Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 5238

www.rsc.org/obc

PAPER

Hyperbranched polymers *versus* dendrimers containing a carbosilane framework and terminal ammonium groups as antimicrobial agents

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Received 28th February 2011, Accepted 15th April 2011
DOI: 10.1039/c1ob05321c

A new family of amine- and ammonium-terminated hyperbranched polycarbosilanes (PCS) and dendrimers has been synthesized. The functionalization of a polycarbosilane matrix was carried out with peripheral allyl groups by two strategies in the case of PCS: 1) hydrosilylation of allyl amines with PCS containing terminal Si–H bonds, or 2) hydrosilylation of PCS–allyl with an aminosilane. Dendrimers with terminal amine groups were synthesized by hydrosilylation of allydimethylamine. Quaternized systems with MeI are soluble and stable in water or other protic solvent. The antibacterial properties of the ammonium-terminated hyperbranched polycarbosilanes and dendrimers have been evaluated showing that they act as potent biocides against Gram-positive and Gram-negative bacterial strains.

1. Introduction

Microbial infection remains one of the most serious complications in several areas, particularly in medical devices, drugs, health care and hygienic applications. In addition, the resistance that bacteria present to conventional antibiotics has made necessary new antibiotics with different modes of actions to combat infectious diseases.[1]

Low molecular weight antimicrobial agents suffer from many disadvantages, such as toxicity to the environment and short-term antimicrobial ability. To overcome these problems continuous efforts have been made to develop new polymeric agents[2] with antimicrobial functional groups supported in the polymer structure. At the present time, the most commonly used antimicrobial reagents are included in four categories: a) oxidants like peroxides or chlorine;[3,4] b) electrophilic agents, such as gold and silver compounds,[5,6] c) formaldehyde and isothiazolones, as organic biocides,[7] d) cationic active biocides, such as quaternary ammonium compounds.[8,9]

The antibacterial properties of quaternary ammonium salts (QAS) were first reported by Jacobs and Heidelberg.[10] QAS can also be chemically bound to polymer carriers, showing a broad spectrum of antimicrobial activity against both Gram-positive and Gram-negative bacteria.[8,11,12] Compared with conventional antibacterial agents of low molecular weight, the advantage of these systems include non-volatility, chemical stability and low permeation through skin,[13] It is generally accepted that the bactericidal activity may be due to a high concentration of cationic charge in the macromolecules that can destabilize the cell membrane and instigate cell lysis as consequence of the negatively charged nature of the cellular membrane.[14] The initial interaction between positively charged polymeric compounds and negatively charged cellular membranes is of an electrostatic nature.[15,16] These polymers displace the divalent surface ions such as calcium and magnesium and may destabilize the membrane structure. This means that biocides behave as surface-active organic cations and therefore have a destabilizing effect on phospholipid systems.[17]

The activity and mechanism of antimicrobial polymers can be affected by several factors such as molecular weight, polydispersity, spacer length between active site and polymer, hydrophilic-hydrophobic balance, and nature of counterions.[18,19] The average molecular weights and the polydispersity of the biocidal polymers sometimes play a crucial role in determining biological functions, especially toxicity.

For that reason, dendrimers, which are well defined macromolecules, with narrow polydispersity and well-characterized molecular weight, have been studied as antibacterial agents.[20–22] For example, the quaternary ammonium terminated poly(propyleneimine) (PPI) dendrimer[23] and PAMAM dendrimers[20,21,24] were found to be biocidal against Gram negative and Gram positive bacteria. However, the main disadvantage of the dendrimers is the synthetic process because it is necessarily

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consists of multistep iterative controlled reactions with tedious isolation and purification procedures.[25,26]

A new class of macromolecular structures are hyperbranched polymers[27,28] that can be prepared by a one pot reaction, usually by self-polymerization of AB_x type monomers.[29,30] The result of this process is a less regularly unified structural conformation, accompanied by broad molecular weight distribution, with a large number of terminal functional groups.[11,31,32]

One type of macromolecule is that containing silicon atoms in their framework. The presence of C–Si bonds endows high stability and also very low hydrophilicity although this property may favour the biopermeability processes. However, this behaviour could be modified by functionalizing the macromolecules with cationic groups, because water solubility is an important requirement for antibacterial studies. It has been reported that polymers such a polysiloxanes[33,34] and polysilsesquioxanes[35] may act as antibacterial biocides. Also, cationic carbosilane dendrimers, have shown their potential to be used as bactericides[22,36] and in other biomedical applications.[37–40] Silicon containing hyperbranched polymers are interesting as new organic–inorganic hybrid materials and they have been previously prepared for AB_2 and AB_3 monomers[41–45] Their ability as drug delivery systems has been published[46] elsewhere but, to the best of our knowledge, no studies concerning the use of hyperbranched polycarbosilane polymers (PCS) as biocide agents have been reported so far.

The aim of this work is the synthesis of hyperbranched polymers and dendrimers based on a carbosilane skeleton with different ammonium groups in the surface and the comparison of the different topologies for biomedical applications, for instance as antibacterial agents.

2. Results and discussion

2.1 Synthesis and characterization of amine and ammonium terminated PCS

The carbosilane matrix with terminal allyl groups has been prepared by polymerization reaction of methyldiallylsilane[47] (AB_2 type monomer) modifying the process described by Muzafarov *et al.* In the present work, the polymerization of the $HSiMe(Allyl)_2$ was carried out in toluene at 60 °C (different solvent and temperature conditions) for 24 h in presence of two drops of Karstedt's catalyst. The disappearance of Si–H bonds was followed by NMR spectroscopy. These polymerization conditions led to polymers with lower molecular weights but similar PDI values as for the PCS–allyl polymers obtained by Muzafarov (see below). The polymers were characterized by ^1H, ^{13}C and ^{29}Si-NMR spectroscopy and exclusion chromatography SEC-MALS in THF solution.[48–50]

The NMR data obtained were consistent with those reported in the literature.[51] The degree of branching (DB), calculated by ^{29}Si-NMR spectroscopy to determine the terminal (T), lineal (L) and dendritic (D) branch point, was 0.65.

With respect to SEC-MALS chromatograms, they were clean and there were no tails or any adsorption effects observed (Fig. 1a). The refractive index (RI) signals are noticeably displaced towards higher elution volumes than those of MALS. This fact is a first hint of the polydispersity of the sample, since the light scattering signals are proportional to the product of molecular

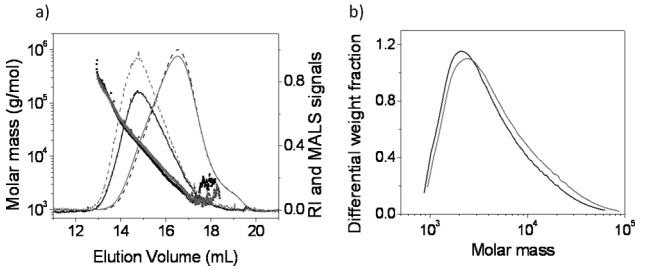


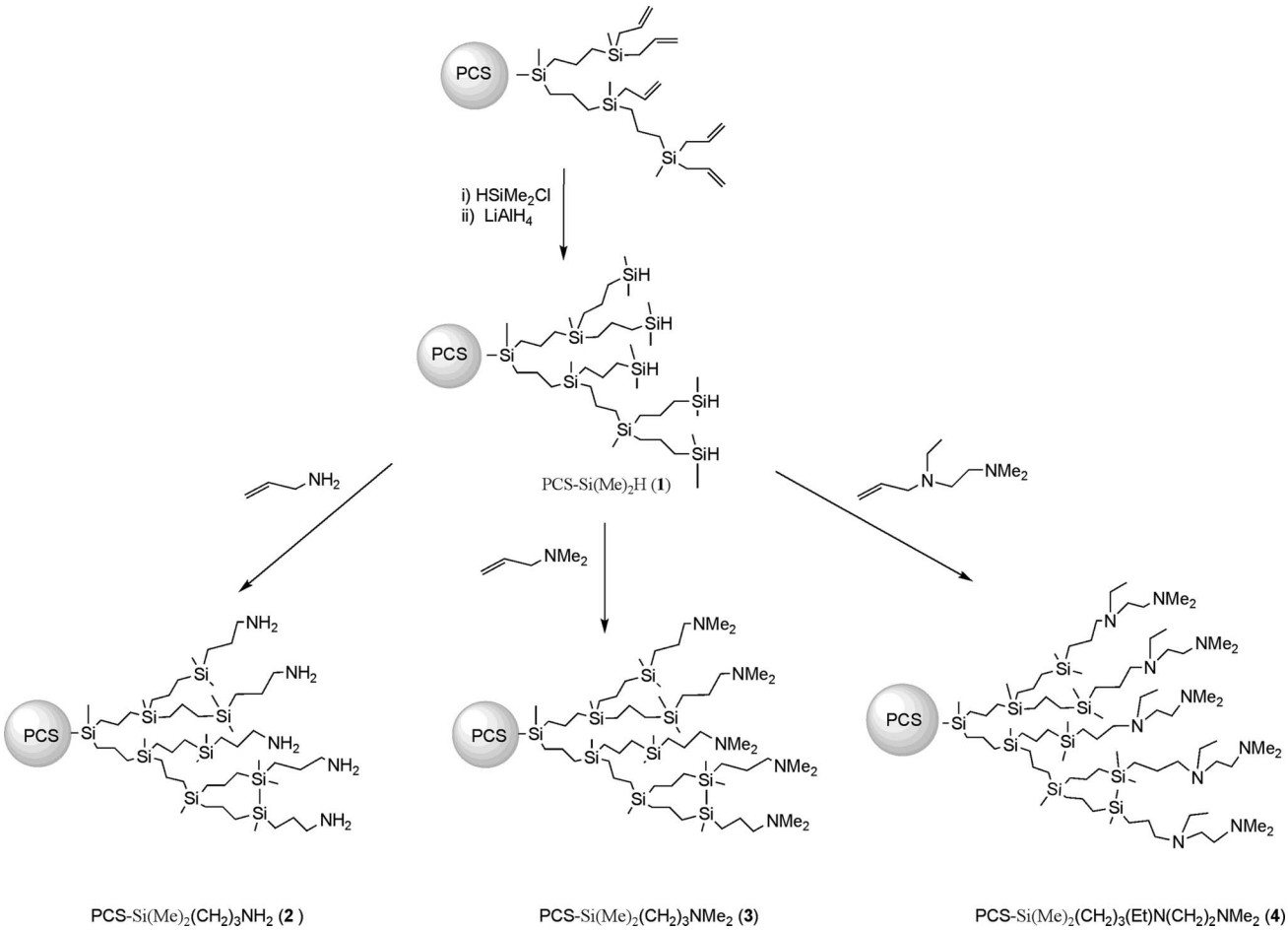
Fig. 1 (a) Chromatograms of two different samples of PCS, in black and gray respectively, showing the MALS signals at 90° (solid lines) and the refractive index, RI, signals (dashed lines), in arbitrary units, *versus* elution volume. Molecular weight (g mol^{-1}) *versus* elution volume also is depicted for both samples (black squares and gray triangles). b) Molecular weight distributions of two different samples of PCS in THF.

weight and concentration. The molecular weight distributions were broad and unimodal (Fig. 1b). The reproducibility of the different batches of synthesized PCS–allyl was fairly good. In all cases polydispersitiy indexes (M_w/M_n) ranged from 2.2 to 2.4 and weight averaged molecular weights (M_w) from 6×10^3 to 7×10^3 g mol^{-1}. These data showed that the molecular weight of the PCS synthesized was similar to third generation carbosilane dendrimers.

Once we had obtained the carbosilane matrix, our next goal was to introduce the ammonium groups at the surface. The functionalization of PCS with amino terminals groups was carried out by two different strategies. First, hydrosilylation of allyl amines with PCS containing terminal Si–H bonds, and second, hydrosilylation of PCS–allyl with an aminosilane.

PCS formed by hydrosilylation of allyl amines. The Si–H terminated hyperbranched polycarbosilane, PCS–$Si(Me)_2H$ (**1**), was synthesized using a similar method to that for analogous carbosilane dendrimers.[52,53] Thus, treatment of PCS–allyl with $HSiMe_2Cl$[54] and the subsequence reaction with $LiAlH_4$ afforded the corresponding polymeric PCS with Si–H bonds (**1**). Three different allyl amines were used in the hydrosilylation reaction: allylamine [$CH_2{=}CHCH_2NH_2$] (I), allyl-dimethylamine [$CH_2{=}CHCH_2NMe_2$] (II), and *N*,*N*-dimethyl-*N*′-allyl-*N*′-ethylethylenediamine [$(CH_2{=}CHCH_2)(Et)N(CH_2)_2NMe_2$] (III).[22] The reactions were performed in ampoules with J. Young valves, using toluene as a solvent and the Karstedt catalyst during 24 h at 120 °C to obtain the PCS–$SiMe_2(CH_2)_3NH_2$ (**2**), PCS–$SiMe_2(CH_2)_3NMe_2$ (**3**) and PCS–$SiMe_2(CH_2)_3(Et)N(CH_2)_2NMe_2$ (**4**) as pale brown oils, soluble in chlorinated solvents and aromatic and aliphatic hydrocarbons but insoluble in water (see Scheme 1). The hydrosilylation reaction occurred exclusively by β-addition and no by-products were detected in the ^1HNMR spectra of the crude products.

The NMR spectroscopic data of derivatives **1–4** were consistent with their proposed structures. The ^1H-NMR spectra of the polycarbosilane framework for PCS **1–4** have almost identical chemical shifts. For the $SiCH_2CH_2CH_2Si$ branches, the middle methylenes are located at 1.28 ppm, whilst the methylene groups bonded directly to silicon atoms are centered at 0.61 and 0.51 ppm and the methyl groups bonded to silicon give signals in the expected zone, around 0 ppm. For the PCS–SiH (**1**) a doublet at 0.04 ppm corresponding to the methyl group bonded to SiH



Scheme 1 Synthesis of amine terminated PCS.

and one multiplet around 3.81 ppm for the hydrogen bonded to the silicon atom was observed. With respect to the outer groups, the methylene groups bonded to nitrogen atoms appear as one multiplet at 2.61 and 2.18 ppm for PCS **2** and **3** respectively, and in case of **4** two multiplets were observed, one at about 2.46 ppm ($SiCH_2CH_2CH_2N$- and -$NCH_2CH_2NMe_2$) and the other at 2.62 ppm (-$NCH_2CH_2NMe_2$ and -NCH_2CH_3) and the methyl fragment of the ethyl group bonded to nitrogen appears as a triplet at 1.04 ppm. The methyl protons of the dimethylamine fragments (**3**, **4**) give a singlet around at 2.10 ppm. In the $^{13}C\{^1H\}$-NMR spectra, for the inner $SiCH_2CH_2CH_2Si$ branches, signals appear in the range of 21.3 to 17.4 ppm. The NMe_2 group gives a signal around 46 ppm and the methylene groups bonded to the nitrogen atoms show a resonance at 45.7 and 63.5 ppm for PCS **2** and **3** respectively, and in case of **4** four resonances at 47.9, 51.2, 57.1 and 57.5 ppm were observed (see Fig. 2a).

While, the ^{29}Si-NMR spectrum for the PCS–allyl shows three resonances for terminal (0.2 ppm, T), lineal (0.7 ppm, L) and dendritic (0.9 ppm, D) branch points, the modified PCS with amino groups in the surface showed in all cases two signals corresponding to dendritic (D) and terminal (T) units at 0.9 and 2.0 ppm respectively.

Finally, ^{15}N-NMR shows one resonance at −355 ppm and −352 ppm for the nitrogen of the PCS **2** and **3** respectively, and for **4** two resonances about −355 and −338 ppm, corresponding to the outer and inner nitrogen atoms.

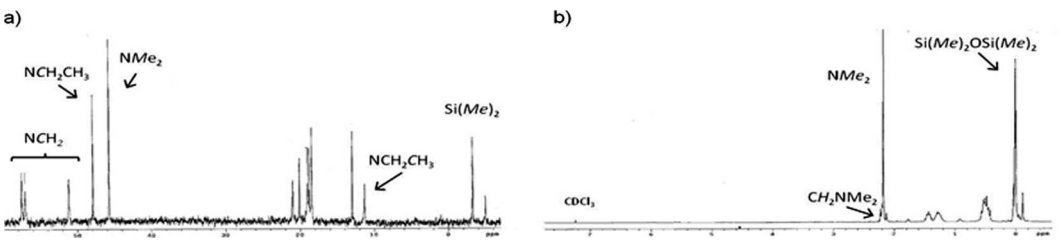
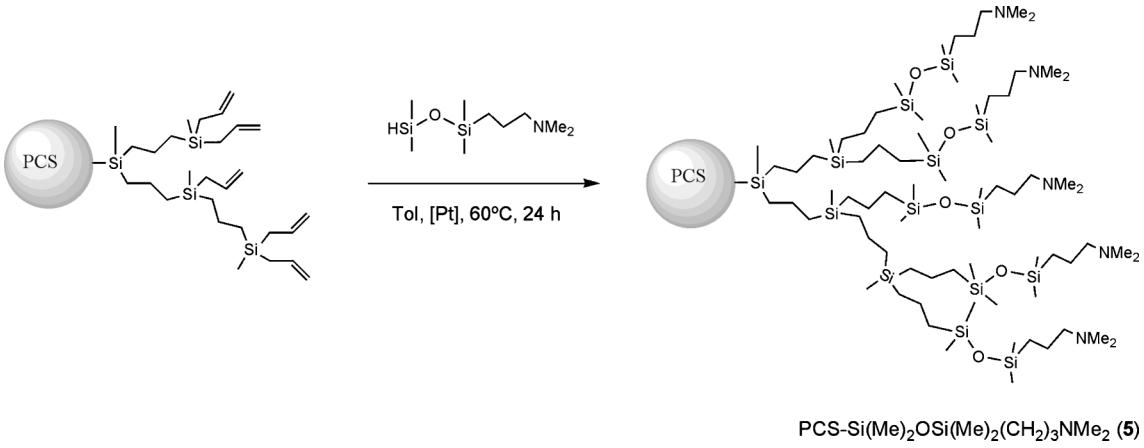


Fig. 2 a) ^{13}C-NMR spectrum of PCS–$SiMe_2(CH_2)_3(Et)N(CH_2)_2NMe_2$ (**4**) in $CDCl_3$ and b) ^{1}H-NMR spectrum of PCS–$Si(Me)_2OSi(Me)_2(CH_2)_3NMe_2$ (**5**) in $CDCl_3$.



Scheme 2 Synthesis of PCS–$Si(Me)_2OSi(Me)_2(CH_2)_3NMe_2$ (**5**).

Attempts have been carried out in order to determine the average molecular weight of PCS with amine groups by SEC-MALS, but strong interactions among the polymers and the column packing came out which preclude a good chromatographic separation. For this reason, the chromatograms of these polymers were neither consistent nor reproducible.

PCS formed by hydrosilylation of PCS–allyl with an aminosilane. The presence of terminal allyl groups in the PCS moved us to introduce the desired functions directly by hydrosilylation with the aim to decrease the number of steps in the synthetic strategy. Thus, we have prepared 1-(*N*,*N*-dimethylaminopropyl)-1,1,3,3-tetramethyldisiloxane (IV) by hydrosilylation of dimethylallylamine with tetramethyldisiloxane.[55] The hydrosilylation reaction between PCS–allyl and IV was carried out in toluene as a solvent at 60 °C during 24 h in presence of Karstedt catalyst to afford the corresponding system PCS–$Si(Me)_2OSi(Me)_2(CH_2)_3NMe_2$ (**5**) as a colorless oil. The process occurred exclusively by β-addition. The hyperbranched polymer **5** is soluble in common organic solvents, but it is insoluble in water (see Scheme 2).

The NMR spectroscopic data are consistent with the proposed structure. The ^{1}H-NMR spectrum (Fig. 2b) shows for the external fragment -$Si(Me)_2OSi(Me)_2(CH_2)_3NMe_2$ a triplet for the methylene group bonded to nitrogen at 2.18 ppm overlapped with the singlet due to the methyl protons of the dimethylamine fragment, and two multiplets centered at 1.41 and 0.51 ppm for the middle methylene group and methylene group bonded to silicon atom respectively. With respect to the methyl groups bonded to silicon atoms two singlets located at –0.01 and 0.01 ppm were observed. The $^{13}C\{^1H\}$-NMR spectrum shows four signals for the external fragment, the resonance for the methylene group bonded to nitrogen appears at 63.5 ppm and the carbon atom of the middle methylene gives a resonance at 22.1 ppm, while the chemical shift of the carbon atom bonded to Si appears around 15.8 ppm. The methyl carbons of the dimethylamine fragment show a resonance at 45.5 ppm. The PCS framework has almost identical chemical shifts to those observed for the PCS **2–4** in both ^{1}H and ^{13}C NMR spectra. ^{29}Si-NMR shows two signals corresponding to silicon atoms bonded to oxygen at 7.2 and 6.9 ppm whereas the dendritic units appear at 0.9 ppm. Finally, the ^{15}N-NMR spectrum shows one signal at –350 ppm.

Ammonium-terminated PCS. Treatment of PCS **2** with HCl at room temperature in diethyl ether led to the formation of a white solid that was insoluble in all organic and protic solvents which precluded its characterization. The ammonium-terminated PCSs were prepared by adding MeI to compounds **3–5** in diethyl ether at room temperature during 48 h to cleanly afford the corresponding quaternized derivatives PCS–$SiMe_2(CH_2)_3N^+Me_3I^-$ (**6**), PCS–$SiMe_2(CH_2)_3(Et)N^+Me(CH_2)_2N^+Me_32I^-$ (**7**) and PCS–$Si(Me)_2OSi(Me)_2(CH_2)_3N^+Me_3I^-$ (**8**) as white solids. The cationic PCS **6** and **7** are soluble and stable in water, alcohols (like methanol or ethanol) and dimethylsulfoxide and can be stored without decomposition for long time periods. The cationic PCS **8**, with Si–O–Si bonds, is soluble in dimethylsulfoxide, methanol and water, although decomposition occurs in protic solvents by hydrolytic breaking of the Si–O bonds. As expected, the ammonium-terminated PCS **6** and **7** showed a positive surface charge density (ζ potential – measured in water) of 69.0 mV for **6** and 73.3 mV for **7**. A positive ζ potential shows a high positive charge in the surface of the PCS which may also be beneficial for enhanced cellular uptake because typical bacterial membranes are negatively charged.

The NMR spectroscopic data for derivatives **6–8** are consistent with their proposed structures (see Fig. 3). The NMR spectra were recorded in DMSO-d_6 or D_2O at room temperature, although in the last solvent the line widths of these spectra tended to be broader. The ^{1}H and ^{13}C NMR spectra show that the carbosilane framework is insignificantly affected by the quaternization reaction. For the external fragments in derivatives **6–8**, the quaternization of the amine groups resulted in a deshielding of the chemical shift of the -CH_2N- groups consistent with the presence of positive charges on the nitrogen atoms. Analogous shifts are observed for the carbons atoms in their ^{13}C NMR spectra. This behavior is also detected in the methyl groups, which appear in the ^{1}H and ^{13}C NMR spectra located at 3.04 and 51.6 ppm (**6**); 3.24 and 52.5 ppm (N^+Me_3), 3.12 and 45.2 ppm (N^+EtMe_2) (**7**); 3.00 and 51.6 ppm (**8**); respectively, downfield with respect to that observed for the amine-terminated-PCS (Fig. 4).

The ^{15}N-NMR spectra of derivatives **6–8** quaternized with MeI shows one signal around –330 for **6** and **8** and two signals at about –331 and –320 ppm, corresponding to the outer and inner nitrogen atoms, respectively for PCS **7**.

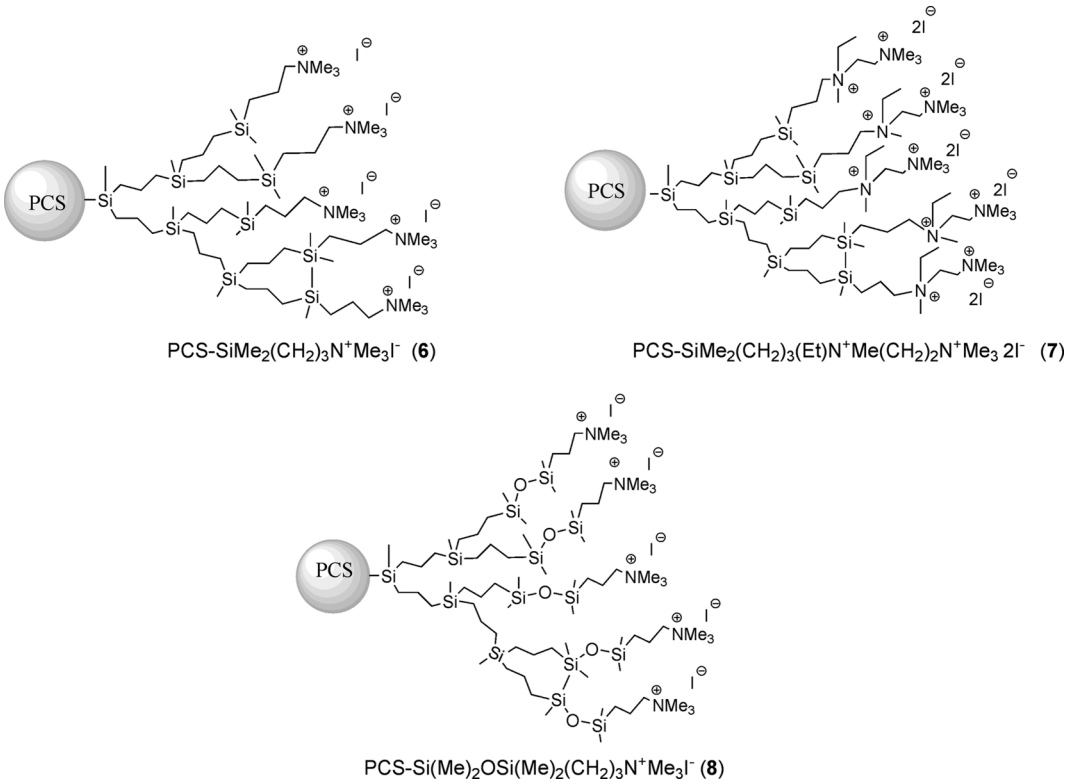


Fig. 3 Ammonium terminated PCS **6–8**.

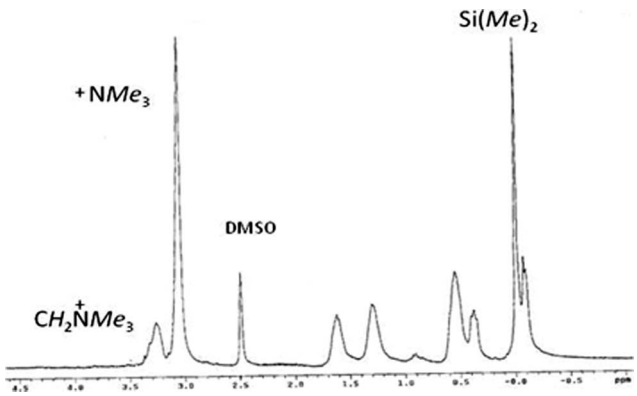


Fig. 4 ^{1}H-NMR spectrum of PCS–$SiMe_2(CH_2)_3N^+Me_3I^-$ (**6**) in DMSO.

2.2 Synthesis and characterization of amine and ammonium-terminated carbosilane dendrimers

In order to compare the antimicrobial activity of the hyperbranched polymers *versus* dendrimers, we have prepared the analogous carbosilane dendrimers with ammonium groups in the surface. The new family of the amine-terminated dendrimers *n*G-$[SiMe_2(CH_2)_3NMe_2]_x$ ($n = 1$, $x = 4$ (**9**); $n = 2$, $x = 8$ (**10**); $n = 2$, $x = 8$ (**11**)) was prepared following the same procedure used for the respective amine–PCS **3**. Thus, reaction of dendrimers *n*G-$(SiH)_x$ with allydimethylamine ($C_3H_5NMe_2$) in THF at 60 °C for 16 h, in the presence of Kardsted's catalyst, afforded the dendrimers **9–11** in high yields as colorless oils. The ammonium salts *n*G-$[SiMe_2(CH_2)_3\ N^+Me_3I^-]_x$ ($n = 1$, $x = 4$ (**12**); $n = 2$, $x = 8$ (**13**); $n = 2$, $x = 8$ (**14**)) were obtained by quaternization of amino groups with an excess of MeI as white solids soluble in water.

With respect to PCS–$SiMe_2(CH_2)_3(Et)N^+Me(CH_2)_2N^+Me_32I^-$ (**7**), this was compared to carbosilane dendrimers previously reported and decorated with the same external fragment.[22]

The NMR spectroscopic and analytical data for derivatives **9–14** are consistent with their proposed structures (see Fig. 5 for some examples). The ^{1}H, ^{13}C and ^{29}Si-NMR spectra of the carbosilane framework for dendrimers **9–14** have almost identical chemical shifts than those analogous PCS (see Experimental Section). The ^{15}N-NMR spectra of **9–11** in $CDCl_3$ show one signal at about –350 ppm and for the cationic derivatives **12–14** in d_6-DMSO one resonance at –330 ppm, similar to those observed in PCS **3** and **6**.

The dendrimers showed a positive surface charge density (ζ potential) of 47.3 mV for **13**, and 67.3 mV for **14**. These values show that PCS **6**, which has a ζ potential of 69.0 mV, presents a higher positive charges on the surface than the second generation dendrimer **13** but similar to the third generation **14**.

Dendrimers with amine groups were also analyzed by mass spectroscopy (MALDI-TOF MS) using 1,8,9-trihydroxyanthracene (dithranol) as the matrix. Very clean MALDI-TOF spectra were obtained for the amino dendrimers **9** and **10**, with fine peaks centered at m/z values matching those for the calculated proton adducts (see Experimental Section). However, for the third generation, **11**, the molecular peaks were not observed because the dendrimers fly with more difficulty in MALDI-TOF MS and the spectrum obtained showed a broader peak, as well as some fragmentation. In case of cationic dendrimers, the first generation, **12**, was analyzed in the same manner than the analogous neutral dendrimer showing the corresponding m/z peak. The second and

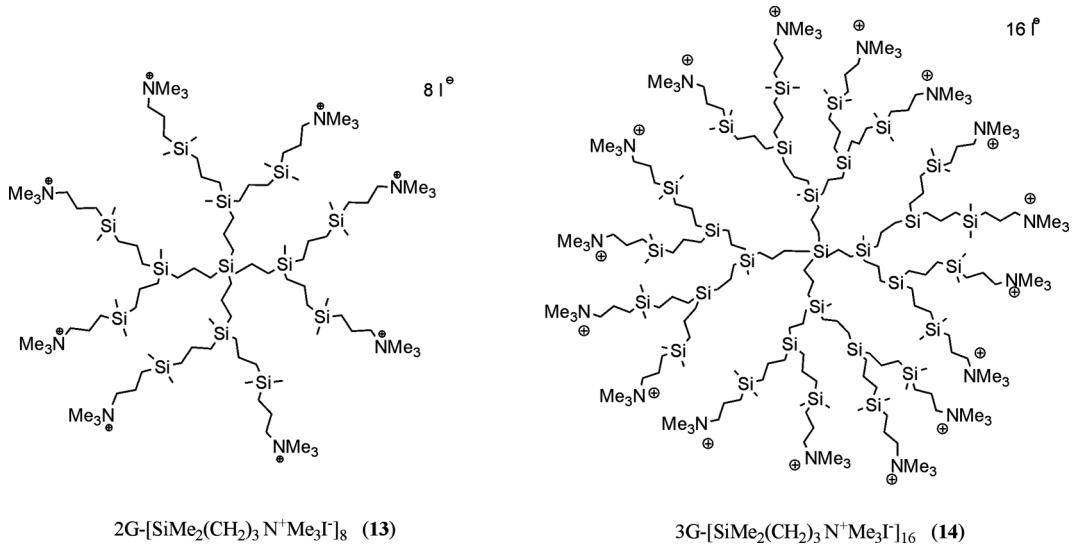


Fig. 5 Molecular representation of dendrimers **13** and **14**.

third generation was analyzed by electrospray, and for **13** it was possible to show the peaks of molecular weight without different numbers of iodine atoms (see Experimental Section), while the molecular peak for **14** was not observed.

2.3 Antimicrobial activity

Polymer biocides with antimicrobial groups chemically bonded to the polymer chain have attracted great interest as they very effectively kill bacteria and other microorganisms; the strong biocidal potency of these polymers is a result of the high local concentration of active groups. Polymers with a silicon containing framework, such a polysiloxanes[33,34] and polysilsesquioxanes[35] may act as antibacterial biocides. In this context, the antibacterial activity of hyperbranched polycarbosilane **6** and **7** has been tested on *Staphylococcus aureus* (Gram-positive) and *Escherichia coli* (Gram-negative) and the activities were compared with analogous carbosilane dendrimers. The biocidal activity for PCS **8** could not be evaluated because it decomposes in protic solvent by hydrolytic breaking of the Si–O bonds as was mentioned. The minimum PCS concentration needed to inhibit bacteria growth for 24 h (minimum inhibitory concentration – MIC) and the minimum polymer concentration required to kill the bacteria (minimum bactericidal concentration – MBC) was determined by measuring both Gram-positive and Gram-negative bacteria growth in the presence of varying concentrations of PCS **6** and **7** and the analogous dendrimers of different generations. The value of MIC is always less than or equal to MBC for the same biocide and microorganism. Data for these activities are show in Table 1.

The results of the antibacterial tests show the high activity of hyperbranched polycarbosilane and dendrimers against both Gram-positive and Gram-negative bacteria. The polycarbosilane PCS **7** showed a higher antibacterial activity than PCS **6** at least for Gram-negative bacteria, probably due to the higher number of functional groups located in its polycationic structure. In the case of dendrimers, the second generation **13** is more active than the third generation **14**. The data show for both topologies lower MIC and MBC values for Gram-positive than Gram-negative bacteria, probably due to the differences in the cell wall structure. In Gram-positive bacteria, there is a membrane formed by a single bilayer, and they are very sensitive to the biocidal action of the polymer, while in Gram-negative bacteria it is composed of two bilayer membranes, making the latter bacteria more resistant to an external attack. Moreover, the strength of the membrane disruption has been reported to depend basically on two parameters: (i) the number of charged groups and (ii) the

Table 1 Bacteriostatic (MIC) and bactericidal (MBC) effects of PCS **6**, PCS **7**, **13**, **14** and other related systems[a]

	Escherichia coli (CECT 515) Gram-negative		*Staphylococcus aureus* (CECT240) Gram-positive	
	MIC	MBC	MIC	MBC
PCS-**6**	16	16	4	4
PCS-**7**	8	8	4	4
2G-CBS[b]	8	16	4	8
3G-CBS[b]	16	16	8	8
13	16	32	4	8
14	64	64	8	8
Siloxane[c]	80	80	20	20
Polysilsesquioxane[d]	2500	—	19.8	—
Penicillin V	256	256	0.016	0.031

[a] All concentrations data are measured as mg L^{-1}. [b] Data taken from ref. 22. [c] Data taken from ref. 34. [d] Data taken from ref. 35.

biopermeability processes (size and molecular weight or lipophilic groups or domains).[2,22]

The activity found for the polycationic hyperbranched carbosilane polymers and dendrimers show that these systems are more potent biocides against Gram-negative than the polysiloxane and polysilsesquioxane[33–35] polymers and slightly less active against Gram-positive bacteria. This fact could be the result of a very lipophilic skeleton compared to the polysiloxane and polysilsesquioxane systems, which may aid in the biopermeability processes.

PCS **6** shows a higher antibacterial activity than that observed for the third generation dendrimer **14** although similar to that for the second generation **13** in both Gram positive and Gram negative. A similar behaviour was found for PCS **7**. As mentioned above, the antibacterial activity depends on the number of charged groups and the size and molecular weight of the macromolecule. The PCS systems present similar molecular weight and ζ potential (positive surface charge density) than the third-generation carbosilane dendrimer, although the antibacterial activity was found to be similar to the second-generation. This feature would indicate that topology could play an important role in the biocide action.

This result implies that the ammonium-terminated polycarbosilane hyperbranched polymers which were synthesized in shorter times and lower cost than the analogous dendrimers are able to exert the same antibacterial effect.

Comparing the data with the antibiotic penicillin V potassium, an effective antibiotic against Gram-positive but not against Gram-negative bacteria, the cationic PCS are much more active against Gram-negative bacteria, while for Gram-positive penicillin shows a higher biocide activity. In this context, the values found for the multivalent PCS systems indicate their high potential as antibacterial agents for both Gram-negative and Gram-positive bacteria.

3. Conclusions

In summary, this work reports on the synthesis of a new family of amine- and ammonium-terminated carbosilane dendrimers and hyperbranched polycarbosilane polymers. The PCS were prepared by functionalization of a polycarbosilane matrix with peripheral allyl groups by two different strategies. The first one entails hydrosilylation of allyl amines with PCS containing terminal Si–H bonds and the second one consists on the hydrosilylation of PCS–allyl with aminosilanes. The subsequent quaternization with MeI in both cases afforded the corresponding ammonium-terminated PCS. Quaternized systems are soluble and in general stable in water or other protic solvent. The antimicrobial studies for PCS **6** and **7** show high antibacterial potency against Gram-positive and Gram-negative bacteria strains when they are in contact with an aqueous suspension of bacteria. In all cases their MIC and MBC values are in range of 4–16 mg L^{-1}. The different behavior observed in the MIC values in Gram-negative and Gram-positive bacteria may be related to the different structure of the cell wall of these systems. The results obtained are comparable to the antibacterial activity of the second generation dendrimers, although certain physical properties such as size and ξ potential make them more similar to the third generation. This would indicate that the dendritic topology could influence the antibacterial action.

Therefore, the shortening of the synthetic procedure for these new ammonium polycarbosilane hyperbranched systems and the subsequent lower economic cost compared to the analogous carbosilane dendrimer counterparts, while maintaining similar antibacterial activity, can be envisaged as the main advantage or reason for their biomedical use.

4. Experimental details

4.1 General remarks

All manipulations of oxygen- or water-sensitive compounds were carried out under an atmosphere of argon using standard Schlenk techniques. Toluene, THF and diethyl ether solvents were dried and freshly distilled under argon prior to use, unless otherwise stated, reagents were obtained from commercial sources and used as received.

4.2. Measurements

Spectroscopic analysis. ^{1}H, ^{13}C, ^{29}Si and ^{15}N-NMR spectra were recorded on Varian Unity VXR-300 and Varian 500 Plus Instruments. Chemical shifts (δ, ppm) were measured relative to residual ^{1}H, ^{13}C, ^{29}Si and ^{15}N resonances for $CDCl_3$, and DMSO-d_6 used as solvents.

Molecular weight. SEC measurements were carried out using a Waters Associates model 510 pump with a 0.1 μm on-line filter (Millipore), a U6 K injector (Waters) and two different detectors, namely an OptiRex Interferometric Refractometer (RI) operating at 632.8 nm and a Dawn DSP-F multiangle light scattering (MALS) photometer, equipped with a He–Ne laser (λ_0 = 632.8 nm), both from Wyatt Technology Corp. The OptiRex refractometer was also used for batch measurements of differential index increment. A value of 0.135 mL g^{-1} was used in all the samples.[56] The eluent used was filtered and degassed tetrahydrofuran, THF (Scharlau, GPC grade). The chromatographic columns used were two styragel linear columns (Waters). Repeated injections of the filtered samples (Millipore, nylon 0.2 μm) were made for each polymer to ensure the reproducibility of the results. The MALS photometer was calibrated with spectrometric grade toluene (Scharlau, GPC grade). The normalization of the detectors in the different organic solutions was performed with a standard sample of polystyrene of low molecular weight. The software used, ASTRA 5.1 from Wyatt Technology, allowed on-line collection of data of molecular mass and radius of gyration, as well as calculation of the MWD distributions and molecular weight averages. Molecular weight averages and the corresponding polydispersity indexes were calculated with the raw data of molecular weights obtained for the different slices of the chromatogram.

ζ potential. The ζ potential of the hyperbranched polycarbosilanes and dendrimers was determined with a dynamic light-scattering particle-size analyzer Zetasizer Nano Series, Malvern Instrument ZEN 3600. The ζ potential was measured in water (1 mg mL^{-1}).

Antimicrobial activity assay. The minimal inhibitory concentration (MIC) of the products were measured in 96-well tray microplates using the international standard methods ISO

20776-1 by microdilution tray preparations.[57] The assays were done in duplicate microplates with three different wells for each concentration analyzed in the microplate. The bacteria used in the analysis were *Escherichia coli* (CECT 515) (Gram-negative) and *Staphylococcus aureus* (CECT 240) (Gram-positive). Both strains were obtained from the "Coleccion Española de cultivos tipo" (CECT). A stock solution of the products was obtained by dissolving 0.01024 g of the compound with 10 ml of distilled water. After that, distilled water was added to obtain the desired concentration. The microplates were incubated at 37 °C using an ultra microplate reader ELX808iu (Bio-Tek Instruments). The minimal bactericidal concentration (MBC) was calculated by inoculating 3 ml of the samples used to calculate the MIC in Petri dish with Mueller-Hinton agar (Ref. 02–136, Scharlau). The samples were put on a drop in the plates. After 48 h of incubation at 37 °C the presence of colonies was tested. The MBC was the minimal concentration where no growth was detected.

4.3 Synthesis

4.3.1 Synthesis of PCS–allyl. Two drops of Karsted's catalyst were added to methydiallylsilane (1.0 g) dissolved in 5 mL of toluene at room temperature. The mixture was warmed to 60 °C, and stirred for 24 h, at which time the ^{1}H-NMR signal of the Si–H group of the methydiallylsilane had disappeared completely, and then evaporated to dryness to remove the solvent to give PCS–allyl as pale yellow oil (0.84 g). ^{1}H-NMR ($CDCl_3$): δ –0.04– –0.07 (s, SiMe), 0.56 (m, -SiCH_2CH$_2$CH$_2$Si-), 1.28 (m, -SiCH$_2$CH_2CH$_2$Si-), 1.54 (m, -SiCH_2CH=CH$_2$), 1.81 (d, -SiCH=CHCH_3), 4.85 (m, -Si CH$_2$CH=CH_2), 5.64 (m, -SiCH=CHCH$_3$), 5.76 (m, -Si CH$_2$CH=CH$_2$). ^{13}C-NMR ($CDCl_3$): δ –5.2 (SiMe), 18.3 (-SiCH$_2$CH$_2$$CH_2$Si-), 22.2 (-Si$CH_2$CH=CH$_2$ and -SiCH$_2$$CH_2CH_2$Si- overlapped), 22.4 (-SiCH=CHCH$_3$), 112.6 (-SiCH$_2$CH=CH$_2$), 113.0 (-SiCH=CHCH$_3$), 134.8 (Si CH$_2$$C$H=CH$_2$), 135.3 (-Si$C$H=CHCH$_3$). ^{29}Si-NMR ($CDCl_3$): δ –8.5 (s, - T′, 2.1%), –7.5 (s, L′, 3.5%), 0.2 (s, T, 21.0%), 0.7 (s, L, 37.2%), 0.9 (s, D, 36.6%).

4.3.2 Synthesis of PCS–SiMe$_2$H. (1). Over a solution of $LiAlH_4$ 2 M in THF (1.5 mL) was added drop by drop a solution of *PCS–SiMe$_2$Cl* in Et_2O at 0 °C (0.94 g). The mixture was stirred at room temperature during 12 h and then the excess of $LiAlH_4$ was neutralized with a solution of NH_4Cl. The organic layer was separated and the aqueous layer extracted with Et_2O (2 × 20 mL). The combined organic layers were dried over $MgSO_4$, filter and concentrated to obtain PCS–SiMe$_2$H as a colorless oil (0.76 g). ^{1}H NMR ($CDCl_3$): δ –0.09 (s, SiMe), 0.04 (d, SiHMe_2), 0.56 (m, -SiCH_2CH$_2$$CH_2$Si-), 1.32 (m, -SiCH$_2$$CH_2CH_2$Si-), 3.81 (m, -SiH). ^{13}C NMR ($CDCl_3$): δ –4.9 (SiMe), –4.3 (SiHMe_2), 18.2 (-SiCH$_2$CH$_2$$CH_2$Si-), 18.5 (-SiCH$_2CH_2$$CH_2$SiH-), 18.9 (-SiCH$_2$$CH_2CH_2$Si- and -SiCH$_2$$CH_2CH_2$SiH-). ^{29}Si-NMR ($CDCl_3$): δ – 14.0 (SiMe$_2$H), δ 0.9 (-*Si*CH$_2CH_2CH_2$Si-),

4.3.3 Synthesis of PCS–SiMe$_2$(CH$_2$)$_3$NH$_2$ (2). The allylamine (1.5 mL) and two drops of Karsted's catalyst were added to a solution of **1** (0.37 g) in toluene (5 mL). The reaction mixture was heated at 70 °C for one night and then evaporated to dryness to remove the solvent to give **2** as a pale yellow oil (0.45 g).^{1}H-NMR ($CDCl_3$): δ –0.11 (s, SiMe), –0.06 (s, SiMe$_2$), 0.53 (m, -SiCH_2CH$_2$$CH_2$Si- and -Si$CH_2CH_2CH_2NH_2$), 1.30 (bs, -NH$_2$), 1.41 (m, -SiCH$_2$$CH_2CH_2NH_2$ overlapped), 2.61 (t, -SiCH$_2$CH$_2$$CH_2NH_2$). ^{13}C-NMR ($CDCl_3$): δ –4.9 (SiMe), –3.3 (SiMe_2), 12.4 (-SiCH$_2$CH$_2$$CH_2$Si-), 18.7–20.1 (-SiCH$_2$$CH_2CH_2$Si- and -Si$CH_2CH_2$$CH_2$Si-), 28.4 (SiCH$_2$$CH_2CH_2NH_2$), 45.7 (-SiCH$_2CH_2$$CH_2NH_2$). ^{29}Si-NMR ($CDCl_3$): δ –7.5 (s, isomerization branch), δ 0.9 (-*Si*CH$_2$CH$_2$CH$_2$Si-), δ 2.0 (-*Si*CH$_2$CH$_2$CH$_2$NH$_2$). ^{15}N-NMR ($CDCl_3$): δ –355 (NH$_2$).

4.3.4. Synthesis of PCS–SiMe$_2$(CH$_2$)$_3$NMe$_2$ (3). This hyperbranched polycarbosilane with terminal dimethylamino groups was prepared using a similar method to that described for **2**, starting from **1** (0.37 g), allyl-dimethylamine in excess (1.5 mL) and two drops of Karsted's catalyst to obtain compound **3** as a pale yellow oil (0.52 g).^{1}H-NMR ($CDCl_3$): δ –0.11 (s, SiMe), –0.07 (s, SiMe$_2$), 0.53 (m, -SiCH$_2$CH$_2$CH_2Si- and -SiCH$_2$CH$_2$CH$_2$NMe$_2$), 1.27 (m, -SiCH$_2$CH_2CH$_2$Si-), 1.41 (m, -SiCH$_2$CH_2CH$_2$NMe$_2$), 2.18 (m, NMe$_2$ and CH$_2$NMe$_2$ overlapped). ^{13}C-NMR ($CDCl_3$): δ –4.9 (SiMe), –3.3 (SiMe_2), 12.9 (-SiCH$_2$CH$_2$CH$_2$NMe$_2$-), 18.7–20.1 (-SiCH$_2$$CH_2CH_2$Si- and -Si$CH_2CH_2$$CH_2$Si-), 22.1 (-SiCH$_2$$CH_2CH_2NMe_2$), 45.5 (-N$Me_2$), 63.5 (-SiCH$_2CH_2$$CH_2NMe_2$). ^{29}Si-NMR ($CDCl_3$): δ –7.6 (s, isomerization branch), 0.9 (-*Si*CH$_2$CH$_2$CH$_2$Si-), 1.8 (-*Si*CH$_2$CH$_2$CH$_2$NMe$_2$). ^{15}N-NMR ($CDCl_3$): δ –352 (NMe$_2$).

4.3.5. Synthesis of PCS–SiMe$_2$(CH$_2$)$_3$NEt(CH$_2$)$_2$NMe$_2$ (4). This hyperbranched polycarbosilane was prepared using a similar method to that described for **2**, starting from **1** (0.24 g), *N*,*N*-dimethyl-*N*′-allyl-*N*′-ethyl-ethylenediamine in excess (1 mL) and two drops of Karsted's catalyst to obtain compound **4** as a pale yellow oil (0.38 g). ^{1}H-NMR ($CDCl_3$): δ –0.10(s, -SiMe), –0.06 (s, -SiMe$_2$), 0.40 (m, -SiCH_2CH$_2$CH$_2$NMe$_2$), 0.52 (m, -SiCH_2CH$_2$$CH_2$Si-), 1.04 (t, -NCH$_2CH_3$) 1.28 (m, -SiCH$_2$$CH_2CH_2$Si-), 1.44 (m, -SiCH$_2$$CH_2CH_2NMe_2$), 2.25 (s, -NMe$_2$), 2.46 (m, SiCH$_2CH_2CH_2$N- and -NC$H_2CH_2NMe_2$), 2.62 (m, NC$H_2CH_3$ and -NCH$_2$CH_2NMe$_2$).^{13}C-NMR ($CDCl_3$): δ –4.9 (SiMe), –3.3 (SiMe_2), 11.3 (NCH$_2$$CH_3$) 12.9 (-Si$CH_2CH_2$-CH$_2$N-), 20.2–18.5 (-SiCH$_2$$CH_2CH_2$Si- and - Si$CH_2CH_2$$CH_2$Si-), 21.0 (-SiCH$_2$$CH_2CH_2$N-), 45.5 (N$Me_2$), 47.9 (-N$CH_2CH_3$), 51.2 (-N$CH_2CH_2NMe_2$), 57.1 (-NCH$_2$$CH_2NMe_2$), 57.5 (-SiCH$_2CH_2$$CH_2$N-). ^{29}Si-NMR ($CDCl_3$): δ –7.6 (s, isomerization branch), 0.9 (-*Si*CH$_2$CH$_2$CH$_2$), 1.8 (-*Si*CH$_2$CH$_2$CH$_2$NMe$_2$). ^{15}N-NMR ($CDCl_3$): δ –355 (-NMe$_2$), -338 (-NCH$_2$CH$_3$).

4.3.6. Synthesis of PCS–Si(Me)$_2$OSi(Me)$_2$(CH$_2$)$_3$NMe$_2$ (5). A solution of PCS–allyl in toluene (0.40 g) was added to 0.98 g to the compound IV and two drops of Karsted's catalyst. The reaction mixture was stirred at room temperature during 24 h. After removal excess of compound IV the hyperbranched carbosilane (**5**) was obtained as a yellow oil (1.19 g).^{1}H-NMR ($CDCl_3$): δ –0.12(s, SiMe), –0.01 and 0.01 (s, OSiMe$_2$), 0.51 (m, -SiCH_2CH$_2$CH_2Si, -SiCH$_2$CH$_2$CH_2SiO- and -OSiCH_2CH$_2$CH$_2$NMe$_2$), 1.27 (m, -SiCH$_2$CH_2CH$_2$Si- and -SiCH$_2$CH_2CH$_2$SiO-), 1.41 (m, -OSiCH$_2$CH_2CH$_2$NMe$_2$), 2.18 (m, NMe$_2$ and CH_2NMe$_2$ overlapped).^{13}C-NMR ($CDCl_3$): δ –5.0 (SiMe), 0.2 and 0.3 (-OSiMe_2), 15.8 (-SiCH$_2$CH$_2$CH$_2$NMe$_2$), 18.7–20.1 (-SiCH$_2$$CH_2$$CH_2$SiO- Si$CH_2$$CH_2$$CH_2$Si-), 22.1 (-OSiCH$_2$$CH_2CH_2NMe_2$), 45.5 (N$Me_2$), 63.5 (-CH$_2NMe_2$). ^{29}Si-NMR ($CDCl_3$): δ 0.9 (-*Si*CH$_2CH_2CH_2$), 7.2 and 6.9 (-*Si*O*Si*CH$_2$CH$_2$CH$_2$NMe$_2$). ^{15}N-NMR ($CDCl_3$): δ –350 (NMe$_2$)

4.3.7. Synthesis of PCS–$SiMe_2(CH_2)_3N^+Me_3I^-$ (6). To a diethyl ether solution of **3** (0.24 g in 100 mL) were added 2 mL of MeI solution. The resulting solution was stirred for 48 h at room temperature and then evaporated under reduced pressure to remove residual MeI. The residue was washed with Et_2O (2 × 10 mL) and dried under vacuum to give **6** as a white solid (0.31 g). ^{1}H-NMR (DMSO): δ –0.09 (s, SiMe), –0.11 (s, SiMe_2), 0.37 (m, Si$CH_2CH_2CH_2N^+Me_3$), 0.54 (m, Si$CH_2CH_2CH_2$Si-), 1.29 (m, -Si$CH_2CH_2CH_2$Si-), 1.62 (m, -Si$CH_2CH_2CH_2N^+Me_3$), 3.04 (s, N^+Me_3), 3.25 (m, -$CH_2N^+Me_3$). ^{13}C NMR (DMSO): δ – 3.9 (Si*Me* and SiMe_2), 11.3 (Si$CH_2CH_2CH_2N^+$Me3), 16.4–17.6 (-Si$CH_2CH_2CH_2$Si- and -Si$CH_2CH_2CH_2$Si-), 22.8 (-Si$CH_2CH_2CH_2N^+Me_3$), 51.6 (N^+Me_3), 67.4 (-Si$CH_2CH_2CH_2N^+Me_3$). ^{29}Si-NMR (DMSO): δ 1.1 (-*Si*$CH_2CH_2CH_2$), 2.5 (-*Si*$CH_2CH_2CH_2NMe_3^+$). ^{15}N-NMR (DMSO): δ –331 (N^+Me_3)

4.3.8. Synthesis of PCS–$SiMe_2(CH_2)_3(Et)N^+Me(CH_2)_2N^+Me_3$ $2I^-$ (7). The PCS **7** was prepared using a similar method to that described for **6**, starting from **4** (0.34 g) and a MeI solution (3 mL). The hyperbranched carbosilane **7** was obtained as a white solid (0.56 g) ^{1}H-NMR (DMSO): δ –0.08(s, -SiMe), –0.00 (s, -SiMe_2), 0.45 (m, -Si$CH_2CH_2CH_2$ N^+), 0.55 (m, -Si$CH_2CH_2CH_2$Si-), 1.04 (t, -$N^+CH_2CH_3$) 1.28 (m, -Si$CH_2CH_2CH_2$Si-), 1.64 (m, -Si$CH_2CH_2N^+$), 2.46 (m, Si$CH_2CH_2CH_2$N- and -NCH_2CH_2 N^+Me_3), 3.24 (m, N^+Me_2 and N^+Me_3), 3.88 (m, CH_2N^+).^{13}C-NMR ($CDCl_3$): δ –5.3 (Si*Me*), –3.8 (SiMe_2), 7.4 ($N^+CH_2CH_3$), 10.6 (-Si$CH_2CH_2CH_2N^+$-), 20.2–18.5 (-Si$CH_2CH_2CH_2$Si-), 18.8 (-Si$CH_2CH_2CH_2N^+$-), 47.2 (N^+Me_2), 52.1 (-$N^+CH_2CH_2N^+Me_3$), 52.5 (N^+Me_3), 56.3 (-$N^+CH_2CH_2N^+Me_3$), 56.7 (-$N^+CH_2CH_3$), 63.2 (-Si$CH_2CH_2CH_2N^+$). ^{29}Si-NMR (DMSO): δ 1.1 (-*Si*$CH_2CH_2CH_2$), 2.6 (-*Si*$CH_2CH_2CH_2N^+$). ^{15}N-NMR (DMSO): δ –331.7 (N^+Me_3), –320.3 (-$N^+CH_2CH_3$).

4.3.9. Synthesis of PCS–$Si(Me)_2OSi(Me)_2(CH_2)_3N^+Me_3I^-$ (8). The PCS **8** was prepared using a similar method to that described for **6**, starting from **5** (0.25 g) and a MeI solution (3 mL). The hyperbranched carbosilane **8** was obtained as a white solid (0.37 g) ^{1}H-NMR (DMSO): δ –0.11(s, SiMe), 0.02 and 0.06 (s, OSiMe_2), 0.49 (m, -Si$CH_2CH_2CH_2$Si, -Si$CH_2CH_2CH_2$SiO- and -OSi$CH_2CH_2CH_2N^+Me_3$), 1.29 (m, -Si$CH_2CH_2CH_2$Si- and -SiCH_2CH_2SiO-), 1.62 (m, -OSi$CH_2CH_2N^+Me_3$), 3.0 (m, N^+Me_3), 3.29 ($CH_2N^+Me_3$).^{13}C-NMR (DMSO): δ –5.4 (Si*Me*), –0.1 and –0.2 (-OSiMe_2), 13.5 (-Si$CH_2CH_2CH_2N^+Me_3$), 16.9–17.8 (-Si$CH_2CH_2CH_2$SiO- Si$CH_2CH_2CH_2$Si-), 22.1 (-OSi$CH_2CH_2N^+Me_3$), 51.6 (N^+Me_3), 67.1 (-$CH_2N^+Me_3$). ^{29}Si-NMR (DMSO): δ 1.1 (-*Si*$CH_2CH_2CH_2$), 8.6 and 7.5 (-*Si*O*Si*$CH_2CH_2CH_2NMe_3^+$). ^{15}N-NMR (DMSO): δ –331.7 (N^+Me_3).

4.3.10. Synthesis of 1G-[$SiMe_2(CH_2)_3NMe_2]_4$ (9). An excess of allyl-dimethylamine (1.2 mL) and two drops of Karsted's catalyst were added to a solution of *1G*-$(CH_2)_3SiMe_2H$ (0.56 g) in THF (2 mL). The reaction mixture was heated at 80 °C for one night and then evaporated to dryness to remove the solvent and residual allyl-dimethylamine. Afterwards, hexane (10 mL) was added and the solution was filtered through active carbon and dried under vacuum to give **9** as a pale yellow oil (0.90 g). ^{1}H-NMR ($CDCl_3$): δ –0.08 (s, 24H, SiMe_2), 0.45 (m, 8H, -Si$CH_2CH_2CH_2NMe_2$), 0.53 (m, 8H, -Si$CH_2CH_2CH_2$Si-), 1.26 (m, 8H, -Si$CH_2CH_2CH_2$Si-), 1.42 (m, 8H, -Si$CH_2CH_2CH_2NMe_2$), 2.19 (s, 24H, -Si$CH_2CH_2CH_2NMe_2$), 2.19 (m, 8H, -Si$CH_2CH_2CH_2NMe_2$ overlapped). ^{13}C-NMR ($CDCl_3$): δ –3.4 (-SiMe_2), 12.8 (-Si$CH_2CH_2CH_2NMe_2$), 17.5 (-Si$CH_2CH_2CH_2$Si-), 18.5 (-Si$CH_2CH_2CH_2$Si-), 20.2 (-Si$CH_2CH_2CH_2$Si-), 22.1 (-Si$CH_2CH_2CH_2NMe_2$), 45.4 (-NMe_2), 63.4 (-Si$CH_2CH_2CH_2NMe_2$). ^{29}Si-NMR ($CDCl_3$): δ (G_0–Si) is not observed, 1.9 (-*Si*$CH_2CH_2CH_2NMe_2$). ^{15}N-NMR ($CDCl_3$): δ –351.5 (-Si$CH_2CH_2CH_2N$$Me_2$). MS: $[M + H]^+$ = 773.64 uma (calcd. = 772.65 uma). Anal. Calc. $C_{40}H_{96}N_4Si_5$ (773.74 g mol^{-1}): C, 62.10; H, 12.51; N, 7.24; Exp.: C, 62.50; H, 12.02; N, 6.87%.

4.3.11. Synthesis of 2G-[$SiMe_2(CH_2)_3NMe_2]_8$(10). Dendrimer **10** was prepared using a similar method to that described for **9**, starting from *2G*-$(CH_2)_3SiMe_2H$ (0.30 g), allyl-dimethylamine in excess (0.5 mL) and two drops of Karsted's catalyst to obtain compound **10** as a pale yellow oil (0.40 g). ^{1}H-NMR ($CDCl_3$): δ –0.11 (s, 12H, Si*Me*), –0.07 (s, 48H, SiMe_2), 0.46 (m, 16H, -Si$CH_2CH_2CH_2NMe_2$), 0.54 (m, 48H, -Si$CH_2CH_2CH_2$Si-), 1.28 (m, 24H, -Si$CH_2CH_2CH_2$Si-), 1.42 (m, 16H, -Si$CH_2CH_2NMe_2$), 2.19 (s, 48H, -Si$CH_2CH_2CH_2NMe_2$), 2.19 (m, 16H, -Si$CH_2CH_2CH_2NMe_2$ overlapped). ^{13}C-NMR ($CDCl_3$): δ –5.0 (Si*Me*), –3.3 (SiMe_2), 12.9 (-Si$CH_2CH_2CH_2NMe_2$), 17.7–21.1 (-Si$CH_2CH_2CH_2$Si- and - Si$CH_2CH_2CH_2$Si-), 22.0 (-Si$CH_2CH_2CH_2NMe_2$), 45.4 (-NMe_2), 63.4 (-Si$CH_2CH_2CH_2NMe_2$). ^{29}Si-NMR ($CDCl_3$): δ (G_0–Si) is not observed, 1.0 (G_1–Si), 1.9 (G_2–Si). ^{15}N-NMR ($CDCl_3$): δ –330 (-Si$CH_2CH_2CH_2N$$Me_2$). MS: $[M + H]^+$ = 1861.01 uma (calcd. = 1858.52 uma). Anal. Calc. $C_{96}H_{228}N_8Si_{13}$ (1860 g mol^{-1}): C, 61.99; H, 12.36; N, 6.02; Exp.: C, 62.43; H, 11.88; N, 5.86%.

4.3.12. Synthesis of 3G-[$SiMe_2(CH_2)_3NMe_2]_{16}$ (11). Dendrimer **11** was prepared using a similar method to that described for **9**, starting from *3G*-$(CH_2)_3SiMe_2H$ (0.26 g), allyl-dimethylamine in excess (0.4 mL) and two drops of Karsted's catalyst to obtain compound **11** as a pale yellow oil (0.36 g). ^{1}H-NMR ($CDCl_3$): δ –0.12 (s, 36H, Si*Me*), –0.07 (s, 96H, SiMe_2), 0.51 (m, 144H, -Si$CH_2CH_2CH_2NMe_2$ and -Si$CH_2CH_2CH_2$Si-), 1.28 (m, 56H, -Si$CH_2CH_2CH_2$Si-), 1.41 (m, 32H, -Si$CH_2CH_2NMe_2$), 2.18 (s, 96H, -Si$CH_2CH_2CH_2NMe_2$), 2.18 (m, 32H, -Si$CH_2CH_2CH_2NMe_2$ overlapped). ^{13}C-NMR ($CDCl_3$): δ –4.9 (Si*Me*), –3.4 (SiMe_2), 12.9 (-Si$CH_2CH_2CH_2NMe_2$), 17.7–20.1 (-Si$CH_2CH_2CH_2$Si- and - Si$CH_2CH_2CH_2$Si-), 22.1 (-Si$CH_2CH_2CH_2NMe_2$), 45.4 (-NMe_2), 63.4 (-Si$CH_2CH_2CH_2NMe_2$). ^{29}Si-NMR ($CDCl_3$): δ (G_0–Si) and (G_1–Si) are not observed, 0.9 (G_2–Si), 1.9 (G_3–Si). ^{15}N-NMR ($CDCl_3$): δ –352.4 (-Si$CH_2CH_2CH_2N$$Me_2$). Anal. Calc. $C_{208}H_{492}N_{16}Si_{29}$ (4032.72 g mol^{-1}): C, 61.95; H, 12.30; N, 5.56; Exp.: C, 61.52; H, 12.08; N, 5.11%.

4.3.13. Synthesis of 1G-[$SiMe_2(CH_2)_3$ $N^+Me_3I^-]_4$ (12). To a diethyl ether solution of **9** (0.29 g in 100 mL) were added 0.19 mL of MeI solution. The resulting solution was stirred for 16 h at room temperature and then evaporated under reduced pressure to give **12** as a white solid (0.50 g). ^{1}H-NMR (DMSO): δ –0.01 (s, 24 H, SiMe_2), 0.37 (m, 8H, Si$CH_2CH_2CH_2N^+Me_3$), 0.58 (m, 8H, Si$CH_2CH_2CH_2$Si-), 1.31 (m, 8H, -Si$CH_2CH_2CH_2$Si-), 1.62 (m, 8H, -Si$CH_2CH_2CH_2N^+Me_3$), 3.04 (s, 36H, N^+Me_3), 3.24 (m, 8H, -$CH_2N^+Me_3$). ^{13}C NMR (DMSO): δ – 3.9 (SiMe_2), 10.7 (Si$CH_2CH_2CH_2N^+$Me3), 16.4 (-Si$CH_2CH_2CH_2$Si-), 17.4 (-Si$CH_2CH_2CH_2$Si-), 17.6

(-SiCH$_2$CH$_2$CH$_2$Si-), 18.8 (-SiCH$_2$CH$_2$CH$_2$N$^+$Me$_3$), 51.6 (N$^+$Me$_3$), 67.4 (-SiCH$_2$CH$_2$CH$_2$N$^+$Me$_3$). ^{29}Si-NMR (DMSO): δ 0.9 (G_0–Si), 2.5 (G_1–Si). ^{15}N-NMR (DMSO): δ –321.5 (NMe_3^+). MS: $[M\text{-}I]^+$ = 1214.49 uma (calcd. = 1213.45 uma). Anal. Calc. $C_{44}H_{108}I_4N_4Si_5$ (1341.4 g mol^{-1}): C, 39.40; H, 8.12; N, 4.61; Exp.: C, 39.52; H, 8.54; N, 4.61%.

4.3.14 Synthesis of 2G-[SiMe$_2$(CH$_2$)$_3$ N$^+$Me$_3$I$^-$]$_8$ (13). Dendrimer **13** was prepared using a similar method to that described for **12**, starting from *2G*-[*SiMe*$_2$(*CH*$_2$)$_3$*NMe*$_2$]$_8$(0.14 g) and MeI (0.1 mL) to obtain compound **13** as a white solid (0.21 g). ^{1}H-NMR (DMSO): δ –0.10 (s, 12H, Si*Me*), –0.08 (s, 48H, Si*Me*$_2$), 0.37 (m, 16H, SiC*H*$_2$*C*H$_2$CH$_2$N$^+$Me$_3$), 0.54 (m, 48H, SiC*H*$_2$*C*H$_2$C*H*$_2$Si-), 1.30 (m, 24H, -SiCH$_2$*CH*$_2$CH$_2$Si-), 1.61 (m, 16H, -SiCH$_2$*CH*$_2$CH$_2$N$^+$Me$_3$), 3.04 (s, 72H, N$^+$*Me*$_3$), 3.25 (m, 16H, -*CH*$_2$N$^+$Me$_3$). ^{13}C NMR (DMSO): δ –5.4 (Si*Me*), – 3.9 (Si*Me*$_2$), 10.6 (Si*C*H$_2$CH$_2$CH$_2$N$^+$Me3), 16.4–17-9 (-SiCH$_2$*C*H$_2$CH$_2$Si- and -Si*C*H$_2$CH$_2$*C*H$_2$Si-), 18.8 (-SiCH$_2$*C*H$_2$CH$_2$N$^+$Me$_3$), 51.6 (N$^+$*Me*$_3$), 67.4 (-SiCH$_2$CH$_2$*C*H$_2$N$^+$Me$_3$). ^{29}Si-NMR (DMSO): δ (G_0–Si) is not observed, 1.1 (G_1–Si), 2.3 (G_2–Si). ^{15}N-NMR (DMSO): δ –322.4 (NMe_3^+). Electrospray (2992.93 g mol^{-1}) $q = 2$ (1370.6; $[M - 2I^-]^{2+}$), $q = 3$ (871.4; $[M - 3I^-]^{3+}$) and $q = 4$ (621.8; $[M - 4I^-]^{4+}$). Anal. Calc. $C_{104}H_{252}I_8N_8Si_{13}$ (2995.51 g mol^{-1}): C, 41.70; H, 8.48; N, 3.74; Exp.: C, 42.19; H, 8.96; N, 3.25%.

4.3.15. Synthesis of 3G-[SiMe$_2$(CH$_2$)$_3$ N$^+$Me$_3$I$^-$]$_{16}$ (14). Dendrimer **14** was prepared using a similar method to that described for **12**, starting from *3G*-[*SiMe*$_2$(*CH*$_2$)$_3$*NMe*$_2$]$_{16}$ (0.13 g) and MeI (0.1 mL) to obtain compound **14** as a white solid (0.18 g). ^{1}H-NMR (DMSO): δ –0.10 (s, 36H, Si*Me*), –0.08 (s, 96H, Si*Me*$_2$), 0.37 (m, 144H, SiC*H*$_2$*C*H$_2$CH$_2$N$^+$Me$_3$), 0.54 (m, 56H, SiC*H*$_2$*C*H$_2$C*H*$_2$Si-), 1.30 (m, 32H, -SiCH$_2$*CH*$_2$CH$_2$Si-), 1.62 (m, 144H, -SiCH$_2$*CH*$_2$CH$_2$N$^+$Me$_3$), 3.08 (s, 32H, N$^+$*Me*$_3$), 3.28 (m, -*CH*$_2$N$^+$Me$_3$). ^{13}C NMR (DMSO): δ –5.4 (Si*Me*), –3.9 (Si*Me*$_2$), 10.6 (Si*C*H$_2$CH$_2$CH$_2$N$^+$Me3), 14.6–17.9 (-SiCH$_2$*C*H$_2$CH$_2$Si- and -Si*C*H$_2$CH$_2$*C*H$_2$Si-), 18.8 (-SiCH$_2$*C*H$_2$CH$_2$N$^+$Me$_3$), 51.7 (N$^+$*Me*$_3$), 67.3 (-SiCH$_2$CH$_2$*C*H$_2$N$^+$Me$_3$). ^{29}Si-NMR (DMSO): δ (G_0–Si) and (G_1–Si) is not observed, 1.1 (G_2–Si), 2.3 (G_3–Si). ^{15}N-NMR (DMSO): δ –321.6 (NMe_3^+). Anal. Calc. $C_{224}H_{540}I_{16}N_{16}Si_{29}$ (6303.74 g mol^{-1}): C, 42.68; H, 8.63; N, 3.56; Exp.: C, 43.14; H, 9.10; N, 3.39%.

Acknowledgements

This work was supported by the Spanish MEC (project CTQ2008-03149) to M.P.T. from UA. MNT-ERA NET 2007 (ref. NAN2007-31135-E), Fondo de Investigación Sanitaria (PI080222), COST Action (TD0802), and CIBER-BBN as an initiative funded by the VI National R&D&i Plan *2008-2011*, *Iniciativa Ingenio 2010*, *Consolider Program*, *CIBER Actions* and financed by the Instituto de Salud Carlos III with assistance from the *European Regional Development Fund* for R.G from U.A.

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