

Pentaerythritol-based Carbosilane Dendrimers

Xin De TANG^{1,2}, Qi Zhen ZHANG^{1*}, Qi Feng ZHOU³

¹School of Chemistry and Chemical Engineering, Shandong University, Ji'nan 250100

²Institute of New Materials, Shandong Jiaotong University, Ji'nan 250023

³College of Chemistry and Molecular Engineering, Peking University, Beijing 100871

Abstract: A series of novel pentaerythritol-based carbosilane dendrimers have been synthesized. Using pentaerythritol-based tetraallyl ether as core molecule, the dendrimers have been prepared up to the third generation with 108 allyl groups on the periphery by alternate allylation-hydrosilylation approach.

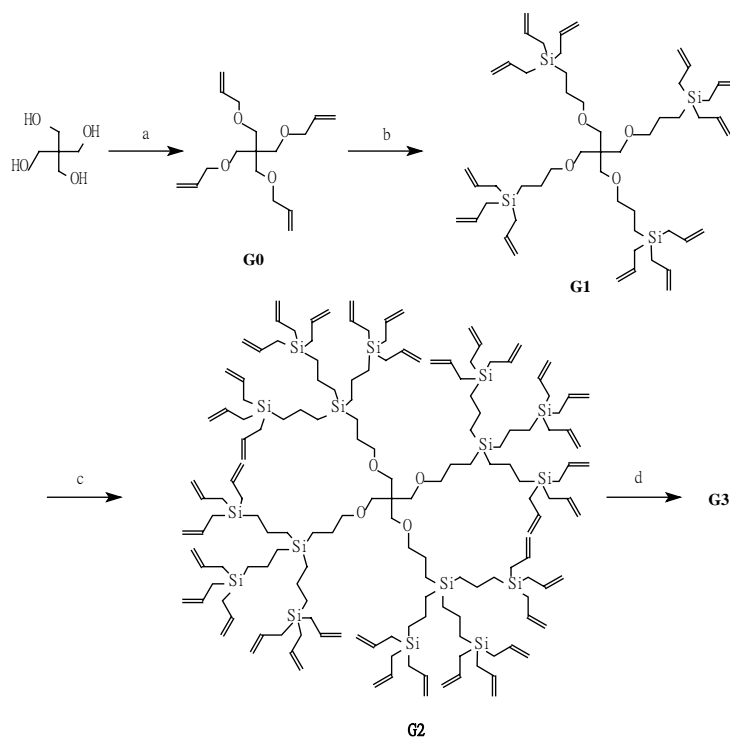
Keywords: Pentaerythritol, carbosilane dendrimer, hydrosilylation, allylation.

Dendrimers, as well-defined, highly branched, and three-dimensional polymers, represent a key stage in the ongoing evolution of macromolecular chemistry¹. Carbosilane dendrimers are the most important class of silicon-containing dendrimers, due to their excellent chemical and thermal stability and to the possibility of synthesizing these molecules to high generations². The divergent method introduced by van der Made³, Roovers⁴, and Seyferth⁵ is the most common and efficient route to synthesize carbosilane dendrimers by repetitive alkenylation-hydrosilylation cycles. Silicon tetrachloride is used as a core in most case to produce carbosilane dendrimers. Kim's group has reported carbosilane dendrimers with other cores, such as $(\text{Me}(\text{CH}_2=\text{CH})\text{SiO})_4$ and $((\text{CH}_2=\text{CHCH}_2\text{O})\text{SiCH}_2)_2$ ^{6,7}. In this paper, we report a series of novel carbosilane dendrimers based on pentaerythritol.

The synthesis of these dendrimers started from pentaerythritol-based tetraallyl ether (**G0**)⁸. The allyl groups of **G0** were hydrosilylated with trichlorosilane (50% excess) in the presence of Karstedt catalyst to give in quantitative yield **G1-Cl** with four $-\text{SiCl}_3$ functional groups. Then all the $-\text{SiCl}_3$ groups reacted with allylmagnesium bromide in THF (reflux, 10 h) to produce the first generation (**G1**) with 12 allyl end-groups. **G1** could be converted into the second generation (**G2**) with 36 allyl end-groups by a repetitive hydrosilylation-allylation cycle. Repeating these reactions gave the third generation (**G3**) with 108 allyl end-groups (**Scheme 1**).

* E-mail: qzzhang@sdu.edu.cn

Scheme 1



a $\text{CH}_2=\text{CHCH}_2\text{Br}$, NaOH, THF;

b, c, d. 1) HSiCl_3 , Karstedt catalyst, THF; 2) $\text{CH}_2=\text{CHCH}_2\text{MgBr}$, THF.

Table 1 Molecular Information of the carbosilane dendrimers

generation	formula	functionality	M_{calcd}	M^{a}
G0	$\text{C}_{17}\text{H}_{27}\text{O}_4$	4	296	282
G1	$\text{C}_{52}\text{H}_{92}\text{O}_4\text{Si}_4$	12	904	860
G2	$\text{C}_{161}\text{H}_{284}\text{O}_4\text{Si}_{16}$	36	2728	2610
G3	$\text{C}_{485}\text{H}_{860}\text{O}_4\text{Si}_{52}$	108	8200	7830

^a Vapor pressure osmometry (VPO) in toluene at 50 °C.

Each generation was purified by chromatography on a silica gel column eluted with a solution of ethyl acetate in hexane. The isolated yields were 55%, 45%, and 32% for **G1**, **G2**, and **G3**, respectively. All these pure products were either oily or viscous liquids. They were characterized by NMR spectroscopy and elemental analysis⁹. The molecular weights of each generation were determined by vapor pressure osmometry (VPO) and summarized in **Table 1**, which showed that the experimental molecular weights were very comparable to their calculated numbers within the experimental errors.

To the best of our knowledge, this is the first report for the synthesis of pentaerythritol-based carbosilane dendrimers with central carbon atom. It is different

from traditional carbosilane dendrimers. These dendrimers may show new physical and chemical properties. They are expected to lead potential applications, the reactive Si-Cl groups on the periphery allow to functionalize the dendrimer surface for the preparation of a diversity of novel materials, such as liquid crystalline dendrimers. Further research into the properties and functionalization of these dendrimers is now under way.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 29874020, 59573029).

References and Notes

1. S. M. Grayson, J. M. Frechet. *Chem. Rev.*, **2001**, *101*, 3819.
2. J.-P. Majoral, A.-M. Caminade. *Chem. Rev.*, **1999**, *99*, 845.
3. A. W. van der Made, P. W. N. M. van Leeuwen. *J. Chem. Soc. Chem. Comm.*, **1992**, 1400.
4. L.-L. Zhou, J. Roovers. *Macromolecules*, **1993**, *26*, 963.
5. D. Seyferth, D. Y. Son, A. L. Rheingold, R. L. Ostrander. *Organometallics*, **1994**, *13*, 2682.
6. C. Kim, A. Kwon. *Synthesis*, **1998**, 105.
7. C. Kim, J. Park. *Synthesis*, **1999**, 1804.
8. X. D. Tang, Q. Z. Zhang, Z. S. Hou, A. X. Li, Q. F. Zhou. *Chin. J. Org. Chem.*, **2004**, *24*, 103.
9. **G0**: ^1H NMR (90 Hz, CDCl_3 , δ ppm): 6.03-5.67 (m, 4H, $\text{CH}=\text{CH}_2$), 5.30-5.06 (m, 8H, $\text{CH}=\text{CH}_2$), 3.94 (d, 8H, $\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2$), 3.46 (s, 8H, $\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2$); ^{13}C NMR (90 Hz, CDCl_3 , δ ppm): 136.25, 134.71, 116.25, 71.98, 70.00, 44.99; IR (KBr, cm^{-1}): 3078, 2909, 2866, 1645, 1420, 1349, 1090, 993, 922.
G1: ^1H NMR (90 Hz, CDCl_3 , δ ppm): 5.97-5.49 (m, 12H, $\text{CH}=\text{CH}_2$), 4.89-4.73 (m, 24H, $\text{CH}=\text{CH}_2$), 3.36 (m, 16H, CH_2OCH_2), 1.57 (m, 8H, $\text{SiCH}_2\text{CH}=\text{CH}_2$), 1.23 (d, 24H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 0.56 (m, 8H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$); ^{13}C NMR (90 Hz, CDCl_3 , δ ppm): 133.99, 113.43, 69.66, 70.48, 45.59, 23.61, 19.47, 7.54. Anal Calcd. For $\text{C}_{52}\text{H}_{92}\text{O}_4\text{Si}_4$: C 69.03; H 10.18. Found: C 68.95; H 10.09.
G2: ^1H NMR (90 Hz, CDCl_3 , δ ppm): 5.96-5.48 (m, 36H, $\text{CH}=\text{CH}_2$), 4.89-4.72 (m, 72H, $\text{CH}=\text{CH}_2$), 3.34 (m, 16H, CH_2OCH_2), 1.56 (m, 72H, $\text{SiCH}_2\text{CH}=\text{CH}_2$), 1.19 (m, 32H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 0.58 (m, 56H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$); ^{13}C NMR (90 Hz, CDCl_3 , δ ppm): 134.09, 113.39, 70.46, 69.70, 44.60, 29.59, 20.86, 19.65, 18.17, 17.39, 16.57. Anal Calcd. For $\text{C}_{161}\text{H}_{284}\text{O}_4\text{Si}_{16}$: C 70.82; H 10.41. Found: C 70.50; H 10.18.
G3: ^1H NMR (90 Hz, CDCl_3 , δ ppm): 5.96-5.48 (m, 108H, $\text{CH}=\text{CH}_2$), 4.89-4.72 (m, 216H, $\text{CH}=\text{CH}_2$), 3.35 (m, 16H, CH_2OCH_2), 1.52 (d, 216H, $\text{SiCH}_2\text{CH}=\text{CH}_2$), 1.20 (m, 104H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 0.69 (m, 200H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$); ^{13}C NMR (90 Hz, CDCl_3 , δ ppm): 134.31, 113.13, 69.90, 70.61, 44.88, 29.65, 22.09, 20.97, 19.80, 18.35, 18.17, 17.87, 17.63, 16.77. Anal Calcd. For $\text{C}_{485}\text{H}_{860}\text{O}_4\text{Si}_{52}$: C 70.98; H 10.49. Found: C 70.54; H 10.26.

Received 16 January, 2004