Hydrophobically modified poly(amidoamine) (PAMAM) dendrimers: their properties at the air–water interface and use as nanoscopic container molecules

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Tri- and tetra-dendron poly(amidoamine) (PAMAM) dendrimers were converted into hydrocarbon-soluble polymers and used as hydrophobic nanoscopic scaffolding by reacting their primary amino chain ends with various epoxyalkanes. These hydrophobically modified modules performed well as nanoscopic transport molecules. They mimicked classical inverse micelle behaviour by transporting copper(II) sulfate from an aqueous solution into an organic phase to form homogeneous, transparent, intensely blue toluene solutions. The modified dendrimers were examined at the air–water interface both with and without copper guest molecules. A number of critical macromolecular design parameters (CMDPs) such as generation (size), core (shape, topology) and surface groups were varied to determine their influence on Langmuir film properties.

Nanostructures are macromolecular assemblies containing from 10^3 to 10^9 atoms with molecular masses of 10^3 to 10^{10} Da. Their dimensions vary from 1 to 10^2 nm. These nanodimensions and masses have very broad implications in such traditional disciplines as polymer science,[1a–b] catalysis,[2] interfacial/colloid science,[3] supramolecular chemistry,[4] electronic microfabrication[5a–b] and molecular biology.[6] It is quite apparent that the development of viable synthetic and characterization methodology which will allow systematic examination of 'structure-controlled nanostructures' would be of significance to these evolving areas.[7–9] For that reason, considerable international interest has focused on these objectives.

Synthetic polymer chemists routinely produce nano-structures as part of a statistical macromolecular product continuum which is associated with most classical covalent polymerization methodology. The major shortcoming of these approaches is the inability to readily isolate precise macromolecular structures or control critical macromolecular design parameters (CMDPs) such as: (*a*) size, (*b*) shape, (*c*) surface chemistry and (*d*) topology. On the other hand, nature solved this problem some 4.5 billion years ago during a critical phase in our natural molecular evolution from atoms to very complex molecular structure. The reproducible synthesis of proteins, DNA, RNA and bio-assemblies possessing precise CMDP controlled features are prime examples of this success.

Using strictly abiotic synthetic methods, it has been widely demonstrated over the past decade that dendrons, dendrimers[10–13] and more recently dendrigrafts[3,14] can be routinely

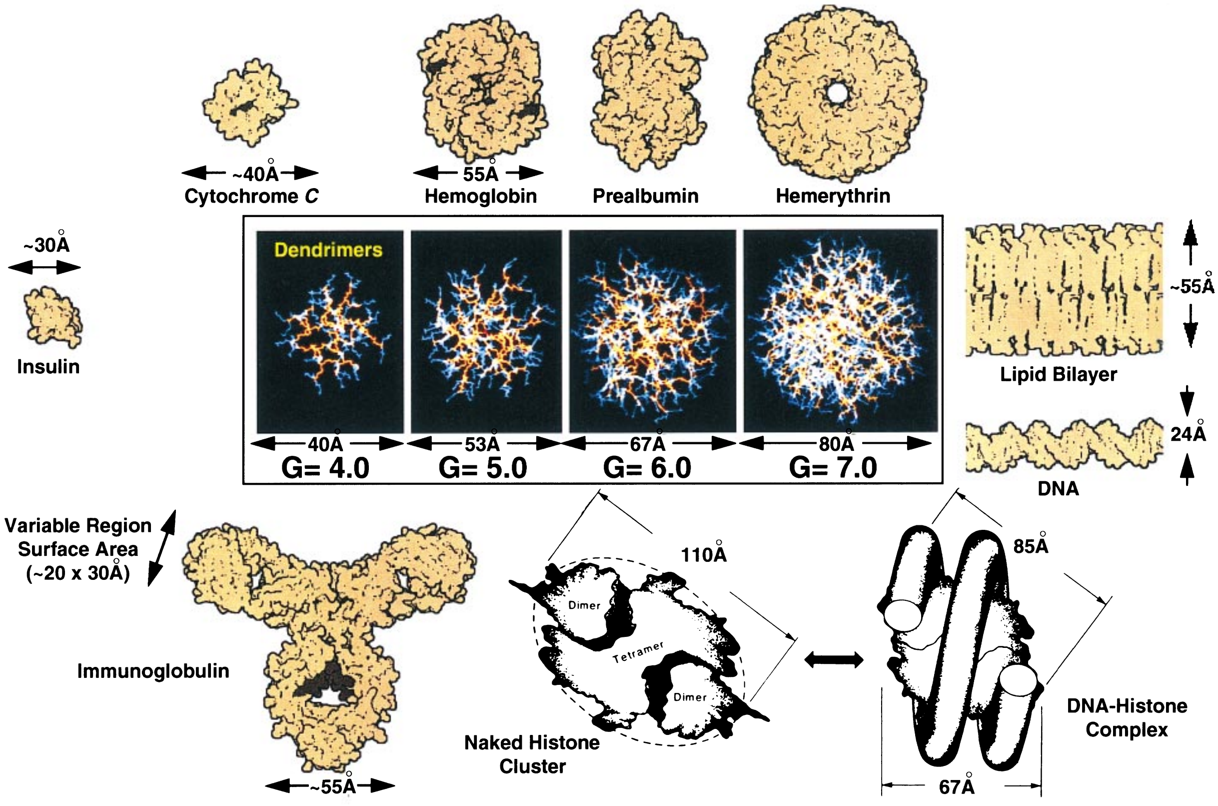


Plate 1 Scaled comparison of tri-dendron (NH_3 core) poly(amidoamine) dendrimers; generation = 4–7, sizes and shapes with various proteins, DNA and bio-assemblies

constructed with CMDP control that rivals the structural regulation found in biological systems. A comparison of various nanoscopic biostructures with tri-dendron poly(amidoamine) (PAMAM) dendrimers clearly illustrates the close scaling of size and shape that is possible (see Plate 1).

The ability to prepare well-defined dendrons and dendrimers[15] leads to the concept of using these materials as fundamental nanoscopic building blocks, suitable for the construction of nanoscopic compounds[16a,b] and other complex assemblies. More recently, these dendritic materials have been identified as nanoscopic scaffolding for catalysis,[17,18] gene vectors,[19–21] magnetic resonance imaging agents,[22] electron conduction,[23] photon transduction,[24a–b] as well as nanoscopic host compartments or 'unimolecular regular micelle mimics' suitable for the containment of pharmaceuticals, agrochemicals, dyes and other guest molecules.[25a–c,32,48]

In this paper, we describe the facile conversion of amine terminated hydrophobic poly(amidoamine) dendrimers into 'unimolecular inverse micelle' modules by surface modification with hydrophobic epoxy reagents. We use the term 'unimolecular inverse micelle' to differentiate these covalently fixed macromolecular structures from the dynamic equilibrium structure of a 'classic' inverse micelle. The resulting hydrocarbon-soluble assemblies functioned as nanoscopically sized container molecules as evidenced by the transport of copper(II) salts into various hydrocarbon solvents. In this fashion, transparent, intensely blue toluene and chloroform solutions were formed. In order to understand better the phase transfer properties of these non-classical micelles, both tri- and tetra-dendron dendrimers were examined with and without copper(II) guest molecules as Langmuir films at the air–water interface.

Experimental

General procedures

The ^{13}C (75.4 or 90.5 MHz) NMR spectra were recorded on either a Varian Unity 300 or a Bruker WM360 SF spectrometer. The ^{13}C NMR spectra were recorded in $CDCl_3$ using the solvent line as the standard (77 ppm) or in D_2O using 1,4-dioxane as an internal standard (66.3 ppm). Electrospray ionization mass spectroscopy was obtained using a Finnigan TSQ-700 spectrometer. The spectra were deconvoluted using the BIOMASS software. Visible spectra were recorded on a Varian Cary 1 spectrometer using matched cells with pure solvent in the reference beam. The PAMAM dendrimers were prepared as previously described.[26a–c] The conditions used to prepare the PAMAM dendrimers employed reaction stoichiometries and rigorous purification procedures which minimize both intramolecular (missing repeat units, intramolecular loops) and intermolecular (dimers, lower generation dendrimers) defects that have been described and characterized previously.[27] The intramolecular defects contained in these samples can be thought of as 'quantized' coproducts, since they are exact multiples of the molecular mass of the desired structure. This is in contrast to defects found in conventional polymers which cover a broad Gaussian distribution, even in the case of polymers prepared by living polymerization techniques. The epoxyalkanes [1,2-epoxyhexane (99%), 1,2-epoxyoctane (99.9%), 1,2-epoxydecane (99.9%) and 1,2-epoxydodecane (99.9%)] were purchased from either Lancaster or Aldrich. Methyl acrylate (99.9%), 1,4-diaminobutane (99.9%), 1,8-diaminooctane (99.9%), and 1,12-diaminododecane (99.9%) were all purchased from Aldrich. Ethylenediamine was received from Fisher and distilled before use.

Surface modification of PAMAM dendrimers

Modification of generation 2, PAMAM dendrimers, ammonia core, $G2(NH_3)$, with 1,2-epoxyhexane is representative of the general method used to prepare hydrophobically modified dendrimers: a $G2(NH_3)$ dendrimer (0.25 g, 2.5 mmol) was dissolved in 10 ml of methanol and 0.35 g (4.0 mmol) of 1,2-epoxyhexane was added. The reaction solution was heated for five days at 40 °C. Additional methanol was added to the reaction solution to give a final dendrimer concentration of 5 mass%, followed by filtering through a 0.2 micron Teflon filter. This solution was ultrafiltered using a flatstock Amicon unit employing a YM3 membrane with a MWCO of 1000. Fourteen recirculations were required to completely remove the excess epoxide. Methanol was removed by rotoevaporation and the dendrimer was dried at room temperature under vacuum to give 0.37 g (80% yield) of modified product. d_c ($CDCl_3$): 172.6–172.9 (m), 69.8, 68.1, 67.8, 67.7, 64.3, 61.9, 56.6, 55.2, 54.9, 52.3, 50.0, 49.1, 38.5, 37.5, 37.2, 34.6, 34.3, 33.7, 33.2, 27.8, 27.7, 22.6, and 13.9. ESI–MS: theoretical $M_W = 4817$; observed $M_W = 4818.5$ (MH^+).

Copper(II) transport studies—'blue toluene-chloroform experiments'

A 3.9 mass% solution of epoxydecane-functionalized G4-(EDA) C_{10} PAMAM dendrimer in toluene was carefully layered on top of a 0.1 M $CuSO_4$ solution. After standing for several hours at room temperature, a dark-blue colour emerged above the aqueous–organic interface. The experiment was continued for several days over which time the toluene solution assumed a very intense, transparent blue colour.

Copper(II)-containing hydrophobically modified dendrimers for Langmuir film studies were prepared by the following procedure: an 1,2-epoxyoctane-modified $G5(NH_3)$ C_8 PAMAM dendrimer (0.30 g) was dissolved in 2 ml of chloroform, and aqueous copper sulfate (30 mg in 2 ml water) was placed on top of the chloroform solution. The mixture was agitated on an orbital shaker for 24 h. After that time, no blue copper colour remained in the aqueous phase. The aqueous phase was decanted and the blue chloroform solution was dried with anhydrous sodium sulfate. Filtration and removal of the solvent by distillation *in vacuo* gave 0.24 g of a blue oil: d_c ($CDCl_3$): 173, 69, 51, 35, 32.0, 29.7, 25.8, 22.8, 14.2.

Over the time frame of these experiments (*ca.* one month), there was no indication that the incorporation of copper ions into these dendrimers resulted in degradation of the dendrimer structure.

Monolayer studies

A Lauda FW-2 film balance was used to examine the properties of the dendrimer monolayers. Distilled water from a Millipore system (18 MV) was used as the subphase and maintained at 23 °C. Millimolar solutions of the dendrimers were prepared in $CHCl_3$. In a typical experiment, dilute dendrimer solutions were added dropwise to the top of the subphase, while the solvent was allowed to evaporate before another drop was added. This procedure was repeated until all the solution was delivered. In order to ensure that residual solvent was not present, dendrimer was equilibrated for 10–20 min before the experiment was initiated. Surface pressure *vs.* area isotherms were measured at a compression rate of 25–30 cm^2 min^{-1}. The limiting areas reported in this paper are an average of at least three measurements.

Results and Discussion

Hydrophobic modification of dendrimers

Perhaps one of the unique features of dendrimeric architecture, compared to classical random coil polymers, is the large number of well-defined chain ends. Several studies have shown that changing the chemical nature of the surface groups can dramatically affect the physical properties of these polymers. For example, Fréchet and co-workers have shown that poly-

(ether) dendrimers can be transformed from organic solvent-soluble polymers to water-soluble materials by a simple surface group transformation.[28a–b] It is important to note that other physical properties such as glass transitions are also influenced by the nature of the surface groups.[29a–b] Critical architectural components of the dendrimers such as the nature of the surface groups/chemistry, repeat unit composition and degree of branching all undoubtedly influence their physical properties and hence many of their eventual applications. At this point, the interplay between these parameters is not totally understood.

In this study, we focused on the surface modification of water-soluble, amine-terminated PAMAM dendrimers to form 'unimolecular inverse micelle' prototypes which would be soluble in organic solvents such as toluene or chloroform. This transformation was easily accomplished by reacting the PAMAM dendrimer's terminal primary amino groups with a variety of hydrophobic epoxyalkanes. These reactions were typically run in methanol, although modifications employing long chain epoxyalkanes, such as 1,2-epoxydodecane, required the addition of a cosolvent (toluene) to maintain homogeneous reaction conditions. We found the reaction could be run either with an excess of epoxide, which was then removed through ultrafiltration of the product, or by simply utilizing stoichiometric amounts of the epoxide. By either method, we saw no indication that an 'all or nothing' distribution of modified and unmodified dendrimers formed, as has recently been reported by Meijer and co-workers for the reaction of alkyl acid chlorides with POPAM dendrimers.[30] Even in experimental runs where sub-stoichiometric quantities of epoxyalkane were used, only a modified product with a statistical distribution of surface alkyl groups centred around the stoichiometric value calculated for the reaction was observed.[31] The products were characterized by ^{13}C NMR spectroscopy, and for the low molecular mass products, electrospray ionization mass spectroscopy was also used.[27b–c]

Transport of copper(II) salts into an organic solvent to form 'blue toluene'

The ability to use dendrimers as container molecules has continued to excite wide scientific interest. Encapsulation of guest molecules into the interior of dendrimer hosts was first demonstrated by the incorporation of acetylsalicylic acid or 2,4-dichlorophenoxyacetic acid into ester-terminated PAMAM dendrimers as early as 1989.[32] We have referred to this phenomenon as 'unimolecular encapsulation.'[33] As an elegant continuation and expansion of this theme, Meijer and co-workers have described a so-called 'dendrimer box' phenomenon.[25] It involves the trapping of certain guest molecules in the interior void spaces by post reaction with bulky surface group reagents.

Dendritic micellar behaviour has been demonstrated on numerous occasions by the dissolution of organic molecules in dendrimers[34a–e] or by the polymerization of water-insoluble monomers in the interiors of carboxy-terminated dendrimers to form novel linear-dendritic composites.[35] On the other hand, some dendrimers have been employed as micellar structures in electrokinetic capillary chromatography.[34f,h] Considerable experimental and characterization work by Turro *et al.*[36–39] has unequivocally demonstrated the 'unimolecular micelle' features of dendrimers. In all of these cases, dendrimers are regarded as regular unimolecular micelles, which consist of a non-polar core and a polar outer shell.

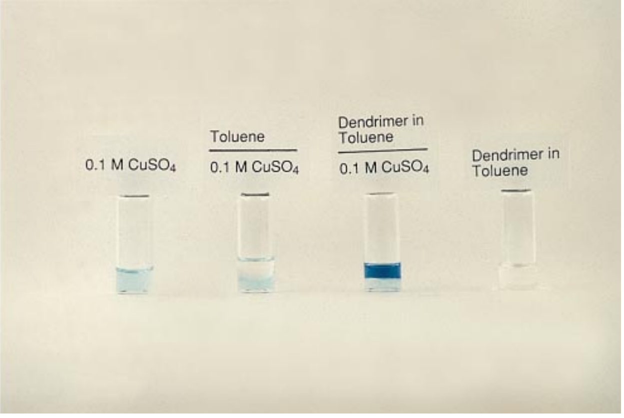


Plate 2

Evidence that modified PAMAM dendrimers behaved as unimolecular inverse micelles, and that the interior space of the dendrimer remains functionally active was clearly demonstrated by the following experiment: a G4(EDA) PAMAM dendrimer which was obtained from the exhaustive reaction of amine-terminated dendrimer with 1,2-epoxyoctane was dissolved in toluene to form a clear solution. This solution was layered on a 0.1 M aqueous $CuSO_4$ solution. During this quiescent experiment, a gradient of a dark-blue colour slowly diffused up from the organic–aqueous interface into the toluene layer. After a period of several days, the entire organic layer took on a dark-blue colour (see Plate 2). As expected, control experiments showed that copper ions were not transported into the organic phase in the absence of dendrimer. Fig. 1 compares the UV–VIS spectrum of the blue toluene layer with that of the starting aqueous $CuSO_4$ solution. The blue-shift of the absorption maximum in the visible region is characteristic of copper coordinated by amine ligands,[40] which in this case could only come from the interior of the dendrimer. The ability of the interior of a dendrimer to coordinate copper ions has been extensively probed recently by EPR spectroscopy.[41] This example clearly shows that the dendrimer acts as a covalently fixed phase transfer agent, with sufficient interaction at the interface between the organic and aqueous solution to allow the interior of the dendrimer to coordinate copper ions. Further studies will be needed to determine the potentially complex solution structure of these dendrimer unimolecular inverse micelles.

Characterization of dendrimer monolayers at the air–water interface

Properties of synthetic polymers at the air–water interface have been studied for many years.[42a–b] Generally, polymers have the ability to act as amphiphiles either through the interaction of polar groups on the chain of the polymer,[43] through the special construction of block/star polymers consisting of both hydrophilic and hydrophobic chains,[44a–b] or by preparing polymer surfactants with hydrophilic chain ends.[45]

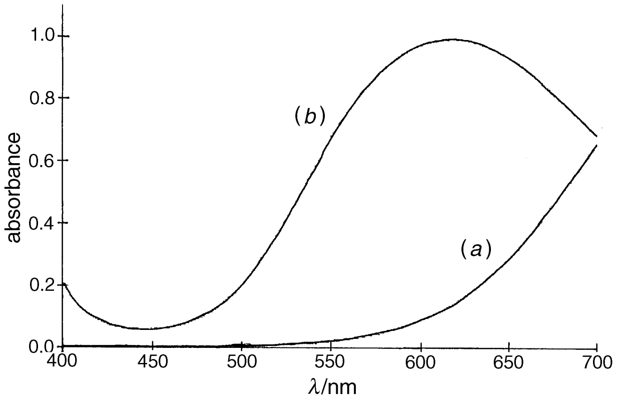


Fig. 1 Visible spectrum of (*a*) an aqueous 0.1 M $CuSO_4$ solution and (*b*) the complex formed between an epoxydecane-modified G4 (EDA) PAMAM dendrimer and $CuSO_4$ in toluene

Polymers that have no amphiphilic character at all can still form films at the air–water interface.[46] Recently, first reports of the properties and structure of poly(ether) dendrimers at the air–water interface were published.[47a–b] Only dendrons of generation 4 and below, with hydroxy groups at the focal point, were found to act as surfactant-like molecules, while the higher generation dendrons and all the poly(ether) tri-dendron dendrimers above generation 1 did not act as surfactant-like polymers or show the ability to form multilayer structures.

For these experiments, PAMAM dendrimers, prepared from both ammonia and various alkylenediamine core molecules, were exhaustively modified with several epoxyalkanes. These cores are illustrated in Scheme 1. The modified dendrimer samples were carefully placed on the water surface of a Langmuir trough as dilute chloroform solutions. In order to ensure total removal of the solvent, the dendrimer was equilibrated at the interface for 10–20 min. A typical isotherm obtained for all of the hydrophobically modified dendrimers we investigated is shown in Fig. 2. As the area available to the molecules decreases, the surface pressure increases until a plateau is reached. Decreasing the area available to the dendrimers beyond this point presumably causes the monolayer film to collapse and form multilayer structures, while the surface pressure remains constant upon further compression. This response is quite different from that observed by Fréchet for poly(ether) dendrimers,[47a–b] where a nucleation phenomenon was observed for the low generation dendrons. The general shape of the isotherms was shown not to be dependent on the compression rate. The isotherms were found to be reversible, with only slight changes in the collapse pressure, as long as the surface pressure applied to the film remained below the collapse point. Addition of sulfuric acid to the subphase (pH = 2) did not strongly affect the shape of the isotherms, although the collapse pressure increased 10–15%.

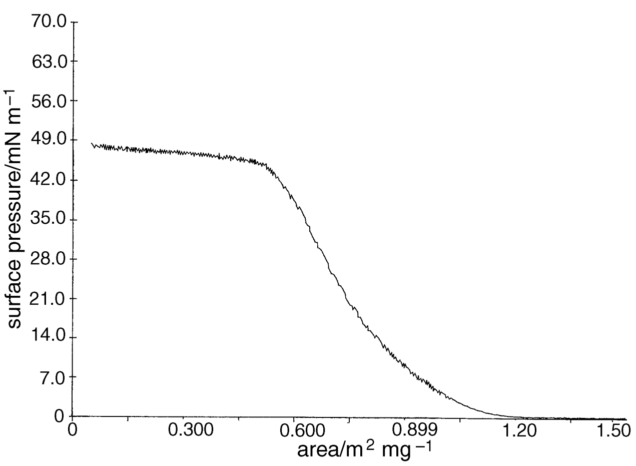
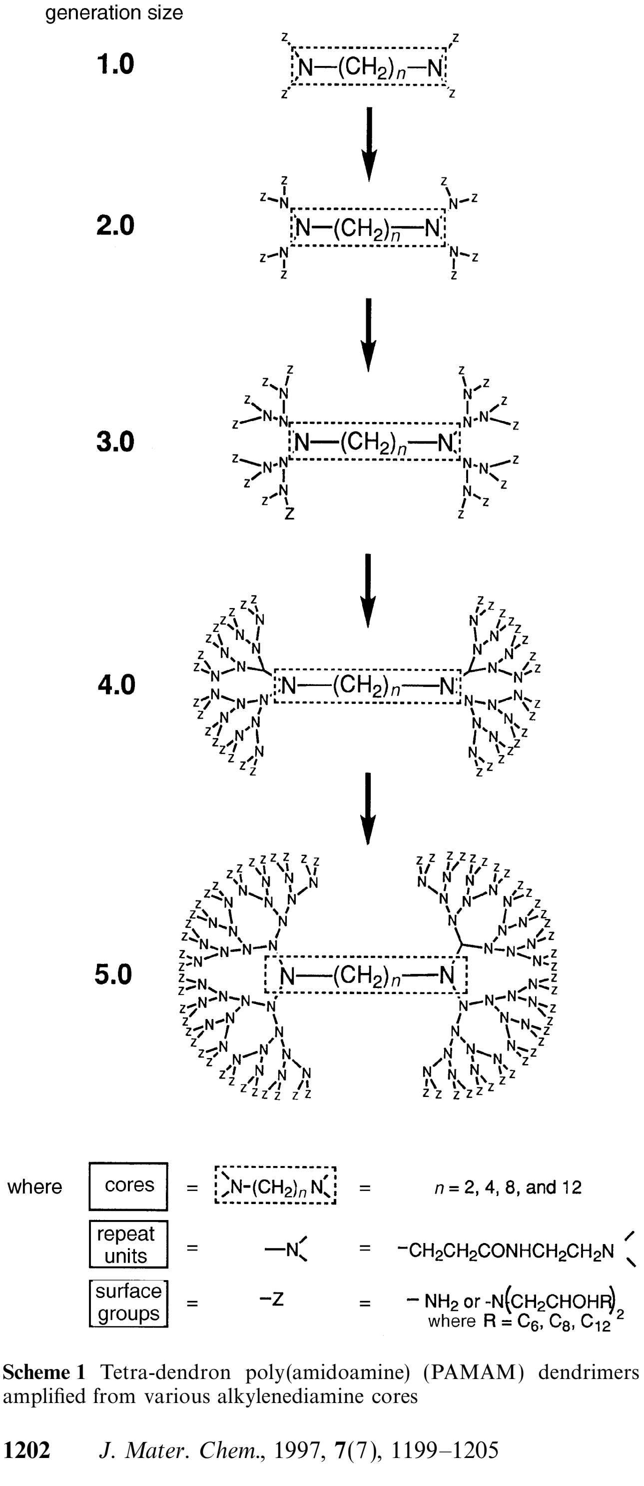


Fig. 2 Langmuir isotherm of a G3(EDA) C_8 PAMAM dendrimer modified with epoxyoctane



Scheme 1 Tetra-dendron poly(amidoamine) (PAMAM) dendrimers amplified from various alkylenediamine cores

One of our goals was to examine the effect of certain critical macromolecular design parameters, such as the core type (multiplicity of branching sites and size of the core), the nature of the surface groups (length of the alkyl chain) and the dendrimer generation (size), in influencing the Langmuir film data. For these experiments, the area occupied per dendrimer molecule was calculated by extrapolating to the x-axis from the point where the collapse curve and the linear region of the increasing pressure part of the isotherm meet. The dendrimers were assumed to be spherical molecules for these calculations.

Table 1 summarizes the isotherm data for three surface modifications and five cores over a range of dendrimer generations. In Fig. 3 the surface radii obtained from the Langmuir data for the epoxyoctane-substituted PAMAM dendrimers are compared to the hydrodynamic radii of unsubstituted ammonia core dendrimers as determined by size exclusion chromatography (SEC).[15b] In general, the agreement is very good. The experimental areas determined from the isotherms increased as a function of generation. It is only at the highest generations that diameters determined from the isotherms differs significantly from the SEC data. Changing the hydrocarbon length on the dendrimer surface does not appear to have a significant effect on the surface area occupied by the dendrimer at the collapse point (Fig. 4). Even at the highest generation studied (generation 5), the limiting surface areas were all the same within the experimental errors associated with the measurements.

We also examined the effect of the core length and multiplicity on the isotherm. Fig. 5 shows the surface area plotted *vs.* dendrimer generation for ammonia and ethylenediamine (EDA) core dendrimers. Both EDA and alkylenediamine core dendrimers build molecular mass 25% faster than dendrimers based on ammonia, since tetravalent cores produce tetradendron dendrimers, while ammonia core leads to tri-dendron

Table 1 Dendrimer isotherm data[a]

sample	surface area/ Å^2 per molecule	sample	surface area/ Å^2 per molecule
G0(NH$_3$) C$_8$	154	G2(EDA) C$_6$	727
G1NH$_3$) C$_8$	284	G2(EDA) C$_8$	877
G2(NH$_3$) C$_8$	756	G2(EDA) C$_{12}$	798
G2(NH$_3$) C$_{12}$	702	G3(EDA) C$_6$	1249
G3(NH$_3$) C$_8$	1211	G3(EDA) C$_8$	1344
G3(NH$_3$) C$_{12}$	1147	G3(EDA) C$_{12}$	1233
G4(NH$_3$) C$_8$	2804	G4(EDA) C$_6$	2363
G4(NH$_3$) C$_{12}$	2848	G4(EDA) C$_8$	2620
G5(NH$_3$) C$_8$	4369	G4(EDA) C$_{12}$	3243
G5(NH$_3$) C$_{12}$	4742	G5(EDA) C$_6$	5779
G2(Butane) C$_{12}$	944	G5(EDA) C$_8$	6449
G2(Octane) C$_{12}$	889	G5(EDA) C$_{12}$	5733
G2(Dodecane) C$_{12}$	871		

[a] *Nomenclature:* the following nomenclature is used to describe the dendrimers prepared for this study. A fifth generation PAMAM dendrimer grown from an ethylenediamine core and modified with 1,2-epoxyhexane is noted as G5(EDA) C$_6$.

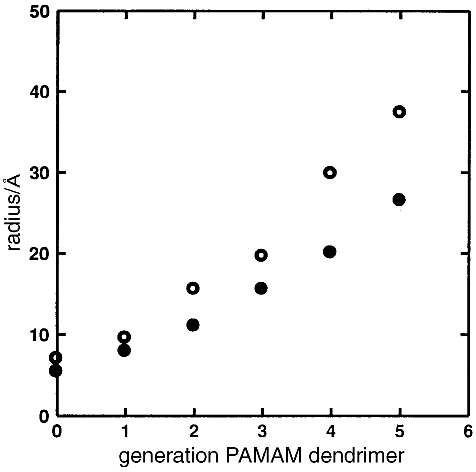


Fig. 3 Comparison of the radii of various generations of PAMAM dendrimers prepared from ammonia cores determined by size exclusion chromatography for the unmodified dendrimers ($) and by the limiting area measurements obtained from the Langmuir film studies for the epoxyoctane-modified dendrimers (#)

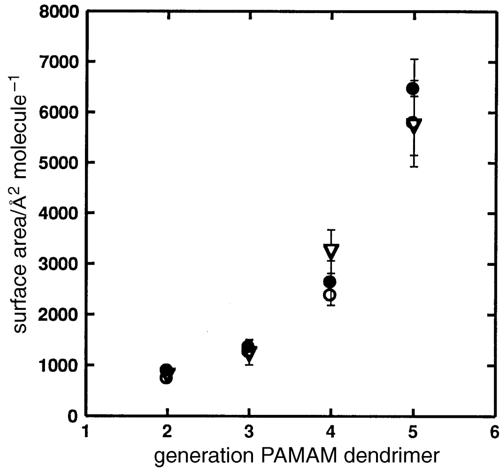


Fig. 4 Plot of surface area *vs.* generation number for PAMAM dendrimers grown from EDA cores and substituted with epoxyhexane (#), epoxyoctane ($) and epoxydecane (( )

dendrimers. There was no significant difference in the limiting surface areas obtained by comparing the two types of cores for generations 2–4. At generation 5, Fig. 6 shows that dendrimers based on EDA cores have a surface area at collapse 20–47% larger than that obtained for the ammonia core dendrimers depending on the length of the surface alkyl chain.

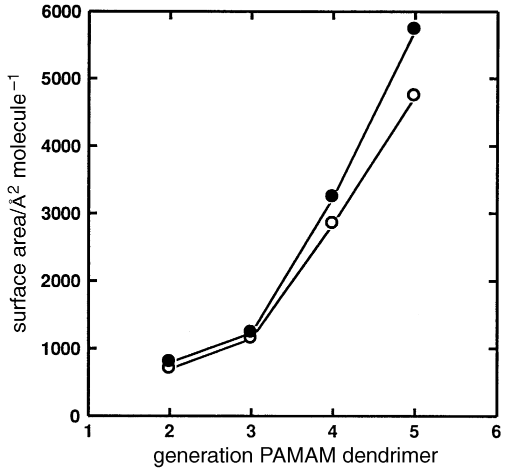


Fig. 5 A surface area *vs.* generation number plot for epoxydecane modified dendrimers grown from ammonia (#) and EDA ($) cores

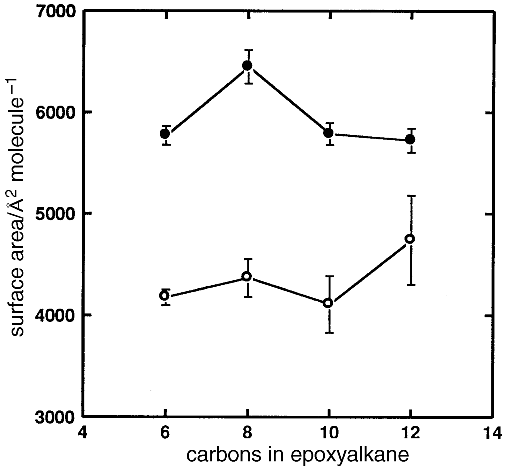


Fig. 6 A plot of surface area *vs.* the number of carbons contained in the epoxyalkane chains for fifth generation dendrimers based on EDA ($) and ammonia (#) cores

Previous theoretical studies have suggested that the shape of PAMAM dendrimer becomes more highly spherical as a function of increasing generation number.[32] Experimental confirmation of the importance of this shape change has shown that a number of physical properties also exhibit dramatic changes coincidental with the shape change.[33] It may be possible that the increasing difference seen in this study between the surface areas of the higher generation dendrimers may be influenced by this shape change. To further investigate the effect of core length, a number of dendrimers with longer tetradendron cores (1,4-diaminobutane, 1,8-diaminooctane and 1,12-diaminododecane) were also examined. These data, presented in Fig. 7, indicate that for the lower generation dendrimers there is no significant difference as a function of the core length. As was seen for the comparison between the ammonia and EDA cores in Fig. 6, it is possible that a greater effect would be seen at higher generations for these dendrimers.

Copper(II) salt-containing dendrimers at the air–water interface

A key question was whether these copper-loaded dendrimers could still be organized at the air–water interface. This issue was examined by using dendrimer copper(II) complexes prepared in chloroform solutions, which were introduced at the air–water interface as described previously. Fig. 8 shows an isotherm obtained for a G5(NH_3) C_8 sample loaded with copper. In general, all the copper-loaded samples exhibit isotherms that are similar in shape to those containing no copper. The collapse pressure increased slightly upon incorporating copper, which may indicate a slight stiffening of the dendrimer interior due to copper complexation. Over the range of dendrimers investigated [*i.e.* G2(NH_3) C_8 to G7(NH_3) C_8], no differences were observed in the isotherms except for the higher collapse pressure noted above. This work clearly demonstrates that metal-loaded dendrimers can be readily organized into two-dimensional layers.

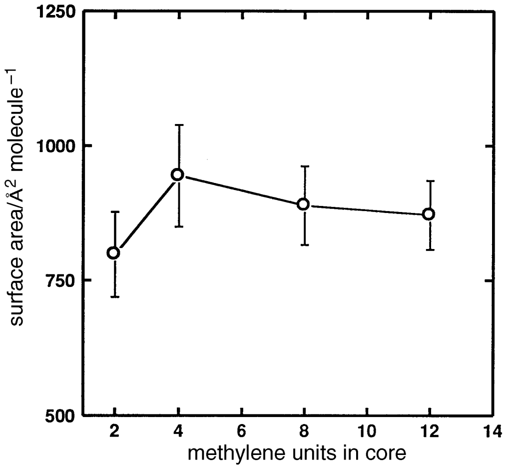


Fig. 7 A plot showing the surface area *versus* the number of methylene units contained in the core for generation two PAMAM dendrimers modified with epoxydodecane

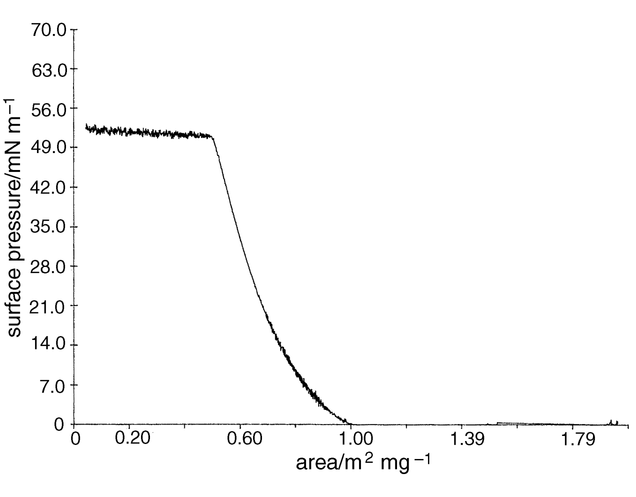


Fig. 8 Langmuir isotherm of a G4 (NH_3) C_8 PAMAM dendrimer surface modified with epoxyoctane and its interior void space loaded with copper ions

Model of hydrophobically modified PAMAM dendrimers at the air–water interface

With these limited data, one can only speculate as to how these hydrophobically modified dendrimers are organized at the air–water interface. Since the surface pressure *vs.* area curves do not show significant shape changes as a function of the dendrimer size, the terminal hydrophobe length or the length/hydrophobicity of the core, it appears that the isotherms are either not sensitive to these structural parameters, or that all of the dendrimers examined are interacting with the subphase in a very similar manner. One model which may be appropriate for the lower generation PAMAM dendrimers is that the accessible hydrophilic dendrimer interior interacts with the aqueous subphase while the hydrophobically modified terminal groups reorganize to extend outward away from the air–water interface. Since the length of the hydrophobic chain does not seem to impact the surface area occupied by the dendrimer, either the chains from adjacent dendrimers are able to interdigitate or they extend upward away from each other. For the low pH experiments (*i.e.* $pH=2$), the subphase was acidic enough to protonate the interior tertiary amines (pK_a *ca.* 4.5), which should help to increase the interaction between the dendrimer interior and the subphase, thereby causing the observed larger collapse pressure. At higher generations, it would seem that a dendrimer reorganization of this type would become increasingly more difficult. A second model one must consider is that the dendrimers are simply acting like hydrophobic spheroids floating at the air–water interface. At this point, it is difficult to tell which of these models is the most probable. Perhaps there is a transition from the first model which may be operable for the lower generations to the floating hydrophobic spheroid model for the more congested higher generations.

Conclusions

Hydrophilic PAMAM dendrimer scaffolds were readily converted to hydrophobic modules by facile reactions of amine groups with epoxyalkanes. The modified dendrimers perform as nanoscopic container molecules, reminiscent of 'unimolecular inverse micelles' as demonstrated by the transport of copper(II) ions from an aqueous solution into toluene or chloroform. These experiments, as well as other work,[25,27,35] clearly show that the interior void spaces of dendrimers are available for the incorporation of guest molecules. The properties of the modified PAMAM dendrimers at the air–water interface were most strongly influenced by the dendrimer generation. Even changing the length of the dendrimer surface hydrophobe from hexyl to dodecyl did not cause any significant differences in the limiting area of the dendrimer at the collapse point. Only for the highest generation dendrimers (generation 5) did the size of the core seem to influence the area taken up by the dendrimer at the collapse point. Further examination of these dendrimers structures at the air–water interfaces will be required to gain a complete understanding of these unique nanoscopic organizations.

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