

Alkylated Hyperbranched Polymers as Molecular Nanosponges for the Purification of Water from Polycyclic Aromatic Hydrocarbons

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ABSTRACT: A series of hyperbranched polymers functionalized with long aliphatic chains has been prepared and characterized. The property of films prepared from these polymers to encapsulate lipophilic polyaromatic pollutants dissolved in water has been established. The level of pyrene and fluoranthene remaining in water after treatment ranged from 1 to 30 ppb for most of the hyperbranched polymers, while for the relatively more water-soluble phenanthrene a final concentration of about 50 to 70 ppb could be attained. The inclusion formation constants determined for the polycyclic aromatics were 2.0×10^8 – 6.3×10^6 M⁻¹ for pyrene, 1.2×10^7 – 1.6×10^6 M⁻¹ for fluoranthene, and 3.8×10^6 – 4

$\times 10^5$ M⁻¹ for phenanthrene. The loading capacities depend on the nature of the polycyclic aromatic compounds and the chemical structure of the parent hyperbranched polymers, ranging from 6 to 31 mg/g of polymer for fluoranthene, 15–54 mg/g for phenanthrene, and 6–35 mg/g for pyrene. Regeneration of the absorbing films was achieved by their treatment with acetonitrile. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2299–2305, 2005

Key words: hyperbranched polymers; functionalization; water purification; polycyclic aromatic hydrocarbons; structure property relations

INTRODUCTION

Hyperbranched polymers received increasing scientific interest during the last decade¹ due to their diversified molecular architecture and prospective applications. They consist of a central core from which emanates a network of repeating branches ending up in characteristic groups, which form the external surface of the polymeric nanoparticle. The polymerization reactions employed for their synthesis lead to polydisperse polymers of nonsymmetric shape. Their properties depend on the structural characteristics of the central core, the branches, and the surface end-groups. The latter are primarily susceptible to functionalization, affording polymers with diversified, tailor-made properties. The development of hyperbranched polymers is closely following the exploitation of dendrimers since both polymers share applications in the field of drug delivery and controlled release,² solvent extraction,³ liquid crystalline materials,⁴ dyes,⁵ antioxidants,⁶ and electroluminescent materials.⁷

Since hyperbranched polymers bear analogous structural features with dendrimers, which can be regarded as unimolecular micelles⁸ or "nanosponges," their branched network favors and may dynamically induce the formation of nanocavities in which a diversity of molecules can be incorporated. The microenvi-

ronment of the nanocavities depends primarily on the structural characteristics of the repeating units and determines the encapsulation potential of the hyperbranched polymers.

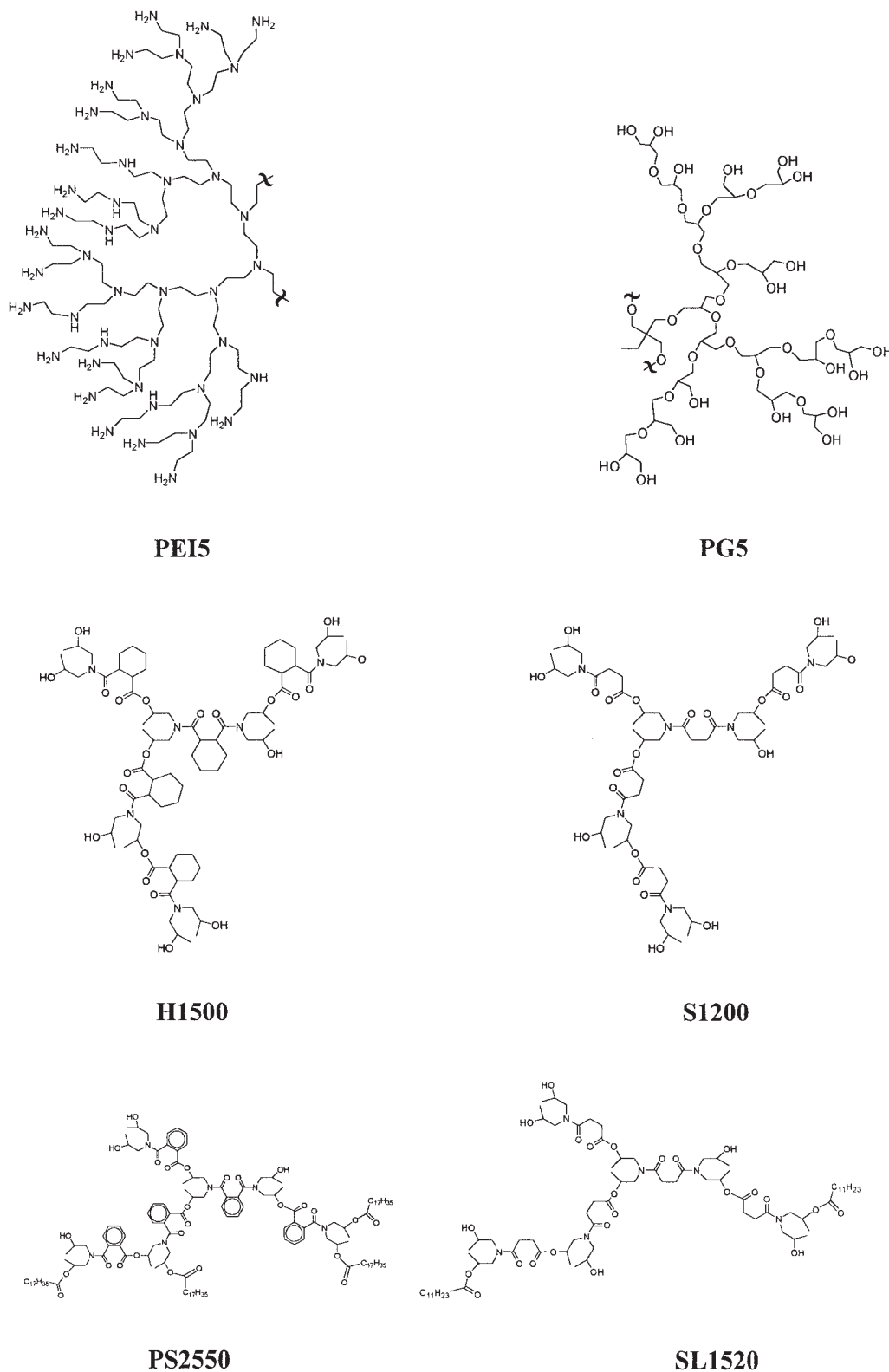
In a recent study,⁹ thin films were formed by solvent evaporation of alkylated diaminobutane poly(propylene imine) dendrimeric (DAB) solutions. These films were subsequently applied to the removal of polycyclic aromatic hydrocarbons (PAHs) contained in water. The pollutants were effectively removed and the films were regenerated. In this connection and aiming at the investigation of analogous properties for the nonsymmetric, low-cost, hyperbranched polymers, this study was undertaken. For this purpose alkylated hyperbranched polymers, originating from poly(ethylene imine), PEI5, polyglycerol, PG5, and hyperbranched polyesteramides,¹⁰ S1200, H1500, PS2550, and SL1520, (Scheme 1) were applied for the removal of polycyclic aromatic hydrocarbons from water. The structural diversity of these hyperbranched polymers determines their nanocavities' microenvironment, which in turn affects encapsulation efficiency and loading capacity, while the presence of aliphatic chains renders them completely insoluble in water.

EXPERIMENTAL

Materials and methods

Poly(ethylene imine), PEI5, (Mn = 5000) and polyglycerol, PG5, (Mn = 5000) hyperbranched polymers

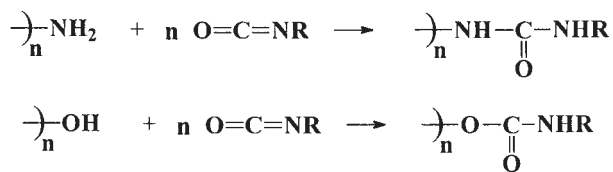
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Scheme 1

were purchased from Hyperpolymers INC. Hyperbranched polyesteramides H1500 ($M_n = 1500$), PS2550 ($M_n = 2500$), S1200 ($M_n = 1200$), and SL1520 ($M_n = 1500$), and poly(propylene imine) dendrimer of the

fifth generation DAB-64 ($MW = 7166$) were purchased from DSM Fine Chemicals Company. Dodecyl and octadecyl isocyanates, phenanthrene, and fluoranthene were purchased from Aldrich and used as re-



Scheme 2 Reactions employed for the synthesis of the alkylated hyperbranched polymers.

ceived. Pyrene (Aldrich) was purified by sublimation followed by recrystallization from ethanol. The concentration of fluoranthene, phenanthrene, and pyrene was determined by fluorescence spectroscopy, employing a Perkin–Elmer LS-5B spectrophotometer following an excitation at 248 nm for phenanthrene, 283 nm for fluoranthene, and 335 nm for pyrene.

General procedure for the preparation of alkylated hyperbranched polymers

The amino and hydroxy groups of PEI5, PG5, and hyperbranched polyesteramides were interacted with long-chain *n*-alkylisocyanates (Scheme 2) for the preparation of fully alkylated, water insoluble derivatives. Thus, to 1 mmol of PEI5, PG5, H1500, S1200, PS2550, or SL1520 dissolved in dry dichloromethane, or pyridine in the case of PG5, a 10% excess of *n*-alkylisocyanate (with chain length 12 or 18 carbon atoms), dissolved in the same solvent, was added drop-wise, under argon, at 0°C in the absence of light. The reaction mixture was kept at this temperature for half an hour and then allowed to reach room temperature, in which it stayed for several hours. The products obtained were precipitated with acetonitrile, separated from the reaction mixture by centrifugation, and dried under vacuum over phosphorus pentoxide affording the alkylated derivatives PEI5-*n* (*n* = 12 or 18), PG5-18, H1500-18, S1200-18, PS2550-18, and SL1520-18. Their chemical structures were established by ¹H and ¹³C NMR. The introduction of long aliphatic chains to all polymers bearing hydroxy or amino terminal groups is established by ¹H and ¹³C NMR spectra (CDCl₃, 250MHz and 62.9 MHz, respectively). Thus, the triplet peak of the methyl group appears at 0.9 ppm while the broad peak at 1.25 ppm corresponds to the methylene groups of the long aliphatic chains. In addition, the peak at 3.25 ppm is attributed to the α-CH₂ relative to the urethane group while the peak at 3.20 ppm is attributed to the α-CH₂ relative to the urea group. In certain cases, the peaks representing the β-CH₂, if not overlapped by the peak at 1.25 ppm, are observed at 1.4 ppm. In the ¹³C NMR spectra, the terminal CH₃ appears at 15 ppm and the CH₂ of the long aliphatic chains between 20 and 30 ppm, while the α-CH₂ and the β-CH₂ appear at 40 and 31 ppm, respectively. The peaks in the ¹³C NMR spectra of the

parent hyperbranched polymers corresponding to the methylenes and methines close to the terminal hydroxy groups are observed at about 60 ppm and 70 ppm, respectively. These are completely absent in the spectra of the products, suggesting completion of the reaction. For PEI5 the peaks at 57 and 40 ppm, representing the β and α methylenes to the external primary amino groups, are replaced by the peaks at 55 and 45 ppm corresponding to the alkylated product. Also, the peaks at 54 ppm (NCH₂CH₂NH) and 41 ppm (HNCH₂CH₂NH₂), related to the methylenes at the vicinity of the secondary NH groups, are replaced by peaks at 47 and 50 ppm, respectively, suggesting that substitution occurs also at the internal secondary amines. The latter is in accordance with what is commonly observed following the reaction of isocyanates with nucleophilic primary and secondary amines.^{11,12}

Determination of absorption rates and inclusion formation constants of alkylated hyperbranched polymers

Slow evaporation of a chloroform solution containing 10 mg of an alkylated hyperbranched polymer resulted in the formation of a thin film covering the walls of a 100 mL round bottom flask. The estimated thickness of the film is approximately 60–70 μm. To these round-bottom flasks, 100 mL of doubly distilled water contaminated with pyrene (100 ppb), phenanthrene (1 ppm), or fluoranthene (200 ppb) were added and agitated for several hours. The so-obtained water was subjected to fluorescence measurements, at regular time intervals, and the absorption of the contaminant was indirectly determined by measuring the concentration of the fluorescent probe in solution. Measurements continued until equilibrium was established. The concentrations at equilibrium were used for the determination of the inclusion formation constants.

Determination of loading capacities of alkylated hyperbranched polymers

To 100 mL round bottom flasks covered by thin films of alkylated hyperbranched polymers (10 mg, estimated thickness of the film approximately 60–70 μm), 50 mL of doubly distilled water containing pyrene (100 ppb), phenanthrene (1 ppm), or fluoranthene (200 ppb) were added. After two hours the concentration of the pollutant still remaining in solution was determined with fluorimetry, and the flasks were emptied and refilled with another 50 mL of contaminated water. This procedure was repeated until no further absorption of the pollutants was observed. In this way saturation of the films was secured. The total quantity of each polycyclic aromatic hydrocarbon loaded was

determined by summing the absorbed pollutant quantities.

Determination of nanocavities' polarity of the nonsubstituted hyperbranched polymers

Thin films of the parent (i.e., nonsubstituted with aliphatic chains) hyperbranched polymers containing pyrene were formed on the surface of round bottom flasks. The flasks were then filled with water and the nonsubstituted hyperbranched polymers incorporating pyrene were allowed to dissolve under agitation for 24 h.

RESULTS AND DISCUSSION

The alkylation of hyperbranched compounds was performed under convenient conditions, facilitated by the accessibility of the amino or hydroxy groups at the external surface of the molecules. Alkylation with long alkyl chain isocyanates renders hyperbranched polymers completely insoluble in water. A crucial requirement of the suitability of these hyperbranched polymers as materials for water purification is to maintain, or even enhance, their solubilizing properties towards lipophilic compounds dissolved in water. Polycyclic aromatic hydrocarbons have in the first place the property to be encapsulated inside hyperbranched polymers because of their insolubility in water, being therefore at a high-energy state. Their inclusion in the lipophilic environment of these polymers is therefore a thermodynamically favorable process. In addition, the presence of tertiary amino groups in PEI5 hyperbranched polymers induces a charge-transfer complexation with PAH.¹³ For testing the encapsulation efficiency of these compounds, inclusion kinetic experiments using the thin film method were performed.

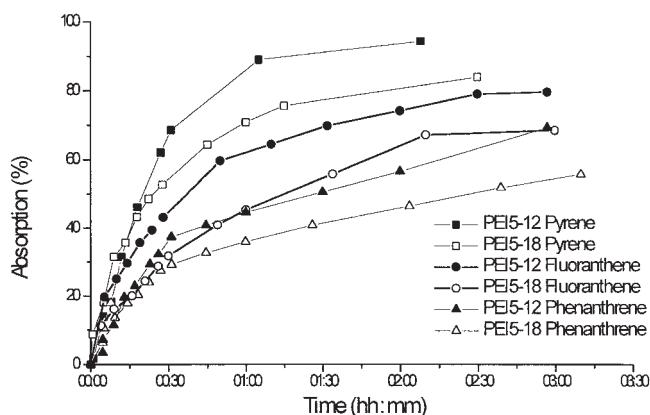


Figure 1 Time dependence of pyrene's, fluoranthene's, and phenanthrene's absorption by thin films of alkylated hyperbranched poly(ethylene imine) polymers (PEI5) bearing 12 and 18 carbon atoms.

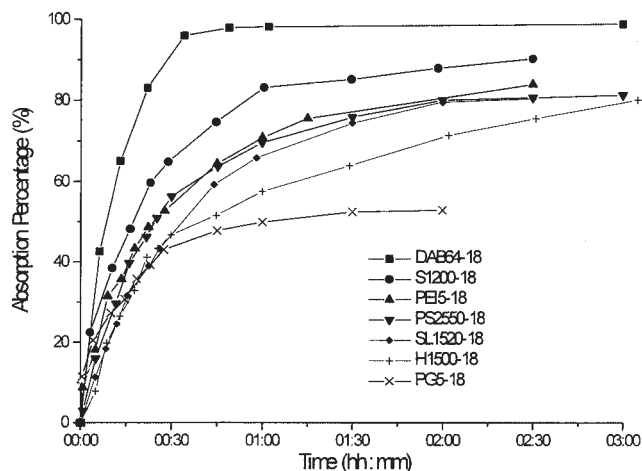


Figure 2 Time dependence of pyrene's adsorption by thin films of alkylated hyperbranched polymers. The corresponding curve for DAB64-18 is plotted for comparison purposes.

For the two PEI5 functionalized derivatives with different aliphatic chain lengths, PEI5-12 and PEI5-18, it was observed that the alkylation of the terminal groups does not prohibit the encapsulation capacity for polycyclic aromatic hydrocarbons as also established for their dendrimeric analogs.⁹ From the results shown in Figure 1, it can be deduced that, in contrast to symmetric dendrimeric analogues, the length of the long aliphatic chains affects considerably the inclusion rate. Derivatives with shorter chains, of 12 carbon atoms, exhibit faster absorption rates.

The absorption rates of pyrene in the structurally different hyperbranched polymers functionalized with an aliphatic chain of 18 carbon atoms are shown in Figure 2. Analogous results were obtained with fluoranthene and phenanthrene. For comparison purposes, the absorption rate of the octadecyl derivative of the fifth generation poly(propylene imine) dendrimer (DAB64-18) is also included.⁹ From these kinetic data the role of the various structural features of hyperbranched polymers affecting the rate of inclusion can be deduced. For all pollutants examined, the symmetrical structure of dendrimers favors fast absorption. Thus, DAB64 alkylated dendrimers exhibit faster absorption rates compared to nonsymmetric analogues, that is, PEI5 alkylated polymers. Encapsulation is therefore a topochemically-affected process.

Another interesting observation is that derivatives of the hyperbranched polymers with flexible branches, that is, having glass transition temperatures below room temperature, exhibit, in general, faster absorption rates than those exhibited by the more rigid ones. Indeed, DAB64 and PEI5 as well as S1200 have low T_g values (-84°C for DAB64, -25°C for PEI, and 20°C for S1200 and SL1520), while on the other hand, H1500 and PS2550 are in a glassy state at room temperature

TABLE I
Inclusion Formation Constants K (M^{-1}) and Concentrations at Equilibrium EC (ppb) Between Polycyclic Aromatic Hydrocarbons and Hyperbranched Derivatives

Hyperbranched derivative	Fluoranthene		Phenanthrene		Pyrene	
	K	EC	K	EC	K	EC
DAB64-18	3.0×10^7	7	1.7×10^6	105	9.0×10^7	2
PEI5-12	1.2×10^7	10	3.8×10^6	47	2.0×10^8	1
PEI5-18	1.0×10^7	20	2.7×10^6	66	2.0×10^8	1
PG5-18	1.6×10^6	126	4.0×10^5	446	6.3×10^6	32
PS2550-18	2.5×10^6	81	1.1×10^6	162	6.7×10^7	3
SL1520-18	1.0×10^7	20	7.1×10^5	251	2.4×10^7	8
S1200-18	4.0×10^6	51	7.0×10^5	253	2.2×10^7	9
H1500-18	4.0×10^6	51	5.6×10^5	318	1.8×10^7	11

($T_g > 40^\circ C$ for H1500 and $> 70^\circ C$ for PS2550). This flexibility favors the formation of adaptable cavities that can be tuned according to the size and shape of the pollutant. Thus, the dynamic character of the flexible dendritic or hyperbranched chains, embracing solutes of various sizes and shapes, induces the encapsulation of pollutants. The flexibility and dynamic character of these dendritic structures are advantageous as far as their ability to incorporate diversified impurities is concerned.

The molecular structure of the parent hyperbranched polymer has also a marked influence on the absorption kinetics. Comparing the octadecyl hyperbranched derivatives of H1500 and PS2550, the presence of aromatic rings inside the cavities of the second one is significantly affecting the absorption rate, apparently due to the higher chemical affinity with the polyaromatic pollutants. On the other hand, the poly(ethylene glycol) hyperbranched derivative, PG5, which has a very hydrophilic chemical structure, leads to low absorption kinetics as well as inclusion formation constants (see below).

The inclusion formation constant K , determined⁹ by thin film experiments, was of the order of 10^8 – $10^6 M^{-1}$ for pyrene and 10^7 – $10^6 M^{-1}$ for fluoranthene (Table I). The constants were many orders of magnitude higher than those typically reported for activated carbon (1.4×10^4 – $3.4 \times 10^5 M^{-1}$)¹⁴ or cyclodextrins (10 – $10^3 M^{-1}$)¹⁵ and comparable to those for cyclodextrin polymers (1×10^8 – 5×10^9).¹⁵ Thus, the formation of the complex in water should be considered as practically irreversible. The inclusion formation constant K of phenanthrene is much lower, that is, of the order of 10^6 – $10^5 M^{-1}$. This can be attributed to the higher solubility of phenanthrene in water since phenanthrene is about one order of magnitude more soluble in water than fluoranthene or pyrene.¹⁶ This molecule is, therefore, in a less unfavorable energy state in water, and the formation of the inclusion complex is not favored. The same conclusion can be reached if the Gibbs free energies ($\Delta G^0 = -RT \ln K$) are calculated (Table II). From these results it becomes evident that the absorp-

tion of the contaminant inside the film is a spontaneous process with a driving force, ΔG^0 , between -7.5 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.

According to our results with these hyperbranched polymers, in most of the cases, the inclusion formation constants were comparable to the ones measured for dendrimeric molecules.⁹ This is very encouraging since hyperbranched compounds are easily prepared, low-cost dendritic analogues, making therefore favorable their application. In addition, it was found that for all the hyperbranched compounds $K_{\text{pyrene}} > K_{\text{fluoranthene}} > K_{\text{phenanthrene}}$. This is in accordance with the order of decreasing solubility in water of these polycyclic aromatics, establishing the validity of the argument that the main driving force behind the inclusion process is the Gibbs free energy obtained for stabilizing the polycyclic aromatic hydrocarbons inside the lipophilic cavities.

Interestingly, the above-mentioned similarity between inclusion formation constants of several hyperbranched compounds to those measured for dendrimeric derivatives is observed despite the fact that the hyperbranched polymers possess more open structures than the dendrimers. In other words, the cavities

TABLE II
Inclusion Formation Gibbs Free Energies (kcal/mol) Between Polycyclic Aromatic Hydrocarbons and Hyperbranched Derivatives

Hyperbranched derivative	Fluoranthene ΔG^0	Phenanthrene ΔG^0	Pyrene ΔG^0
PEI5-12	-9.8	-8.8	-10.9
PEI5-18	-9.4	-8.6	-10.9
PG5-18	-8.3	-7.5	-9.1
PS2550-18	-8.6	-8.1	-10.5
SL1520-18	-9.4	-7.8	-9.9
S1200-18	-8.9	-8.0	-10.0
H1500-18	-8.9	-7.7	-9.7

TABLE III
 I_1/I_3 Ratio of the Principal Vibronic Bands of Pyrene Encapsulated in Dendrimeric and Hyperbranched Polymers

Hyperbranched polymer	I_1/I_3
DAB64	1.41
PEI5	1.37
PG5	1.61
S1200	1.56
H1500	1.47

are not fully developed. An explanation that can be provided is the solid nature of the absorbing material. For the solid absorbent polymeric thin films, inclusion formation constants are independent of the concentration of the dendrimeric or hyperbranched compound, which is taken as unity. Thus, inclusion constants are independent of the number of available absorption sites because these constants have been determined far below the saturation level. The factors that seem to critically affect the inclusion formation constants are the stability of the pollutant into the cavity and the Gibbs free energy for the inclusion process.

To further study and predict the key factors affecting inclusion formation constants, the polarity of the interior of the hyperbranched polymers was investigated. Fluorescence measurements of pyrene encapsulated in the parent, nonsubstituted hyperbranched polymers were performed, and the I_1/I_3 ratio of the first and third principal vibronic band intensities of pyrene was determined (Table III); this ratio is related to the polarity of the environment in which pyrene is solubilized.¹⁷ The corresponding ratio of pyrene in DAB64 is included for comparison purposes. A comparison of the data in Table III indicates that the polarities of DAB64 and PEI5 are roughly the same. This is expected since both polymers have similar structures, explaining also the fact that DAB64 and PEI5 derivatives exhibit about the same K and ΔG values. In addition, PG5 nanocavities exhibit the highest I_1/I_3 ratio as a result of their polar poly(ethylene

TABLE IV
 Loading Capacities (mg/gr) of the Alkylated Hyperbranched Derivatives

Hyperbranched derivative	Fluoranthene	Phenanthrene	Pyrene
PEI5-12	31	44	20
PEI5-18	21	44	11
PG5-18	6	15	8
PS2550-18	24	54	35
SL1520-18	21	35	19
S1200-18	11	14	6
H1500-18	12	15	20

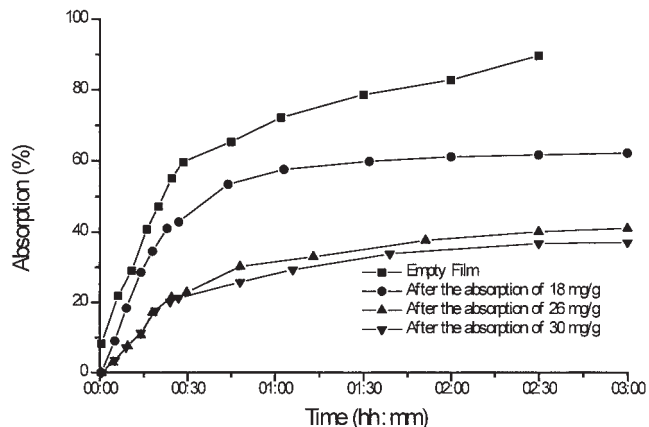


Figure 3 Absorption kinetics of PEI5-12 film, empty and gradually filled with fluoranthene.

glycol) environment. The low K and ΔG values of the inclusion process exhibited by this polymer are therefore rationalized. Although the inclusion of polycyclic aromatic hydrocarbons in PG5 derivatives is clearly inadequate, there is possibly the potential of incorporating polar pollutants inside their nanocavities. The derivatives of S1200 and H1500 that exhibit intermediate I_1/I_3 values also show intermediate inclusion formation constants. Furthermore, as already discussed for inclusion kinetics experiments, the chemical compatibility between the interior of hyperbranched polymers and the pollutants positively affects inclusion constants. Comparing the results (Table II) obtained for PS2550-18, which bears phenyl groups in the interior, with H1500-18, S1200-18, and SL1520-18, which have a similar structure but no phenyl groups, it is clear that the former exhibits higher inclusion formation constants for phenanthrene and pyrene. This does not, however, apply for fluoranthene, possibly due to its shape, which may not fit properly into the nonflexible cavity of PS2550.

For evaluating the applicability of these polymers as water purification materials, two more parameters should be considered, that is, their maximum loading

TABLE V
 Desorption Gibbs Free Energies (kcal/mol) in Acetonitrile of Pyrene Absorbed in Hyperbranched Polymers

Hyperbranched derivative	ΔG^0 (Kcal/mol)
PEI5-12	-2.6
PEI5-18	-2.6
PG5-18	-1.7
PS2550-18	-2.5
SL1520-18	-2.5
S1200-18	-2.1
H1500-18	-2.4

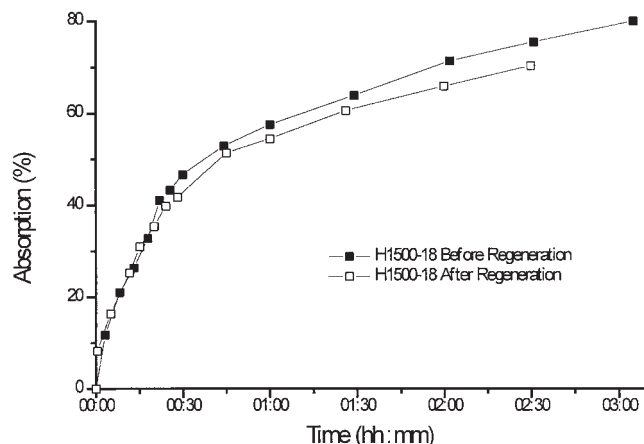


Figure 4 Time dependence of pyrene's adsorption by thin films of alkylated hyperbranched polymer H1500-18 before and after regeneration.

capacity and the possibility of regenerating saturated materials. The loading capacities of the alkylated hyperbranched polymers at saturation have been determined, and the results (Table IV) show that alkylated hyperbranched polymers have a maximum capacity, ranging from 6 to 54 mg of pollutant per g of polymer depending mainly on the polycyclic aromatic compound. During the encapsulation process of the pollutants in thin films' nanocavities, inclusion rate was monitored and found to be decreasing as the quantity of the absorbed polycyclic aromatic hydrocarbon was increasing. This is depicted for PEI5-12 absorbing fluoranthene in Figure 3.

Furthermore, as mentioned above, the inclusion of the polycyclic aromatic compounds is 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 can be reversed in less polar organic solvents. Thin films loaded with pyrene were regenerated with acetonitrile, and the calculated ΔG° (Table V) indicates that regeneration is a spontaneous exothermic process. The polymers with the most hydrophilic cavities exhibited the smallest ΔG° values, as expected. It should be noted that after regeneration, inclusion proceeds at a slightly lower rate (Figure 4).

CONCLUSIONS

Alkylated hyperbranched polymers are easily prepared and exhibit "nanosponge" properties. They can encapsulate toxic polycyclic aromatic compounds dissolved in water and they are, therefore, promising

systems for water purification. They are alternatives of the expensive, symmetric dendrimeric compounds prepared by a multi-step process. Reduction of the concentration of polycyclic aromatic hydrocarbons in water to the level of a few ppb was achieved. Structural features, such as symmetry of the polymers, flexibility of their branches, intermolecular interactions, and chemical compatibility between the pollutants and the chemical moieties of the nanocavities, are the parameters determining encapsulation capability. The encapsulated pollutants are effectively removed from the hyperbranched nanosponges by treating the saturated materials with organic solvents; they are therefore regenerated. 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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