www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 599 (2000) 123–127

Journal of Organo metallic Chemistry

Preparation of double-layered dendritic carbosilanes

Chungkyun Kim *, Seongmo Son

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

Received 12 August 1999; received in revised form 22 November 1999; accepted 2 December 1999

Abstract

Preparation of double-layered carbosilane dendrimers using hydrosilylation and alkenylation as well as alkynylation is described. The dendritic molecule is developed up to the fourth generation, which is composed of one propylene and two ethenyl layers in the inner shell and 96 phenylethynyl groups on the outermost periphery. The dendrimers are characterized by the use of NMR, MALDI-TOF mass spectroscopy, and elemental analysis. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Dendrimer; Carbosilane; Ethynyl silane; Hydrosilylation; Platinum catalyst

---

1. Introduction

Highly branched dendritic macromolecules have received considerable attention in recent years [1]. New materials with characteristic chemical and physical properties can be prepared when these functions carry out specific characters. The synthesis of the double-layered dendritic macromolecules by the use of two different generating methods for inner and outer shells was able to introduce the functionalization of the molecular surface [2]. Recently, carbosilane dendrimers have attracted great attention as a base for materials that are used for the simple construction of molecular architecture [3]. We observed a few methods for the preparation of carbosilane dendrimers possessing allyl, allyloxy and ethynyl groups by the use of hydrosilation, alcoholysis, and alkenylation as well as alkynylation procedures [4–7]. Dendrimers with two different layers for inner and outer shells have been focused on the modification of the dendritic peripheral property [8]. But very little is known about the synthetic approach of the two-layered dendritic macromolecules, and in most cases the studies are limited to the synthesis of the unified molecules with great terminal macromolecular species [9]. In this report, we will show that double-layered carbosilane dendrimers can be made by the use of hydrosilation and subsequently alkenylation as well as alkynylation.

2. Results and discussion

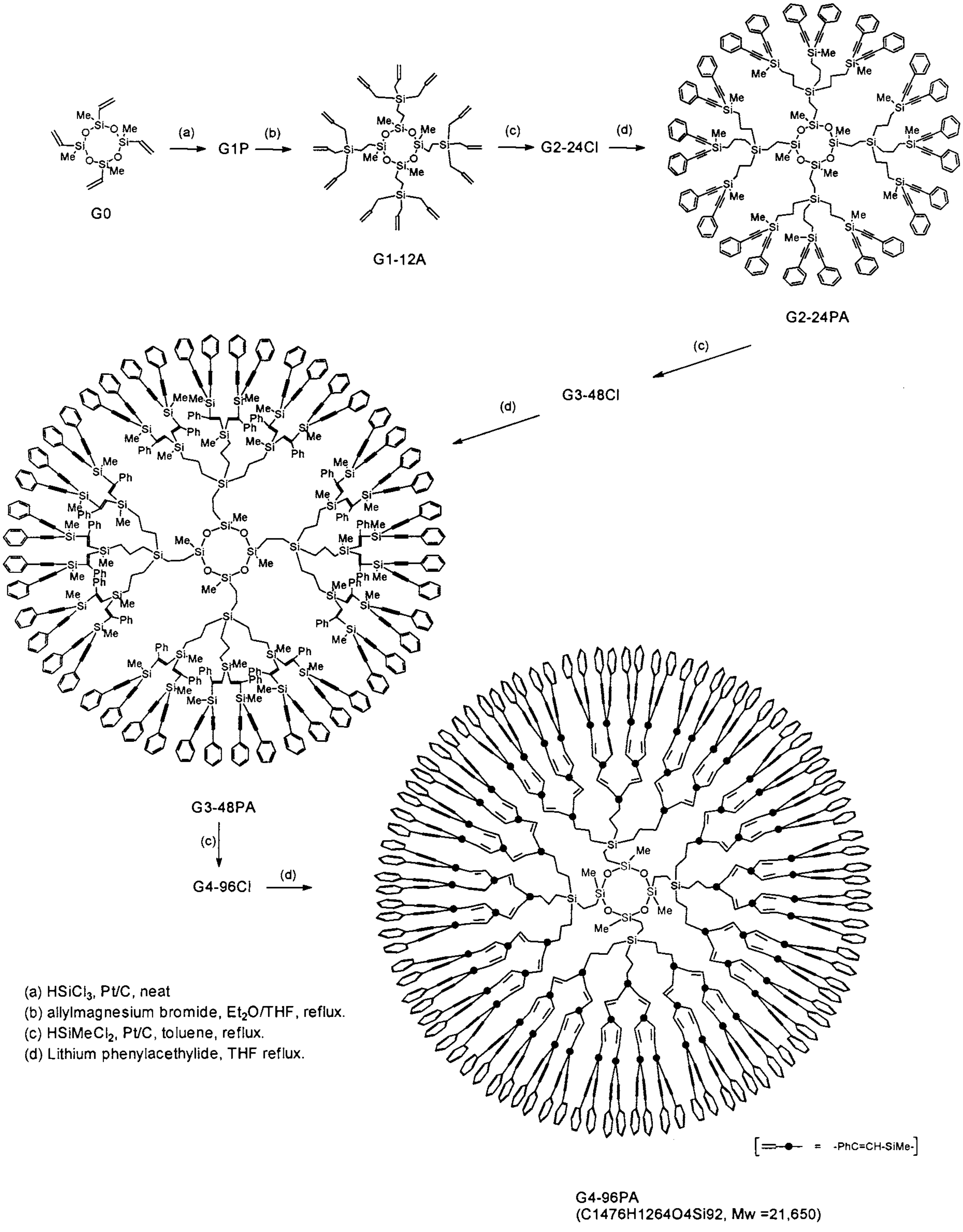
The synthesis of carbosilane dendrimers is based on the complete hydrosilation and alkenylation as well as alkynylation of double and triple bonds as shown in Scheme 1. The quantitative hydrosilation of double bonds in $(SiOMeCH{=}CH_2)_4$ with hydrosilanes ($HSiMe_nCl_{3-n}$; $n = 0–2$) and alkenylation as well as alkynylation have already been recorded [4]. The 12 Si–Cl bonded chlorosilylated generation (G1-12Cl) is obtained as a pure molecule by the reaction of $(SiOMeCH{=}CH_2)_4$ and $HSiCl_3$ in the presence of Pt–C (Pt–C; 10% Pt content on activated carbon) which is obtained quantitatively. The first generation with 12 allylic end groups (G1-12A) is obtained as a pure molecule by the reaction of $(SiOMeCH_2CH_2SiCl_3)_4$ and allylmagnesium bromide. The reaction of G1-12A with dichloromethylsilane under a platinum catalyst quantitatively provided the second generation with the 24 Si–Cl bond-containing dendrimer (G2-24Cl). The reaction of G2-24Cl with lithium phenylacethylide provided the second generation with the 24 phenylethynyl group-containing dendrimer (G2-24PA) on the periphery. Subsequently, the transition of triple bonded G2-24PA to G3-48Cl is carried out by hydrosilation that is observed with quantitative yields. By the repetition of hydrosilation with G*n*-*m*PA ($n = 2$, $m = 24$; $n = 3$, $m = 48$) with dichloromethylsilane under a platinum catalyst and alkynylation with lithium phenylacethylide in reflux condition, the ethynyl group-containing den-

---

* Corresponding author. Fax: + 82-51-2007259.

E-mail address: ckkim@mail.donga.ac.kr (C. Kim)

PII: S0022-328X(99)00746-9



Scheme 1. Overview of reaction route of dendrimers.

drimers were prepared up to the fourth generation with good yields. The formation of the fifth generation with 192 Si–Cl bonds by the application of the same reaction mechanism did not give a uniformly ordered structure.

The identification and decision of the degree of reaction of all branches in dendrimers are very important. NMR spectroscopy clearly reveals the transition from old generations to new generations. For example, information about the transition of G2-24Cl to G2-24PA

Table 1
MALDI mass, EA, UV and SEC data of G*n*-*m*PA type dendrimers

G*n*-*m*PA	Formula	MALDI (Found/Calc.)	EA (Found/Calc.) (%)		UV		SEC	
			C	H	λ_{max}	$E_{max}\times 10^5$	Rt (min)	PD (M_w/M_n)
G1-12A	$C_{48}H_{88}O_4Si_8$	954/954	60.70/60.44	9.50/9.30	–	–	–	–
G2-24PA	$C_{252}H_{256}O_4Si_{20}$	3910/3911	77.08/77.40	6.42/6.60	243	0.840	16.41	1.19 (2719/2272)
G3-48PA	$C_{660}H_{592}O_4Si_{44}$	9831/9824	79.54/80.69	5.97/6.07	243	1.619	15.60	1.14 (4331/3786)
G4-96PA	$C_{1476}H_{1264}O_4Si_{92}$	–[a]/21650	79.93/81.88	5.83/5.88	243	3.215	14.90	1.15 (7161/6199)

[a] Not observed.

can be obtained from the observation of the ^{1}H-NMR spectrum. The decay of methyl signals of G2-24Cl at 0.72 ppm and the formation of G2-24PA at 0.35 ppm were clearly observed. Furthermore, ^{13}C-NMR spectroscopic attachments of the hydrosilation procedure clearly revealed the transition of triple bond signals at 90.05 and 106.37 ppm to double bonds at 140.39 and 157.04 ppm.

The MALDI mass spectroscopic determination of G2-24PA and G3-48PA dendrimers mainly showed the M^+ signal that is clearly due to the structural perfection of the prepared dendrimers. The *m*/*z* value of G2-24PA showing the dominant signal at 3910 amu corresponds to the calculated value 3911. G3-48PA is observed, respectively, at 9831 (calcd. 9824) amu (Table 1). However, the MALDI spectrum of G4-96PA with 21 650 amu does not show an M^+ ion peak in this condition. As a related result, we observed that the tendency of the increasing number of triple bonds has been in direct proportion to the increasing molar absorbities of the given dendrimers (see Fig. 1). This method in any case can assist the determination of molecular weight, because the MALDI-TOF mass spectroscopic determination of high-molecular-weight dendrimers is not available in many cases. Size-exclusion chromatography (SEC) provided additional information on the perfect building and purity of each generation. As expected, the calculated molecular weight of dendrimers was in indirect proportion to retention time (see Fig. 2), but the molecular weights determined were not in agreement with the theoretical molecular weight. This is explained by differences in the linear polystyrene standards and the synthesized ball-type dendrimers. SEC analyzed polydisphersity values (M_w/M_n: 1.14–1.19) for the dendrimers G2-24PA to G4-96PA explain that the prepared dendrimers have a very narrow molecular-weight range. The plot of the observed molecular weights of G2-24PA to G4-96PA versus retention time revealed straight linearity. This means the prepared dendrimers have regularly increased molecular weight. Moreover, this SEC attachment could be an indirect method for the determination of the molecular weight of dendrimers.

The techniques used for the characterization of dendrimers were ^{1}H- and ^{13}C-NMR, and UV spectroscopy, size-exclusion chromatography, and elemental analysis. The simplicity of the ^{1}H- and ^{13}C-NMR spectra is an indication of the high purity of dendrimers. Different generations may be readily seen in the ^{1}H- and ^{13}C-NMR spectra.

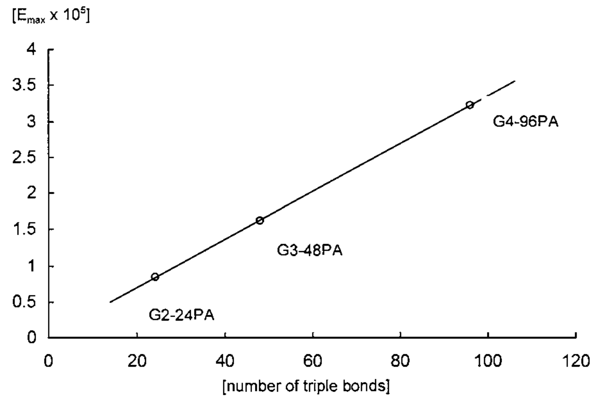


Fig. 1. Graphical view of UV data.

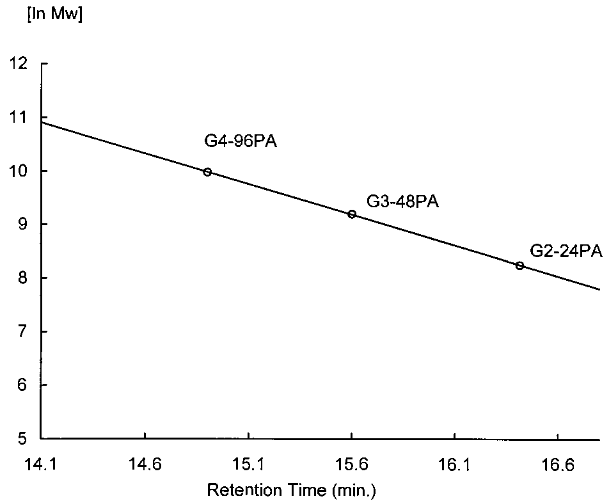


Fig. 2. Graphical view of SEC data.

3. Experimental

All reactions were carried out under a dried N_2 atmosphere. Ether and THF were dried by sodium–benzophenone ketyl, while solvents such as toluene were dried and distilled from sodium metal. The NMR spectra were recorded on a Bruker AC-200 Spectrometer. The UV spectra were measured by an HP 8452A diode array UV–visible spectrophotometer. Elemental analysis and MALDI mass spectroscopy (KRATOS KOMPACKT MALDI 2) attachments were performed in the Pusan and Taejon Branches of the Korean Basic Science Institute.

3.1. G2-24Cl

A mixture of 6.11 g (6.57 mmol) of G1, 15.93 g (138.47 mmol) of $HSiMeCl_2$, and 0.10 g of a hydrosilation catalyst (Pt–C, 10% content on activated carbon) was refluxed for 5 h. The excess dichloromethylsilane was removed by vacuum. The catalyst was filtered off and volatile components were removed by vacuum, leaving 13.78 g of pure G2P, as a white precipitate. Further purification was not available because of sensitivity to moisture. By the NMR spectroscopy, the yielded compound was a single dendrimer. Yield: 13.78 g (5.09 mmol, 90%) of pure G2-24Cl. ^{1}H-NMR (ppm, $CDCl_3$): $\delta = 0.10$ (s, 12H, MeSi, G0), 0.72 (s, 36H, MeSi, G2), 0.44 (m, 16H, CH_2, G0), 0.69 (m, 24H, CH_2, G1), 1.19 (m, 24H, CH_2, G1), 1.54 (m, 24H, CH_2, G1). ^{13}C-NMR (ppm, $CDCl_3$): $\delta = -1.34$ (MeSi, G0), 5.53 (MeSi, G2P), 3.23, 8.96 (CH_2, G0), 15.45, 17.34, 25.93 (CH_2, G1).

3.2. G2-24PA

A total of 80 ml (80 mmol) of a lithium phenylacetylide in THF was added slowly to 2.81 g (2.95 mmol) of G2P in 50 ml toluene. After the addition was finished, the reaction mixture was refluxed for 5 h. Volatile components were removed under reduced pressure, leaving a yellow precipitate and salt was precipitated in toluene and filtered off. The prepared compounds were chromatographed on silica gel with chloroform. The product G2-24PA was obtained as a clear, yellow–brown glass (7.52 g, 1.92 mmol, 65%). ^{1}H-NMR (ppm, $CDCl_3$): $\delta = -0.30$ (s, 12H, MeSi, G0), 0.35 (s, 36H, MeSi, G2), 0.48 (m, 16H, CH_2, G0), 0.73 (m, 24H, CH_2, G1), 0.87 (m, 24H, CH_2, G1), 1.60 (m, 24H, CH_2, G1), 7.44–7.55 (m, 120H, Ph, G2). ^{13}C-NMR (ppm, $CDCl_3$): $\delta = -1.58$ (MeSi, G0), -1.12 (MeSi, G2), 3.78, 9.27 (CH_2, G0), 16.12, 18.38, 20.80 (CH_2, G1), 90.05, 106.37 ($C{\equiv}C$, G2), 122.68 (C_{quart}), 128.19 (C-*o*), 128.74 (C-*p*), 132.11 (C-*m*). Anal. Calc. (%) for $C_{252}H_{256}O_4Si_{20}$: C, 77.40; H, 6.60. Found: C, 77.08; H, 6.42. UV (in THF): λ_{max} (243 nm), ε_{max}, 0.840×10^5 mol^{-1} cm^{-1}. MALDI-TOF MS: (Found/Calc.) (3910/3911). IR (cm^{-1}, KBr): 2160 ($\nu_{C\equiv C}$). SEC: Rt (min), 16.41; PD, 1.19 (M_w/M_n).

3.3. G3-48Cl

The same procedure was used in the reaction of 3.76 g (0.96 mmol) of G2-24PA, 5.74 g (49.86 mmol) of $HSiMeCl_2$, and 0.08 g of a platinum catalyst in 25 ml toluene for 17 h reflux. Yield: 6.08 g (0.91 mmol, 95%) of pure G3-48Cl. ^{1}H-NMR (ppm, $CDCl_3$): $\delta = -0.61$ (s, 12H, MeSi, G0), -0.48 (s, 36H, MeSi, G2), 0.71 (s, 72H, MeSi, G3P), -0.09 (m, 16H, CH_2, G0), 0.08 (m, 24H, CH_2, G1), 0.32 (m, 24H, CH_2, G1), 1.06 (m, 24H, CH_2, G1), 6.51 (m, 24H, SiCH, G3), 7.02–7.27 (m, 120H, Ph, G2). ^{13}C-NMR (ppm, $CDCl_3$): $\delta = -1.21$ (MeSi, G0), -2.98 (MeSi, G2), 4.53 (MeSi, G3), 3.82, 9.12 (CH_2, G0), 16.48, 18.31, 20.31 (CH_2, G1), 140.39, 157.04 (C=C, G3P), 127.51 (C_{quart}), 127.73 (C-*o*), 128.12 (C-*p*), 148.80 (C-*m*).

3.4. G3-48PA

The same procedure was used in the reaction of 3.04 g (0.45 mmol) of G3-48Cl and 30 ml (30 mmol) of $LiC{\equiv}CPh$ in 25 ml THF for 5 h reflux. Yield: 2.09 g (0.29 mmol, 64%) of pure G3-48PA. ^{1}H-NMR (ppm, $CDCl_3$): $\delta = -0.50$ (s, 12H, MeSi, G0), -0.50 (s, 36H, MeSi, G2), 0.39 (s, 72H, MeSi, G3), -0.07 (m, 16H, CH_2, G0), -0.07 (m, 24H, CH_2, G1), 0.09 (m, 24H, CH_2, G1), 0.93 (m, 24H, CH_2, G1), 6.62 (m, 24H, SiCH, G3), 7.16–7.35 (m, 360H, Ph, G2–G3). ^{13}C-NMR (ppm, $CDCl_3$): $\delta = -1.48$ (MeSi, G0), -2.88 (MeSi, G2), -0.86 (MeSi, G3), 3.86, 9.12 (CH_2, G0), 16.62, 18.31, 20.53 (CH_2, G1), 147.92, 157.93 (C=C, G3), 89.19, 107.55 ($C{\equiv}C$, G3), 126.47, 127.60, 128.07, 143.17 (Ph, G2), 122.57 (C_{quart}), 128.18 (C-*o*), 128.84 (C-*p*), 132.02 (C-*m*). Anal. Calc. (%) for $C_{660}H_{592}O_4Si_{44}$: C, 80.69; H, 6.07. Found: C, 79.54; H, 5.97. UV (in THF): λ_{max} (243 nm), ε_{max}, 1.619×10^5 mol^{-1} cm^{-1}. MALDI-TOF MS: (Found/Calc.) (9831/9824). IR (cm^{-1}, KBr): 2160 ($\nu_{C\equiv C}$). SEC: Rt (min), 15.60; PD, 1.14 (M_w/M_n).

3.5. G4-96Cl

The same procedure was used in the reaction of 1.37 g (0.14 mmol) of G3-48PA, 2.20 g (19.12 mmol) of $HSiMeCl_2$, and 0.05 g of a platinum catalyst in 25 ml toluene for 17 h reflux. Yield: 2.02 g (0.13 mmol, 94%) of pure G4-96Cl. ^{1}H-NMR (ppm, $CDCl_3$): $\delta = -0.67$ (s, 12H, MeSi, G0), -0.53 (s, 36H, MeSi, G2), -0.67 (s, 72H, MeSi, G3), 0.64 (s, 144H, MeSi, G4), -0.14 (m, 16H, CH_2, G0), 0.01 (m, 24H, CH_2, G1), 0.27 (m, 24H, CH_2, G1), 0.92 (m, 24H, CH_2, G1), 6.05 (m, 24H, SiCH, G3), 6.49 (m, 48H, SiCH, G4), 6.84–7.22 (m, 360H, Ph, G2–G3). ^{13}C-NMR (ppm, $CDCl_3$): $\delta = -3.14$ (MeSi, G0), -3.08 (MeSi, G2), -2.62 (MeSi, G3), 4.51 (MeSi, G4), 3.87, 9.17 (CH_2, G0), 16.98, 18.30, 20.95 (CH_2, G1), 145.91, 161.86 (C=C, G3), 139.98, 157.33 (C=C, G4), 126.42, 127.90, 144.23 (Ph, G2), 127.48 (C_{quart}), 128.09 (C-*o*), 128.19 (C-*p*), 146.46 (C-*m*).

3.6. G4-96PA

The same procedure was used in the reaction of 2.13 g (0.14 mmol) of G4-96Cl and 20 mml (20 mmol) of LiC≡CPh in 25 ml THF for 6 h reflux. Yield: 1.71 g (0.08 mmol, 56%) of pure G4-96PA. ^{1}H-NMR (ppm, $CDCl_3$): $\delta = -0.53$ (s, 12H, MeSi, G0), -0.67 (s, 36H, MeSi, G2), -0.67 (s, 72H, MeSi, G3), 0.34 (s, 144H, MeSi, G4), -0.10 (m, 24H, CH_2, G1), 0.10 (m, 24H, CH_2, G1), 0.95 (m, 24H, CH_2, G1), 6.04 (m, 24H, SiCH, G3), 6.72 (m, 48H, SiCH, G4), 7.17–7.59 (m, 840H, Ph, G2–G4). ^{13}C-NMR (ppm, $CDCl_3$): $\delta = -1.50$ (MeSi, G0), -3.17 (MeSi, G2), -2.64 (MeSi, G3), -0.97 (MeSi, G4), 3.82, 9.20 (CH_2, G0), 16.81, 18.80, 20.93 (CH_2, G1), 144.85, 163.04 (C=C, G2), 145.60, 158.31 (C=C, G3), 89.24, 107.45 (C≡C, G4), 126.48, 127.64, 131.41, 142.74 (Ph, G2–G3), 122.55 (C_{quart}), 128.16 (C-*o*), 128.82 (C-*p*), 131.99 (C-*m*). Anal. Calc. (%) for $C_{1476}H_{1264}O_4Si_{92}$: C, 81.88; H, 5.88. Found: C, 79.93; H, 5.83. UV (in THF): λ_{max} (243 nm), ε_{max}, 3.215×10^5 mol^{-1} cm^{-1}. IR (cm^{-1}, KBr): 2159 ($\delta_{C\equiv C}$). SEC: Rt (min), 14.90; PD, 1.15 (M_w/M_n).

Acknowledgements

This study is supported by the Korean Science and Engineering Foundation (Grant no. 995-0300-009-2) and Dong-A University (1998).

References

[1] (a) J. Issberner, R. Moore, F. Vögtle, Angew. Chem. Int. Ed. Engl. 33 (1994) 2413. (b) M.K. Lothian-Tomalia, D.M. Hedstrand, D.A. Tomalia, A.B. Padias, H.K. Hall, Jr., Tetrahedron 53 (1997) 15495. (c) M. Fischer, F. Vögtle, Angew. Chem. Int. Ed. 38 (1999) 884. (d) J.-P. Majoral, A.-M. Caminade, Chem. Rev. 99 (1999) 845. (e) F. Vögtle, Müllen, Abstract of First International Dendrimer Symposium (IDS-1), Dechema, 1999, p. 1.

[2] (a) D.J. Pesak, J. Moore, Angew. Chem. Int. Ed. Engl. (1997) 1636. (b) L. Groenendaal, J.M.J. Fréchet, J. Org. Chem. 63 (1998) 5675. (c) P.R. Ashton, S.E. Boyed, C.L. Brown, N. Jayaraman, F. Stoddart, Angew. Chem. 109 (1997) 756.

[3] (a) S.W. Krska, D. Seyferth, J. Am. Chem. Soc. 120 (1998) 3604. (b) K. Lorenz, H. Frey, B. Stühn, R. Mülhaut, Macromolecules 30 (1997) 6860. (c) M. Veith, R. Elsassaser, R.-P. Kruger, Organometallics 18 (1999) 656. (d) M. Nanjo, A. Sekiguchi, Organometallics 17 (1998) 492. (e) J. Nakajama, J.-S. Lin, Tetrahedron Lett. 34 (1997) 6043.

[4] C. Kim, K. An, J. Organomet. Chem. 547 (1997) 55.

[5] (a) C. Kim, A. Kwon, Synthesis (1998) 155. (b) C. Kim, Y. Jeong, I. Jung, J. Organomet. Chem. 570 (1998) 9.

[6] (a) C. Kim, M. Kim, J. Organomet. Chem. 563 (1998) 43. (b) C. Kim, I. Jung, Inorg. Chem. Commun. 1 (1998) 427.

[7] C. Kim, K. An, Bull. Korean Chem. Soc. 18 (1997) 164.

[8] (a) M.T. Reetz, G. Lohmer, R. Schwickhardi, Angew. Chem. Int. Ed. Engl. 36 (1997) 1526. (b) D.J. Pesak, J.S. Moore, Angew. Chem. Int. Ed. Engl. 36 (1997) 1636.

[9] K. Lorenz, R. Mülhaut, H. Frey, U. Rapp, F.J. Mayer-Posner, Macromolecules 28 (1995) 6657.