be obtained by NMR spectroscopy, analysis of MALDI mass spectra, analysis of UV spectrum as well as elemental analysis.

## EXPERIMENTAL

All reactions were carried out under a dried N<sub>2</sub> atmosphere. NMR spectra were measured using samples in the CDCl<sub>3</sub> solution: <sup>1</sup>H NMR spectra at 200.13 MHz and <sup>13</sup>C NMR spectra at 50.32 MHz by Bruker AC-200 Spectrophotometer. UV spectra were measured by HP 8452A Diode Array UV/Vis. Spectrophotometer. Elemental analysis (Carlo Erba

1108) and MALDI mass (Kratos Kompact MALDI 2) attachments were performed in the Pusan and Taejeon Branch of the Korean Basic Science Institute.

Ether and THF were dried by distillation from a blue solution of sodium benzophenone ketyl and solvents such as pentane and hexane were dried and distilled from sodium metal. Siloxane tetramer (Me(CH<sub>2</sub>=CH)SiO)<sub>4</sub> was purchased from Fluka Chemical Co. Platinum catalysts (Pt on activated carbon, 10% Pt content) were used after vacuum dry at room temperature. Full experimental details for hydrosilylation and ω-alkenylation will appear elsewhere<sup>1,6</sup> but the following may serve as examples:

Table 1. NMR data of terminated dendrimers

	MeSi	CH <sub>2</sub>	Ph	
G4P-PA*	<sup>1</sup> H	-0.67 (s, 24H, G2) -0.05 (s, 48H, G3) -0.02 (s, 12H, G1) -0.01 (s, 12H, G0) 0.38, 0.41 (d, 96H, G4)	0.48, 0.66 0.92, 1.25, 1.58 (m)	7.24-7.29 (m) 7.44-7.49 (m)
	<sup>13</sup> C	-4.97 (G0-G3) -1.05 (G4)	18.04, 18.89, 20.63 (G3) 18.35 (G2)	122.71 (C-q) 128.17 (C-o) 128.75 (C-p) 132.08 (C-m)
	<sup>1</sup> H	-0.63 (s, 72H, G2-G3) -0.12 (s, 12H, G1) 0.07 (s, 12H, G0) 0.27 (s, 96H, G4)	0.48 (m) 0.84 (m) 1.36 (m)	6.72, 6.76 (d) 7.25, 7.30 (d)
	<sup>13</sup> C	-0.40 (G0-G3) -0.37 (G4)	17.10, 17.90, 18.49 (G3) 17.80-18.60 (G0-G2)	114.62 (C-q) 121.43 (C-o) 132.55 (C-m) 153.08 (C-Br)
	<sup>1</sup> H	-0.15 (G2-G3, 72H) -0.13 (G1, 12H) 0.07 (G0, 12H) 0.27 (G4)	0.47, 0.88 1.25, 1.44	6.90-6.94 7.17-7.42
G4P-PP	<sup>13</sup> C	-5.18 (G0-G3) -3.70 (G4)	17.22, 17.95, 18.72 (G4) 18.49	119.98, 126.64, 128.18, 128.60 134.99, 140.53, 153.68
	<sup>1</sup> H**	-0.06 (s, H, G2-G3, 72H) -0.10 (s, H, G4, 96H) 0.07 (G1, 12H) 0.40 (G0, 12H)	0.60 (m, H) 1.30 (m, H) 1.52-1.53, 1.56-1.57 (d, H, G4)	
G4	<sup>13</sup> C* <sup>3</sup>	-5.69 (G4) -5.03--4.95 (G0-G3)	17.94, 18.22, 18.78 (G3) 18.22, 18.56, 18.99 (G2) 19.18 (G1)	

\*δ(C≡C): 90.06, 106.34 ppm, \*\*δ(HC=CH<sub>2</sub>): 4.80 (s, CH<sub>2</sub>=), 4.86, 4.88, 4.89, 4.90 (dd, CH<sub>2</sub>=), 5.79 (septet, CH=),  
\*<sup>3</sup>: 113.08 (CH<sub>2</sub>=), 134.78 (CH=).

**Alkenylation: G1.** 103 mmol of allylmagnesium bromide (1.3 equiv. number of chlorine) was slowly added to 8.49 g (9.95 mmol) of **G1P** in 25 ml THF. After the addition was finished, the reaction mixture was refluxed for 2 h and solvents were removed under reduced pressure. The magnesium salt was precipitated in pentane and filtered off. The volatile components were removed under reduced pressure, leaving 8.10 g of a colorless liquid. Yielded compounds were chromatographed on silica gel with chloroform as an eluent. The product, **G1** ( $\text{MeSiCH}_2\text{CH}_2\text{SiMe}(\text{CH}_2\text{CH}=\text{CH}_2)\text{O}$ )<sub>4</sub>, was obtained as a clear, colorless oil (5.10 g, 6.00 mmol, 60%). Spectroscopic data of **Gn** types dendrimers ( $n=1\sim 3$ ) based on siloxane tetramer are reviewed in ref. 1c and **G4** in Table 1.

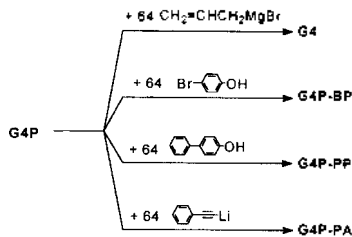
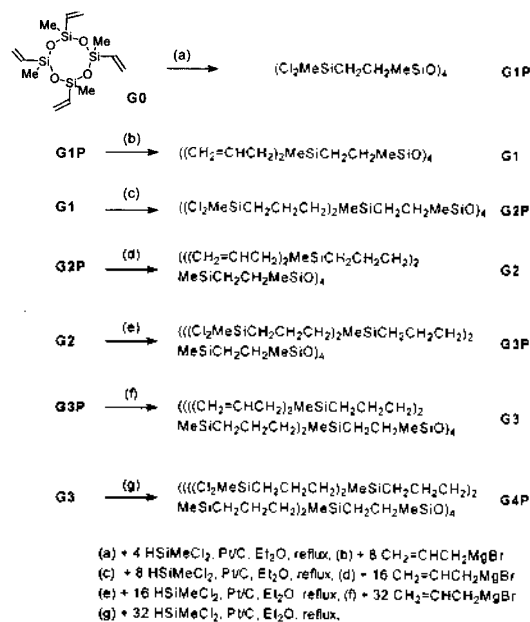
**Hydrosilation: G1P.** A mixture of 3.70 g (10.37 mmol) of **G0**, 7.41 g (64.38 mmol, 1.5 equiv.) of  $\text{HSiMeCl}_2$  and 0.10 g of a dried platinum catalyst (Pt on activated carbon, 10% Pt content) in 25 ml THF was stirred for 12h at room temperature. The excessive  $\text{HSiMeCl}_2$ , and THF were removed under vacuum. The catalyst was filtered off in pentane and the pentane was evaporated, leaving 8.49 g (9.95 mmol, 93%) of **G1P** ( $\text{Cl}_2\text{MeSiCH}_2\text{CH}_2\text{MeSiO}$ )<sub>4</sub> as a clear, colorless oil, which was very sensitive to moisture. **GnP** types dendrimers ( $n=1\sim 3$ ) based on siloxane tetramer are reviewed in ref. 1c.

**G4P-PA.** 15 ml (1 M in THF) of a lithium phenylacetylide solution was slowly added to 1.36 g (0.18 mmol) of **G4P** in 25 ml THF. After the addition was completed, the reaction mixture was refluxed for 4 h and solvents were removed under reduced pressure. The compounds were chromatographed on silica gel with chloroform as an eluent. The product **G4-PA** was obtained as a clear, yellow-brown glass (1.75 g, 0.14 mmol, 77%). Spectroscopic data are described in Table 1.

**G4P-BP.** 15 mmol of a *p*-bromophenol solution (1 M in THF) was slowly added to the solution of 1.36 g (0.18 mmol) of **G4P** and 5 g of TMED in 25 ml toluene. After the addition was completed, the reaction mixture was stirred for 5 h. When the reaction was done by <sup>1</sup>H-NMR, solvents and unreacted TMED were removed under reduced

pressure. The TMED HCl salt was precipitated in pentane and filtered off. All yielded compounds were chromatographed on silica gel with chloroform as an eluent. The product **G4-BP** was obtained as a clear, colorless glass (1.92 g, 0.12 mmol, 66%). Spectroscopic data are described in Table 1.

**G4P-PP.** 20 mmol of a *p*-phenylphenol solution (1 M in THF) was slowly added to the solution of 1.36 g (0.18 mmol) of **G4P** and 5 g of TMED in 25 ml toluene. After the addition was completed, the reaction mixture was stirred for 5 h. When the reaction was done by <sup>1</sup>H-NMR, solvents and unreacted TMED were removed under reduced pressure. The TMED HCl salt was precipitated in pentane and filtered off. All yielded compounds were chromatographed on silica gel with chloroform as an eluent. The product **G4-PP** was obtained



Scheme 1. Synthetic methods of dendrimeric silanes.

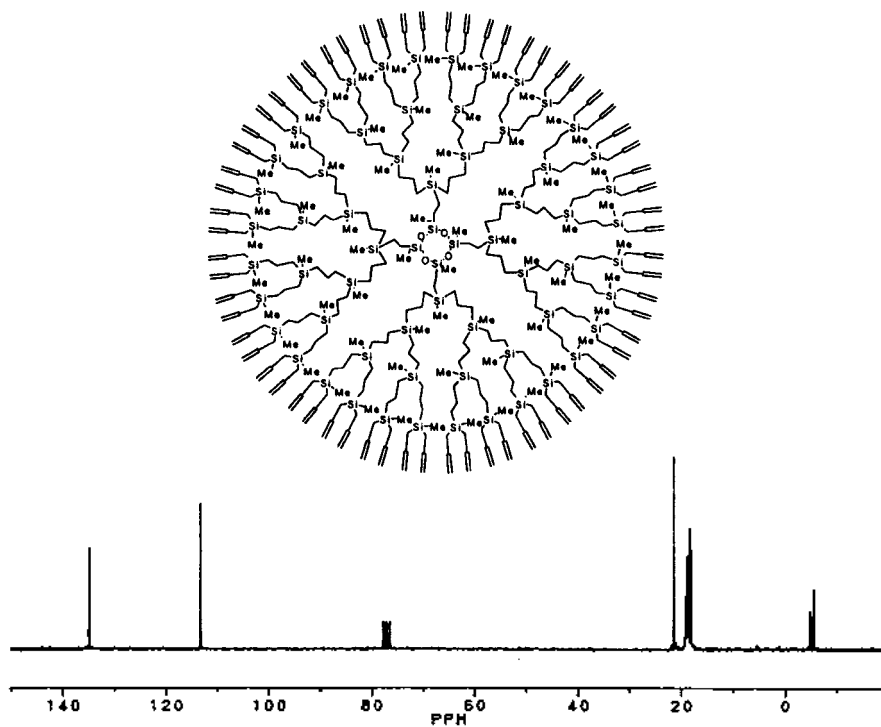


Fig. 1. Planar view and  $^{13}\text{C}$  NMR spectroscopic view of G4.

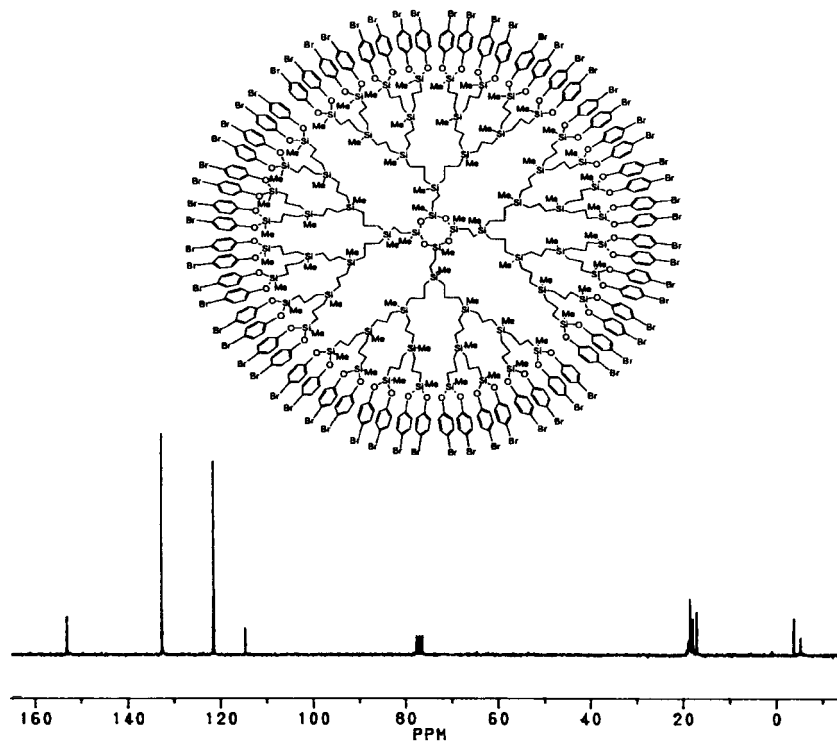


Fig. 2. Planar view and  $^{13}\text{C}$  NMR spectroscopic view of G4P-BP.

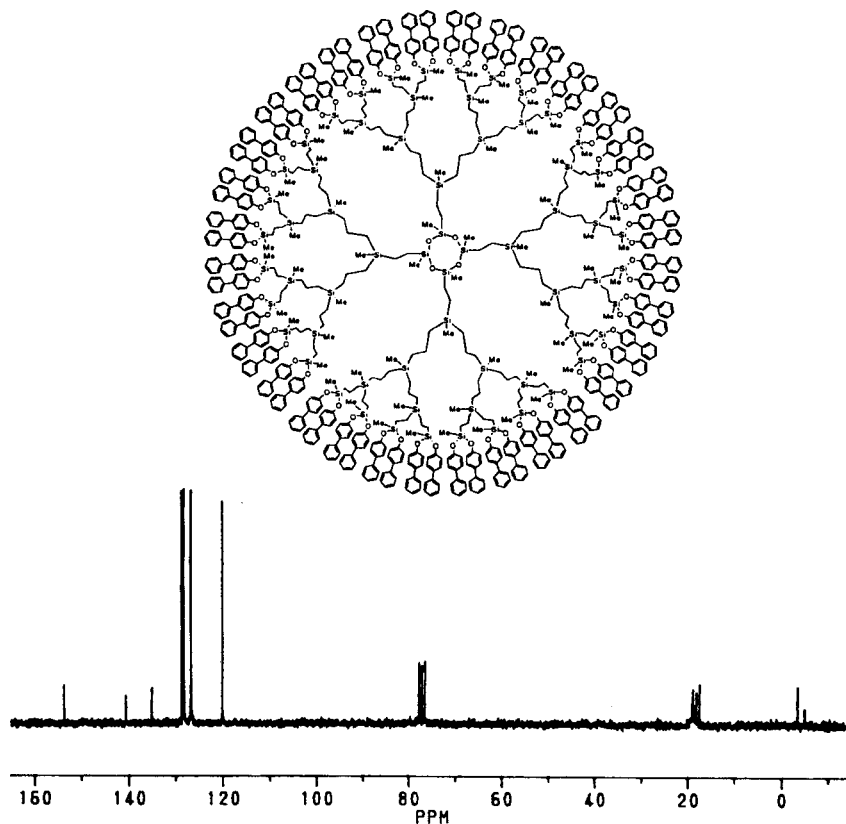
as a clear, colorless glass (2.45 g, 0.15 mmol, 83%). Spectroscopic data are described in *Table 1*.

**Results and discussion.** The synthesis of carbosilane dendrimers (**G0-G4** and **G1P-G4P**) is based on the complete hydrosilation<sup>15</sup> and alkenylation of allylsilane and chlorosilane groups on its periphery as shown in *Scheme 1*.

Two well-known reactions involving dichlorosilyl-capped **G4P** generation with 64 Si-Cl bonds were investigated. The reactions were performed with *p*-bromophenol and *p*-phenylphenol in order to anchor specifically on the periphery of respective dendrimers, while the reactions were also attempted with lithium phenylacetylide in order to cover the surface of dendrimers with 64 groups phenylethynyl units. The treatment of a toluene solution of **G4P** 1.1 equiv. of lithium phenylacetylide at refluxing THF for 4 h gave rise to the dendrimers **G4P-PA** in quantitative yields (*Fig. 4*).

The reactions were monitored by <sup>1</sup>H and <sup>13</sup>C NMR which showed the disappearance of the signal due to the MeSiCl<sub>2</sub> groups of **G4P** on behalf of a new signal at 0.41 ppm corresponding to the terminal MeSi groups. The same reactions were conducted with **G4P** and *p*-phenylphenol and *p*-bromophenol in the presence of TMED leading in quantitative yields to **G4P-BP** (*Fig. 2*) and **G4P-PP** (*Fig. 3*) dendrimers, respectively, here also, reaction needed 2 h at 50°C to go to completion. The purification of the dendrimers (**G4**, **G4P-PP**, **G4P-BP** and **G4P-PA**) by chromatography was necessary after each reaction step.

MALDI mass spectroscopy has recently found an application in this area.<sup>12</sup> This is demonstrated by the investigation of polyacetylene dendrimers,<sup>13</sup> polyesters<sup>16</sup> and carbosilane-based dendritic polyols<sup>5</sup> with excellent results. The MALDI mass spectrum of **G4** with 64 allylic end groups (Mw: 7,



*Fig. 3.* Planar view and <sup>13</sup>C NMR spectroscopic view of **G4P-PP**.

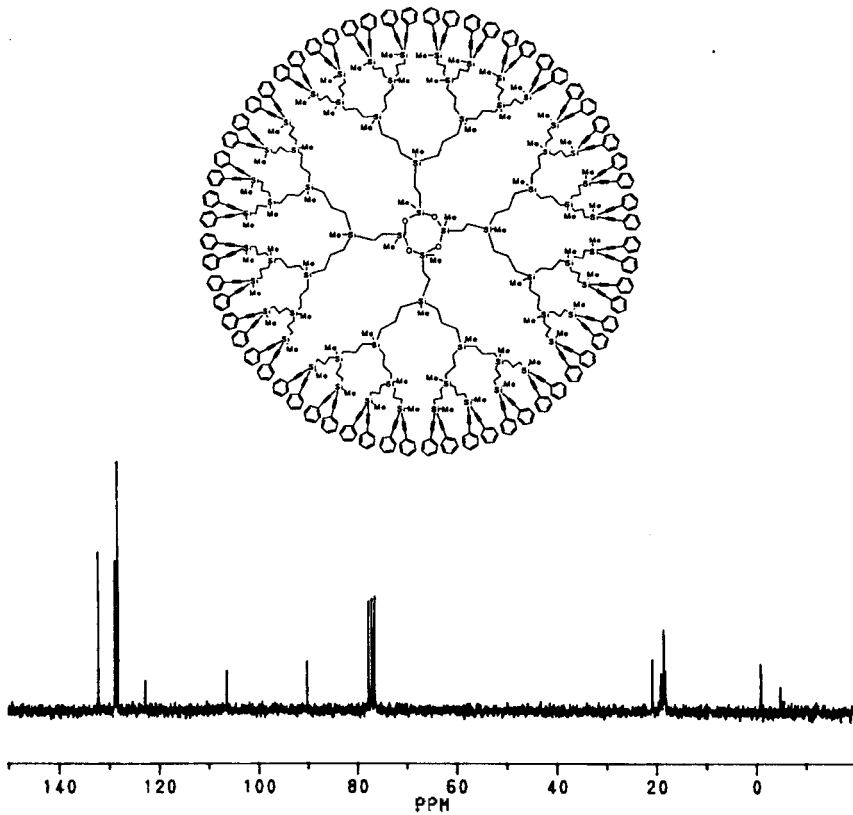


Fig. 4. Planar view and  $^{13}\text{C}$  NMR spectroscopic view of G4-PA.

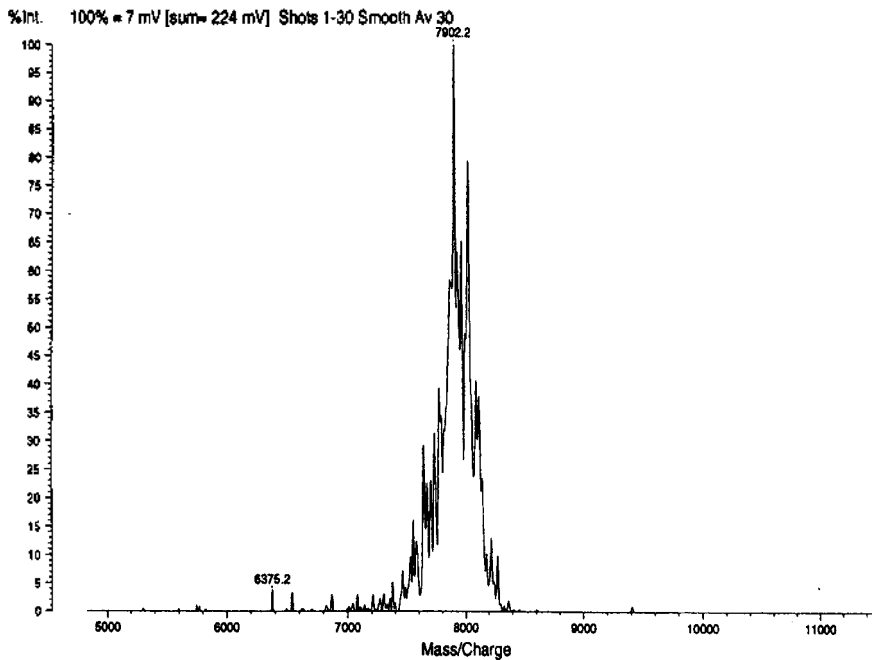
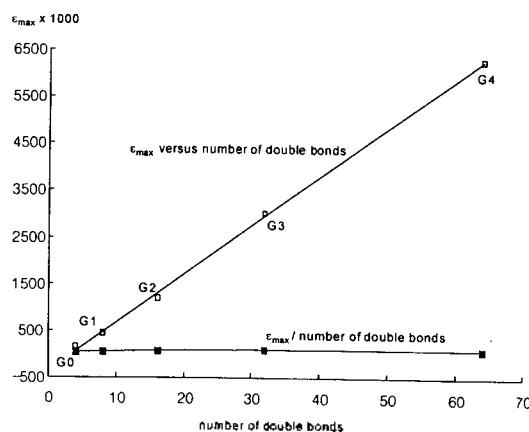


Fig. 5. MALDI mass spectroscopic view of G4 dendrimer.

Table 2. UV/VIS spectroscopic data of dendrimers

Compds.	$\chi^*$	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (l $\cdot$ mol $^{-1}$ cm $^{-1}$ )	$\epsilon_{\max}/\chi$
G0	4	224	158	39.50
G1	8	224	437	54.63
G2	16	224	1,187	74.19
G3	32	224	3,005	93.91
G4	64	224	6,290	98.29
G4P-PA	-	283	36,193	-
G4P-BP	-	285	55,117	-
G4P-PP	-	288	56,908	-

\*number of double bonds

Fig. 6. Graphical view of the maximal coefficient of absorption ( $\epsilon_{\max}$ ) in each generation ( $G_n$ -type dendrimers  $n=0-4$ ) vs. number of double bonds.

913) shows main signals at  $m/z=7902.2$  that are clearly due to the 64 allylic end groups containing dendrimers (Fig. 5). The  $m/z$  value of the dominant signal corresponds to the calculated value of  $m/z$  for G4 dendrimer. But, the MALDI mass spectrum of G4P-BP with 64 *p*-bromophenoxy end groups ( $M_w$ : 16,300), G4P-PP with 64 *p*-phenylphenol end groups ( $M_w$ : 16,121) and G4P-PA with 64 *p*-phenylethynyl end groups ( $M_w$ : 11,746) showed no molecular ion peaks.

The information concerning a perfect building block of  $G_n$  ( $n=1-4$ ) type dendrimers can be obtained, such as a direct comparison of its UV absorption spectra at ( $\lambda_{\max}$  at 224 nm. The increasing number of double bonds for each generation is in direct proportion to molar absorption coefficients ( $\epsilon_{\max}$ ). We expect a good possibility of determining the molecular mass of  $G_n$ -type dendrimers by the

use of these phenomena (Table 2 and Fig. 6). Also, the increasing generation leads to an increase of  $\epsilon_{\max}$ , due to the increased double bonds on the periphery. All terminated dendrimers were soluble in THF, Et<sub>2</sub>O, and toluene, but practically insoluble in hydrocarbons and alcohol.

**Acknowledgment.** This study is supported by the Korean Ministry of Education through Research Fund (BSRI-96-3446) and Dong A University (1997).

## REFERENCES

1. The previous publications: (a) Kim, C.; An, K. *Bull. Korean Chem. Soc.*, **1997**, *18*, 347-356. (b) Kim, C.; Choi, S. K. *Main Group Met. Chem.* **1997**, *20*, 143-150. (c) Kim, C.; An, K. *J. Organomet. Chem.* **1997**, *547*, 55-63. (d) Kim, C.; Kwon, A. *Synthesis*, **1998**, 105-108.
2. (a) Buhleier, E.; Wehner, W.; Vögtle, F. *Synthesis* **1978**, 155. (b) Lambert, J. B.; Pflug, J. D.; Stern, C. L. *Angew. Chem.* **1995**, *107*, 106-108; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 98-99. (c) Uchida, H.; Kabe, Y.; Yoshino, K.; Kawamata, A.; Tsumuraya, T.; Masamune, A. *J. Am. Chem. Soc.* **1990**, *112*, 7077-7079. (d) Jansen, J. F. G. A.; de Brabander van der Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *32*, 1226. (e) Morikawa, A.; Kakimoto, M.; Imai, Y. *Macromolecules* **1991**, *24*, 3469-3474. (f) Tomalia, D. A.; Naylor, A. M.; Goddard III, W. A. *Angew. Chem.* **1990**, *102*, 119-157; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138. (g) Issberner, J.; Moore, R.; Vögtle, F. *Angew. Chem.* **1994**, *107*, 2507-2521; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2413-2420.
3. (a) Dagani, R. *C&EN* **1996**, *June 3*, 30-38. (b) Frey, H.; Lorenz, K.; Lach, C. *Chem. Unser. Zeit* **1996**, *30*, 75-85. (c) Linderhorst, T. K. *Nachr. Chem. Tech. Lab.* **1996**, *44*, 1073-1079.
4. Kim, Y. H. *J. Am. Chem. Soc.* **1992**, *114*, 4947.
5. Lorenz, K.; Hölter, D.; Stühn, B.; Mülhaupt, R.; Frey, H. *Adv. Mater.* **1996**, *8*, 414-416.
6. (a) van der Made, A. W.; van Leeuwen, P. W. N. M.; de Wilde, J. C.; Brandes, R. A. C. *Adv. Mater.* **1993**, *5*, 466-468. (b) van der Made, A. W.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1400-1402.

7. Roovers, J.; Toporowski, P. M.; Zhou, L. L. *Polymer Preprints* **1992**, *33*, 182.
8. (a) Son, D. Y.; Rheingold, A. L.; Ostrander, R. L. *Organometallics* **1994**, *13*, 2682-2690. (b) Seyferth, D.; Kugita, T.; Rheingold, A. L.; Yab, G. P. A. *Organometallics* **1995**, *14*, 5362-5366.
9. (a) Tomalia, D. A.; Durst, H. D. *Top. Curr. Chem.* **1993**, *165*, 193-313. (b) Newkome, G. R. *Advances in Dendritic Macromolecules*; JAI Press: Greenwich, CT, 1994; Vol. 1, p 1-68.
10. (a) Kim, C.; Sung, D. D.; Chung, D. I.; Park, E.; Kang, E. J. *Korean Chem. Soc.* **1995**, *39*, 789-798. (b) Kim, C.; Park, E.; Kang, E. J. *Korean Chem. Soc.* **1995**, *39*, 799-805. (c) Kim, C.; Park, E.; Kang, E. *Bull. Korean Chem. Soc.* **1996**, *17*, 419-424. (d) Kim, C.; Park, E.; Kang, E. *Bull. Korean Chem. Soc.* **1996**, *17*, 592-597.
11. (a) Muzafarov, A. M.; Gorbatsevich, O. B.; Rebrov, E. A.; Ignat'eva, G. M.; Chenskaya, T. B.; Myakushev, V. D.; Bulkin, A. F.; Papkov, V. S. *Polym. Sci.* **1993**, *35*, 1575. (b) Ponomarenko, S. A.; Rebrov, E. A.; Bioka, N. I.; Vasilenko, N. G.; Muzafarov, A. M.; Freidson, Y. S.; Shivaev, V. P. *Polym. Sci.* **1994**, *36*, 896. (c) Krasovskii, V. G.; Sadovskii, N. A.; Gorbatsevich, O. B.; Muzafarov, A. M.; Il'ina, M. N.; Dubovik, I. I.; Strelkova, T. V.; Papkov, V. S. *Polym. Sci.* **1994**, *36*, 589.
12. Loo, R. R. O.; Winger, B. E.; Smith, R. D. *J. Am. Chem. Soc. Mass Spectrom.* **1994**, *5*, 1064-1071.
13. Xu, Z.; Kahr, M.; Walker, K. L.; Wilkins, C. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4537-4550.
14. Lorenz, K.; Mülhaupt, R.; Frey, H.; Rapp, U.; Mayer-Posner, F. *J. Macromolecules* **1995**, *8*, 6657-6661.
15. Larson, G. L. *Advances in Silicone Chemistry*; JAI Press: Greenwich, CT, 1991; Vol. 1, p 327-387.
16. Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *Angew. Chem.* **1994**, *106*, 123-126.