Functional Dendrimeric "Nanosponges" for the Removal of Polycyclic Aromatic Hydrocarbons from Water

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A series of poly(propylene imine) dendrimers functionalized with long aliphatic chains has been prepared and characterized. The property of these dendrimers to encapsulate polycyclic aromatic hydrocarbons from water down to a few ppb level has been established. The inclusion formation constants are orders of magnitude higher than those reported for activated carbon (from 1.4×10^4 to 3.4×10^5 M^{-1}) or cyclodextrins ($10-10^3$ M^{-1}) while they are comparable to those of cyclodextrin polymers (from 1×10^8 to 5×10^9). Furthermore, the loading capacities depend on polycyclic aromatic compounds and the type of alkylated dendrimeric derivatives, that is, 6−19 mg/g for fluoanthrene, 44−67 mg/g for phenanthrene, and 34−57 mg/g for pyrene. Regeneration is also feasible using nonpolar solvents.

Introduction

The structural features of dendrimers favor or rather dynamically induce the formation of nanocavities, which can incorporate a diversity of molecules, leading to the formation of molecular nanocomposites. Dendrimers[1] are highly branched macromolecules of well-defined symmetrical structures consisting of a central core, repeating units, and terminal functional groups, which can be properly functionalized so as to fulfill requirements for a diversity of applications including that of encapsulation of various molecules. The nature of the internal generations of dendrimers determine the microenvironment of nanocavities and consequently the solubilization properties while the external groups determine the solubility and chemical behavior of dendrimers in the external medium.

Recent studies have established that diaminobutane poly(propylene imine) dendrimers[2] and some of their water-soluble derivatives[3] encapsulate pyrene, which is reversibly released upon acidification. In this connection and with the aim at the removal of organic impurities from water and the production of ultrapure water, diaminobutane poly(propylene imine) dendrimers were functionalized with long aliphatic chains to render these molecules lipophilic, that is, completely insoluble in water. It is understandable that the encapsulating properties of these new dendrimeric derivatives for lipophilic molecules should not be hindered by the introduction of the alkyl chains.

In the present work poly(propylene imine) dendrimers with 32 and 64 primary amino groups, that is, DAB-32 and DAB-64 with 32 and 64 surface groups, respectively, were interacted with long-chain *n*-alkylisocyanates for the preparation of fully alkylated, water-insoluble dendrimeric derivatives (Scheme 1). The reaction is facile and it is also accelerated by the accessibility of the amino groups at the external surface of the dendrimeric molecules coupled with the local high concentration of the same groups. The development of these materials, described as "nanosponges", is aiming at water treatment for the production of ultrapure water.

Experimental

Materials and Methods. Amine-terminated diaminobutane poly(propylene imine) dendrimers, that is, DAB-32 and DAB-64, were purchased from DSM Fine Chemicals Company and used as received. Pyrene (Aldrich) was purified by sublimation followed by recrystallization from ethanol. Phenanthrene and fluoranthene were purchased from Aldrich and used as received. The concentration of solubilized aromatics was determined by fluorescence spectroscopy, employing a Perkin-Elmer LS-5B spectrophotometer after excitation at 248 nm for phenanthrene, 283 nm for fluoranthene, and 335 nm for pyrene.

General Procedure for Preparation of *n*-Alkylurea-Diaminobutane Poly(propylene imine) Dendrimers. The reaction with *n*-alkylisocyanates was performed cautiously under the hood. To 0.001 mol of diaminobutane poly(propylene imine) dendrimers, DAB-32 or DAB-64, dissolved in dry dichloromethane, 0.035 or 0.070 mol of *n*-octyl or *n*-octadecylisocyanate, dissolved in the same solvent, was slowly added under argon at 0 °C. The reaction mixture was held at this temperature for half an hour and then allowed to reach room temperature. The octadecyl derivatives were precipitated with methanol and the octyl analogues with acetonitrile, separated from the reaction mixture by centrifugation, followed by repeated washings with the precipitating solvents. The materials were exhaustively dried under vacuum over phosphorus pentoxide.

Complete transformation of the external primary amino groups of the dendrimers to amide urea moieties was estab-

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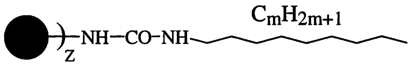
10.1021/cm030214q CCC: $25.00

Scheme 1



Z = 32 or 64 is the number of surface groups
m = 8 or 18

lished by ^{1}H and ^{13}C NMR, elemental analysis, and the fluorescamine test. Specifically, α-CH2 and β-CH2 protons at 2.55 and 1.45 ppm relative to amino groups of the unfunctionalized dendrimers were shifted to 3.15 and 1.55 ppm for the alkylated dendrimers. Also the protons of urea moiety appeared at 6.40 and 6.00 ppm as two broad peaks (due to the dissimilar character of the substituents). Similarly, the ^{13}C NMR peaks of α and β carbons relative to amino groups at 30.8 and 39.7 ppm, respectively, were not detected anymore (25000 scans) and were replaced by two new peaks at 27.9 and 37.8 ppm, respectively. Also the α-carbon relative to the urea group and the carbonyl group of urea were observed at 42.3 and 159.7 ppm, respectively.

^{1}H NMR (250 Hz, $\mathrm{CDCl_3}$): δ 6.00 and 6.40 (s, $\mathrm{N}H\mathrm{CON}H$), 3.15 (m, $\mathrm{C}H_2\mathrm{NHCONHC}H_2$), 2.34 (m, $\mathrm{NC}H_2\mathrm{CH_2C}H_2\mathrm{N}$, $\mathrm{NC}H_2\mathrm{CH_2CH_2C}H_2\mathrm{N}$, $\mathrm{NC}H_2\mathrm{CH_2CH_2NHCONH}$), 1.55 (m, $\mathrm{NCH_2C}H_2\mathrm{CH_2N}$, $\mathrm{NCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2N}$, $\mathrm{NCH_2C}H_2\mathrm{CH_2NHCONH}$), 1.44 (m, $\mathrm{NHCONHCH_2C}H_2\mathrm{CH_2}$), 1.23 (m, $\mathrm{NHCONHCH_2CH_2(C}H_2)_9\mathrm{CH_2}$), 0.85 (t, $\mathrm{CH_3}$). ^{13}C NMR (62.9 Hz, $\mathrm{CDCl_3}$): δ 159.7 ($C\mathrm{O}$), 52.5 ($\mathrm{N}C\mathrm{H_2CH_2CH_2}C\mathrm{H_2N}$, $\mathrm{N}C\mathrm{H_2CH_2}C\mathrm{H_2N}$), 50.6 ($\mathrm{N}C\mathrm{H_2CH_2CH_2NHCONH}$), 42.3 ($\mathrm{NHCONH}C\mathrm{H_2CH_2}$), 37.8 ($\mathrm{NCH_2CH_2}C\mathrm{H_2NHCONH}$), 31.9 ($C\mathrm{H_2CH_2CH_3}$), 30.6 ($C\mathrm{H_2CH_2CH_2CH_3}$), 29.8−29.4 ($\mathrm{CH_2(}C\mathrm{H_2)_5CH_2}$), 27.9 ($\mathrm{NCH_2}C\mathrm{H_2CH_2NHCONH}$), 27.2 ($\mathrm{NHCONHCH_2}C\mathrm{H_2CH_2}$), 24.8 ($\mathrm{NCH_2}C\mathrm{H_2CH_2N}$, $\mathrm{NCH_2}C\mathrm{H_2}C\mathrm{H_2CH_2N}$), 22.7 ($\mathrm{CH_2}C\mathrm{H_2CH_3}$), 14.1 ($\mathrm{CH_3}$). Elemental analysis. Calcd for octylurea DAB-32, $\mathrm{C_{472}H_{976}N_{94}O_{32}}$: C, 66.84; H, 11.60; N, 15.52. Found: C, 66.56; H, 11.81; N, 15.43. Calcd for octadecylurea DAB-32, $\mathrm{C_{792}H_{1616}N_{94}O_{32}}$: C, 73.34; H, 12.56; N, 10.15. Found: C, 72.96; H, 12.84; N, 10.63. Calcd for octylurea DAB-64, $\mathrm{C_{952}H_{1968}N_{190}O_{64}}$: C, 66.86; H, 11.60; N, 15.56. Found: C, 66.5; H, 11.93; N, 15.45. Calcd for octadecylurea DAB-64, $\mathrm{C_{1592}H_{3248}N_{190}O_{64}}$: C, 73.32; H, 12.55; N, 10.20. Found: C, 73.64; H, 12.50; N, 10.22.

Further proof for the completion of this modification was offered by the fluorescamine test,[4] which has shown that for all the alkylated derivatives the reaction proceeded almost to completion, that is, exceeding 99% conversion for the DAB-32 and 97.7% conversion for the DAB-64 derivatives. Fluorescamine and ninhydrin tests have been commonly used for the accurate determination of primary amino groups as described in the literature for analogous molecules.[5,6]

Determination of Absorption Rates and Inclusion Formation Constants of Functional Dendrimers. Slow evaporation of 0.5% dendrimeric chloroform solutions resulted in the formation of thin films, covering round-bottom flasks, with an estimated thickness of ≈60−70 μm. To these films, 50 mL of doubly distilled water contaminated with 100 ppb of either pyrene or phenanthrene, or fluoranthene, was added and stirred. Fluorescence measurements were performed at regular time intervals and the absorption percentage of the contaminant was deduced by measuring the concentration of the fluorescent probe in solution.

The inclusion formation constants were also determined by thin film experiments as described above. In this case 5 mg of the dendrimeric derivatives was dissolved in chloroform in 50-mL round-bottom flasks and films were formed following evaporation of the solvent. In these flasks 50 mL of doubly distilled water contaminated with 100 ppb of pyrene, phenanthrene, or fluoranthene was added. The solutions in the flasks were stirred and the pollutants' concentration was monitored until equilibrium was reached.

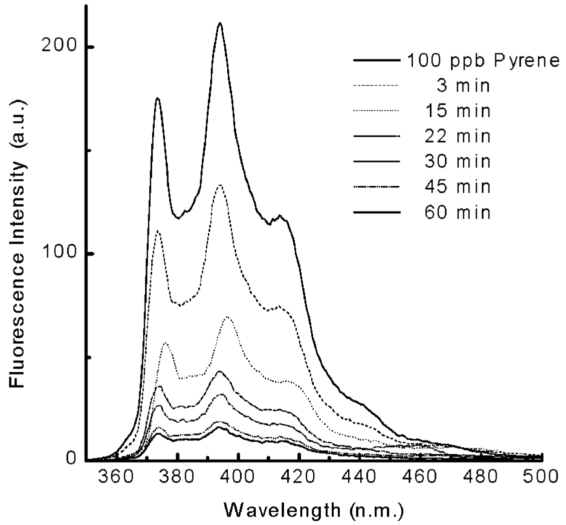


Figure 1. Time dependence of the fluorescence of a pyrene solution added to a glass vial covered by a film of octylurea DAB-64.

Determination of Loading Capacities of Functional Dendrimers. To 1-L round-bottom flasks, covered by thin films deposited from 10 mg of each dendrimer, were added consecutively doubly distilled water polluted with fluoranthene, phenanthrene, or pyrene. The saturation of the films was proved when no further absorption of the pollutants was observed. Subsequently, the water was removed and the films were repeatedly washed with 50 mL of hexane until no traces of the pollutant was detected. The absorbed quantities for each polycyclic aromatic hydrocarbon were determined by measuring their concentration in hexane using fluorescence spectroscopy.

Results and Discussion

The alkylation of diaminobutane poly(propylene imine) dendrimers, easily achieved via interaction with lipophilic isocyanates, drastically changes their solubility profiles, rendering these dendrimers completely insoluble in water. A crucial requirement for these functional dendrimers is to maintain or even enhance their solubilizing properties toward lipophilic compounds dissolved in water.

For testing the encapsulation efficiency of these lipophilic dendrimers, inclusion kinetics using thin dendrimeric films was performed. A typical example showing the decrease of fluorescence intensity of a water sample contaminated with pyrene due to its encapsulation in octylurea DAB-64 dendrimer is shown in Figure 1. It is evidenced that the alkylation of the terminal $\mathrm{NH_2}$ groups does not prohibit the encapsulation capacity for pyrene as established for the water-soluble parent[2] and quaternized[3] derivatives.

The degree of inclusion of contaminants inside the octyl and octadecyl dendrimeric derivatives of DAB-32 and DAB-64 is depicted in Figures 2−4. It can be deduced from these diagrams that the length of the long aliphatic chains and the generation of the dendrimers only slightly affect the inclusion rate. Functionalized derivatives of DAB-64 with long aliphatic chains incorporate a slightly higher percentage of pyrene, although the adsorption rate remains the same. Also, the inclusion of phenanthrene is slightly affected by the length

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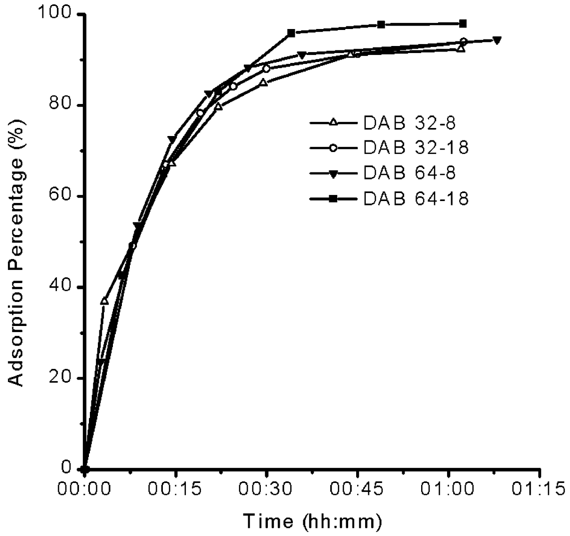

Figure 2. Time dependence of pyrene's adsorption percentage by thin films of dendrimeric derivatives.

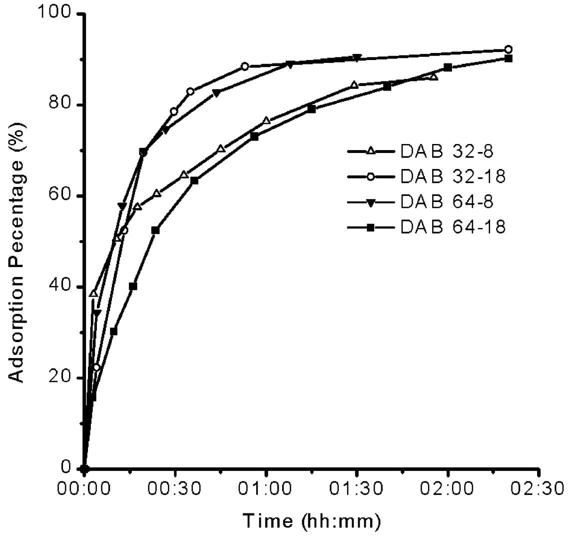

Figure 3. Time dependence of phenanthrene's adsorption percentage by thin films of dendrimeric derivatives.

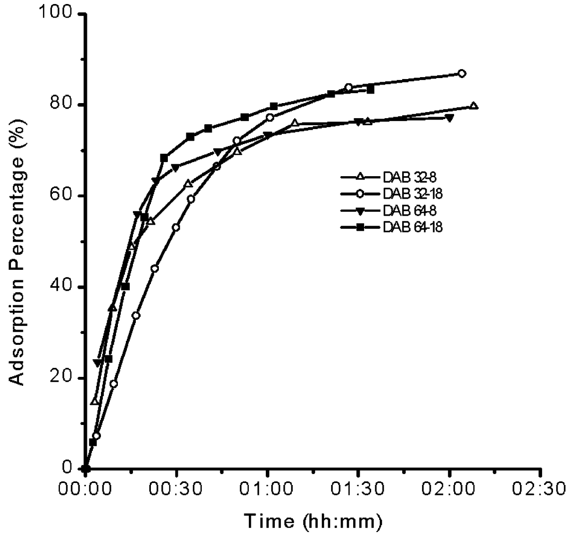

Figure 4. Time dependence of fluoranthene's adsorption percentage by thin films of dendrimeric derivatives.

Table 1. Inclusion Formation Constants *K* (M^{-1}) and Concentrations at Equilibrium EC (ppb) between Polycyclic Aromatic Hydrocarbons and Alkylated Dendrimeric Derivatives

	fluoranthene		phenanthrene		pyrene	
	K	EC	*K*	EC	*K*	EC
octylurea DAB-32	0.4×10^8	5	1.5×10^6	119	0.2×10^8	10
octadecylurea DAB-32	0.2×10^8	10	1.8×10^6	99	1.1×10^8	2
octylurea DAB-64	0.3×10^8	7	1.6×10^6	111	1.3×10^8	2
octadecylurea DAB-64	0.3×10^8	7	1.7×10^6	105	0.9×10^8	2

of the aliphatic chains while octadecyl-substituted dendrimers show a higher adsorption percentage. Furthermore, alkylated derivatives of DAB-32 exhibit a smaller inclusion rate; the entrapment of fluoranthene requires a longer period of time than the other polycyclic aromatic hydrocarbons (PAHs).

Judging from these results, according to which dendrimer generation and length of alkyl chain do not drastically affect the removal of organic contaminants, one is tempted to comment on the solubilization mode of dendrimers. Thus, the inclusion of molecules is determined by the dynamic character of the flexible dendritic chains, which embrace solutes of various sizes and shapes. According to this model, the terminal groups are not only found on the surface but also in the whole volume of the dendrimer.[7,8] This behavior could be an advantage for these polymers as far as their ability to incorporate impurities is concerned since water contaminants of different sizes and shapes can be effectively removed.

Polycyclic aromatic hydrocarbons (PAHs) are solubilized inside dendrimers since they are practically insoluble in water and they are, therefore, in a high-energy state. Thus, their inclusion in the lipophilic environment of these dendrimers is a thermodynamically favorable process. Second, solubilization in the hydrophobic environment is further amplified by the formation of charge-transfer complexes between polyaromatics and the tertiary amino groups.[9]

The inclusion formation constants[10] determined by thin film experiments, as described in the Experimental Section, were of the order of 10^8 M^{-1} for pyrene and fluoranthene (Table 1). The constants are many orders of magnitude higher than those typically reported for activated carbon (from 1.4×10^4 to 3.4×10^5 M^{-1})[11] or cyclodextrins ($10-10^3$ M^{-1})[12] and comparable to those

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[10] According to the equation DAB + PAH $\rightleftharpoons$ [DAB−PAH] the inclusion formation constant is given by the following: K = [DAB−PAH]/{[DAB][PAH]}, where [PAH] is the activity of the polycyclic aromatic hydrocarbon that remained dissolved in water and [DAB−PAH] and [DAB] are the activities of the dendrimer (film) with and without the incorporated pollutant, respectively. The solid film [DAB] has certainly an activity of 1 while the activity of the "complex" [DAB−PAH] was also taken as 1 since it is also the solid film state (by convention the activities of solids are taken as 1 irrespective of the amount of the solid present). The complex is formed by the incorporation of the PAHs in the film. With these assumptions the equation is further simplified as follows: K = 1/[PAH].

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Table 2. Inclusion Formation Free Gibbs Energies (kcal/mol) between Polycyclic Aromatic Hydrocarbons and Alkylated Dendrimeric Derivatives

	fluoranthene	phenanthrene	pyrene
octylurea DAB-32	−10.2	−8.3	−10
octadecylurea DAB-32	−9.8	−8.4	−10.8
octylurea DAB-64	−10	−8.3	−10.9
octadecylurea DAB-64	−10	−8.4	−10.7

for cyclodextrin polymers (from 1×10^8 to 5×10^9).[12] It should be noted that a chemical reaction is considered irreversible when K is of the order of 2×10^9 M^{-1},[12] but in this case it must be taken into account that formation of a conventional chemical bond does not take place. Thus, the formation of the complex in the solid film should be considered as practically irreversible. The inclusion formation constant K of phenanthrene is much smaller, that is, of the order of 1×10^6 M^{-1}. This can be attributed to the higher solubility of phenanthrene in water since phenanthrene is about 1 order of magnitude more soluble in water than fluoranthene or pyrene.[13] This molecule is therefore in a less unfavorable energy state in water and the formation of the inclusion complex is less favored. The same conclusion can be reached if the Gibbs free energies ($\Delta G° = -RT \ln K$) are calculated (Table 2). From these results it is evident that the absorption of the contaminant inside the nanoporous film is a spontaneous process with a driving force, $\Delta G°$, between −8 and −11 kcal/mol, in contrast to other water purification procedures such as reverse osmosis or filtration, which require energy to drive the process to completion.

Finally, to evaluate whether these materials could be promising candidates for water purification, two more parameters should be considered, that is, their maximum inclusion capacities and possible regeneration of the dendrimers. The loading capacities of the alkylated dendrimeric derivatives at saturation have been determined and the results (Table 3) show that dendrimeric polymers have a maximum capacity ranging from 6 to 67 mg of pollutant per g of dendrimer depending mainly on the polycyclic aromatic compound.

Table 3. Loading Capacities (mg/g) of the Alkylated Dendrimeric Derivatives

	fluoranthene	phenanthrene	pyrene
octylurea DAB-32	6	44	34
octadecylurea DAB-32	19	67	57
octylurea DAB-64	12	57	38
octadecylurea DAB-64	12	49	34

In addition, as mentioned above, the inclusion of the PAHs is due to a noncovalent host−guest interaction, which is energetically favored by the high energy of the pollutant when dissolved in water. Therefore, this nonreversible inclusion reaction in water should be reversible in nonpolar organic solvents. Indeed, the binding constants between the dendrimeric derivatives and the pollutants in hexane are 11.2, 11.1, and 10.9 M^{-1} ($\Delta G° \approx 1.4$ kcal/mol) for pyrene, phenanthrene, and fluoranthene, respectively. Thus, films from functional dendrimeric materials can be readily regenerated if washed by the appropriate nonpolar solvent.

Concluding Remarks

Long-chain alkylated dendrimeric derivatives are effective nanosponge materials for the inclusion of toxic polycyclic aromatic compounds dissolved in water. Reduction of the concentration of these contaminants to the level of a few ppb was achieved. The encapsulated pollutants can be effectively removed from the dendrimeric nanosponges by treating them with nonpolar solvents, resulting in the regeneration of the dendrimeric material. Furthermore, these compounds proved to be far more effective than active carbon and the overall process takes place spontaneously, in contrast to reverse osmosis or filtration.

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