

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

## Water-Soluble Carbosiloxane Dendrimers

Bettina Lühmann; Heinrich Lang; Karin Brüning

**To cite this Article** Lühmann, Bettina , Lang, Heinrich and Brüning, Karin(2001) 'Water-Soluble Carbosiloxane Dendrimers', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 169: 1, 157 — 160

**To link to this Article:** DOI: 10.1080/10426500108546614

**URL:** <http://dx.doi.org/10.1080/10426500108546614>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Water-Soluble Carbosiloxane Dendrimers

BETTINA LÜHMANN, HEINRICH LANG\* and KARIN BRÜNING

*Technische Universität Chemnitz, Fakultät für Naturwissenschaften, Institut für Chemie, Lehrstuhl für Anorganische Chemie, Strasse der Nationen 62, D-09111 Chemnitz (Germany)*

This article focuses on the preparation of water-soluble carbosiloxane dendrimers by the divergent growth method using repetitive hydrosilylation-alcoholysis cycles as well as ammonolysis and ionexchange reaction steps.

**Keywords:** Carbosiloxane; Dendrimers; Water-Solubility

## INTRODUCTION

In recent years the number of studies on perfectly branched, highly symmetrical, tree-like macromolecules assigned dendrimers have exponentially increased.<sup>[1,2,3]</sup>

At first, great effort was concentrated on the preparation of dendritic molecules with organic skeletons while the development of heteroatom-containing dendrimers has only become of rising interest in the last few years.<sup>[4,5,6,7]</sup> Among the latter one carbosiloxane dendrimers containing Si-O-C units in the dendritic scaffold are of considerable interest.<sup>[8,9]</sup>

In this paper the construction of water-soluble dendrimers is described based on a carbosiloxane skeleton by repeated hydrosilylation-alcoholysis cycles using the divergent growth method.<sup>[10]</sup>

\* Corresponding author. E-mail: heinrich.lang@chemie.tu-chemnitz.de

## RESULTS AND DISCUSSION

Due to the hydrophobic character of the Si-O-C sub-units, carbosiloxane dendrimers are insoluble in common polar organic solvents and water, respectively. Figure 1 shows an example for this kind of dendritic species prepared by the alcoholysis of a 2<sup>nd</sup> generation Cl-terminated carbosiloxane dendrimer with  $\text{HO}(\text{CH}_2)_7\text{CH}_3$  in the presence of  $\text{NEt}_3$  as a base.<sup>[11]</sup>

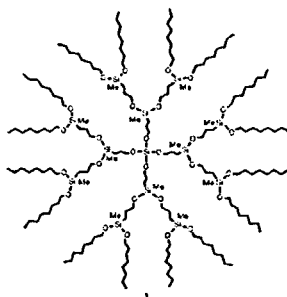


FIGURE 1 2<sup>nd</sup> generation carbosiloxane dendrimer 1.<sup>[11]</sup>

One example of a more hydrophilic carbosiloxane dendrimer is shown in Figure 2. The 1<sup>st</sup> generation carbosiloxane polyol 2 is accessible by the substitution of terminal Cl atoms in  $\text{Si}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{SiMeCl}_2)_4$  by  $\text{HOCH}(\text{CH}_3)\text{COOCH}_3$  followed by reduction with  $\text{LiAlH}_4$ .<sup>[11]</sup>

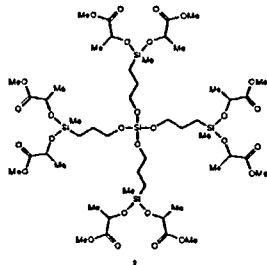
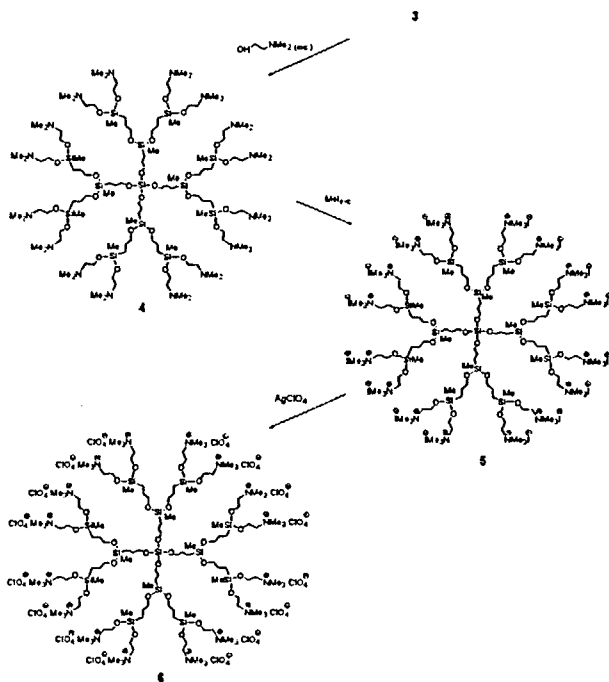


FIGURE 2 Dendritic carbosiloxane polyol 2.<sup>[11]</sup>

Dendrimer **2** is soluble in common polar organic solvents like  $\text{CH}_3\text{CN}$ , but insoluble in water. To obtain water soluble carbosiloxane dendrimers, the terminal Cl-functionalities of *e.g.* the 2<sup>nd</sup> generation dendrimer  $\text{Si}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{Me})\text{O}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMeCl}_2)_2)_4$  (**3**) were reacted with an excess of  $\text{HOCH}_2\text{CH}_2\text{NMe}_2$  to produce the  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{O}$ -functionalised dendrimer **4** (Scheme 1). The latter molecule can be transformed into the surface modified  $[\text{O}(\text{CH}_2\text{CH}_2\text{NMe}_3)^+ \text{I}^-]$  quaternary ammonium derivative **5** by its reaction with  $\text{CH}_3\text{I}$ . Furthermore, the iodide counter-ions of the  $\text{NMe}_3^+ \text{I}^-$  surface bound entities can be replaced by *non*-coordinating anions such as  $\text{ClO}_4^-$  via treatment with  $\text{AgClO}_4$  to yield molecule **6** (Scheme 1).<sup>[11,12,13]</sup>



SCHEME 1 Synthesis of the water-soluble carbosiloxane dendrimers **5** and **6**.<sup>[11,12,13]</sup>

Dendrimers **5** and **6** possess a micell-like structure which could be used for the solubilization of lipophilic compounds in aqueous solutions.<sup>[8,14]</sup>

All compounds described were fully characterised by NMR (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>29</sup>Si{<sup>1</sup>H}) and IR spectroscopic studies, as well as elemental analysis.

#### Acknowledgement

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. We also would like to thank Degussa-Hüls AG (Hanau) and Wacker Chemie GmbH (Burghausen) for generous chemical donations.

#### References

- [1] G.R. Newkome, C.N. Moorfield, F. Vögtle, *Dendritic Molecules, Concepts, Synthesis, Perspectives*, VCH, Weinheim (1996).
- [2] H.F. Chow, T.K.K. Mong, M.F. Nongrum, C.W. Wan, *Tetrahedron*, **54**, 8543 (1998).
- [3] C. Gorman, *Adv. Mater.*, **10**, 295, (1998).
- [4] H. Frey, C. Lach, K. Lorenz, *Adv. Mat.*, **10**, 279 (1998).
- [5] D. Gudat, *Angew Chem.*, Int. Ed. Engl. **36**, 1951, (1997).
- [6] J.-P. Majoral, A.-M. Caminade, *Chem. Rev.*, **99**, 845 (1999).
- [7] E.A. Rebrov, A.M. Muzafarov, V.S. Pabkov, A.A. Zhdanov, *Dokl. Nauk. SSSR*, **309**, 376 (1989).
- [8] H. Frey, Ch. Schlenk, "Silicon-Based Dendrimers" in *Topics in Current Chemistry*, **210**, 69, Springer, New York (2000).
- [9] C. Kim, Y. Jeong, I. Jung, *J. Organomet. Chem.*, **570**, 9 (1998).
- [10] K. Brüning, H. Lang, *Synthesis*, 1931 (1999).
- [11] B. Lühmann, *Ph. D. Thesis*, Technische Universität Chemnitz.
- [12] B. Lühmann, *Diplomarbeit*, Technische Universität Chemnitz (1998).
- [13] K. Brüning, *Dissertation*, Technische Universität Chemnitz (2000).
- [14] S.W. Krska, D. Seyferth, *J. Am. Chem. Soc.*, **120**, 3604, (1998).