

# Organosilicon Dendritic Networks in Porous Ceramics for Water Purification

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Triethoxysilyl-functionalized poly(propylene imine) (DAB32) dendrimer and poly(ethylene imine) (PEI5) hyperbranched polymer were conveniently prepared in chloroform and were subsequently allowed to impregnate porous ceramic filters. Following hydrolysis of triethoxysilyl moieties to Si–OH, polycondensation occurred affording networks containing Si–O–Si bridges with simultaneous formation of Si–O–M bridges resulting from the interaction of Si–OH with M–OH of the ceramic surface. In this manner, covalent binding of the organosilicon dendritic polymers is achieved at the ceramic surface. These porous ceramic filters, impregnated with organosilicon dendritic polymers, were employed for water purification. The concentration of polycyclic aromatic compounds in water was reduced to the level of a few ppb by continuous filtration of contaminated water through these filters. The filters loaded with pollutants were effectively regenerated by treatment with acetonitrile.

## Introduction

Dendrimers<sup>1</sup> are highly branched polymers with a well-defined symmetrical structure consisting of a central core, repeating units, and terminal functional groups while hyperbranched polymers<sup>2</sup> share analogous structural features but are nonsymmetric. The latter are conveniently prepared in contrast to the tedious procedures employed for the synthesis of dendrimers. The scientific and technological interest of these dendritic polymers stems from their property of exhibiting nanocavities and also from the facile functionalization of their terminal groups.<sup>3</sup> The nanocavities of dendrimers can encapsulate a diversity of molecules including catalysts, active drug compounds, organic pollutants, and so forth giving rise to the development of novel catalytic

complexes,<sup>4</sup> drug delivery systems,<sup>5</sup> or the newly developed method<sup>6</sup> for the purification of water, respectively. Encapsulation efficiency<sup>7</sup> is determined by the microenvironment of nanocavities, which is primarily dependent on the structural characteristics of their repeating units. On the other hand, the multifunctionality of the external surface of dendritic polymers determines their solubility and, most importantly, their reactivity with other molecules,<sup>2e,3b</sup> molecular aggregates,<sup>8</sup> or reactive surfaces.<sup>9</sup> The so-called polyvalency effects<sup>10</sup> are crucially associated with the chemistry of dendrimers and they are exercised because of the accumulation of the functional groups at their external surface. Because of these effects, enhanced binding with

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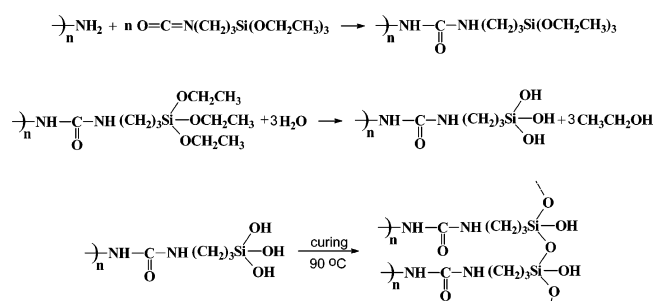
other substrates is achieved.

Recently, it has been established that dendrimeric polymers rendered insoluble in water by alkylation and processed into thin films can encapsulate organic pollutants dissolved in water. Specifically, thin films were formed from alkylated diaminobutane poly(propylene imine) dendrimers (DAB)<sup>6</sup> or alkylated hyperbranched poly(ethylene imine)<sup>11</sup> polymer. Organic pollutants dissolved in water were encapsulated in their nanocavities affording ultrapure water, which contained pollutants down to few ppb levels. The filled dendrimeric films were regenerated with acetonitrile.

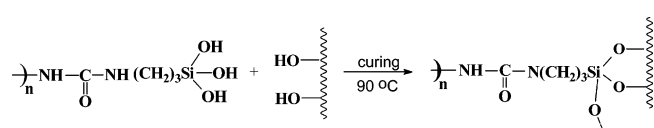
Aiming at investigating novel dendritic systems for encapsulating organic pollutants, it was decided to use cross-linked dendritic derivatives chemically attached on ceramic filters. A similar strategy was recently developed and extensively published by Dvornic et al. Specifically, at a first stage, alkoxy-silylated groups were introduced either on dendrimeric<sup>12</sup> or hyperbranched polymeric<sup>13</sup> surfaces. The so-prepared dendritic polymers were hydrolyzed and subsequently cross-linked via the sol-gel approach affording nanostructured dendritic based networks<sup>14</sup> which were subsequently employed by Dvornic et al.<sup>14f,15</sup> for hosting organic or inorganic guests.

On the basis of the previously mentioned innovative work<sup>12-15</sup> on organosilicon dendritic polymers, in the present study we report the synthesis of analogous polymers and nanostructured networks which are applied for the preparation of ultrapure water. For this purpose, the amino groups of poly(propylene imine) dendrimer (DAB32) and hyperbranched poly(ethylene imine) (PEI5) are now interacted under extremely mild conditions with 3-(triethoxysilyl)propyl isocyanate. The triethoxysilyl derivatives obtained being susceptible to facile hydrolysis afford silanols which they polycondensate, by loss of water, with other neighboring hydroxy groups either intramolecularly or intermolecularly, Scheme 1. These dendritic silanols can also condensate with hydroxyl groups, which are present on the surface of activated ceramics, forming a chemically bound film, Scheme 2. Specifically, titanium dioxide ceramic filters were subjected to treatment with triethoxysilyl derivatives affording, after curing, a nanostructured dendrimeric network covalently bound on the ceramic filter. The formation and characteriza-

Scheme 1



Scheme 2



tion of this network together with its ability to encapsulate organic pollutants are, in detail, investigated in the present study.

## Experimental Section

**Materials and Methods.** Diaminobutane poly(propylene imine) dendrimer, DAB32 (fourth generation, 32 primary amino groups), was purchased from DSM while poly(ethylene imine) hyperbranched polymer, PEI5 (Mn = 5000, ~68 primary and secondary amino groups), was purchased from Hyperpolymers INC. 3-(Triethoxysilyl)propyl isocyanate (Aldrich) was used as received. Titanium dioxide filters (porosity 37.3%, median pore diameter 8 μm) were provided by Céramiques Techniques et Industrielles (France). The hydrolysis of the ethoxysilyl groups and the formation of the siloxane bridges were established by FTIR spectroscopy employing a Nicolet Magna-IR Spectrometer 550. Phenanthrene, pyrene, and β-naphthol, which were used as model pollutants, were purchased from Aldrich and were purified by recrystallization. Their concentration in water was determined by fluorescence spectroscopy employing a Perkin-Elmer LS-5B spectrophotometer with excitation wavelengths at 248 nm for phenanthrene, 270 nm for β-naphthol, and 335 nm for pyrene.

**Preparation of Triethoxysilyl Dendritic Derivatives, DAB32-Si and PEI5-Si.** Diaminobutane poly(propylene imine) dendrimer (DAB32), 0.001 mol, or poly(ethylene imine) hyperbranched polymer (PEI5), 0.001 mol, was dissolved in dry chloroform under argon at 0 °C. To this solution, 0.032 or 0.068 mol of 3-(triethoxysilyl)propyl isocyanate, dissolved in the same solvent, was added and the reaction mixture was held at this temperature for half an hour and then was allowed to reach room temperature in which it remained for several hours. This solution was used for impregnating the ceramic filters as will be described in the next section. For identifying the materials obtained, the same reaction was performed in deuterated chloroform, and NMR spectra were obtained during the reaction course. The reaction was complete since terminal amino groups were not detected by NMR while peaks attributed to the newly formed urea moiety appear as shown below.

**Silylated Dendrimeric Material (DAB32-Si).** <sup>1</sup>H NMR (500 Hz, CDCl<sub>3</sub>): δ = 6.12 (s NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCONH), 5.84 (s SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCONH), 3.74 (m CH<sub>3</sub>CH<sub>2</sub>OSi), 2.96 (m NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCO, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCO), 2.21 (m NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCO), 1.41 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N, NC-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCO, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCO), 1.05 (t CH<sub>3</sub>CH<sub>2</sub>OSi), 0.45 (m NCH<sub>2</sub>CH<sub>2</sub>Si). <sup>13</sup>C NMR (125 Hz, CDCl<sub>3</sub>): δ = 159.9 (CO), 58.5 (CH<sub>3</sub>CH<sub>2</sub>O), 52.7 (NCH<sub>2</sub>CH<sub>2</sub>-

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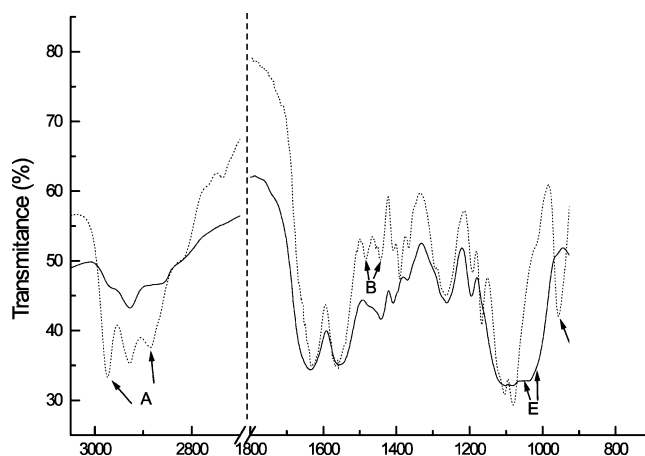
CH<sub>2</sub>CH<sub>2</sub>N), 52.1 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 51.2 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCO), 43.1 (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCO), 38.2 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCO), 28.2 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCO), 24.9 (N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 24.1 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 18.4 (CH<sub>3</sub>CH<sub>2</sub>OSi), 8 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si).

**Silylated Hyperbranched Material (PEI5-Si).** <sup>1</sup>H NMR (500 Hz, CDCl<sub>3</sub>): δ = 6.81 (s NCH<sub>2</sub>CH<sub>2</sub>NHCONH), 5.96 (s SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCONH), 3.74 (m CH<sub>3</sub>CH<sub>2</sub>OSi), 3.15 (m NCH<sub>2</sub>CH<sub>2</sub>NHCO), ((N-CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCO), 3.08 (m SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCO), 2.47 (m NCH<sub>2</sub>CH<sub>2</sub>N, NCH<sub>2</sub>CH<sub>2</sub>NHCO, (NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCO), 1.53 (m SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH-CO), 1.15 (t CH<sub>3</sub>CH<sub>2</sub>OSi), 0.57 (m NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si). <sup>13</sup>C NMR (125 Hz, CDCl<sub>3</sub>): δ = 159.4 ((NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCO), 158.8 (NCH<sub>2</sub>CH<sub>2</sub>NCO) 58.3 (CH<sub>3</sub>CH<sub>2</sub>O), 54.4 (NCH<sub>2</sub>CH<sub>2</sub>NH) 53.4 (NCH<sub>2</sub>CH<sub>2</sub>N), 48.5 (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCO), 43.6 (NCH<sub>2</sub>CH<sub>2</sub>NHCO), 42.8 (NHCONCH<sub>2</sub>CH<sub>2</sub>NHCO) 23.8 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 18.3 (CH<sub>3</sub>CH<sub>2</sub>OSi), 7.7 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si).

**Impregnation of Titanium Oxide Ceramic Filter Modules with Organosilicon Dendritic Polymers and Formation of Dendritic Siloxane Networks.** Titanium oxide ceramic filters in the form of multichannel tubes (25 mm diameter, 25 mm or 250 mm length, 52 channels) were subjected to etching by immersion into 1 N NaOH solution for several hours; they were repeatedly washed with water and methanol and dried under vacuum as described by Ottenbrite.<sup>16</sup> These filters were immersed into the previously described triethoxysilyl dendrimeric or hyperbranched polymer solutions and were held at 60 °C for 6 h under argon. Subsequently, they were allowed to dry in open air, cured at 90 °C for up to 50 h, and washed with acetonitrile to remove possible traces of the unreacted 3-(triethoxysilyl)propyl isocyanate. The weight increase of the modules was initially 6.5% whereas after the curing process the polymer weight was 5.2% of the ceramic because of hydrolysis/condensation reactions. The progress of curing was monitored separately, by applying the above-mentioned solution on KBr or KBr/TiO<sub>2</sub> pellets and following the same drying/curing procedure as above. FT-IR spectra of these pellets were recorded at regular time intervals until no changes between successive spectra were observed. When pure TiO<sub>2</sub> pellets were employed, it was not possible to record FT-IR spectra in the wavelength region of interest (1000–400 cm<sup>-1</sup>) because of its strong absorption. For this reason, several pellets with different weight ratios of KBr/TiO<sub>2</sub> were tested for FT-IR studies. It was found that optimum spectra were obtained by using 2% w/w of TiO<sub>2</sub> in KBr.

**Determination of Inclusion Rates and Inclusion Formation Constants for Model Organic Pollutants in Dendritic Siloxane Networks.** The triethoxysilyl dendrimeric or hyperbranched polymer solution discussed above (10 mL) was slowly evaporated into a glass round-bottom flask (100 mL) for the formation of a thin film. The flask was placed in an oven at 90 °C for 50 h for the formation of the polymeric network via siloxane bridges. To this round-bottom flask, 100 mL of doubly distilled water contaminated with pyrene (100 ppb), phenanthrene (1 ppm), or β-naphthol (300 ppb) was added and subjected to fluorescence measurements, at regular time intervals. The inclusion of the contaminant was indirectly determined by measuring the concentration of the fluorescent probe in solution. The inclusion formation constants were determined by registering the aromatics concentration after equilibrium was reached.<sup>6</sup>

**Evaluation of Impregnated Porous Ceramic Filter Modules for the Removal of Water Pollutants.** The evaluation of the ceramic filters impregnated with the dendritic networks as far as their ability to remove organic pollutants from water is concerned was performed by continuous filtration experiments of the above-



**Figure 1.** FTIR spectra of the PEI5-Si on a KBr pellet before (dotted line) and after (straight line) curing at 90 °C for 30 h.

mentioned water solutions, employing an appropriate stainless steel housing for the filter module and an HPLC pump operating at different flow rates (2–7 mL/min). The concentration of the pollutants at the outlet was also monitored by fluorescence spectroscopy.

## Results and Discussion

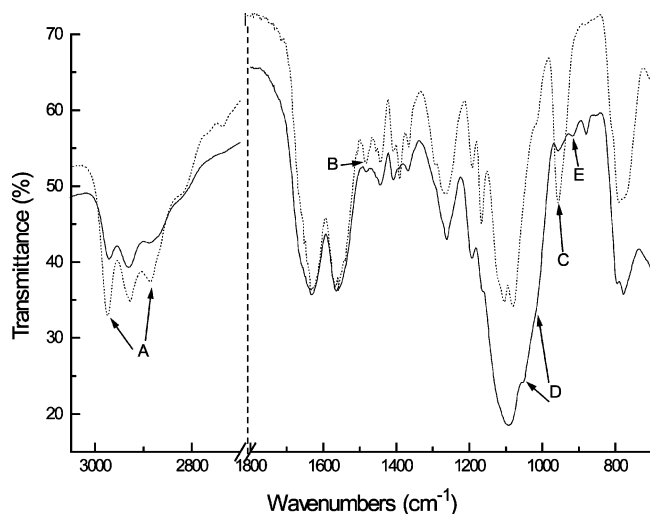
The reaction of the dendritic polymers with the 3-(triethoxysilyl)propyl isocyanate was facilitated by the polyvalency effect because of accessibility of the amino groups at their external surface.<sup>10</sup> The reaction is performed under anhydrous conditions to prevent hydrolysis of the isocyanate group to amino group and of the ethoxysilyl group to silanol; the latter reaction would lead to polymerization and gelation. Following the impregnation step of the ceramic filters with the previously mentioned reaction mixture, ambient humidity is required for silanol formation, which subsequently polycondensates via formation of Si–O–Si bonds at 90 °C. These reactions were monitored by FT-IR measurements of thin films as described in the Experimental Section.

The spectra recorded before and after curing for 30 h at 90 °C are shown in Figure 1. Hydrolysis of the ethoxysilane groups to SiOH groups can be established by the disappearance of the asymmetric (2974 cm<sup>-1</sup>) and symmetric (2885 cm<sup>-1</sup>) stretching vibrations (Figure 1, A) as well as of the asymmetric (1484 cm<sup>-1</sup>) and symmetric (1391 cm<sup>-1</sup>) deformation vibrations (Figure 1, B) of the methyl groups and the bending vibration 783 cm<sup>-1</sup> of the Si–O–C groups<sup>14e</sup> (Figure 1, C). The presence of the band at 950 cm<sup>-1</sup> corresponding to the stretching vibrations of the Si–OH groups<sup>14e,17</sup> in the initial spectrum indicates that hydrolysis of the siloxane groups is taking place as soon as the reaction mixture is exposed at ambient humidity. This band initially increases in intensity because of the hydrolysis of the ethoxysilane groups, but after approximately 10 h it starts decreasing in intensity (Figure 1, D) indicating that the silanol groups are being transformed into siloxane groups. This transformation is almost quantitative after about 30 h. The characteristic Si–O–Si asymmetric and symmetric stretching vibrations at 1050 and 1010 cm<sup>-14e,17,18</sup> are progressively

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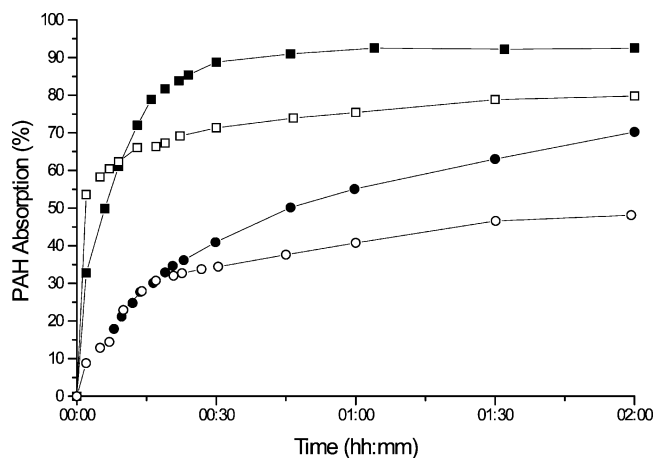


**Figure 2.** FTIR spectra of the PEI5-Si on a KBr/TiO<sub>2</sub> pellet before (dotted line) and after (straight line) curing at 90 °C for 50 h.

observed in the spectra of the films (Figure 1, E), partially overlapping the Si-C stretching vibrations.

Polycondensation of the hydrolyzed organosilicon dendrimers or hyperbranched polymers at the ceramic TiO<sub>2</sub> supports was monitored, as above, employing KBr pellets containing TiO<sub>2</sub>. The spectra obtained before and after curing for 50 h at 90 °C are shown in Figure 2. The spectrum of TiO<sub>2</sub> was subtracted to avoid overlapping of the peaks at the 1000–400 cm<sup>-1</sup> region by the broad band of Ti-O-Ti linkage in the amorphous state.<sup>19</sup> Hydrolysis of ethoxysilane groups was observed as described above (Figure 2, A and B). Also, the SiOH peak at 950 cm<sup>-1</sup> is significantly reduced in intensity (Figure 2, C), while the Si-O-Si bond formation is established by the presence of the two asymmetric and symmetric stretching bands at 1050 and 1000 cm<sup>-1</sup>, respectively (Figure 2, D). A small peak at 920 cm<sup>-1</sup> (Figure 2, E), which appears only after 50 h of curing, is attributed to Ti-O-Si stretching vibration<sup>19,20</sup> suggesting chemical bond formation between the ceramic support and the polymeric dendritic network after prolonged curing at high temperatures.

Polycondensation of the hydrolyzed organosilicon dendritic polymers leads to the formation of materials completely insoluble in water. This is a requirement for materials to be applied for the removal of lipophilic contaminants from water as it was recently established with long-chain alkylated dendrimeric derivatives.<sup>6</sup> In the present case, the organosilicon dendritic network is covalently bound on the ceramic support, becoming therefore nonleachable while retaining its inclusion capacity. Polycyclic aromatic hydrocarbons have in the first place the property to be encapsulated inside the nanocavities of dendritic polymers because of their insolubility in water. Their inclusion in the lipophilic environment of this network is therefore a thermodynamically favorable process. For testing the encapsulation efficiency of the networks, three different polycyclic aromatic hydrocarbons



**Figure 3.** Time dependence of the absorption of pyrene (square symbols) and phenanthrene (circles) in thin films of dendrimeric DAB32-Si (open symbols) and hyperbranched PEI5-Si (solid symbols) siloxane networks.

are employed, their water solubility of which differs significantly.<sup>21</sup>

For evaluating the encapsulation efficiency of these compounds, inclusion kinetic experiments were performed using a thin film method analogous to the one employed for the alkylated dendrimers.<sup>6</sup> It is evident (Figure 3) that the polymers have the capacity to absorb polycyclic aromatic hydrocarbons from water. Specifically, the PEI5-Si siloxane network removes 92% of pyrene and 70% of phenanthrene from water after 2 h. For the same period of time, DAB32-Si siloxane network removes 80% of pyrene and 48% of phenanthrene. On the other hand, the absorption of  $\beta$ -naphthol is significantly slower and equilibrium is reached after several days. The high pyrene absorption compared to that of phenanthrene can be attributed to the higher solubility of phenanthrene in water which is 1 order of magnitude higher than that of pyrene.<sup>21</sup> The same behavior was also observed when alkylurea poly(propylene imine) dendrimers<sup>6</sup> or alkylated hyperbranched polymers<sup>11</sup> were used for the encapsulation of polycyclic aromatic compounds from water. As far as  $\beta$ -naphthol is concerned, its lower absorption is due to its even higher water solubility compared to both pyrene and phenanthrene not favoring its absorption inside the dendrimer.

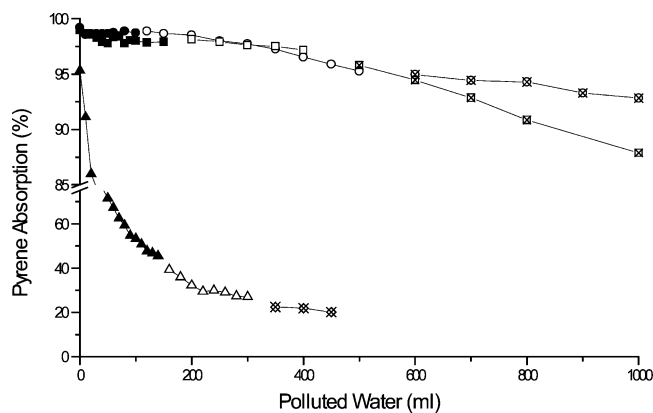
The inclusion formation constants were also determined by model thin film experiments (Table 1), as described in the Experimental Section. Their order of magnitude,  $10^7$  M<sup>-1</sup> for pyrene,  $10^6$  M<sup>-1</sup> for phenanthrene, and  $10^5$  M<sup>-1</sup> for  $\beta$ -naphthol, is correlated with the water solubility of contaminants while it is only weakly correlated with the type of dendritic architecture. This behavior also applies to the Gibbs free energies ( $\Delta G^\circ = -RT \ln K$ ); the relatively water-soluble  $\beta$ -naphthol exhibits the lowest absolute value. Relatively hydrophilic molecules are in a less unfavorable energy state in water and the formation of the inclusion complex is not therefore favored. It is therefore established that the main driving force behind the inclusion process is the Gibbs free energy required for stabilizing the aromatic compounds inside the lipophilic cavities of the dendrimeric or the hyperbranched polymer network. The negative values

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**Figure 4.** Pyrene absorption by continuous filtration through ceramic  $\text{TiO}_2$  filters (25-mm length) either empty (triangle symbols) or impregnated with dendrimeric (DAB32-Si, square symbols) or hyperbranched (PEI5-Si, circles) siloxane networks as a function of polluted water volume at various flow rates (2 mL/min, solid symbols; 4 mL/min, open symbols; 7 mL/min, x centered symbols).

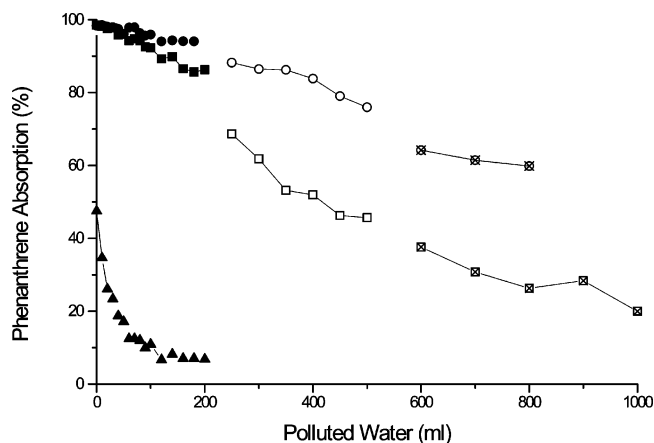
**Table 1. Inclusion Formation Constants  $K$  ( $\text{M}^{-1}$ ), Concentrations at Equilibrium EC (ppb), and Inclusion Formation Gibbs Free Energies (kcal/mol) between Polycyclic Aromatic Compounds and Dendritic Siloxane Networks**

pollutant	thermodynamic parameters	networks	
		PEI5-Si network	DAB32-Si network
pyrene	$K$	$2.2 \times 10^7$	$2.5 \times 10^7$
	EC	9	8
	$\Delta G^\circ$	-9.2	-9.2
phenanthrene	$K$	$9.7 \times 10^5$	$1.0 \times 10^6$
	EC	184	172
	$\Delta G^\circ$	-7.5	-7.5
$\beta$ -naphthol	$K$	$6.1 \times 10^5$	$7.2 \times 10^5$
	EC	235	200
	$\Delta G^\circ$	-7.3	-7.3

of  $\Delta G^\circ$  demonstrate that the absorption of the contaminant inside the nanoporous film is a spontaneous process, with a  $\Delta G^\circ$  ranging from -7.3 to -9.2 kcal/mol. This is in contrast to other water purification procedures such as reverse osmosis, which require energy to drive the process to completion.

Following these results, experiments were performed employing ceramic filters, which were impregnated with silylated dendrimeric and hyperbranched derivatives and polymerized by curing at 90 °C for 50 h. These hybrid materials were used for continuous filtration of polluted water containing pyrene, phenanthrene, or  $\beta$ -naphthol. Comparing the results with those obtained from the empty (nonimpregnated) filters, it is evident that the impregnation with dendrimeric or hyperbranched networks largely enhances the absorption efficiency of polycyclic aromatic contaminants. The less soluble pyrene<sup>21</sup> is almost completely absorbed by 25-mm-long hybrid filters even at high filtration rates (4 and 7 mL/min), whereas the pyrene retained by the empty filters dramatically decreases with eluted water volume (Figure 4). No significant differences are observed between the two dendritic networks. However, at higher flow rates the dendrimeric network is less effective, which is in line with the kinetic experiments.

For phenanthrene, which is 1 order of magnitude more soluble than pyrene,<sup>21</sup> 95–90% of the pollutant was retained at low flow rates (2 mL/min) using 25-mm filters; however, when the flow rate was increased to 4 mL/min, the retention

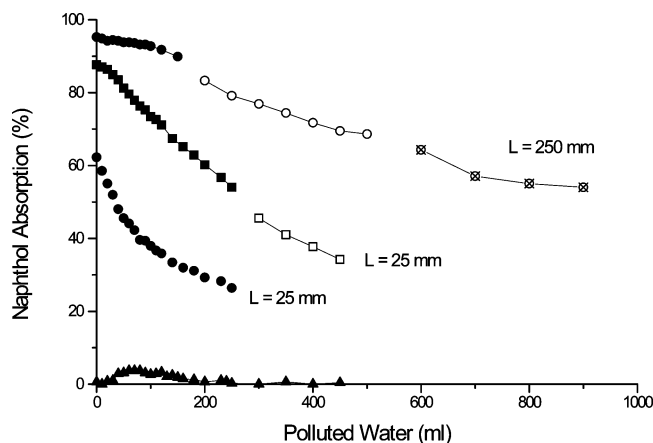


**Figure 5.** Phenanthrene absorption by continuous filtration through ceramic  $\text{TiO}_2$  filters (25-mm length) either empty (triangle symbols) or impregnated with dendrimeric (DAB32-Si, square symbols) or hyperbranched (PEI5-Si, circles) siloxane networks as a function of polluted water volume at various flow rates (2 mL/min, solid symbols; 4 mL/min, open symbols; 7 mL/min, x centered symbols).

percentage of phenanthrene absorbance drops from 90% for the PEI5-Si network to 75% for the DAB32-Si network as a result of the decrease of the contact time between the pollutant and the absorbing polymer networks (Figure 5). In addition, in both cases a notable decrease of the retention percentage is observed with accumulation of absorbed phenanthrene. At higher flow rates (7 mL/min), the retention percentage decreases to 65 and 40% for PEI5-Si and DAB32-Si networks, respectively. It is therefore obvious that for an effective purification from phenanthrene, at higher flow rates, a longer filter is required, to secure adequate contact time.

Another observation meriting discussion and requiring explanation is that the overall performance of DAB32-Si network for polycyclic aromatic hydrocarbon absorption is inferior to that of PEI5-Si network especially at high flow rates (4–7 mL/min). It seems that the fully developed symmetrical structure of DAB32 and the complete functionalization of the amino groups with the introduction of ethoxysilanes result, following their hydrolysis, in the accumulation of silanol groups at the external surface of the dendrimers. The latter favors the subsequent formation of many intermolecular siloxane bridges after curing. The structure of the polymeric network becomes comparatively more rigid to that originating from the hyperbranched polymer, inhibiting therefore the inclusion rate of bulky molecules. However, the rigidity of the polymeric structure affects only the inclusion rate and not the inclusion constant.

These promising results with the hybrid filters triggered interest for investigating the absorption capacity of a more water-soluble aromatic hydrocarbon. For this purpose,  $\beta$ -naphthol was selected having solubility in water of about 1000 ppm, that is, 3 orders of magnitude higher than that of phenanthrene. The results of continuous filtration experiments of  $\beta$ -naphthol are shown in Figure 6. Although  $\beta$ -naphthol is not at all absorbed by the empty ceramic support (25 mm), the hybrid filters significantly retained it at low flow rates, the DAB32-Si network exhibiting the best absorbing behavior. This difference is in line with the respective difference in the determined  $K$  values (Table 1), which



**Figure 6.**  $\beta$ -Naphthol absorption by continuous filtration through ceramic  $\text{TiO}_2$  filters (25- or 250-mm length) either empty (triangle symbols) or impregnated with dendrimeric (DAB32-Si, square symbols) or hyperbranched (PEI5-Si, circles) siloxane networks as a function of polluted water volume at various flow rates (2 mL/min, solid symbols; 4 mL/min, open symbols; 7 mL/min, x centered symbols).

suggest that its absorption in DAB32-Si is thermodynamically more favored than in PEI5-Si. In contrast to the previous experiments with pyrene and phenanthrene where the DAB32-Si network in continuous filtration experiments is not absorbing as efficiently as the PEI5-Si network, because of rigidity of the polymeric network of DAB32-Si which inhibits the inclusion rate of bulky molecules, absorption of  $\beta$ -naphthol is not affected apparently because of its considerably smaller size.

Furthermore, a 10-fold increase in contact time between  $\beta$ -naphthol and the hyperbranched polymer network achieved by employing a filter tube of 250 mm results in a dramatic enhancement of absorption capacity, that is, up to 90% at a flow rate of 2 mL/min. It should therefore be concluded from these results that although, as mentioned above, the main

driving force for the inclusion process is the Gibbs free energy required for stabilizing the aromatic compounds inside the lipophilic cavities, the size and shape of the absorbed molecules should not be disregarded because they are affecting the kinetics of the experiments.

For a final evaluation of the applicability of these organosilicon dendritic networks as water purification materials, their regeneration capability should be investigated. Since the inclusion of contaminant is a noncovalent host-guest interaction, which is energetically favored by the high energy of the contaminant when dissolved in water, this irreversible inclusion reaction in water can be reversed in less polar organic solvents. Tube filters contaminated with pyrene, phenanthrene, and  $\beta$ -naphthol were successfully regenerated with acetonitrile with gentle heating ( $<50\text{ }^\circ\text{C}$ ). After regeneration, repeated inclusion of contaminants proceeds with no apparent change in the binding efficiency.

### Conclusions

The synthesized organosilicon dendrimeric and hyperbranched networks were employed for impregnating porous ceramic filters, which proved promising devices for water purification. These filters encapsulate toxic polycyclic aromatic compounds dissolved in water having also the potential for application to relatively water-soluble toxic pollutants. Thus, reduction of the concentration of polycyclic aromatic compounds in water, to the level of a few ppb, was achieved by continuous filtration of contaminated water at different flow rates. The filters were effectively regenerated by treating them with acetonitrile.

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