AFM STUDIES OF MONOLAYERS OF HYDROPHOBICALLY-MODIFIED POLY(PROPYLENE IMINE) DENDRIMERS

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AFM STUDIES OF MONOLAYERS OF HYDROPHOBICALLY-MODIFIED POLY(PROPYLENE IMINE) DENDRIMERS

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PREFACE

Dendrimers are highly symmetric and branched macromolecules. The properties of dendrimers are very different from those of small organic molecules and linear macromolecules because they are determined mostly by the terminal functional groups. These well-engineered dendritic molecules offer scientists with challenges and exciting opportunities. Dendrimers have numerous potential applications in chemical, biological, medicinal and materials research which have been facilitated by their commercial availability.

In this work, we chose the second generation poly(propylene imine) (PPI, $DAB\text{-}dendr\text{-}(NH_2)_8$) dendrimer as starting material. A series of hydrophobically-modified dendrimers were prepared by using fatty acid chlorides. The modified dendrimers are amphiphiles which contain a hydrophilic (water-loving) core (head) and eight hydrophobic (water-fearing) tails. These dendrimers are designed to be interfacial stabilization agents between electrode and electrolyte in lithium batteries, and so how these dendrimers behave on flat surface is very intriguing to us. The Langmuir-Blodgett (LB) technique and atomic force microscopy (AFM) are two major tools to study interfacial behavior of these dendrimers at the air/water and air/solid interfaces. When amphiphilic compound solution is spread on the air-water interface of a Teflon trough, the hydrophilic polar head of the amphiphilic molecule is in contact with the water surface, while the hydrophobic parts extend away from the water surface. Thus a

monolayer is formed at the interface. The monolayer can be transferred to a solid substrate by the LB technique, where the substrate is vertically dipped into and pulled out of the water subphase. The LB technique allows researchers to analyze and manipulate features of monomolecular organic layers, for example amphiphilic molecules, fatty acids and lipids. AFM is a method of microscopy that maps the topography of a surface at a resolution as small as atomic lattice [Angstrom (Å) level] in the real space and allows researchers to obtain molecular and atomic level properties.

In this work, surface pressure–area isotherms were measured to study the stability, the mean molecular areas of these amphiphilic dendrimers on water. Monolayers of these amphiphiles were transferred to mica by the LB film method and the properties of monolayers were studied by AFM. The C_{12}-fatty acid modified dendrimers formed stable monolayers of smooth and homogenous surface. The C_{18}-fatty acid modified dendrimers formed relatively stable films and showed island structures at surface pressure of 10 mN/m, and the monolayers were collapsed at surface pressure of 25 mN/m. The formation of monolayers on mica suggests that the dendrimers may also form stabilizing monolayers at the electrode-electrolyte interface of solid state lithium ion batteries.

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CHAPTER I

DENDRIMERS REVIEW

ABSTRACT

This chapter discusses the most important structural features and properties of dendrimer materials. The two most common methods used to synthesize dendrimers, divergent and convergent, are briefly reviewed. Typical reactions of poly(propylene imine) (PPI) dendrimers are summarized due to their importance in this thesis. The modified PPI dendrimer monolayers at air/water interfaces are briefly discussed. The potential applications of dendrimers for drug delivery and as medical diagnostic agents, high-performance polymers and separation agents, dendritic catalysts and light harvesting and energy transfer in dendrimers are also reviewed.

INTRODUCTION

Dendrimers are *tree-like* compounds. They have very unique structural features, such as many branches, high symmetry, monodispersity, globular shape, and void space in the interior.[1] Compared to the well known behavior of linear macromolecules, dendrimers have very low intrinsic viscosity because of the high density of atoms in a limited volume.[2] The properties of dendrimers are very different from those of small organic molecules and those of linear macromolecules because they are determined mostly by the terminal functional groups.[3]

Since the first synthetic dendrimer was reported in 1979,[4] this kind of materials has attracted great attention of researchers in different fields. During the1980-90's, researchers made great efforts to synthesize new families of dendrimers with higher generations. Poly(amido amine) (PAMAM) and poly(propylene imine) (PPI) dendrimers are the most common and are commercially available. Hydrophobically modified PAMAM and PPI dendrimers are amphiphiles and have received extensive attention because of their unique behavior at the air/water and air/solid interfaces. In the last few years, interest in the application of these materials has risen rapidly. So far, dendrimers have found applications in medicinal chemistry, high-performance polymers and separation agents, catalysis, energy transfer and other fields.[5]

SYNTHESIS OF DENDRIMERS

The synthesis of dendritic macromolecules is unlike the synthesis of regular polymers. Perfect dendrimers are synthesized by a two-step repetitive synthetic approach, are ideally branched and have the same chain lengths. Regular polymers usually are synthesized by chain or step polymerization. Two major approaches, convergent and divergent synthesis, are employed to prepare dendrimers as illustrated in Figure 1.[1,6,7]

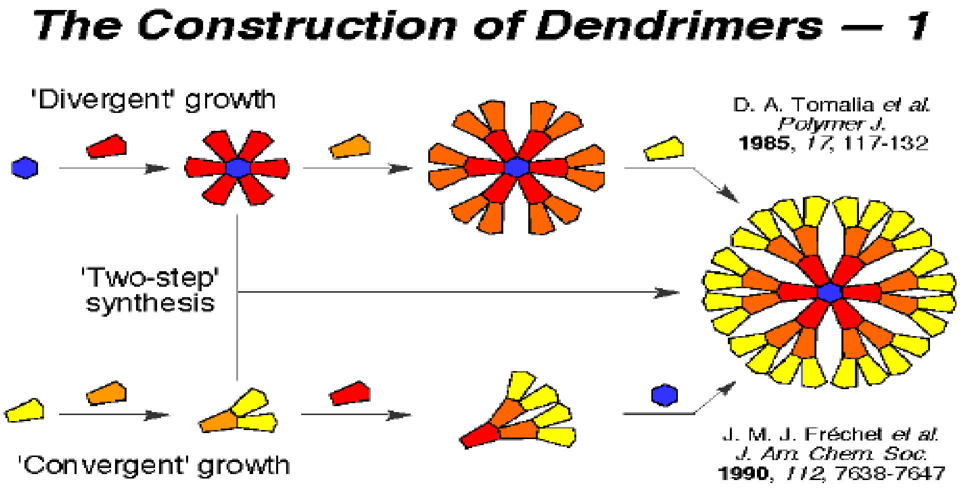


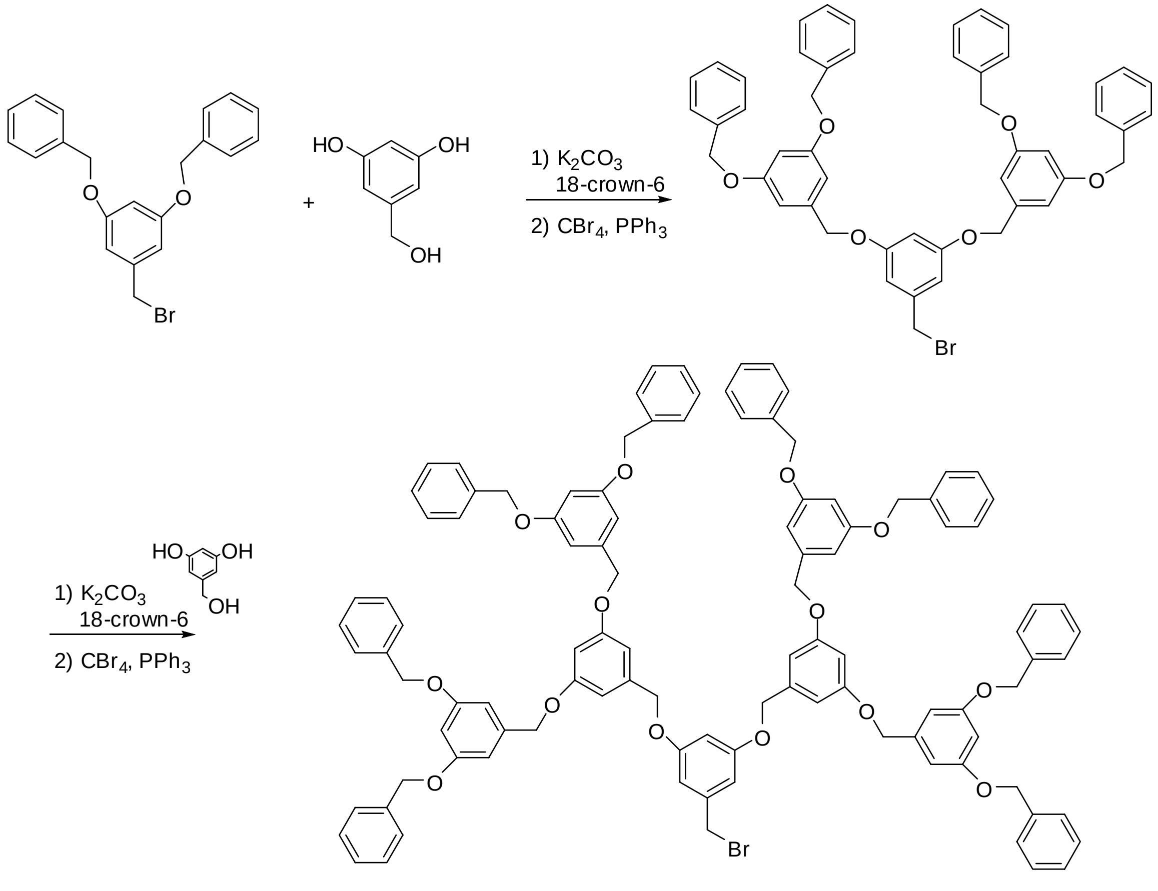
Figure 1. The two major methods of synthesis of dendrimers[8]

Divergent Synthesis. The divergent method is an "inside out" method. In this strategy, a dendrimer begins with a core molecule and grows outwards toward the periphery from the core. The reactive groups on the dendrimer surface react with monomer units to grow a new generation to the dendrimer in a stepwise manner as shown in Figure 1.[8] Thus, the number of coupling reactions increases exponentially with each successive generation. In this way dendrimers can be constructed step by step until spatial crowding prevents further reactions of the end functional groups.[9] This synthesis method allows easy analysis of lower generation materials after each step of the reaction. However, higher generation dendrimers synthesized by the divergent approach often contain structural defects because the reactions between end functional groups and monomers become more difficult with the increasing surface congestion of the dendrimers. Examples of this synthetic method can be found in the work of Meijer,[10] Tomalia,[11] Diederich[12] and Newkome[13]. The synthesis of poly(propylene imine) dendrimers will be addressed in detail (Meijer's and Worner's work).[10,14]

Convergent Synthesis. In contrast to the divergent method, the convergent method is an "outside in" strategy. The convergent approach prepares dendrimers from the periphery toward the core. In this method, different individual dendrimer branches (wedges or dendrons) are synthesized first. When the growing dendrons are large enough, several dendrons are *tied* to a suitable core to build up a new complete dendrimer. The starting blocks end up being on the periphery of dendrimers, while the succeeding blocks take the position of a *focal point*. Hawker and Fréchet reported the first example of convergent method to synthesize polybenzyl ether dendrimers (Scheme 1).[7,15] In their work, two iterative synthetic steps were employed: (1) a benzyl bromide group of a dendritic synthon was used to alkylate phenolic hydroxyl groups, (2) carbon tetrabromide (CBr_4) was used to convert a benzylic alcohol group of the higher generation dendron to a benzylic bromide. The highest generation synthesized is the sixth generation.[15]

Other examples of the convergent strategy come from Miller,[16] Stoddart,[17] Wolf[18] and Yoshida.[19] The advantage of convergent growth over divergent growth stems from the fact that convergent synthesis gives more homogeneous and defect-free dendrimers, since by-products and dendrons are smaller than the complete dendrimers and could be easily removed. However, it is very difficult to synthesize dendrimers of much higher generation by the convergent synthesis strategy. The reason is that the reactions between dendrons and the core become less and less efficient with the increasing generations.

Scheme 1. Hawker and Fréchet's Convergent Synthetic Method[15]



The commercially available poly(propylene imine) (PPI) family dendrimers are synthesized by the divergent approach.[10,14] A short view of the synthesis is given in the following paragraph because of its importance in this thesis. The synthesis starts from a 1,4-diaminobutane core as shown in Scheme 2. It proceeds as a series of two repetitive reactions: a Michael addition reaction of amino groups to acrylonitrile, followed by reduction of the nitriles to primary amines. The nitrile-ended materials are denoted as "half-generation" $G_{n.5}$ and the full-generation amine-terminated dendrimers are considered as G_n. So far, the highest generation synthesized is the fifth generation. Although only 23% of the fifth generation PPI dendrimers are perfect due to the steric problem on the surface of the higher generation dendrimers, this is the highest known for any 64-end-group dendrimers synthesized by a divergent method.[5] Nevertheless, the polydispersity of PPI dendrimers is still very low compared to hyperbranched polymers.

The molecular weight and the number of terminal groups increase exponentially with the dendrimer increasing generation. But the dendrimer diameter does not increase exponentially, it increases near linearly. This fact leads the density of dendrimer end groups to increase nonlinearly: the higher the dendrimer generation, the more densely packed the surface. Table 1.1 shows general properties of PPI dendrimers related to the dendrimer generations.[10,14] Another consequence of the exponential growth pattern of dendrimers is a change of shape with generation. As the dendrimer generation increases, the dendrimer becomes more crowded, and the shape changes from an open expanded configuration (G_2) to a spherical or globular structure.

Scheme 2. Divergent Synthesis of Poly(propylene imine) Dendrimers

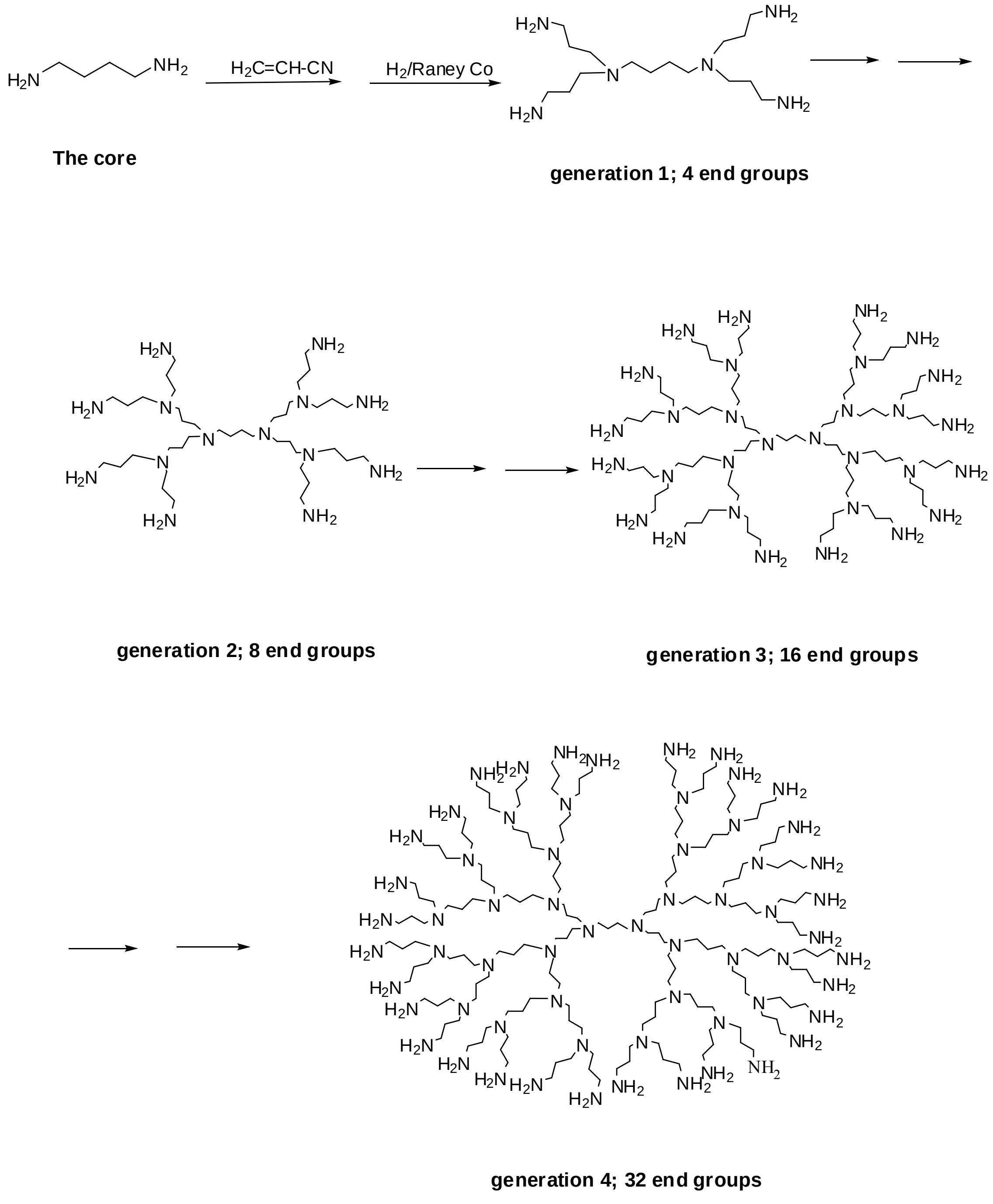


Table 1. General Features of PPI Dendrimers[10,14]

Generation	End Groups	Tertiary Amines	Molecular Weight[a]	Diameter[b], nm	End groups/surface area($1/nm^2$)
1	4	2	317	0.9	0.39
2	8	6	773	1.4	0.32
3	16	14	1687	1.9	0.35
4	32	30	3514	2.4	0.44
5	64	62	7168	2.8	0.65

[a] Molecular weight is based on perfect dendrimers.

[b] The dimensions of PPI were determined by small-angle neutron scattering (SANS).[20]

MODIFICATION OF PPI DENDRIMERS

As mentioned above, the terminal groups of PPI dendrimers are amines and most modifications take place at the end groups. Some modifications also happen at core and branch points since the interior amines are tertiary amines.

Chain End Modifications (Exterior Modification). Amine groups can react with many different organic groups. Figure 3 gives a summary of typical reactions.[21] The consequent products such as polynitriles, polyesters, polyamides, and perfluorinated dendrimers have been studied and applied in a variety of fields.

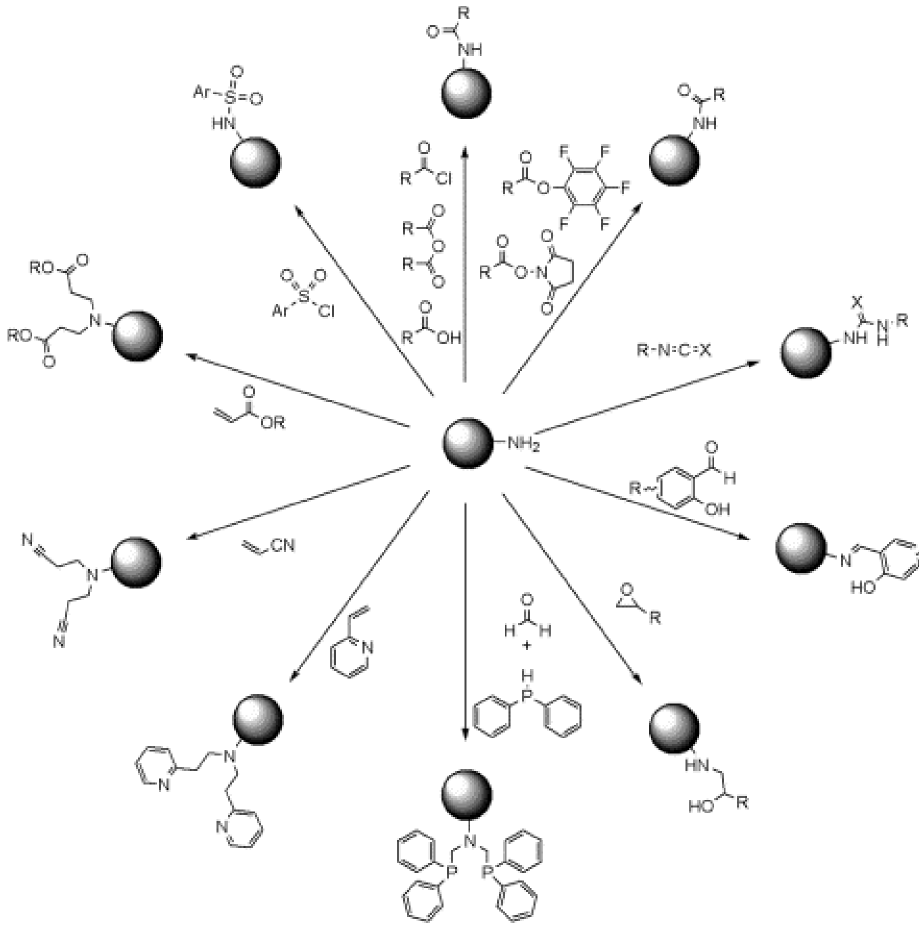


Figure 2. Reactions coupling functional groups and polyamino dendrimers[21]

PPI dendrimers modified with long hydrophobic chains are a new class of surfactants: amphiphilic dendrimers. This kind of dendrimers has been reported as organic molecular hosts. Alkyl-amidated and PEGylated (polyethylene glycol modified) PPI dendrimers are two examples.[22,23]

PPI dendrimers modified with both PEG and octyl groups at chain ends were reported by our research group.[23] In this work, four steps were employed. First, PPI chain ends were amidated by octanoyl chloride followed by reduction with $LiAlH_4$ to give the secondary octylamine. Then the secondary octylamines were amidated with an acid chloride derivative of triethylene glycol methyl ether followed by reduction to obtain dendrimers with both octyl and triethylene glycol methyl ether at every chain end. PPI dendrimers modified by fatty acids such as octadecanoic, dodecanoic, and hexadecanoic acids through covalent interactions are also reported.[22,24,25] Water solubility and internal organic character are the main concern in preparing these dendrimers.

Chain End and Branch Point Modification (Complete Modification). In addition to modification of the exterior, it is also possible to modify the interior of PPI-dendrimers by quaternizing the internal tertiary amines to generate multiple cationic ammonium sites. Elissen-Roman and our research group have presented complete quaternization of PPI dendrimers (modified at the exterior and quaternized at interior).[26-28] Meijer and coworkers also introduced several PPI dendrimers modified at both the exterior and the interior with the aim to make water soluble, hydrolytically stable and non-toxic transfection agents.[29] In the work, the end groups of PPI dendrimers were modified with acetyl or with triglycol gallate (PEG-like) groups which keep water solubility and produce non-toxic species. The PPI dendrimers were modified at the interior by reacting the internal tertiary amines with methyl iodide to construct a micro-environment with multiple quaternary charge sites. The number of charge sites is between 2 and 60 with the variation of dendrimer generation. The higher local concentration of charge (cationic) sites, the better capability of forming complexes with DNA and other multi-anionic species such as RNA.

Core and Branch Point Modifications (Interior Modifications). Due to greater steric hindrance and less reactivity than the chain ends, core and branch point modifications are not as common as chain end modifications. Because the properties of dendrimers are mainly determined by the end groups, core and branch point modifications are less attractive. In order to successfully internally modify dendrimers, chain end reactions should be blocked by using protecting groups to make internal sites selectively available or prepare the PPI dendrimers by using a new amine source.

PPI DENDRIMER MONOLAYERS AT AIR/WATER INTERFACES AND SOLID SURFACES

Saville and his coworkers first reported studies of dendrimers at the air – water interface.[30] They used convergent Fréchet-type poly (benzyl ether) dendrons which contain a hydrophilic alcohol part at the focal point and hydrophobic benzyl groups at the periphery. The isotherms (surface pressure *vs*. molecular area, Π – A) showed the higher molecular weight dendrons could better stand the increased pressure.[30]

Poly(propylene imine) (PPI) dendrimers of generations 1-5 have been modified with alkyl hydrophobic chains and dialkyl sulfide chains to form amphiphilic dendrimers.[25,31,32] On water, these dendrimers can form very stable monolayers with hydrophobic alkyl groups tipping to the air and hydrophilic core pointing to the aqueous phase (Figure 3). The isotherms collected by LB techniques show sharp increases of the surface pressure under compression. This phenomenon indicated the formation of stable monolayers with no significant change in the total surface area at a constant pressure with time.[32] Some examples are PPI dendrimers with palmitoyl, {4-(4-hexyloxyphenylazo)}undecanoyl chains and dialkyl sulfide chains.[25,31,32] The Π – A characteristics of monolayers of these dendrimers are very close to each other and they have been found to be stable up to pressure of 55-65 mN/m. The areas per end group are analogous for these studied dendrimers and are comparable to those of monolayers formed by alkylthiocarboxylic acids or alkylcarboxylates.[31] Meijer and co-workers explained the behavior of these amphiphilic dendrimers by the following model: the flexible dendrimers adopt a flattened conformation in which the hydrophilic part (the core) is associated with the water surface, while the hydrophobic end groups point upwards and away from the water surface.[25] The model of hydrophobic chains involving a parallel-packed array oriented perpendicular to the water surface was further supported by examination (UV-vis spectroscopy) of a monolayer that was formed with dendrimer containing an azobenzene chromophore.[25]

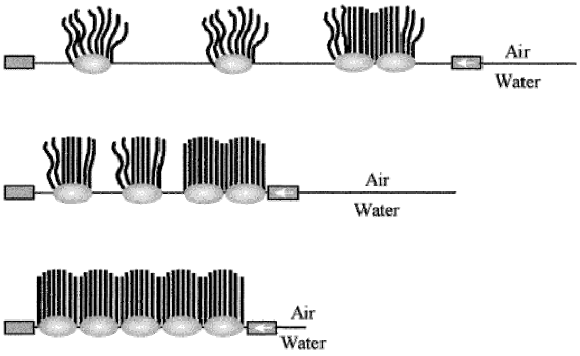


Figure 3. Schematic representation of the organization of amphiphilic dendrimers with increasing pressure in a monolayer on the water surface.[25]

The monolayers on the water surface can be transferred to solid substrates such as mica, metal surfaces and silicon wafers by vertical deposition. Hydrophobically modified poly(amido amine) (PAMAM) dendrimers in the Langmuir-Blodgett films deposited on mica and silicon wafer surfaces have been studied by atomic force microscopy (AFM).[33,34] Meijer and his coworkers reported AFM studies of LB films based on the fifth generation PPI denderimer modified randomly with ratio 1:1 of palmitoyl and azobenzene –containing alkyl chains.[32] The photoreponsive dendrimer formed regular pressure-area isotherms ($\Pi - A$), and the monolayers were transferred to a silicon wafer at a constant surface pressure of 20 mN/m. The AFM images of the dendrimer showed the presence of a smooth and homogeneous surface with an average film thickness of 3.1 nm.[32]

Organized surface monolayers at the air-water and the air-solid interfaces play important roles in the field of nanoscience and nanotechnology.[35,36] The amphiphilicity created by the inclusion of hydrophobic and hydrophilic segments facilitates the study of the molecular ordering in monolayers at the air-water interface.[37-39] Experimental detection at both the air-water and the air-solid interface help us comprehend the molecular ordering and reorganization of segments at both interfaces.[40] Hydrophobically modified dendrimers will form monolayers at the air-water interface too. Dendrimer films on supporting materials may find applications in holographic data storage, organic LEDs, lithography, and biomedical sensors.[41-46] Thicker layers of dendrimers on solid surfaces have been prepared by the polyelectrolyte layer-by-layer method[47] and by synthesis of dendrons starting with functional groups on various solid surfaces.[48]

FILMS ON THE SURFACE OF SOLID POLY(ETHYLENE OXIDE)

The use of lithium batteries as portable electricity sources is growing due to their high energy densities and a large electrochemical window. One problem is that the interface between electrode and solid polymer electrolyte is not stable. A passivating layer forms after a high number of charge/discharge cycles.[49,50] Research in Teeters's group showed the presence of crystalline in hydrocarbon monolayers stabilized at the electrode/electrolyte interface by using attenuated total reflection (ATR) FT-IR spectroscopy.[51] Ford and Teeters have proposed to synthesize amphiphilic PPI dendrimers and add the dendrimers in solid electrolyte systems to enhance the stabilization of the interface in lithium batteries. An additional benefit could be that ion conduction increases in the bulk solid polymer electrolyte. The work is in progress in the University of Tulsa.

APPLICATIONS OF DENDRIMERS

Due to their structural features such as high branches, symmetry, globular shape, dendrimers have potential applications in a wide range of areas. These include drug delivery, molecular recognition,[9] chemical sensors, medical diagnostic agents, high-performance polymers, catalysts,[52] and building blocks of supermolecules, just name a few. There are many review articles[1,5,53,54] published since the first report of successful synthesis of dendritic molecules. Here only a few typical applications are briefly described, especially with the very recent developments; any earlier work can be found from those earlier review and research articles.

Drug and Gene Delivery Agents. An ideal drug carrier must be biochemically inert and non-toxic, but still able to protect the drug within the carrier until it reaches the desired site of action, and then release the drug. Over the years, many polymeric drug-delivery systems (carriers) have been developed to enhance the aqueous solubility and circulation half-time of a drug, target the drug to certain tissues, improve drug transit across biological barriers and slow drug metabolism.[55] Recently, dendrimer-based drug carriers including both *in vitro* efficacy and *in vivo* therapeutic studies have gained researchers' attention.[29,56] Dendrimers as carriers, especially poly(amido amide) (PAMAM), are useful in this application because of their desirable chemical and physical properties, including: uniform size, biocompatibility, water solubility, modifiable surface functionality, and available internal cativities.[56,57]

PAMAM and PPI dendrimers and their derivatives have been studied as potential transfection agents for gene delivery, because this kind of dendrimers are positively charged and can bind DNA in a physiological environment.[29] For instance, plain G_3 and quaternized G_2 PPI dendrimers favored to target gene to the liver.[28] However, their toxicity in cell cultures, their binding capabilities to DNA and their transfection efficiency are big concerns. According to Malik et al.[58] the terminal or surface groups of dendrimers determine the toxicity of the overall dendritic structure; therefore it is very promising to chemically modify the surface of dendrimers to create delivery systems with low toxicity, good water solubility, and improved hydrolytic stability.[29]

High-performance Polymers and Separation Agents. Synthetic dendrimer membranes are promising for use in gas separation systems. Polyimides are one class of polymeric materials heavily investigated for gas separation. Due to the economic concerns related to developing new polyimides, academic scientists and industrial developers have shifted their research focus to chemical and physical modifications of commercially available polyimides to improve the overall gas separation performance. Cross-linking methods have gained the most attention.[59,60] PAMAM and PPI dendrimers have been employed as cross-linking agents to modify the commercially available polyimides.[61-63] Sirkar and co-workers[64] opened a new door of research and development of dendrimer-modified membrane materials. They developed a high-performance CO_2 selective poly(vinylidene fluoride) (PVDF) flat membrane by using PAMAM as a CO_2 selective molecular gate. After that researchers have paid attention to chemically modify membranes with a variety of dendrimers.[61]

Dendritic Catalysts. Catalysis is one of the important potential applications of dendrimers. Studies show that dendrimer-metal complexes can act as either heterogeneous or homogeneous catalysts in organic reactions. They find very promising catalytic applications in hydrogenation,[65,66] hydroformylation,[67-69] olefin metathesis,[70,71] Heck reaction,[68] polymerization,[72] alkylation[73] and oxidation[74] because of their easy tuning of structure, size and location of catalytically active sites.[52] Dendrimer-metal complexes (metallodendrimers) are very active catalysts in a lot of reactions. The properties of the dendritic catalysts are determined by the location and the nature of the metal. Figure 4 presents the four most common configurations of the dendritic catalysts.

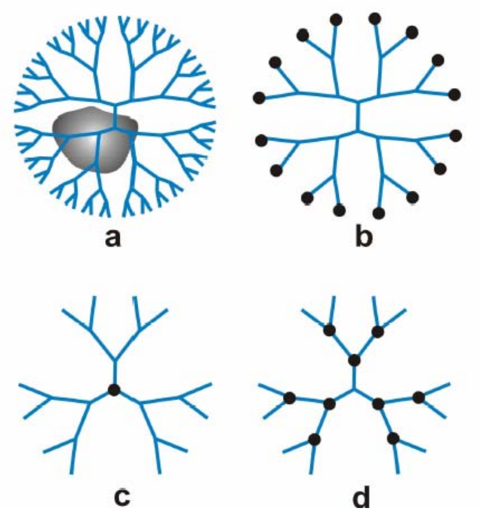


Figure 4. Types of metallodendrimer complexation: (a) dendrimer-encapsulated metal nanoparticles, (b) periphery metallodendrimers, (c) core metallodendrimers, (d) branch point metallodendrimers.[52]

The synthesis of dendrimer-encapsulated metallic nanoparticles has been reported by Crooks and others.[75-79] Dendrimers are promising materials for hosting catalytically active metal nanoparticles for the following reasons: (1) fair uniformity of composition and structure, (2) excellent stability of the nanoparticles by encapsulation without agglomeration during reactions, (3) good retention of the nanoparticles by steric effects with metal active surface, (4) good flexibility of the dendrimer periphery to tailor solubility of the nanocomposite, and (5) the outstanding ability of the branches to selectively control the access of small molecules to the encapsulated nanoparticles. These materials have been demonstrated to be very good homogeneous catalysts for the electrochemical reduction of oxygen.[75-79]

Reetz and his co-workers modified poly(propylene imine) (PPI) G_3 dendrimer by using diphenylphosphine ligands and prepared periphery metallodendrimer type catalysts.

This type catalyst is very active in hydroformylation.[68] Since the active catalytic sites are on the surface of the periphery metallodendrimer catalysts, substrates can easily reach these active spots and then speed up the reactions.

Dendrimers also have been reported as chiral catalysts, micellar and phase – transfer catalysts, enzyme mimics and membrane reactors.[52] Our research group has found that a dendrimer unimolecular micelle is a good catalytic medium for the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate.[23,80] Our research group also have converted poly(propylene imine) dendrimers (PPIs) iodide quaternized at the chain ends or/and the branch points to chloride counter ion. These quaternary ammonium chloride dendrimers improved the speed of the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate about 500 times.[81,82]

Light Harvesting and Energy Transfer in Dendrimers. Light harvesting and energy transfer play vital roles in photosynthesis in plants, in which the energy of photons absorbed by a light-absorbing antenna moiety is transferred to a nearby secondary energy acceptor species. Thus, it is very valuable that artificial light-harvesting systems can convert solar radiation into a useful source of energy with similar efficiency. Dendrimers can be artificial light-harvesting systems because of their unique structures: (1) an energy gradient for the funneling process because of tree-like structure, (2) the number of peripheral absorbing units that grows exponentially with increasing generation, and (3) the relatively short distance between the core and the periphery.[83] One example of photonic molecular assemblies in which light absorption is followed by nearly quantitative energy transfer have been reported by Moore and coworkers.[84] They reported that energy was transferred through the dendrimer to a core chromophore in a host-guest system. Another example of energy-transfer is presented by Meijer *et al*.[85] In their work, they demonstrated that energy was transferred between the arms of dendrimers and encapsulated dye molecules. Functionalized PPI dendrimers conjugated to oligo(p-phenylene vinylene) (OPV) groups pull water-soluble anionic dyes into organic phases efficiently and can reach an energy transfer efficiency of 90%.

Dendrimers are significantly different from linear polymers. They have numerous beneficial properties, such as variable size and conformation, high structural and chemical homogeneity, high functionality and binding density, as well as controllable degradation; therefore, we expect those unique properties should be used in a variety of applications. We also face the same challenges when we move from the laboratory to industry for dendrimers as that of linear polymers. Reducing cost may be the biggest challenge: high cost is likely to prevent any large volume applications.

In this work, PPI G_2 dendrimer was modified by lauroyl and stearoyl chlorides to give amide dendrimers which were further reduced by lithium aluminum hydride and methylated by large excess of formic acid and formaldehyde. These hydrophobically modified dendrimers showed good solubility in chloroform. Interfacial behavior of those dendrimers at the air/water interface was investigated by the Langmuir technique using a Langmuir trough. The films of the dendrimers were transferred to newly cleaved mica by Langmuir-Blodgett method and characterized by atomic force microscopy (AFM).

Surface pressure-area isotherms and AFM measurements showed that the lauroyl-modified amphiphilic dendrimers formed stable monolayers of smooth and homogenous surface with roughness < 0.5 nm. High resolution AFM images showed a tetragonal motif with spacing of between 0.4 and 0.5 nm, indicating crystalline two dimensional packing of the alkyl chains on a mica surface.

The films of the stearoyl-modified dendrimers were transferred to the newly cleaved mica at surface pressures of 10 mN/m and 25 mN/m. The Langmuir films transferred at the surface pressure of 10 mN/m were relatively stable and showed island structures. The monolayers were collapsed on mica after transfer at the surface pressure of 25 mN/m, which is below the collapse pressure observed on the surface pressure-area isotherms.

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CHAPTER II

SYNTHESIS OF HYDROPHOBICALLY MODIFIED DENDRIMERS

INTRODUCTION

Meijer and coworkers have reported poly(propylene imine) (PPI) dendrimers with hydrophobic chain end groups as inverted unimolecular micelles. These dendrimers can be used as hosts for hydrophilic molecules such as Bengal Rose. They are very effective at extractions of hydrophilic compounds from the polar solvent ethanol.[1] PPI dendrimers with hydrophobic end groups are amphiphiles with a hydrophilic core. At air-water interfaces, these amphiphiles can form monolayers with the hydrophilic core contacting water and the hydrophobic tails pointing to air. In other words, they can form well organized monolayers at an air/water interface.[2] The monolayers can be transferred to a solid substrate, and how these amphiphilie monolayers arrange on air/solid interfaces are very intriguing to us.

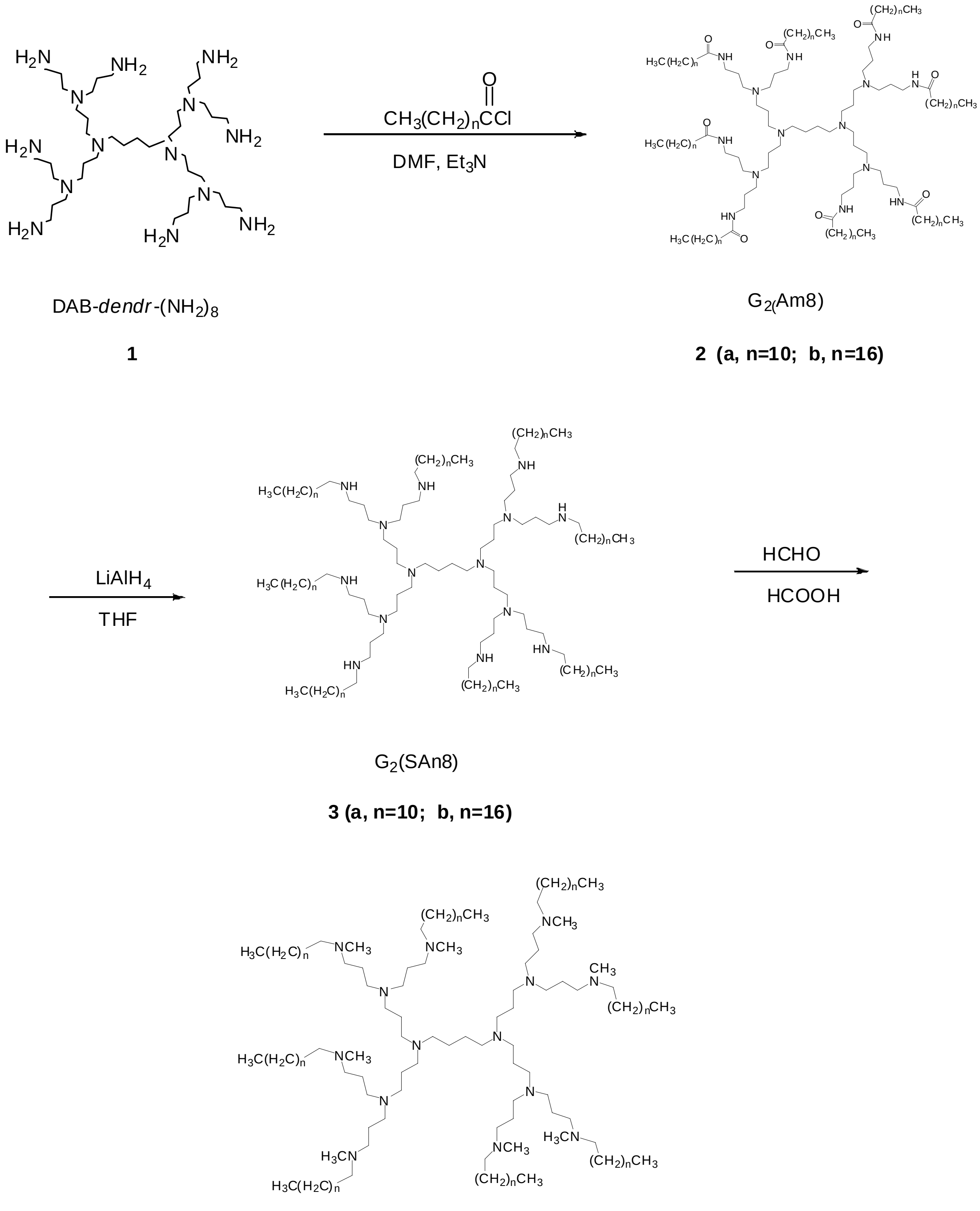
The objective of this part of the project was to modify end groups of poly(propylene imine) PPI *DAB-dendr-*$(NH_2)_8$ **1** to obtain dendrimers with long aliphatic hydrocarbon chain ends in order to study the effects of the hydrocarbon chains on the interface stabilization between electrode/electrolyte in lithium batteries. The commercial

PPI dendrimers have tertiary amines at the cores and branch points and primary amines as end groups. The cores, branch points and end groups all can be reactive.

RESULTS AND DISCUSSION

Synthesis of Hydrophobically Modified Dendrimers. As shown in Scheme 1, we modified end groups (primary amines) of PPI dendrimer, *DAB-dendr-*$(NH_2)_8$**1**, by using lauroyl and stearoyl chlorides to form amide dendrimers **2**. We reduced the amide dendrimers to secondary amine dendrimers **3**. The secondary amine dendrimers were methylated to tertiary amines **4** by the Eschweiler-Clarke reaction using a large excess formic acid and formaldehyde. Under these conditions, the tertiary amines were final products and no quaternary ammonium salts were formed. The mechanism of the Eschweiler-Clarke reaction is shown below in Scheme 2.[3-6] The driving force of the reaction is the formation of carbon dioxide gas (CO_2). The methylation of the amines begins with imine formation with formaldehyde. The formic acid acts as a source of hydride and reduces the iminium ions to tertiary amines. Based on this mechanism, the final products are not quaternary ammonium salts, because it is not possible for a tertiary amine to form another imine or iminium ion.

SCHEME 1. Hydrophobic Modification of Poly(propylene imine) Dendrimers



DAB-*dendr*-$(NH_2)_8$

1

$G_2(Am8)$

2 (a, n=10; b, n=16)

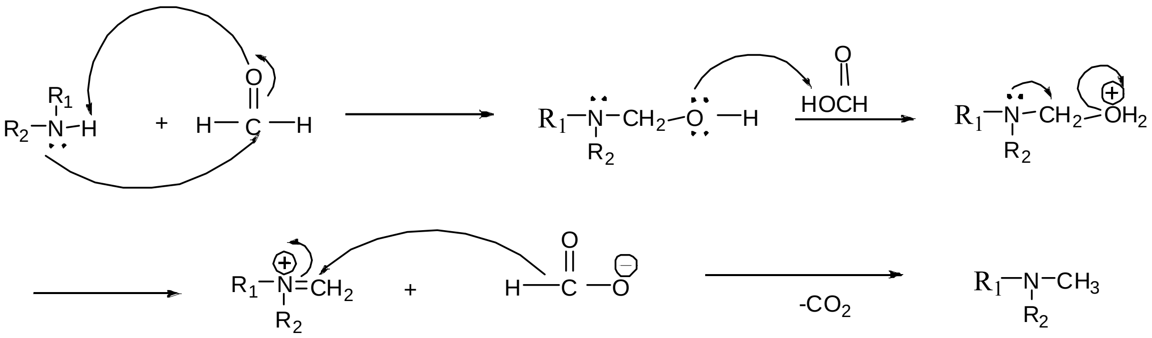
$G_2(SAn8)$

3 (a, n=10; b, n=16)

$G_2(TAn8)$

4 (a, n=10; b, n=16)

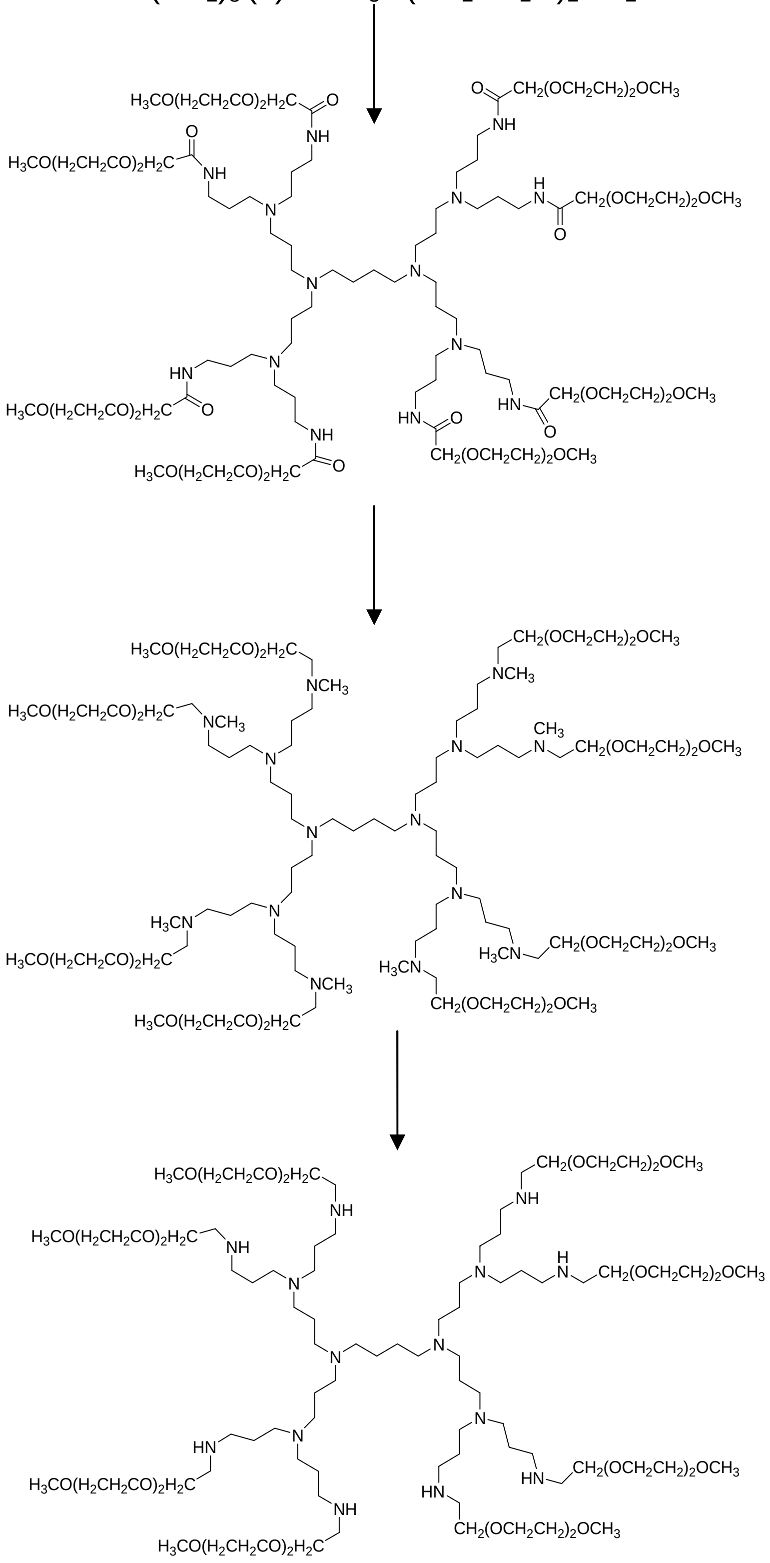
SCHEME 2. Mechanism of Eschweiler-Clarke Reaction



We also modified *DAB-dendr-(NH$_2$)$_8$* **1** by using 2-[2-(2-methoxyethoxy)ethoxy]acetyl (TEO) chloride as shown in Scheme 3. The procedures of these reactions were very similar to those of Scheme 1. The solubility of dendrimer **5** in polar solvents such as water and alcohols was high due to the hydrophilic TEO end groups.[7] Pan reported that the purification and further reaction of dendrimer **5** was very difficult due to its poor solubility in common organic solvents.[7] But in this work, amide dendrimer **5** was successfully reduced to amine dendrimer **6** in anhydrous THF.

SCHEME 3. Hydrophilic Modification of the Poly(propylene imine) Dendrimers

$PPI(NH_2)_8$ (**1**) + $CH_3O(CH_2CH_2O)_2CH_2COCl$



5

6

7

Characterization. Some of the products were purified by flash chromatography using a basic aluminum oxide column (methanol/$CHCl_3$:5:95), and the purity was examined by thin layer chromatography (TLC, silica gel plates pretreated with trimethylamine). All products were characterized by ^1H and ^{13}C NMR analysis. Product **2a** in Scheme 1 was characterized by matrix assisted laser deposition/ionization time of flight (MALDI-TOF) mass spectroscopy.

NMR Analysis. Figures 1 and 2 show the ^1H and ^{13}C NMR spectra of dendrimers **1, 2a, 3a and 4a**. NMR spectra of stearoyl modified PPI dendrimers are showed in the appendix (Figures 2-7). NMR analysis showed the primary amine groups at chain ends of DAB-*dendr*-$(NH_2)_8$ (PPI) were amidated by lauroyl and stearyol chloride to give the amide dendrimers. The new peaks on the proton NMR spectrum (Figure 1) were $CH_2NHC{=}O$ at 3.26 ppm, $NHCOCH_2$ with a triplet signal at 2.18 ppm, and amide N*H* at 6.97 ppm. The ^{13}C NMR also showed several new peaks: several alkyl carbons (from 14.09 ppm to 32.00 ppm), and the carbonyl group at 173.64 ppm. NMR analysis also showed that all the amide (C(=O)NH) groups were completely reduced to secondary amine groups by $LiAlH_4$, as indicated by the absence of peaks at 6.97 ppm (N*H*CO), and 3.24 ppm ($NHCOCH_2$) in ^1H NMR , and 173.64 ppm (*C*O) in ^{13}C NMR spectra (Figure 1 and Figure 2).

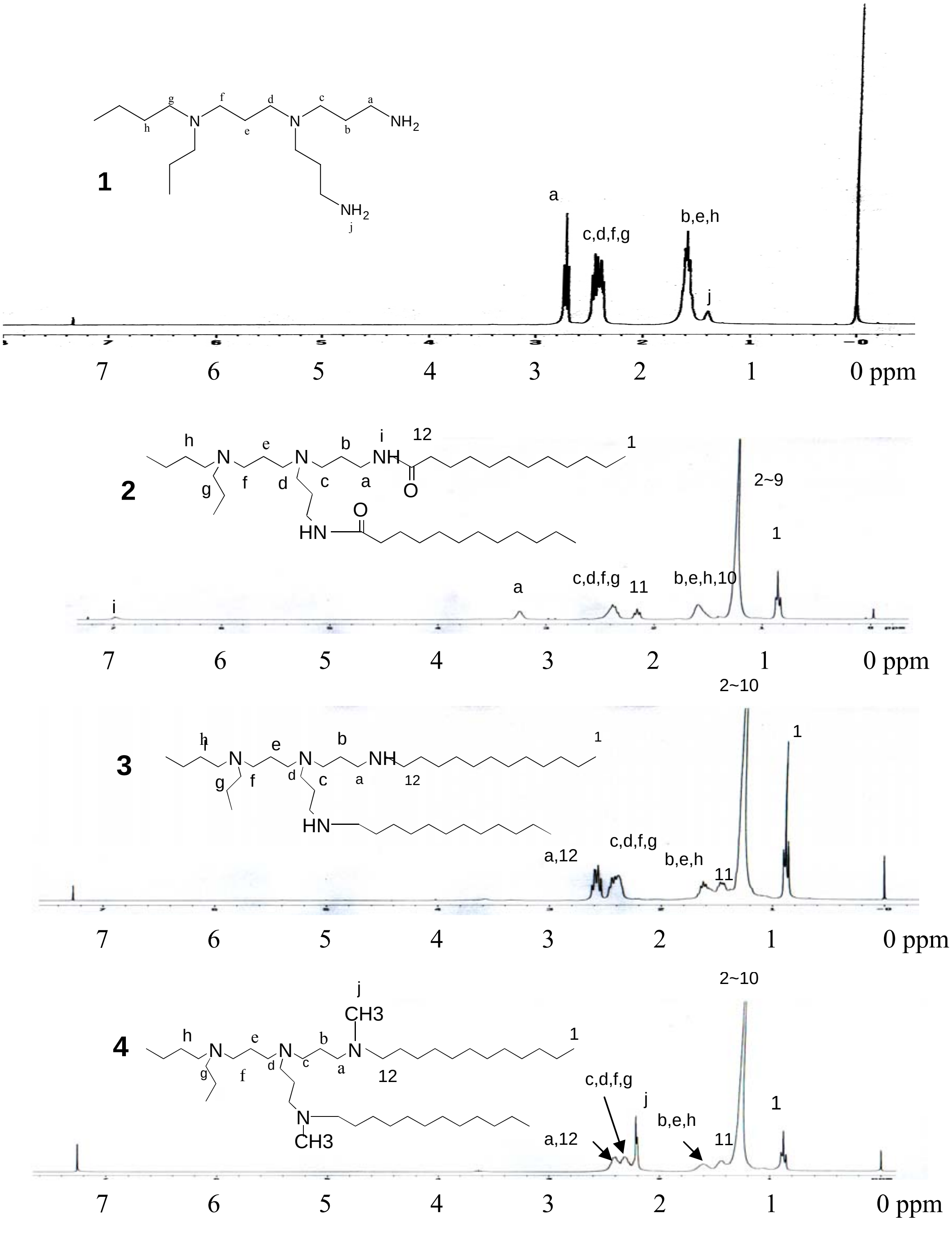


Figure 1. ^{1}H NMR spectra of dendrimers **1, 2a, 3a** and **4a**

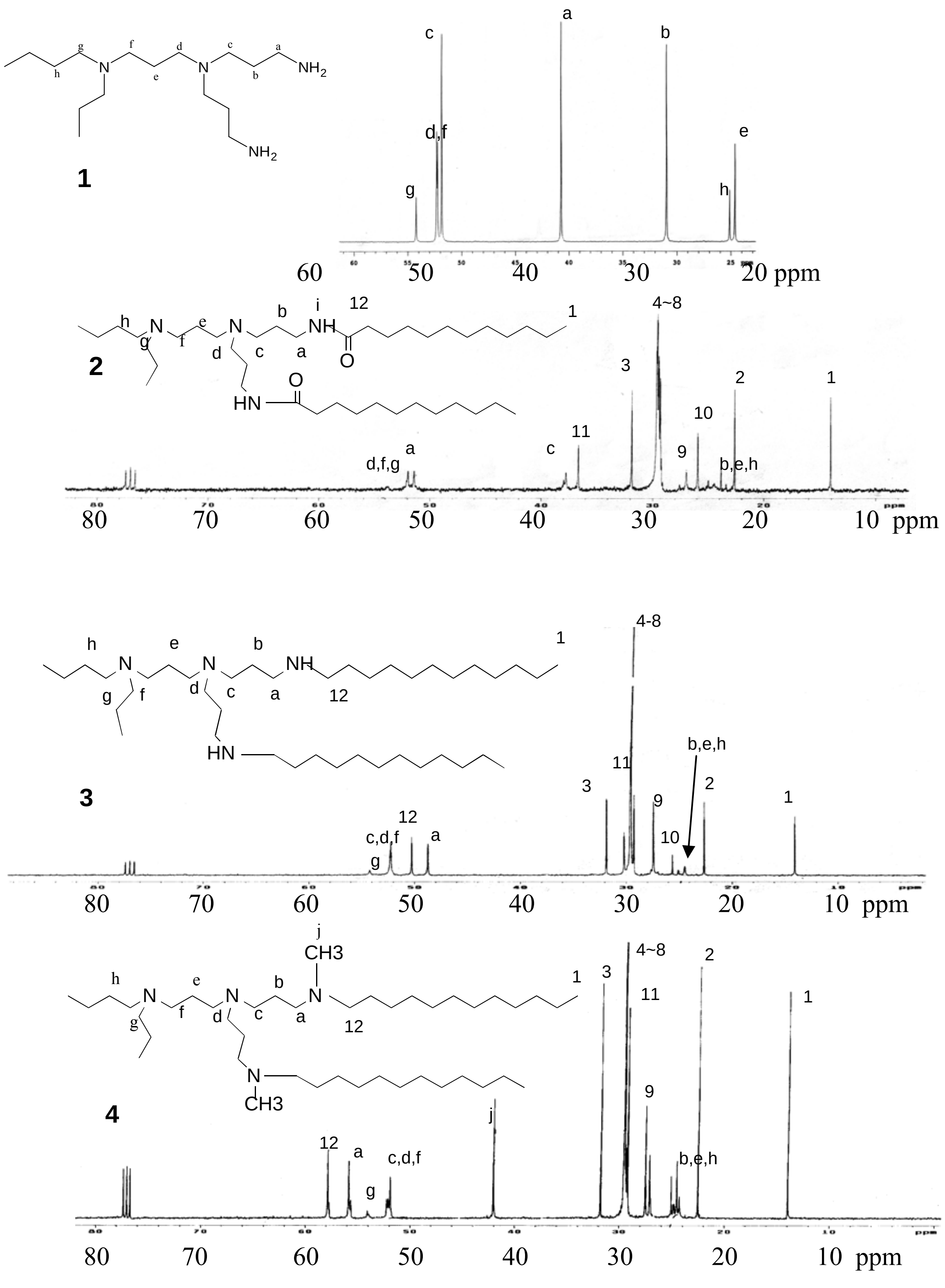


Figure 2. ^{13}C NMR spectra of dendrimers **1, 2a, 3a** and **4a**

The NMR spectra show that the secondary amines were methylated by a large excess formic acid and formaldehyde to give the tertiary amine dendrimers. The appearance of the characteristic strong peak at 2.2 ppm in the ^1H spectrum corresponding to the methyl protons of the R-N-CH_3 (R is an aliphatic hydrocarbon group) demonstrates the complete methylation of the secondary amines. Also, a large new sharp peak at 42.0 ppm which belongs to CH_3-N- R, shifts of carbon a and carbon 12 downfield and no remaining peaks of the secondary amine in the ^{13}C NMR spectrum are evidence of high conversion to NCH_3 (Figure 1 and Figure 2).

The formation of the amide groups and the subsequent conversion of the amide groups to amine groups were also screened by FT-IR. The strong absorption peak of the amide carbonyl stretching band at about 1640-1650 cm^{-1} indicated the formation of the new functional amide groups, and the disappearance of the same peak after $LiAlH_4$ reduction proved that reduction was complete.

The series of TEO-modified dendrimers (Scheme 3) were studied by NMR and the results were similar to those of dendrimers prepared in Scheme 1 (see appendix Figures 8-13).

MALDI-TOF MS Analysis. MALDI-TOF results revealed the presence a peak of the calculated molecular weight of **2a.** (See appendix Figure 1). However, none of the other dendrimers (**3a, 4a, 2b, 3b, 4b**) had a peak for the molecular weight.[2] Besides the presence of a molecular ion for **2a**, there are some very interesting peaks: 1143.09 Da, 1325.50 Da, 1508.32 Da, 1690.70 Da, 1872.05 Da, 2046.74 Da. The differences between these peaks are about 182 Da, which corresponds to the calculated formula weight of one chain ($COC_{11}H_{23}$). From the MS alone, there are two possible explanations for this. One is that different numbers of the chain ($COC_{11}H_{23}$) were lost by fragmentation in the mass spectrometer. Another is that the *DAB-dendr-*$(NH_2)_8$ (PPIs) dendrimers were not completely amidated by acid chlorides. But the NMR analysis shows that the primary amine was completely amidated (Figures 1 and 2).

Solubilities of the Hydrophobically Modified Dendrimers. The hydrophobically modified dendrimers are soluble in THF, toluene, dichloromethane and chloroform. They are not soluble in acetone or acetonitrile. Compounds **2a**, **3a** and **2b** are slightly soluble in hexane at 25 ºC and completely soluble at 50 ºC. Compounds **4a**, **3b** and **4b** are soluble in hexane (Table 1).

Table 1. **Solubilities of the Hydrophobically Modified Dendrimers** [a]

dendrimer	acetone	ether	acetonitrile		hexane	
	25 ºC	25 ºC	25 ºC	50 ºC	25 ºC	50 ºC
2a	-	-	-	-	ss	+
3a	-	-	-	-	ss	+
4a	-	+	-	-	+	+
2b	-	-	-	-	ss	+
3b	-	-	-	-	+	+
4b	-	+	-	-	+	+

a “+”: soluble; ss: slightly soluble; “-”: insoluble.

CONCLUSIONS

Dendrimers which are designed for polymer/electrode interface studies in lithium batteries have been successfully synthesized and characterized by NMR, IR and MALDI-TOF MS. Poly(propylene imine) amide dendrimers were prepared from commercial *DAB-dendr-*$(NH_2)_8$ (PPIs) in DMF or toluene using lauroyl and stearoyl chlorides. These amide dendrimers in THF were completely reduced by $LiAlH_4$ to secondary amine dendrimers. The secondary amine dendrimers in toluene were methylated using a large excess formic acid and formaldehyde to give the tertiary amine dendrimers.

EXPERIMENTAL SECTION

Poly(propylene imine) G_2 dendrimer (PPI) was used in this work. Amine-terminated G_2, PPI *DAB-dendr-*$(NH_2)_8$ dendrimer was purchased from Aldrich (WI, USA) and Symo-chem (Eindhoven, The Netherlands) and used as received. Lauroyl chloride ($CH_3(CH_2)_{10}COCl$), stearoyl chloride ($CH_3(CH_2)_{16}COCl$), oxalyl chloride (ClCOCOCl), lithium aluminum hydride ($LiAlH_4$) in tetrahydrofuran (THF) solution (1.0 M), and 2-[2-(2-methoxyethoxy)ethoxy] acetic acid ($CH_3O(CH_2CH_2O)_2CH_2COOH$) were purchased from Aldrich (WI, USA).Triethylamine (TEA, anhydrous) and tetrahydrofuran (THF, anhydrous) were purchased from ACROS. All chemicals were used as received unless otherwise stated. All aqueous solutions were prepared with DI water (18 MΩ·cm Barnstead E-pure).

G_2(Am8) (2a). Lauroyl chloride (2.63 g, 12.02 mmol) was added to a 100 mL three-necked round bottomed flask with 0.773 g (1.0 mmol) of *DAB-dendr-(NH$_2$)$_8$* **1**, 3.0 mL of anhydrous DMF, and 2.1 mL (1.51 g, 15.0 mmol) of anhydrous TEA under nitrogen at 0 ^{o}C in an ice bath. After 10 min, the solution was stirred under nitrogen at 70 ^{o}C for 24 h. Water (2.0 mL) was added, and the solution was stirred for 10 min; then 20 mL of CH_2Cl_2 was added to the mixture. The CH_2Cl_2 solution was washed (1% K_2CO_3, 15 mL × 2, saturated NaCl solution, 15 × 1 mL), dried (K_2CO_3) and filtered by gravity. The CH_2Cl_2 was removed by vacuum rotary evaporation. The residue was dissolved in toluene (10 mL × 3) and toluene was removed by vacuum rotary evaporation. The product was dried under vacuum at 60 ^{o}C overnight to get 1.504 g (85%) of yellow sticky ointment. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (t, CH_3), 1.25 (m, CH_2), 1.62 (m, $NCH_2CH_2CH_2NCO$, $NCH_2CH_2CH_2N$, $NCH_2CH_2CH_2CH_2N$), 2.18 (t, $NHCOCH_2$), 2.40 (m, $CH_2N(CH_2)_2$, $NCH_2CH_2CH_2CH_2N$), 3.26 (q, CH_2NHCO), 6.97 (br, N*H*CO).^{13}C NMR (75 MHz, $CDCl_3$, δ): 14.04 (alkyl *C*1), 22.64 (alkyl *C*2), 29.43-29.62 (alkyl *C*4-*C*8), 25.78 ($NCH_2CH_2CH_2NH$, $NCH_2CH_2CH_2CH_2N$, $NCH_2CH_2CH_2NHCO$), 25.91 (alkyl *C*10), 27.0 (alkyl *C*9), 31.85 (alkyl *C*3), 36.64 (alkyl *C*11), 37.77 ($NCH_2CH_2CH_2NHCO$), 51.41 ($NCH_2CH_2CH_2NHCO$), 51.94 ($NCH_2CH_2CH_2N$, $NCH_2CH_2CH_2CH_2N$), 173.64 (*C*=O). Calcd MW: 2229. MALDI-TOF MS (matrix, 2,5-dihydroxybenzoic acid) found: 2232.

G_2(SAn8) (3a). To a magnetically stirred solution of amide **2a** (0.755g, 0.36 mmol) in anhydrous THF (32 mL) maintained at 0 ^{o}C under N_2, lithium aluminum hydride (10 mL of a 1.0 M solution in THF, 10.0 mmol) was added dropwise by addition funnel over a period of 30 min. The resulting mixture was allowed to warm to room temperature for a few minutes, then heated, and stirred under gentle reflux. After 7 h, an extra portion of $LiAlH_4$ (4.9 mL of a 1.0 M solution in THF, 4.9 mmol) was added, and the reaction mixture was heated under reflux for a further 17 h. After being cooled to room temperature, the above mixture was slowly transferred into saturated aqueous Na_2SO_4 solution (40 mL) at 5-10 ^{o}C. Since the mixture seemed a little greasy, 20 mL of 2.0 M aqueous NaOH solution was added. After gravity filtering, the THF layer was collected, washed with 4% aqueous K_2CO_3 (3 × 20 mL), dried (anhydrous K_2CO_3) and concentrated under reduced pressure. The product was dried under vacuum overnight to give 0.610 g (0.27 mmol, 80 %) of yellow oily **3a**. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (t, CH_3), 1.26(m, CH_2), 1.44-1.62 (m, $NCH_2CH_2CH_2N$, $NHCH_2CH_2CH_2$), 2.38-2.44 (m, $CH_2N(CH_2)_2$), 2.54 (m, CH_2NH). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 14.05 (alkyl *C*1), 22.62 (alkyl *C*2), 24.46 ($NCH_2CH_2CH_2$), 24.0 ($NCH_2CH_2CH_2NH$), 24.99 ($NCH_2CH_2CH_2CH_2N$), 27.45 (alkyl *C*9), 29.29-29.68 (alkyl *C*4-*C*8), 30.22 (alkyl *C*11), 25.91 (alkyl *C*10), 31.86 (alkyl *C*3), 48.75 ($NHCH_2CH_2CH_2N$), 50.28 (alkyl *C*12), 52.24 ($NCH_2CH_2CH_2NH$), 54.22 ($NCH_2CH_2CH_2CH_2N$).

G_2(TAn8) (4a). A mixture of the secondary amine **3a** (0.831 g , 0.4 mmol), 37% formaldehyde (1.251 g, 15.2 mmol) of, 88% formic acid (2.714 g, 51.9 mmol) and 16 mL of toluene was heated to 80 ^{o}C under N_2 with stirring. After 20 h, 0.634 g (7.8 mmol) of formaldehyde and 1.341 g (25.6 mmol) of formic acid were added. The mixture was heated at 80 ^{o}C for 4 h. After being cooled to room temperature, the resulting mixture was treated with sodium hydroxide (20 mL of a 2.0 M aqueous solution) to make the pH>14. The dendrimer was extracted into dichloromethane (20 mL). The organic phase was dried by anhydrous K_2CO_3. After solvent was removed under reduced pressure, 0.703 g (0.30

mmol, 75%) of an oily yellow **4a** was recovered.^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, δ): 0.88 (t, $\mathrm{C}\mathit{H}_3$, 1), 1.26 (m, $\mathrm{C}\mathit{H}_2$), 1.41-1.60 (br, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2N}$, $\mathrm{NHCH_2C}\mathit{H}_2\mathrm{CH_2}$), 2.2 (s, $\mathrm{C}\mathit{H}_3$, a), 2.3 (br, $\mathrm{C}\mathit{H}_2\mathrm{N(CH_2)_2}$), 2.40 (m, $\mathrm{C}\mathit{H}_2\mathrm{NH}$).^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, δ): 13.91 (alkyl *C*1), 22.48 (alkyl *C*2), 22.48-25.00 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_2N}$, $\mathrm{NCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2N}$, $\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2NH}$), 27.45 (alkyl *C*9), 27.12 (alkyl *C*10) 29.12-29.47 (alkyl *C*4-*C*8), 29.00 (alkyl *C*11), 27.12 (alkyl *C*10), 31.71 (alkyl *C*3), 42.2 ($\mathrm{N}\mathit{C}\mathrm{H_3}$), 51.87 ($\mathrm{NH}\mathit{C}\mathrm{H_2CH_2CH_2N}$), 54.20 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2N}$). 55.83 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2NH}$), 57.80 (alkyl *C*12).

$\mathbf{G_2}$(Am8) (2b). By the procedure used to prepare **$\mathbf{G_2}$(Am8) (2a),** stearoyl chloride (2.424 g, 8.0 mmol), *DAB-dendr-*$(\mathit{NH_2})_8$ **1** (0.773 g, 1.0 mmol), freshly distilled toluene (3.0 mL) and anhydrous TEA (0.888g , 8.8 mmol) was heated under underflux for 24 h. After cooling, the mixture was dissolved in 30 mL of chloroform and was centrifuged for more than 1 h. The undissolved solid and solvents were removed to give 2.207 g (76%) of yellow/white solid product. IR (film on NaCl) ν_{max}: 3295, 3089, 1651cm^{-1}. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, δ): 0.88 (t, $\mathrm{C}\mathit{H}_3$), 1.30 (m, $\mathrm{C}\mathit{H}_2$), 1.62 (m, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2NCO}$, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2N}$, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$), 1.84 ($\mathrm{NHCOCH_2C}\mathit{H}_2$), 2.18 (t, $\mathrm{NHCOC}\mathit{H}_2$), 2.40 (m, $\mathrm{CH_2N(C}\mathit{H}_2\mathrm{)_2}$, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{N}$), 3.24 (q, $\mathrm{C}\mathit{H}_2\mathrm{NHCO}$), 6.90 (br, $\mathrm{N}\mathit{H}\mathrm{CO}$).^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, δ): 14.20 (alkyl *C*1), 23.00 (alkyl *C*2), 29.50-29.82 (alkyl *C*4-*C*15), 26.20 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_2NH}$, $\mathrm{NCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2N}$, $\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_2NHCO}$), 32.20 (alkyl *C*3), 37.00 (alkyl *C*17), 38.10 ($\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2NHCO}$), 51.94 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2}\mathit{C}\mathrm{H_2N}$) $\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2N}$), 52.50 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2NHCO}$), 174.00 (*C*=O).

$\mathbf{G_2}$(SAn8) (3b). By the procedureused to prepare **$\mathbf{G_2}$(SAn8) (3a),** dendrimer **2b** (0.963 g, 0.332 mmol), anhydrous THF (32 mL), lithium aluminum hydride (12 mL of a

1.0 M solution in THF, 12.0 mmol) gave 0.563 g (0.20 mmol, 66 %) of the yellow secondary amine dendrimer **3b.** The yellow crude product was purified on an aluminum oxide column (methanol/$CHCl_3$: 5:95) to give 0.453 g (81%) of **3b**.^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (t, C*H*$_3$), 1.26 (m, C*H*$_2$), 1.44-1.62 (m, $NCH_2CH_2CH_2N$, $NHCH_2CH_2CH_2$), 2.40-2.44 (m, C*H*$_2$N (CH_2)$_2$), 2.60 (m, C*H*$_2$NH). ^{13}C NMR (75 MHZ, $CDCl_3$, δ): 15.00 (alkyl *C*1), 23.90 (alkyl *C*2), 25.80 ($NCH_2CH_2CH_2$), 24.99 ($NCH_2CH_2CH_2CH_2N$), 28.30 (alkyl *C*15 and $NCH_2CH_2CH_2NH$), 30.40-31.00 (alkyl *C*4-*C*14), 30.82 (alkyl *C*17), 26.41 (alkyl *C*16), 32.86 (alkyl *C*3), 49.75 ($NHCH_2CH_2CH_2N$), 50.88 (alkyl *C*18), 53.84 ($NCH_2CH_2CH_2NH$), 54.22 ($NCH_2CH_2CH_2CH_2N$).

G_2(TAn8) (4b). By the procedure used to prepare **G_2(TAn8) (4a),** dendrimer **3b** (0369 g, 0.13 mmol), 37% formaldehyde (1.281 g, 15.6 mmol), 88% formic acid (2.903 g, 55.5 mmol) and toluene (14 mL) gave 0.293 g (0.1 mmol, 79%) of the yellow tertiary amine dendrimer **4b.** The product was purified on an aluminum oxide column (methanol/$CHCl_3$:5:95) to give 0.200 g (66%) of **4b**. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (t, C*H*$_3$, 1), 1.26 (m, C*H*$_2$), 1.41-1.60 (br, $NCH_2CH_2CH_2N$, $NHCH_2CH_2CH_2$), 2.20 (s, C*H*$_3$, a), 2.34 (br, C*H*$_2$N(CH_2)$_2$), 2.42 (m, C*H*$_2$NH). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 14.41 (alkyl *C*1), 23.08 (alkyl *C*2), 24.88-25.00 ($NCH_2CH_2CH_2N$, $NCH_2CH_2CH_2CH_2N$, $NCH_2CH_2CH_2NH$), 28.05 (alkyl *C*16), 28.12 (alkyl *C*15, *C*16), 30.12-29.47 (alkyl *C*4-*C*14), 29.20 (alkyl *C*17), 31.21(alkyl *C*3), 52.87 ($NHCH_2CH_2CH_2N$), 54.20 ($NCH_2CH_2CH_2CH_2N$). 56.23 ($NCH_2CH_2CH_2NH$), 58.20 (alkyl *C*18).

2-[2-(2-Methoxyethoxy)ethoxy]acetyl chloride. A solution of 2-[2-(2-methoxy ethoxy)ethoxy]actetic acid (5.34 g, 30.0 mmol) and oxalyl chloride (6.35 g, 50.0 mmol) in 3 mL of toluene was stirred for 4 h at 65 °C. The solvent and excess reagent were removed under reduced pressure, and the residue was dried at 40 °C under vacuum to give a light yellow oil (5.24 g, 90%) which was used without further purification.[6]

$\mathbf{G_2}$(Am8) (5). By the procedure used to prepare **$\mathbf{G_2}$(Am8) (2a)**, 2-[2-(2-methoxyethoxy)ethoxy]acetyl chloride (3.000 g, 15.3 mmol), $\mathit{DAB\text{-}dendr\text{-}(NH_2)_8}$ (1000 mg, 1.29 mmol) and anhydrous TEA (0.99 g, 8.9 mmol) in anhydrous DMF (5.0 mL) gave 2.128 g (10.4 mmol, 81%) of light yellow oil. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, δ): 1.40-1.78 (br, $\mathrm{NCH_2C\mathit{H}_2CH_2NCO}$, $\mathrm{NCH_2C\mathit{H}_2CH_2N}$, $\mathrm{NCH_2C\mathit{H}_2C\mathit{H}_2CH_2N}$), 2.40 (m, $\mathrm{CH_2N(C\mathit{H}_2)_2}$, $\mathrm{NC\mathit{H}_2CH_2CH_2C\mathit{H}_2N}$) 3.25 (q, $\mathrm{C\mathit{H}_2NHCO}$), 3.40 (s, $\mathrm{OC\mathit{H}_3}$), 3.60-3.78 (m, $\mathrm{OC\mathit{H}_2C\mathit{H}_2}$), 4.0 ($\mathrm{COC\mathit{H}_2O}$), 8.0 (br, $\mathrm{N\mathit{H}CO}$). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, δ): 24.4 ($\mathrm{NCH_2\mathit{C}H_2CH_2NH}$), 25.6 ($\mathrm{NCH_2\mathit{C}H_2\mathit{C}H_2CH_2N}$), 27.8 ($\mathrm{NCH_2\mathit{C}H_2CH_2NHCO}$), 38.0 ($\mathrm{NCH_2CH_2\mathit{C}H_2NHCO}$), 51.0 ($\mathrm{N\mathit{C}H_2CH_2CH_2NHCO}$), 51.4 ($\mathrm{N\mathit{C}H_2CH_2\mathit{C}H_2N}$), 52.2 ($\mathrm{N\mathit{C}H_2CH_2CH_2\mathit{C}H_2N}$), 58.8 ($\mathrm{O\mathit{C}H_3}$), 70-71.8 ($\mathrm{O\mathit{C}H_2\mathit{C}H_2O}$), 72.2 ($\mathrm{CO\mathit{C}H_2O}$), 170.0 ppm ($\mathit{C}$=O).

$\mathbf{G_2}$(SAn8) (6): By the procedure used to prepare **$\mathbf{G_2}$(SAn8) (3a)**, lithium aluminum hydride (10 mL of a 1.0 M solution in THF, 10.0 mmol) and amide **5** (1.600 g, 0.78 mmol) in anhydrous THF (23 mL) gave 1.25 g (0.64 mmol, 83 %) of yellow oily secondary amine dendrimer **6**. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, δ): 1.40-1.75 (br, $\mathrm{NCH_2C\mathit{H}_2CH_2NCO}$, $\mathrm{NCH_2C\mathit{H}_2CH_2N}$, $\mathrm{NCH_2C\mathit{H}_2C\mathit{H}_2CH_2N}$), 2.43 (m, $\mathrm{CH_2N(C\mathit{H}_2)_2}$, $\mathrm{NC\mathit{H}_2CH_2CH_2C\mathit{H}_2N}$) 2.62 (t, $\mathrm{C\mathit{H}_2NHCH_2CH_2O}$), 2.78 (t, $\mathrm{CH_2NHC\mathit{H}_2CH_2O}$), 3.40 (s, $\mathrm{OC\mathit{H}_3}$), 3.60-3.78 (m, $\mathrm{OC\mathit{H}_2C\mathit{H}_2O}$). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, δ): 24.20 ($\mathrm{NCH_2\mathit{C}H_2CH_2NH}$), 24.84 ($\mathrm{NCH_2\mathit{C}H_2\mathit{C}H_2CH_2N}$), 27.26 ($\mathrm{NCH_2\mathit{C}H_2CH_2NH}$), 48.28 ($\mathrm{NH\mathit{C}H_2CH_2O}$), 49.16 ($\mathrm{NCH_2CH_2\mathit{C}H_2NH}$), 51.79 ($\mathrm{N\mathit{C}H_2CH_2CH_2NH}$), 52.10

$(\mathrm{N}\mathit{C}\mathrm{H_2CH_2}\mathit{C}\mathrm{H_2N})$, 54.00 $(\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2N})$, 58.80 $(\mathrm{O}\mathit{C}\mathrm{H_3})$, 70-70.40 $(\mathrm{O}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2O})$. 71.68 $(\mathrm{NHCH_2}\mathit{C}\mathrm{H_2O})$.

$\mathrm{G_2}$(TAn8) (7): By the procedure for used to prepare **$\mathrm{G_2}$(TAn8) (4a),** mixture of the secondary amine **6** (1.25 g , 0.64 mmol), 2.030 g (27.9 mmol) of 37% formaldehyde, 4.180 g (79.9 mmol) of 88% formic acid and 15 mL of toluene gave 0.863 g (0.42 mmol, 67%) of the oily tertiary amine **7**. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, δ): 1.40-1.75 (br, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2NCO}$, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2N}$, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$), 2.21 (m, $\mathrm{CH_2N(C}\mathit{H}_2)_2$, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{N}$) 2.40 (m, $\mathrm{C}\mathit{H}_2\mathrm{N(CH_3)CH_2CH_2O}$), 2.58 (t, $\mathrm{CH_2N(CH_3)C}\mathit{H}_2\mathrm{CH_2O}$), 3.38 (s, $\mathrm{OC}\mathit{H}_3$), 3.50-3.70 (m, $\mathrm{OC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{O}$).^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, δ): 24.20 $(\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_2N}$, 24.84 $(\mathrm{NCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2N})$, 27.26 $(\mathrm{NCH_2}\mathit{C}\mathrm{H_2CH_2N})$, 42.80 $(\mathrm{N(}\mathit{C}\mathrm{H_3)CH_2CH_2O})$, 51.79 $(\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2N})$, 52.10 $(\mathrm{N}\mathit{C}\mathrm{H_2CH_2}\mathit{C}\mathrm{H_2N})$, 54.00 $(\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2N})$, 57.00 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2O}$, $\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2N}$), 58.80 $(\mathrm{O}\mathit{C}\mathrm{H_3})$, 70-70.40 $(\mathrm{O}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2O})$. 71.68 $(\mathrm{N(CH_3)CH_2}\mathit{C}\mathrm{H_2O})$.

Solubilities of Dendrimers. Solubilities were tested by adding 4-5 mg of sample into 1.0 mL of solvent in a 4 mL vial and stirring magnetically for 30 min. The sample was judged soluble if a clear solution formed, slightly soluble if a cloudy solution formed, and insoluble if the oil or solid remain unchanged.

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CHAPTER III

HIGHLY ORDERED LANGMUIR FILMS OF AMPHIPHILIC POLY(PROPYLENE IMINE) DENDRIMERS AT THE WATER-AIR INTERFACE

ABSTRACT

Three amphiphilic poly(propylene imine) (PPI) dendrimers were synthesized by attaching lauroyl chains to a commercial PPI (*DAB-dendr-*$(NH_2)_8$) dendrimer core in DMF. Interfacial behavior of those dendrimers at the air/water interface was investigated using a Langmuir trough. The films of the dendrimers were transferred to newly cleaved mica by the Langmuir-Blodgett method. Surface pressure-area isotherms and atomic force microscopy (AFM) measurements showed that the amphiphilic dendrimers formed stable monolayers of smooth and homogenous surface with roughness < 0.5 nm. High resolution AFM images showed a tetragonal motif with spacing of between 0.4 and 0.5 nm, indicating crystalline two dimensional packing of the alkyl chains on a mica surface.

INTRODUCTION

Dendrimers are highly branched and monodisperse polymers that have attracted increasing interest due to their special properties and potential diverse applications ranging from chemical sensing to molecular transfer in biological environments.[1-5] Among the dendrimer studies, the modification of dendrimers and the supramolecular chemistry of dendrimers are two of the most studied fields.[6] The modification of dendrimers can take place at the periphery or at the branch points or at the core and will change the properties of the dendrimers. Assembly of dendrimers, such as self-assembled monolayers (SAMs) and Langmuir-Blodgett (LB) films which are highly ordered supramolecular systems, will bring new and promising properties to the interfaces.[1,7]

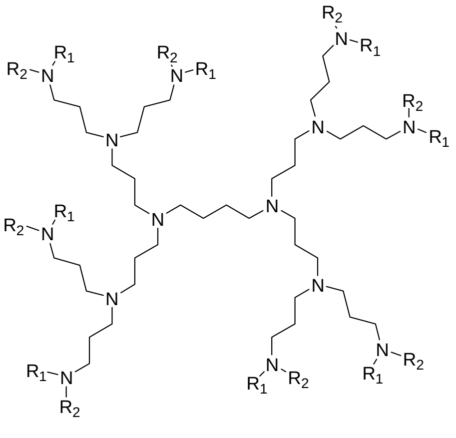
Langmuir and Langmuir-Blodgett (LB) technology are the leading tools to study the surface and interface behavior, especially novel molecule architecture arrangements at the air-water interface. When amphiphilic compounds are dissolved in a volatile organic solvent and the solution is spread on the air-water interface of a trough, the volatile organic solvent evaporates and the hydrophilic polar head of the amphiphilic molecule is in contact with the water surface, while the hydrophobic non-polar part points to air and extends away from the water surface. Thus a monolayer is formed at the interface. The Langmuir monolayer is an ideal two-dimensional (2D) system for the study of chemistry and thermodynamics at the surface and interface.[8] The monolayer has three 2D phases (gas, expanded liquid, condensed liquid) depending on the intermolecular distance, the pH, the ionic content of water and the experimental temperature. The monolayer can be transferred to a solid substrate layer by layer by the

LB technique, where the substrate is vertically dipped into and pulled out of the water subphase. Recently, the use of dendrimers at surfaces and interfaces has received increased attention.[9,10] Several research groups have prepared amiphiphilic dendrimer Langmuir films.[11-16] Studying the behavior of amphiphilic dendrimers at the air-water interface allows researchers to gain important information about their size, shape, compressibility, and flexibility.[11-16] Meijer and coworkers modified the end groups of PPI dendrimers using long hydrophobic chains.[11,12] The conformational flexibility of dendrimer branches allowed folding of the dendritic structure to form a pancake shape of the polar cores at the air-water interface.[11,12] The modified dendrimers form monolayers at the air/water interface with the hydrophilic pancake core contacting with the water subphase and the hydrophobic end groups perpendicularly extending away from the water surface.[11,12] This implies that significant flexibility of the dendritic core allows the conformation to reorganize and match with the planar air-water interface.[11,12]

Atomic force microscopy (AFM) makes understanding of surface and interface behavior and molecular organization possible because it is a high-resolution imaging technique that provides surface topography information as small as the atomic lattice in the real space. It allows researchers to obtain molecular and atomic level properties.

Significant progress has been made in the study the surface morphology of poly(amidoamine) dendrimers (PAMAM) by AFM, including imaging of different generations of PAMAM,[17,18] investigation of self-assembled monolayers and mutilayers of PAMAM by electrostatic deposition technique,[19] and study of individual PAMAM dendrimers absorbed on a Au(111) substrate.[20] Especially Tomalia and coworkers systematically studied molecular properties, such as size, shape, and rigidity after deposition on a mica surface, of PAMAM by using AFM.[17]

There are few AFM studies of poly(propylene imine) (PPI) dendrimers. Previous studies by the Langmuir Blodgett (LB) film method showed that PPI dendrimers amidated by acid chlorides can form very stable monolayers at the air-water interface.[12] Meijer and coworkers reported that a LB monolayer of *DAB-dendr-*$(NH_2)_{64}$ with 32 palmitoyl and 32 azobenzene alkyl chains on a silicon wafer had a smooth and homogeneous surface with an average film thickness of about 3.1 nm by using AFM technique.[11] Recently we successfully modified a second-generation PPI dendrimer with lauroyl chloride and studied the adsorption behavior of the modified PPI dendrimer on a mica surface.[21] The dendrimer formed fractal aggregates on mica at the very beginning of adsorption. With the adsorption time increase, the dendrimer molecules diffuse and integrate into the fractal structures and form a continuous film.



2a: $R_1 = CH_3(CH_2)_{10}CO$-; $R_2 = H$
3a: $R_1 = CH_3(CH_2)_{10}CH_2$-; $R_2 = H$
4a: R1 = $CH_3(CH_2)_{10}CH_2$-; $R_2 = CH_3$-

Figure 1. Structure of PPI dendrimers modified by lauroyl chloride

In this study, we report our systematic investigation of the assembly of hydrophobically modified PPI dendrimers at the air/water interface. The PPI dendrimers were functionalized with lauroyl chloride (**2a**) and then the amide units were further transformed to secondary and tertiary amine (**3a, 4a**). The modified dendrimers can form monolayers on water surfaces due to their amphiphilicity. Surface pressure-area isotherm measurements and AFM observations revealed that the amphiphilic dendrimers formed stable monolayers of smooth and homogeneous surface with roughness <0.5 nm at 10×10 μm scan scale. At the condensed state, especially when the compression reached 25 mN/m, the alkyl chains packed tightly and formed a 2D crystal with chain-to-chain spacing of between 0.4 nm and 0.5 nm and an aliphatic chain titling angle of 30º.

EXPERIMENTAL SECTION

Surface Pressure-Area Isotherms. Measurements were carried out at 24 ºC by using a NIMA Langmuir-Blodgett trough (Model 712 BAM, Serial 035, Nima Technology Ltd, England). The LB trough, which was protected by a glass box, was cleaned with TX™ 304 TexWipe® wipers (Engineered Fabrics® for Critical Environments, The Texwipe Company LLC, Upper Saddle River, NJ) and chloroform as a cleaning solvent, waiting 15 minutes until all the cleaning solvent evaporates. Chloroform (reagent grade) was used as received within half a year. The surface pressure was measured using the Wihelmy plate method. The water used as the subphase was purified to a specific resistivity of 18 MΩ.cm in our lab. The amphiphilic dendrimers were dissolved in chloroform at a concentration of 2.0 mg/mL and the solutions were used without further filtration. Scintillation vials for holding solutions were used as received. Spatulas for transferring dendrimers were also cleaned with the TexWipe® wipers and chloroform. On the water subphase (pH=7, surface area: 710 cm^2), 30 μL of dendrimer solution was spread using a 50 μL Finnpipette and allowed to equilibrate for 20 min before compression was started. Isotherms were recorded with a compression speed of 50 cm^2/min at room temperature.

Surface Film Transfer. The deposition of the dendrimer monolayer from the water surface to mica was carried out at a surface pressure of 25 mN/m. Newly cleaved mica was vertically placed in the water subphase; the monolayer was created and compressed as stated above. Then the pressure was released and the monolayer was recompressed at the same speed until the surface pressure reached 25 mN/m. Mica was withdrawn at a speed of 2 mm/min (upstroke) at the constant surface pressure of 25 mN/m. The mean molecular area was 160 Å^2/molecule during the time of transfer.

AFM Measurements. The dendrimer films were transferred onto newly cleaved mica surfaces by the LB method at 25 mN/m. After 8 to 48 h, the films were imaged by AFM (Digital Instruments Multimode Scanning Probe Microscope with Nanoscope IIIa controller, Digital Instruments, Santa Barbara, CA) operated in either tapping mode or contact mode. For tapping mode imaging, the AFM was operated at the set point ratio of 0.9 and the scanning rate of 1.0 Hz /line. The silicon probe (MikroMasch, Portland, Oregon) had a spring constant of 2-5 N/m, a resonance frequency of 120 - 170 kHz, and a nominal tip radius of curvature of 5-10 nm. Contact mode AFM was employed and Si_3N_4 cantilevers with a nominal spring constant of 0.38 N/m were used for high-resolution imaging. A high-pass and low-pass filtering process as well as a Fast Fourier Transfer

(FFT) process were applied to the raw image data to remove most of the noise that may possibly be due to air flow and acoustic noise in our laboratory.

RESULTS AND DISCUSSION

Dendrimers at the Air/Water Interface. The compression of the amphiphilic dendrimers, **2a**, **3a**, and **4a**, at the air-water interface was investigated using Langmuir techniques. The results are shown in **Figure 2**. The surface pressure versus area (Π~A**)** isotherms of the amphiphilic dendrimers showed the formation of stable Langmuir monolayers with expanded and condensed liquid 2D phases typical for amphiphiles.[8] The isotherms exhibited a sharp increase of the surface pressure upon compression, which indicate the formation of stable monolayers.

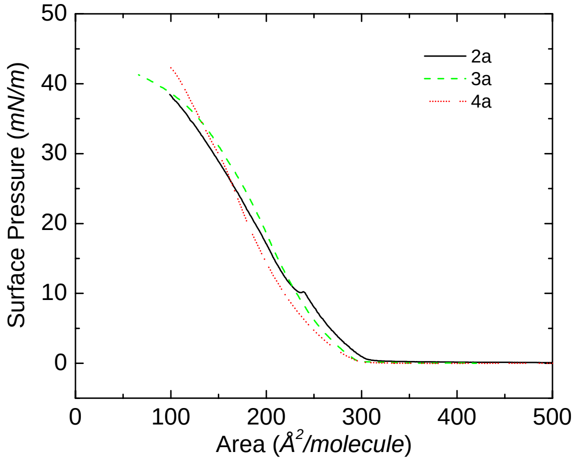


Figure 2. Pressure-area isotherms (Π ~A) of modified dendrimers.

Table 1. Areas for Modified *PPI-$(NH_2)_8$*-dendrimers from Extrapolation of First Compression Isotherms to Zero Pressure

Dendrimers	**2a**	**3a**	**4a**
Area, (Å^2)/molecule	271	264	243

The surface areas per molecule for the hydrophobically modified dendrimers were estimated by extrapolation of the steep rise in surface pressure to zero pressure in reference to a usual method[12,22,23] and listed in Table 1. The isotherms of the amphiphilic molecules strongly depend upon the numbers of hydrophobic groups attached to the hydrophilic core.[23] If a molecular area of 20 Å^2, a value usually found for alkylcarboxylates,[12] is assumed for one lauroyl chain, the ideal surface area per molecule for the lauryol modified dendrimers (each dendrimer has 8 hydrophobic chains) should be 160 Å^2 (20 Å$^2 \times$ 8). The observed surface areas per molecule (Table 1) are larger than the theoretical value (160 Å^2). This implies that the modified dendrimers “spread out” a little bit and flatten on the water surface in the expanded liquid phase.[7] According to Tomalia[24] and Meijer[12] the hydrophilic dendrimer core associates closely with the aqueous subphase while the hydrophobic alkyl tails reorganize themselves and point outward to the air. Providing that the poly(propylene imine) core has a nearly flat and oblate conformation, all the attached hydrophobic chains make up the observed molecular area.[25]

AFM Studies of LB Films. For topographic studies of the hydrophobically modified PPI dendrimers by AFM, Langmuir-Blodgett films were prepared by the vertical dipping method on mica surfaces. Newly cleaved clean mica sheets were dipped vertically downward into the Langmuir trough before the Langmuir film formation so that deposition only occurred at the upright stroke of the mica sheets. The films were kept in ambient condition to allow water to evaporate naturally and imaged in more than 8 but less than 48 h.

The film transfer of dendrimers **2a**, **3a**, and **4a** was carried out at a constant pressure of 25 mN/m after the second compression, shown in Figure 3. The second compression exhibited similar hysteresis for all three dendrimers, indicating irreversibility of compression due to the formation of compact domains on the water surface.[12] The molecular areas of the dendrimers on water from the second compression to 25 mN/m were about 160 Å^2 (Figure 3), which is equal to that of 8 tightly packed alkyl chains perpendicular to the surface. The transfer ratio of the film to mica was almost unity, which suggests that the surface structure of the transferred film on mica is equal to that at the air-water interface. The transfer ratio is defined by the following formula:[8]

$$\gamma = A_1 / A_2$$

where A_1 is the decrease of water subphase area during the deposition process, and A_2 is the mica surface area covered (two sides). The monolayers were never at equilibrium in our experiments. Since the monolayers were compressing slowly on water at the same time as dendrimers were being transferred to mica, the defined formula needs to be modified. The area of water covered decreased by an average of 14.5 cm^2 without deposition during the same time period as deposition. The transfer ratio was calculated by the modified formula:

$$\gamma = (A_1 - 14.5) / A_2$$

Table 2 reports the calculated results.

Table 2. The Calculated Transfer Ratio for Dendrimers 2a-4a

Dendrimer	**2a**	**3a**	**4a**
A_1 (cm^2)	29.2	31.6	33.0
A_2 (cm^2)	15.1	16.5	17.3
Transfer ratio	0.97	1.07	1.06

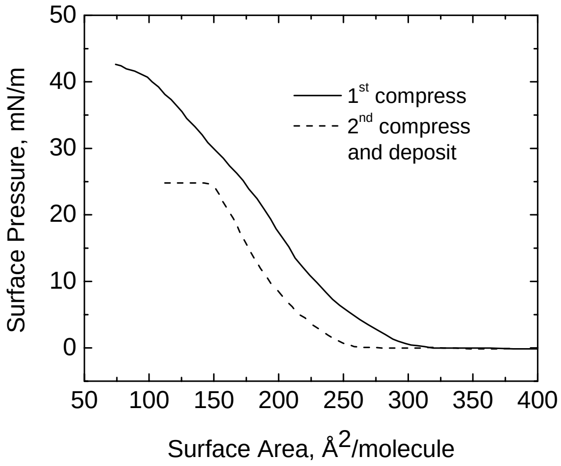


Figure 3. Representative isotherm of C_{12}-modified PPI dendrimer **4a**. Isotherms of **2a**, **3a** were similar to this.

AFM scans at different locations and scan sizes of showed the transferred LB film of **2a** was very flat with a roughness < 0.5 nm at a scan size of 10 × 10 μm, shown in Figure 4a. Scratching experiments were carried out on the same film by switching the operation from tapping mode to contact mode. Figure 4b shows the height image of the LB film of **2a** captured after scratching the transferred LB film at ~100 nN on an area of 0.5 μm × 0.5 μm. A rectangular groove of 0.1 μm × 0.5 μm was formed by scratching, and the surrounding area of that groove didn't change in height. This points out that the LB film of **2a** is very stable and hard to penetrate by the AFM tip due to the dense molecular packing on the mica.[26] The section analysis indicated the LB film transferred from the water/air interface to mica had a thickness of 1.2 nm. The length of an extended zigzag C_{11} aliphatic chain is 1.37 nm. Providing there was no effect of the tapping pressure of the AFM operation on the height measurement of such an orderly packed LB film, the measured thickness of the transferred dendrimer film corresponds to a tilting of 30° of the aliphatic chains related to an ideal perpendicular packing. The results are very consistent with the literature reports on LB films of amphiphilic compounds with alkyl chains of different length transferred from the water/air interface onto a silicon surface.[11]

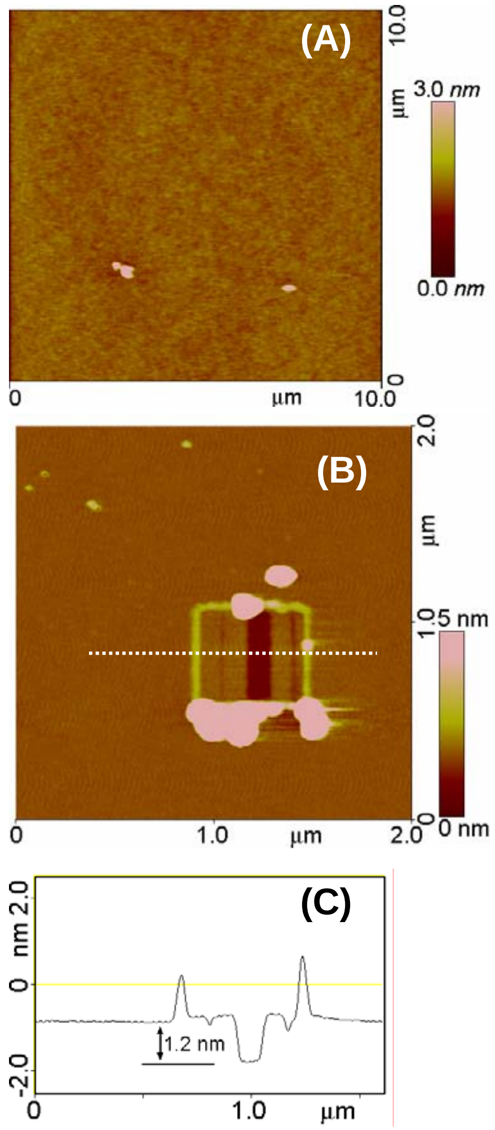


Figure 4. (A) AFM height images of a LB film of dendrimer **2a** deposited on mica at a surface pressure of 25 mN/m. (B) AFM height image of a LB film of dendrimer recorded after continuously scratching at ~100 nN in a 0.5 μm × 0.5 μm area. While a rectangular groove of 0.1 μm × 0.5μm was formed by scratching, the surrounding area of that groove did not change obviously with regard to the height.

A representative high-resolution AFM image of **2a** on mica is shown in Figure 5. Partially because of the environment settings of our laboratory, such as vibration, air flow, and acoustic noise, the raw atomic resolution images were noisy. After removing most of the noise by high-pass and low-pass filtering, the Fast Fourier Transform (FFT) process gave a nice FFT spectrum, shown in the corner in Figure 5A, indicating a highly ordered structure of the transferred dendrimer films. The FFT processed image, shown in Figure 5B**,** indicates that the aliphatic chains chemically bonded onto the dendrimers formed 2D crystals on the mica surface with a chain-to-chain spacing of 0.45 nm in both directions on the surface plane. A high-resolution AFM image of mica is shown in Figure 5C and 5D. A hexagonal structure with a spacing of 0.54 was clearly identified for the mica surface, which was used for deposition of dendrimer monolayer. The appearance of a tetragonal motif after the Langumuir-Blodgett film transfer when mica has a hexagonal motif proves that the dendrimers deposited onto the mica.

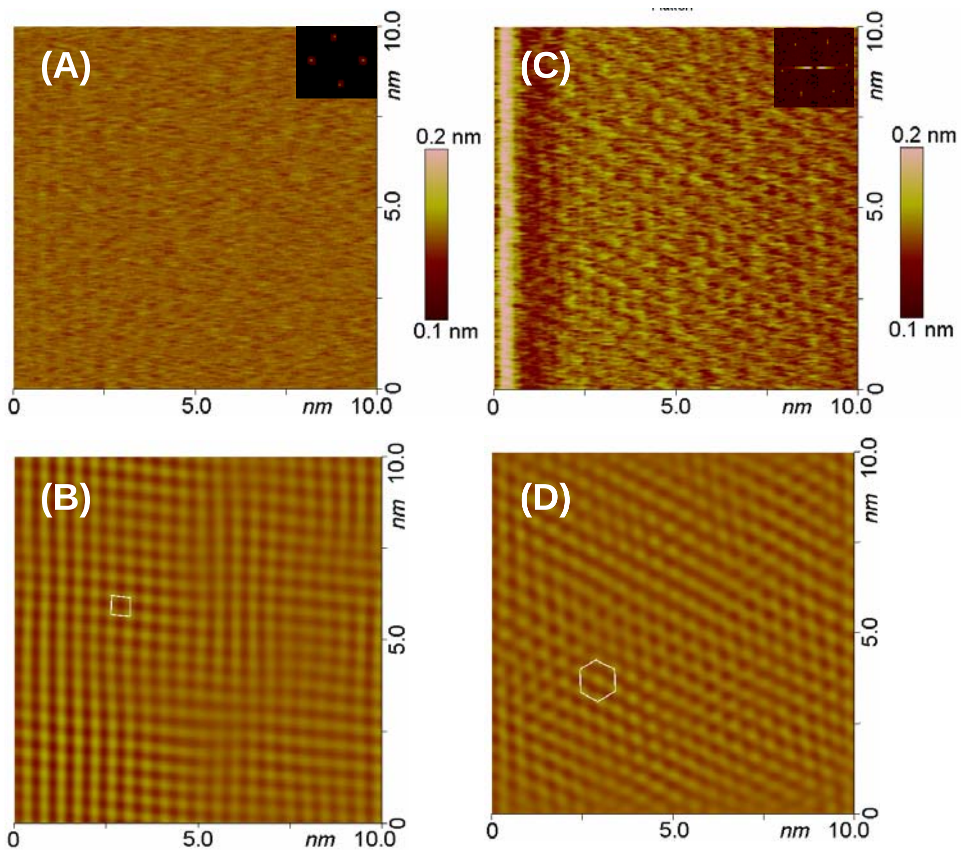


Figure 5. High-resolution AFM images of the LB film of dendrimer **2a** deposited on mica at a surface pressure of 25 mN/m (A and B) and newly cleaved mica (C and D) before (A, C) and after (B, D) Fast Fourier Transform (FFT) processing. The 2-D FFT spectrum was inserted at the top-right corner of the raw data.

The AFM images of dendrimers **3a** and **4a** are shown in Figures 6, 7, 8 and 9. Similar to dendrimer **2a** the LB films of **3a** and **4a** exhibited very flat surfaces with roughness < 0.5 nm at scan size of 10 × 10 μm, shown in Figures 6A and 8B. The film thickness as estimated by AFM scratching for the LB films of **3a** and **4a** were 1.9 nm and 1.7 nm, respectively, shown in Figures 6b, 6c, 8b, and 8c, which were thicker than that of **2a**. The dendrimers **3a** and **4a** are derivatives of **2a** with the carboxyl group being reduced to a methylene unit; therefore the aliphatic chain is one unit longer (~1.25 Å). This modification in chemistry may also influence the deformability of the hydrophilic dendrimer core, so that the compression at 25 mN/m makes the aliphatic chains more compact and also reduces the area covered by the oblate hydrophilic core. Both the change in chemistry of dendrimers **3a** and **4a** and the possibly forced deformation induced by compression on the dendrimer core contribute to the increase of the film thickness.

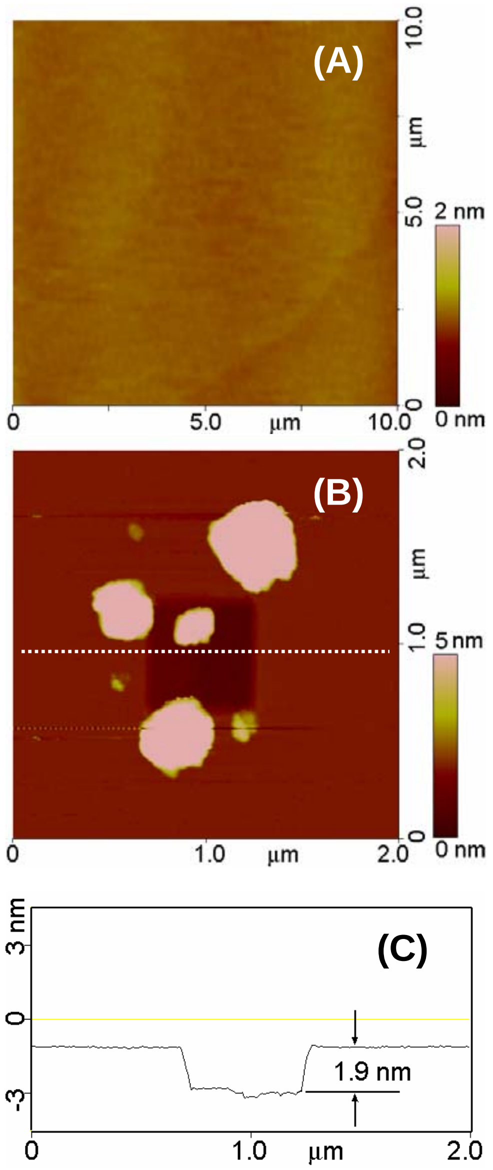


Figure 6. AFM height images of a LB film of dendrimer **3a** deposited on mica at a surface pressure of 25 mN/m (A) and after scratching on the transferred LB film at ~100 nN in a 0.5 μm × 0.5 μm square area (B). (C) is a profile of image (B).

High resolution FFT AFM images obtained from regions of the **3a** and **4a** monolayers on mica, shown in Figures 7 and 9, indicated that the aliphatic tails were still well packed with lateral spacing between neighboring tail ends of 0.44 nm and 0.41 nm, respectively. However, more defects were observed on those LB films, as seen in Figures 7 and 9. These defects may be caused by the dislocation of neighboring aliphatic chains during the compression to both the hydrophilic dendrimer core and the hydrophobic alkyl chains.

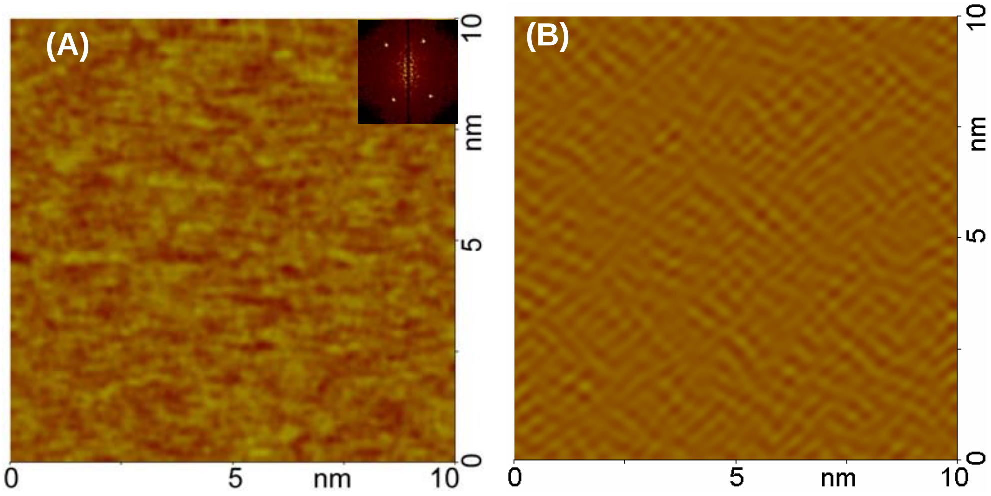


Figure 7. High-resolution AFM image of the LB film of dendrimer **3a** deposited on mica at a surface pressure of 25 mN/m.

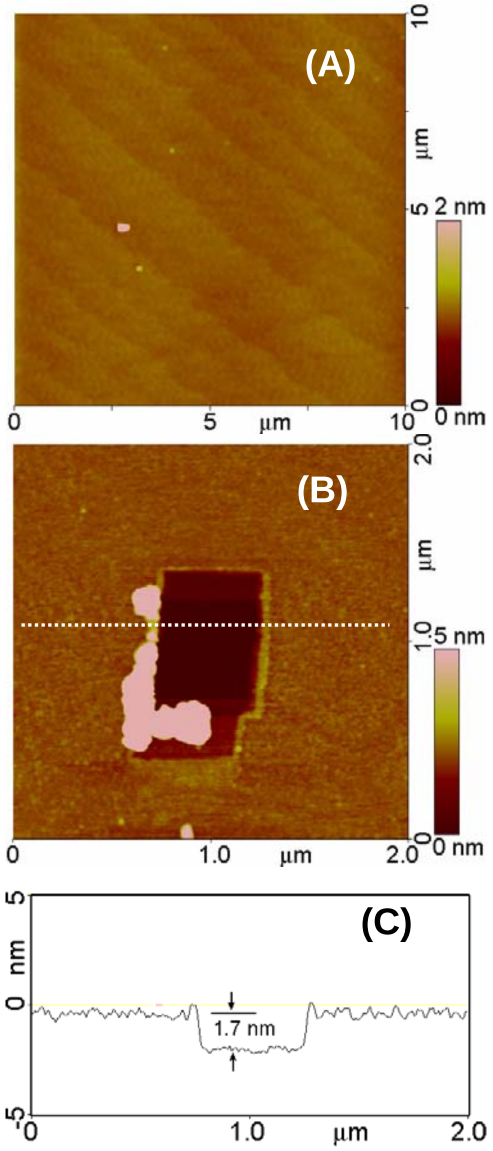


Figure 8. AFM height images of LB film of dendrimer **4a** deposited on mica at a surface pressure of 25 mN/m (A) and after scratching on the transferred LB film at ~100 nN in a 0.5 μm × 0.5 μm square area (B). (C) is a profile of image (B).

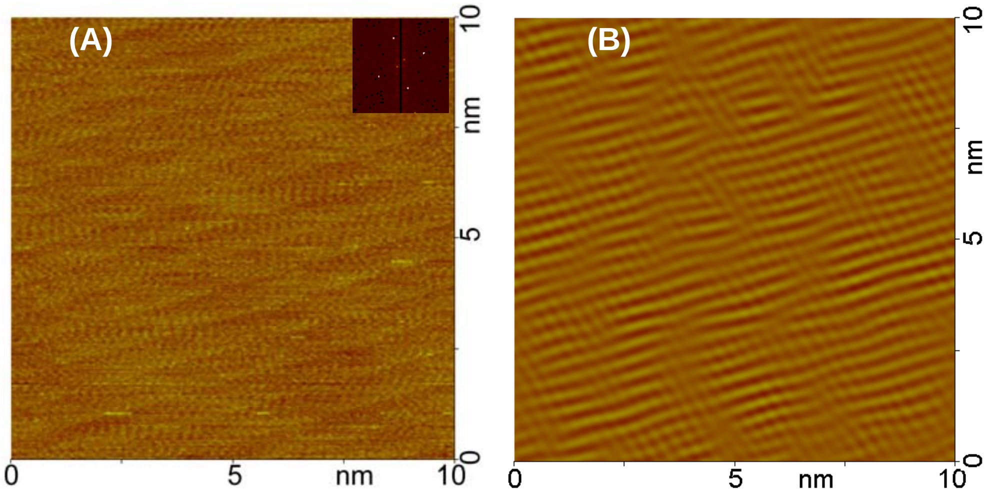


Figure 9. High-resolution AFM image of the LB film of dendrimer **4a** deposited on mica at a surface pressure of 25 mN/m.

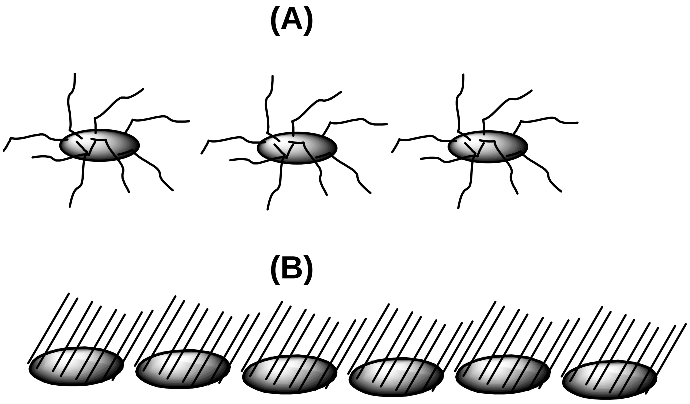


Figure 10. Schematic representation of the molecular organization of the amphiphilic PPI dendrimers at the air/water interface. (A) At surface pressure ~0 mN/m, the dendrimers spread well on the surface with relatively planar conformation. (B) Well ordered, close-packed monolayer at a surface pressure of 25 mN/m.

From the Π -A isotherm and AFM results, the self-assembly of the lauroyl modified PPI dendrimer **2a** and its derivatives **3a** and **4a** at the air-water interface is depicted in Figure 10. At surface pressure of ~0 mN/m, the dendrimers spread well on the surface with relatively planar conformation (Figure 10A). As surface pressure builds up, the molecules are forced to fill the gaps between molecules and condensed monolayer domains appear. Further compression results in a well-ordered condensed monolayer with alkyl groups standing away from the water surface (Figure 10B).

For other low-generation monodendrons with peripheral alkyl chains, the Π -A isotherms show a wide limiting area and a low critical monolayer pressure.[27] Grazing-incident X-ray diffraction studies[28-30] as well as high-resolution AFM measurements[26] indicate that the alkyl chains form very ordered lattices with molecular axes tilted toward nearest neighbors. Generally the hydrophilic core is at or beneath the water surface, and the alkyl chains form a high-density sublayer above the surface with the chains pointed away from the air/water interface.[12,24] Our results are in good agreement with the literature reports in showing packing and tilting of the peripheral alkyl chains.

In summary, lauroyl modified PPI dendrimers **2a** and its derivatives **3a** and **4a** exhibited strong amphiphilic behavior. They can form well packed monolayers at the surface pressure of 25 mN/m. The AFM scratching experiments indicated that the lauroyl modified PPI dendrimer **2a** was oriented with a tilting angle of 30º to the aliphatic chain axis to fill gaps in the empty region in the dendrimer core, while the hydrophilic dendrimer core adopts a flattened conformation that associates with water molecules by hydrogen bonding. Derivatives **3a** and **4a** formed more compact monolayers at the air/water interface with less tilting of the aliphatic chains and more squeezed hydrophilic dendrimer cores.

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CHAPTER IV

LANGMUIR AND LANGMUIR–BLODGETT FILMS OF STEAROYL MODIFIED POLY(PROPYLENE IMINE) G_2 DENDRIMER AND ITS DERIVATIVES

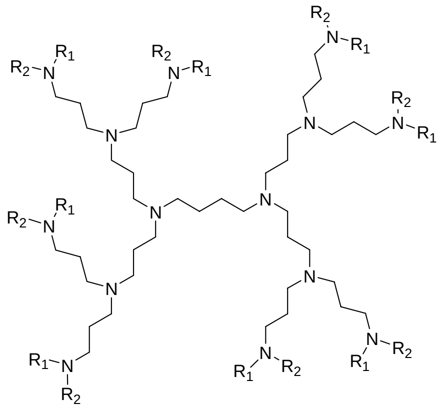
ABSTRACT

Amphiphilic poly(propylene imine) (PPI) dendrimers were synthesized by amidation of a commercial PPI (*DAB-dendr-*$(NH_2)_8$) dendrimer with stearoyl chloride in DMF. The amidated PPI dendrimer was further modified to form secondary and tertiary PPI amines. Interfacial behavior of these dendrimers at the air/water interface was investigated using a Langmuir trough. The films of the dendrimers were transferred to freshly cleaved mica by the Langmuir-Blodgett method at surface pressures of 10 mN/m and 25 mN/m and characterized by atomic force microscopy (AFM) measurements. The Langmuir films transferred at the surface pressure of 10 mN/m were relatively stable and showed island structures. The monolayers were collapsed on mica after transfer at the surface pressure of 25 mN/m, which is below the collapse pressure observed on the surface pressure-area isotherms.

INTRODUCTION

Langmuir and Langmuir-Blodgett films have been investigated extensively for their potential applications in nonlinear optical, piezoelectric, pyroelectric, semiconducting, sensing and barrier devices.[1-5] Dendrimers have been recognized as promising building blocks of Langmuir-Blodgett films for the surface groups of dendrimers can be chemically functionalized through the synthetic manipulation and application of the resulting dendrimers in the related areas has been expanding.[6-14]

Several research groups have prepared Langmuir films from amiphiphilic dendrimers.[15-20] Previous studies showed that PPI dendrimers amidated by acid chlorides can form very stable monolayers at the air-water interface.[16] Meijer and coworkers reported that a LB monolayer of $DAB\text{-}dendr\text{-}(NH_2)_{64}$ with 32 palmitoyl and 32 azobenzene end groups on a silicon wafer had a smooth and homogeneous surface with an average film thickness of about 3.1 nm by using AFM technique.[15] Recently we successfully modified a second-generation PPI dendrimer with lauroyl chloride and studied the adsorption behavior of the modified PPI dendrimer at different interfaces.[21,22] The dendrimers form fractal aggregates on mica at the very beginning of physical adsorption. With the adsorption time increase, the dendrimer molecules diffuse and integrate into the fractal structures and form continuous film.[21] At the air/water interface, these amphiphilic dendrimers form monolayers at a surface pressure of 25 mN/m.[22]



2b: $R_1 = CH_3(CH_2)_{16}CO$, $R_2 = H$
3b: $R_1 = CH_3(CH_2)_{16}CH_2$, $R_2 = H$
4b: $R_1 = CH_3(CH_2)_{16}CH_2$, $R_2 = CH_3$

Figure 1. Structures of the hydrophobically modified PPI G_2 dendrimers.

In this study, we report our systematic investigation of the assembly of stearoyl modified PPI dendrimer **2b** and its derivatives **3b** and **4b**, shown in Figure 1, at the air/water interface. The PPI dendrimer **1**, DAB-*dendr-*$(NH_2)_8$, was functionalized with stearoyl chloride to give amide **2b** and then the amide units were further transformed to secondary amine **3b** and tertiary amine **4b** These hydrophobically-modified PPI dendrimers form monolayers on a water surface due to their amphiphilicity. Surface pressure-area isotherm measurements indicated that the dendrimers exhibited fast transition from gas phase to condensed phase. AFM observations revealed that the amphiphilic dendrimers formed stable monolayers as island structures in which some of the dendrimer molecules lie relatively flat on and some of the dendrimer molecules extend away from the mica surface. In the condensed liquid state on water, especially when the compression reached 25 mN/m, the alkyl chains were pushed up and extended almost perpendicularly away from the water subphase. Collapse of the monolayers was revealed by formation of dense islands of various areas and heights in the AFM images of the Langmuir-Blodgett films.

EXPERIMENTAL

The methods for preparation of monolayers on water, Langmuir-Blodgett films transfer onto mica, and AFM imaging are reported in Chapter III.

Determination of Dendrimer Size in Solution. Dynamic light scattering based High Performance Particle Size Analyzer (Malvern Instruments, UK) was used to measure the size and size distribution of dendrimers in chloroform. The measurements were carried out at 25ºC with a solution concentration of 2 mg/mL, the same concentration as used in Langmuir film formation.

RESULTS

Dendrimers at the Air/Water Interface. The self-assembly of the amphiphilic dendrimers **2b**, **3b**, and **4b** at the air/water interface was investigated by the Langmuir technique. The results are shown in Figures 2-4. The surface pressure versus area (Π-A**)** isotherms of the amphiphilic dendrimers showed typical features of amphiphiles at the air/water interface.[5] The isotherms had a sharp increase of the surface pressure upon compression, which indicates steady transition from a liquid-expanded phase to a liquid condensed phase. The reversibility of the compression of the amphiphilic dendrimers at the air/water interface was characterized by measuring the isotherms during compression-expansion cycles. The Π-A isotherms of **3b** are shown in Figure 3. The dendrimers **2b** and **4b** exhibited similar behavior at the air/water interface during the compression-expansion cycling. The second compression showed a clear hysteresis with the second Π-A isotherm curve displaying a smaller molecular area than the preceding one. By repeated compression-expansion cycling, however, a relatively small hysteresis was reached. Furthermore, as shown in Figure 4, when the compression pressure was controlled to 10 mN/m, the Π-A isotherms of dendrimers **2b**, **3b**, and **4b** exhibited very small hysteresis during the compression-expansion cycling, indicating excellent reversibility of the monolayer formation at low surface pressure. The large hysteresis of the first cycle, especially when the first compression reached a surface pressure above 25 mN/m, may be due to the influence of domain formation by the solution-spreading and solvent-evaporation process. This indicates that the initial state of the monolayer is slightly changed and that reorganization takes place during the compression-expansion cycles.

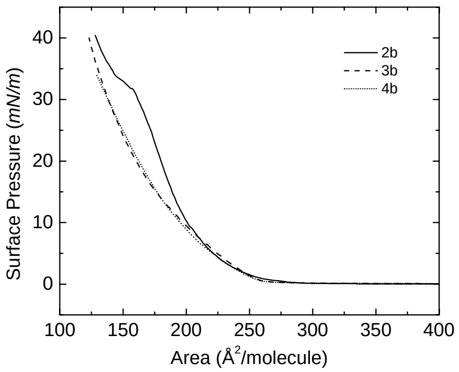


Figure 2. Pressure-area isotherms (Π ~A) of hydrophobically modified dendrimers **2b**, **3b**, and **4b**.

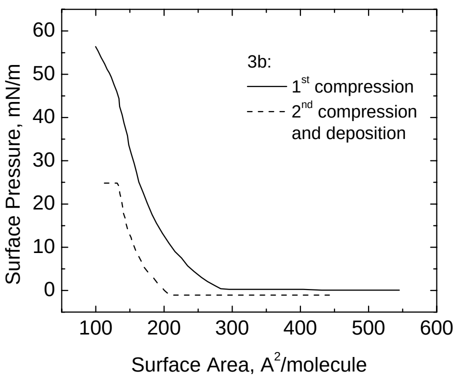


Figure 3. Isotherms of dendrimer **3b** from two successive compressions. The monolayer at the air/water interface was first compressed to 55 mN/m and then expanded to the surface pressure of 0 mN/m. After equilibrating for 10 min, a second compression to a surface pressure of 25 mN/m was carried out in the same way as in the first run.

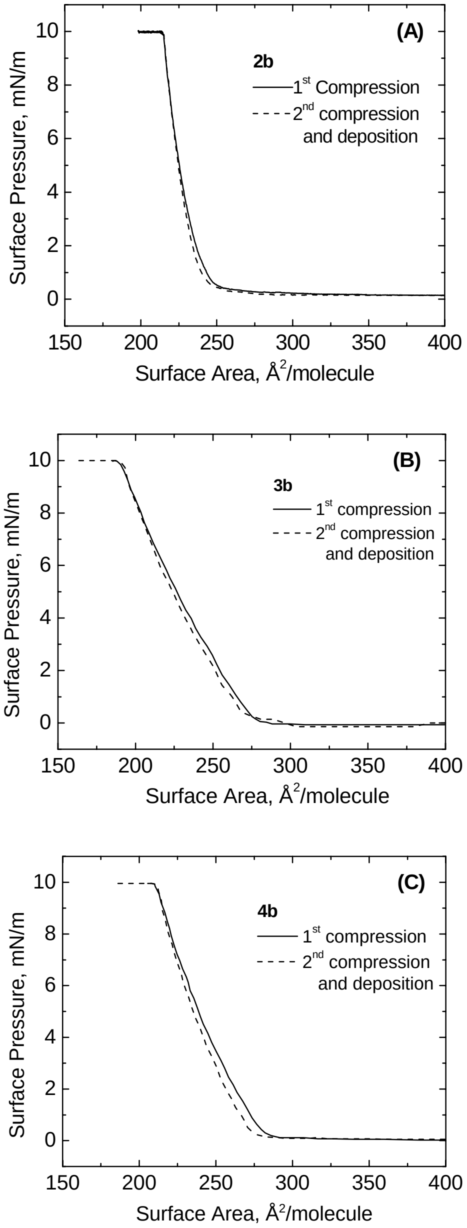


Figure 4. Isotherms of hydrophobically modified PPI dendrimers **2b** (A), **3b** (B), and **4b** (C) with maximum surface pressure of 10 mN/m.

The surface areas per molecule for the hydrophobically modified dendrimers **2b**, **3b**, and **4b** were estimated from Figures 2-4 by extrapolation of the steep rise in surface pressure to zero pressure [16,23,24] and listed in Table 1. The isotherms of the amphiphilic molecules strongly depend upon the numbers of hydrophobic groups attached to the hydrophilic core.[24] If a molecular area of 20 Å^2, a value usually found for alkylcarboxylates,[16,25] is assumed for one stearyol chain, the ideal surface areas per molecule for the stearyol modified dendrimer **2b** and its derivatives **3b** and **4b** (each dendrimer has 8 hydrophobic chains) should be 160 Å^2 (20 Å^2× 8). The observed surface areas per molecule (Table 1) are larger than the theoretical value (160 Å^2). This implies that the modified dendrimers "spread out" a little bit and flatten on the water surface at the initial transition from an expanded to a condensed liquid phase.[12] The alkyl-terminated PPI dendrimers underwent internal reorganization upon compression. We believe that the rigidity of the dendrimers will increase with increasing length of hydrophobic chains,[26] which leads to the observed mean molecular areas of 225-235 Å^2/molecule for stearoyl modified PPI dendrimer **2b**

Table 1. Areas of Modified PPI-$(NH_2)_8$-dendrimers from Extrapolation of First Compression Isotherms to Zero Pressure

Dendrimers	**2b**	**3b**	**4b**
Area (Å^2)/molecule	225	235	235

and its derivatives **3b** and **4b** smaller than the 243-271 Å^2/molecule of lauroyl modified PPI dendrimer and its related derivatives.[22]

AFM Studies of Dendrimer LB Films. For topographic studies of the hydrophobically modified PPI dendrimers **2b**, **3b**, and **4b** by AFM, LB films were prepared on mica surfaces by the vertical dipping method. Newly cleaved clean mica sheets were dipped vertically in the Langmuir trough before spreading the dendrimer solution onto the water subphase so that deposition only occurred at the upright stroke of the mica sheets after the Langmuir film formed on the water subphase at fixed surface pressure. The films were kept under ambient condition to allow water to evaporate naturally and imaged in more than 12 and less than 36 hours.

The Langmuir films of stearoyl modified PPI G_2 dendrimer **2b** and its derivatives **3b** and **4b** were transferred at surface pressures of both 10 mN/m and 25 mN/m. The transfer ratio was about 1.0 at both surface pressures, based on the reduced surface area of the monolayer on the Langmuir trough and the deposited areas on the mica. The images of the monolayers transferred at the two different pressures are shown in Figures 5-7 (deposited at 10 mN/m) and Figures 8-12 (deposited at 25 mN/m). Island domains were clearly observed on all of the films. The size, shape, and density of the islands formed on the LB films of **2b**, **3b**, and **4b** were different.

LB Films Transferred at 10 mN/m. The heights of the islands on the LB films of dendrimers **2b**, **3b**, and **4b** measured from mica are about 2 nm, and the heights of the seas of films around the islands ranged from 0.8 to 1.1 nm, as shown in Figures 5B, 6C, 7D, and 7F. The theoretical length of a C_{18} chain is 2.3 nm.[27] Therefore, the measured heights of the islands on the LB films are lower than the theoretical value, if we presume the alkyl chains extended away from the water surface and pointed toward the air vertically. The dendrimer organization on the water surface at the surface pressure of 10 mN/m may be different from that of dendrimers or other amphiphilic compounds with shorter alkyl chains. Scratching experiments were done in the regions between the islands. The section analysis of the AFM images recorded after scratching indicated that continuous film of thickness of 1.2 nm were formed under compression reaching a surface pressure of 10 mN/m, shown in Figures 5E, 6F, and 7E. From this value, the thicknesses of the islands will be between 2.0 nm and 2.3 nm, close to the value of the length of a C_{18} chain. This simple analysis points out that the side chains of the dendrimers **2b**, **3b**, and **4b** either lie on the water surface for the lower regions or extend away from the water surface at a tilting angle of ~25° for the island locations.

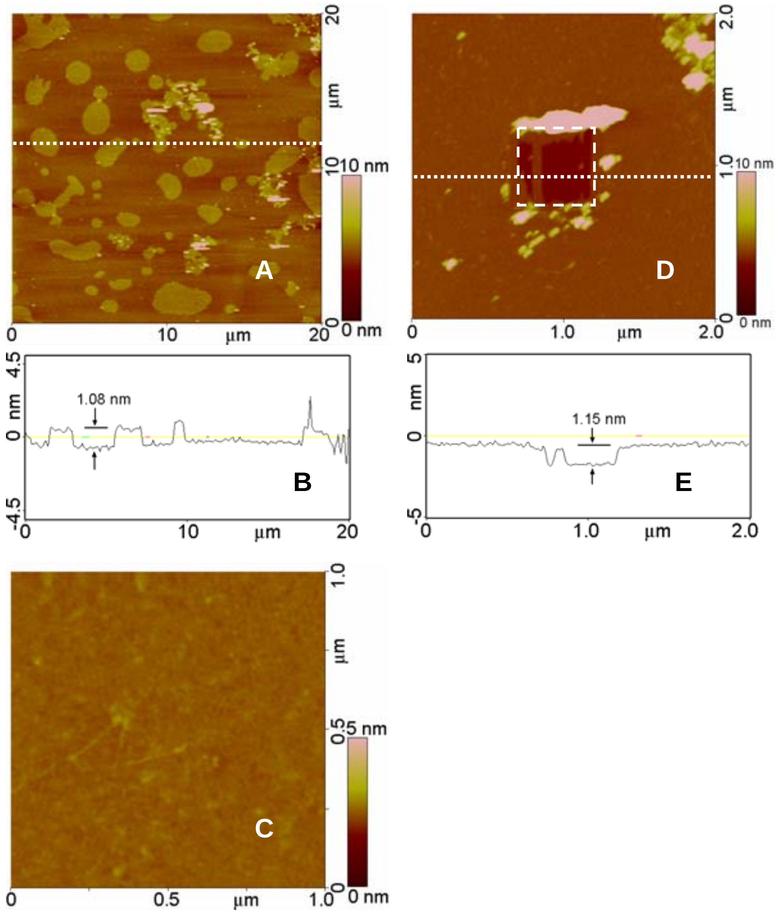


Figure 5. AFM height images (A, C, D) of the LB film of dendrimer **2b** deposited on mica at a surface pressure of 10 mN/m. B and E are the profiles of images A and D. Image D was recorded after scratching on the transferred LB film at ~100 nN in a 0.5 µm × 0.5 µm square area.

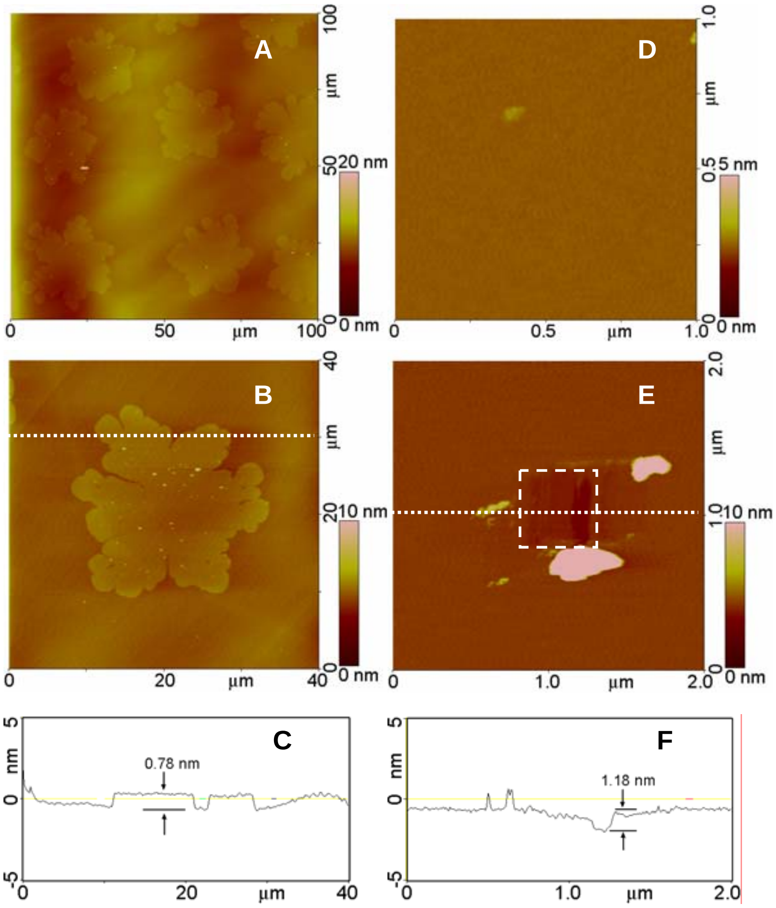


Figure 6. AFM height images (A, B, D, E) of the LB film of dendrimer **3b** deposited on mica at a surface pressure of 10 mN/m. C and F are the profiles of images B and E. Image E was recorded after scratching on the transferred LB film at ~100 nN in a 0.5 µm × 0.5 µm square area.

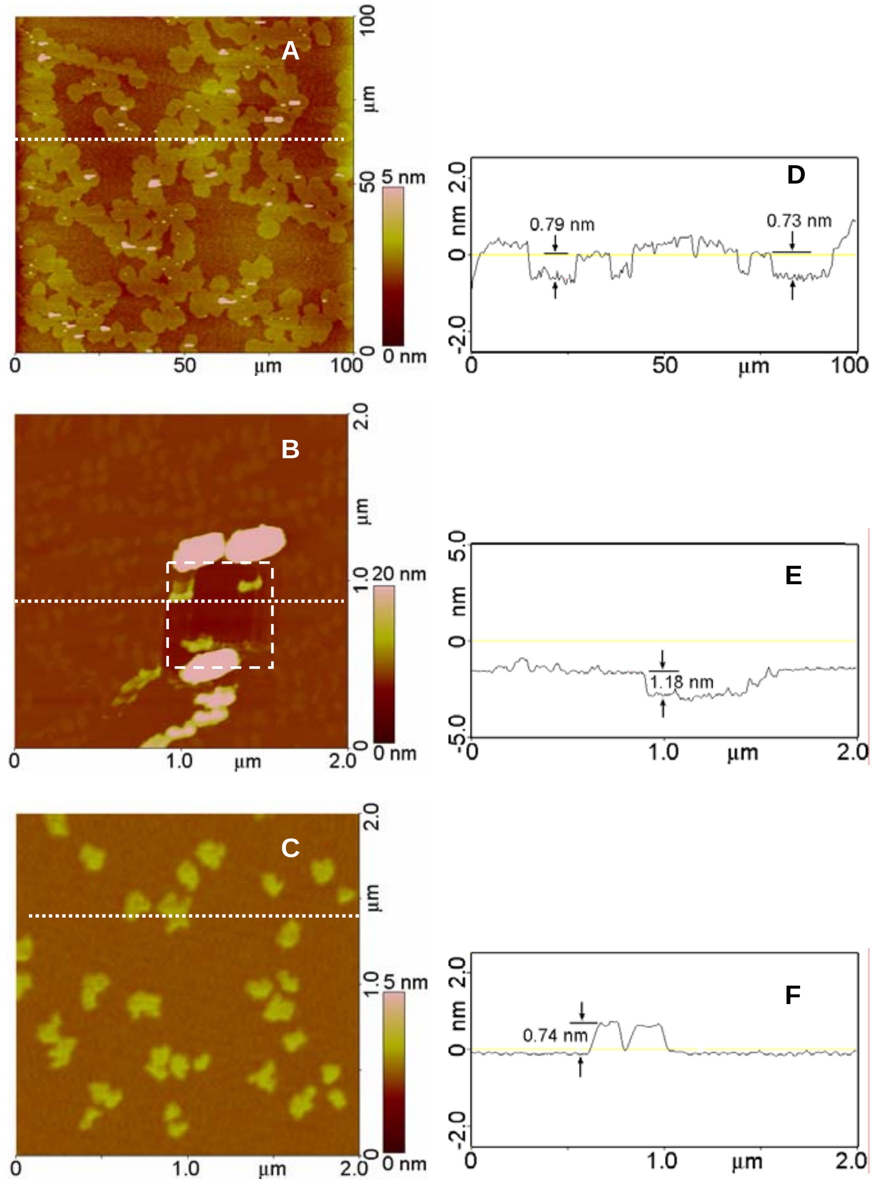


Figure 7. AFM height images (A, B, C) of the LB film of dendrimer **4b** deposited on mica at a surface pressure of 10 mN/m. D, E, and F are the profiles of images A, B, and C. Image B was recorded after continuingly scratching on the transferred LB film at ~100 nN in a 0.5 µm × 0.5 µm squared area.

LB Films Transferred at 25 mN/m. Although steady increase of the surface pressures up to 40 mN/m were observed for all three amphiphilic dendrimers during compression, as shown in Figure 2, the LB films of **2b**, **3b**, and **4b** deposited at 25 mN/m exhibited multi-layer heterogeneous structures. Both lower islands with height between 0.7 nm and 1.0 nm and higher islands with height between 3.0 nm and 4.5 nm, shown in Figures 8, 10, and 11, were observed. Further scratching experiments indicated that the underlying films surrounding the islands had thicknesses between 1.2 nm and 2.8 nm, shown in Figures 9, 10D, and 12. This implies that the thicknesses of the islands on the LB films of **2b**, **3b**, and **4b** will be up to 5.5 nm, 5.7 nm, and 7.3 nm, respectively. Thus the monolayers of **2b**, **3b**, and **4b** at the air/water interface have already changed and partially collapsed at the surface pressure of 25 mN/m.

Based on the isotherms of the dendrimers (Figures 3 and 4), the mean molecular areas were about 160 $Å^2$ at 25 mN/m and about 200 $Å^2$ at 10 mN/m. Clearly only reorganization or dislocation of the solid crystalline phases in the LB films of **2b**, **3b**, and **4b** can be attributed to the reduction of surface area from 200 $Å^2$/molecule to 160 $Å^2$/molecule forming scattered multilayers at the air/water interface. So when the surface pressure was increased up to 25 mN/m, solid dendrimers were pushed to stack up to form islands because the monolayers were not stable under increased compression force.

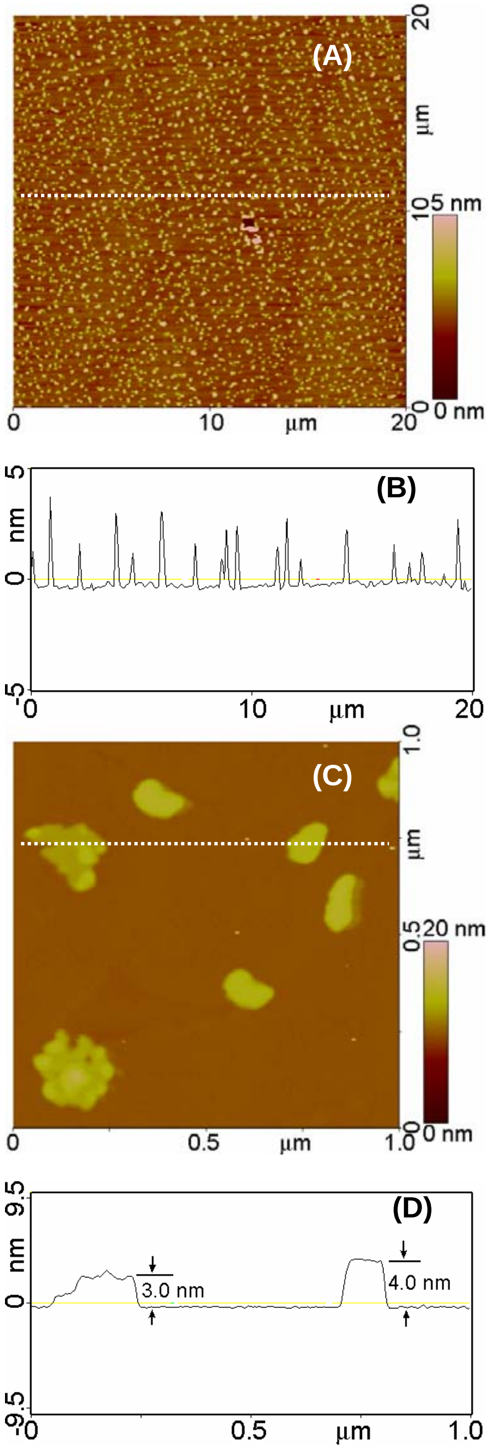


Figure 8. AFM height images (A and C) of a LB film of dendrimer **2b** deposited on mica at a surface pressure of 25 mN/m. B and D are line profiles of A and C.

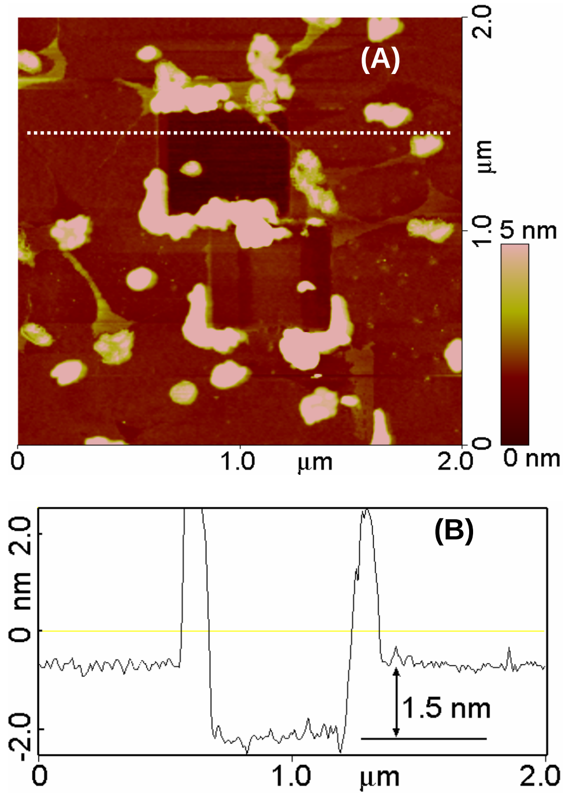


Figure 9. (A) AFM height image of a LB film of dendrimer **2b** deposited on mica at a surface pressure of 25 mN/m. The images were recorded after scratching on the transferred LB film at ~100 nN in a 0.5 µm × 0.5 µm squared area. B is a line profile of image A.

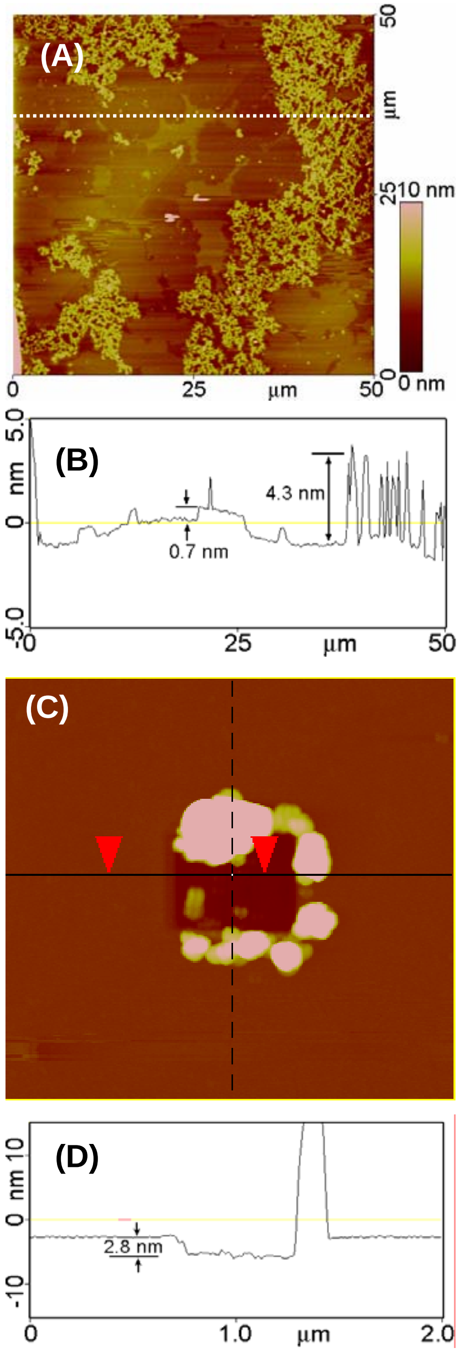


Figure 10. AFM height images of a LB film of dendrimer **3b** deposited on mica at a pressure of 25 mN/m (A and C). C was recorded after scratching on the transferred LB film at ~100 nN in a 0.5 µm × 0.5 µm squared area. B and D are the profiles of A and C.

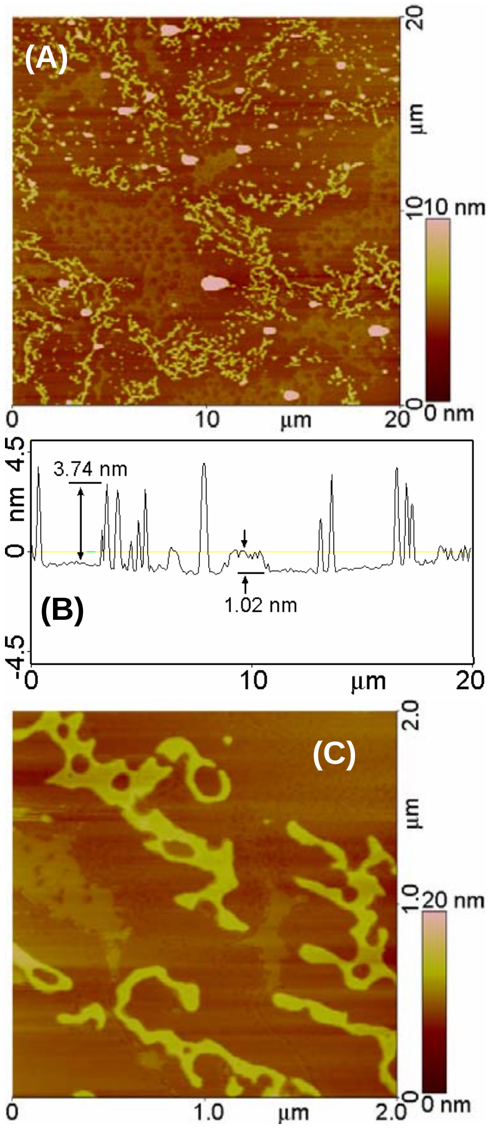


Figure 11. AFM height images (A and C) of a LB film of dendrimer **4b** deposited on mica at a compression pressure of 25 mN/m. B is a line profile of A.

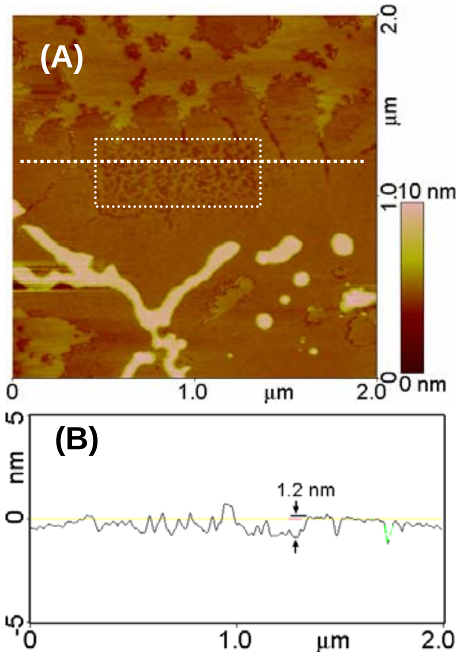


Figure 12. (A) AFM height image of a LB film of dendrimer **4b** with C_{18} chains after scratching. (B) is a line profile of a cross section of A.

Dendrimers in Dilute Solution. Dynamic light scattering was used to determine whether there were aggregations of dendrimers in the solution of 2 mg/mL in chloroform. Figure 13 showed the size distribution of dendrimers **2b**, **3b** and **4b**. The instrument we used is from Malvern Instruments and has a lower detection limit of 0.6 nm. From Figure 13, we can see, the average value of particle diameters for the three hydrophobically modified PPI dendrimers was 0.8 nm with an average width of 0.3 nm at half peak height, which is close to the diameter of the second generation PPI dendrimer core (1.4 nm). However, since the lower limit of the detectable range of the Malvern HPPS is 0.6 nm, the absolute values of the measurements are only approximate. The important result is that the dendrimers were not aggregated in the solutions used to prepare the Langmuir films.

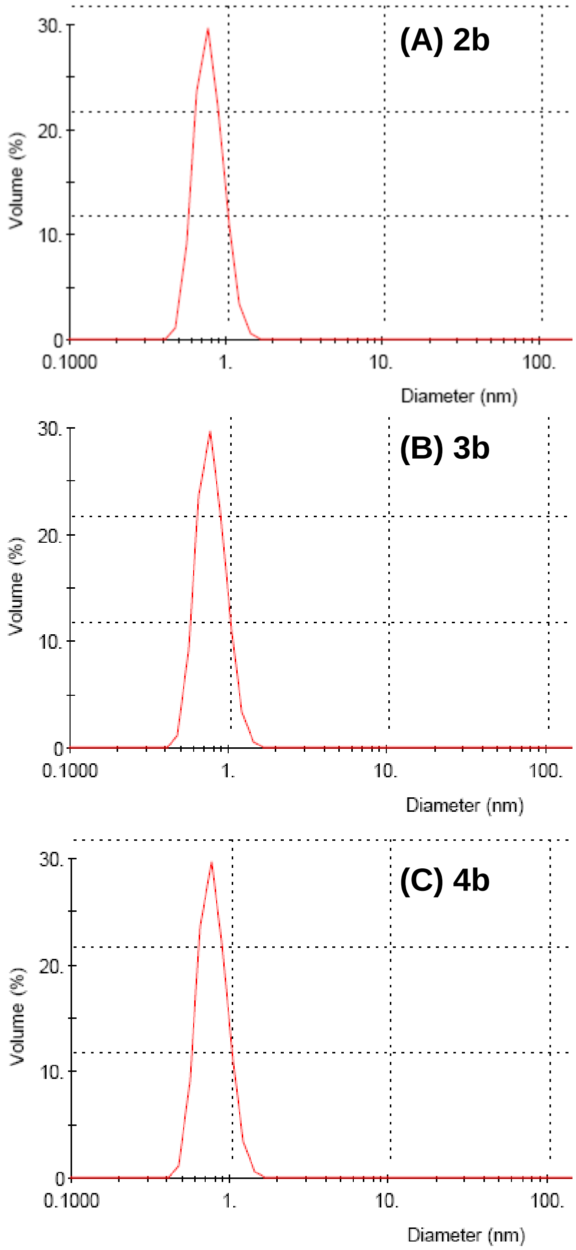


Figure 13. Size distribution of dendrimers **2b**, **3b**, and **4b** in chloroform at 25 ºC at a concentration of 2 mg/mL. [Volume (%) is percent of volume of the particles (dendrimers) in the measured volume of the system (solution)].

DISCUSSION

Generally the cohesive force of molecules having a long alkyl side chain is very strong, which showed decrease mobility of the stearyl chains of dendrimers **2b**, **3b**, and **4b**.[27,28] The stearyl side-chains maintain crystallinity below the side-chain melting temperature of 60 ºC in poly(stearyl glutamate).[29-33] The reorientation and further crystallization of the side chains occurs during evaporation of the solvent at the air/water interface. Miyano and coworkers[30,31] report that the side-chains of poly(stearyl glutamate) undergo instantaneous intercrossing and crystallization just after spreading a chloroform solution of the poly(stearyl glutamate) at the air/water interface, which causes the poly(stearyl glutamate) to form multi-domain phases at the air/water interface. Evaporation of the solvent acts as the driving force to introduce the reorganization of the side chains by capillary force and further crystallization by the strong cohesive force between the long alkyl chains.[29] There are eight alkyl chains bonded to the PPI dendrimer ends, the eight alkyl chains therefore reorganize themselves into small crystalline bundles and molecular crystals. Providing that the hydrophilic PPI dendrimer core has a nearly flat and oblate conformation and associates closely with the water subphase, all the attached hydrophobic chains in the crystalline form pack more tightly making the observed molecular area close to the idea molecular area of 200$Å^2$.[16,34,35]

Because the stearoyl chains grafted at the PPI dendrimer ends tend to crystallize, at the air/water interface even individual dendrimers **2b**, **3b**, and **4b** may form cylindrical or disk-like two dimensional molecular crystals. The cylindrical or disk-like shapes can arrange themselves to lie relatively flat or stand vertically on the water subphase.[36-38] The size of the crystalline aggregates of the dendrimers **2b**, **3b**, and **4b** determines the orientation of dendrimer molecules in the Langmuir film at the air/water interface. Individual molecular crystals of the dendrimers may intend to adopt edge-on conformation at the water surface, while bigger crystalline islands formed by further compression may choose face-on arrangement.

When the barrier of the Langmuir trough was subject to compression, the domain sizes of dendrimer molecular crystals were fixed at the first spreading of the solution. Edge-on dendrimer crystals with high titling merged together and formed a possibly homogeneous monolayer at or before the lift-off point in the Π-A isotherms. As the monolayer was compressed further, especially up to 25 mN/m, the rigid dendrimer crystals could not respond to the compression force instantly because of the low compressibility of crystalline solids, at some places the dendrimer domains therefore were pushed up to form higher islands in order to release the internal stress in the monolayer.[39] After the Langmuir films were transferred to hydrophilic mica, the configuration of the PPI dendrimer with long hydrophobic alkyl chains could be assumed the same as that at the air/water interface. It is reasonable that the monolayers of dendrimers **2b**, **3b**, and **4b** collapsed at the surface pressure of 25 mN/m that was well below the collapsed pressure based on the π-A isotherms.

CONCLUSIONS

Surface pressure-area isotherm measurements combined with AFM analysis of amphiphilic PPI G_2 dendrimers **2b**, **3b**, and **4b** at the air/water interface indicate inhomogeneous monolayers. Multidomain structure on the level of submicron to tens of microns was revealed by AFM. The Langmuir films transferred at a surface pressure of 10 mN/m were relatively stable and showed island structures. The monolayers were collapsed on mica after transfer at a surface pressure of 25 mN/m, which is below the collapse pressure observed on the surface pressure-area isotherms. At low surface pressure of 10 mN/m, the amphiphilic C_{18}-modified dendrimers formed disordered thin films on the water surface with island domains rising out of the continuous film. At the surface pressure of 25 mN/m, all the hydrophobic alkyl chain aggregates were pushed up and extended away from the water surface; monolayer collapse was observed because of the low compressibility of crystalline dendrimer bundles, which resulted in formation of denser islands of different height and size.

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APPENDIX

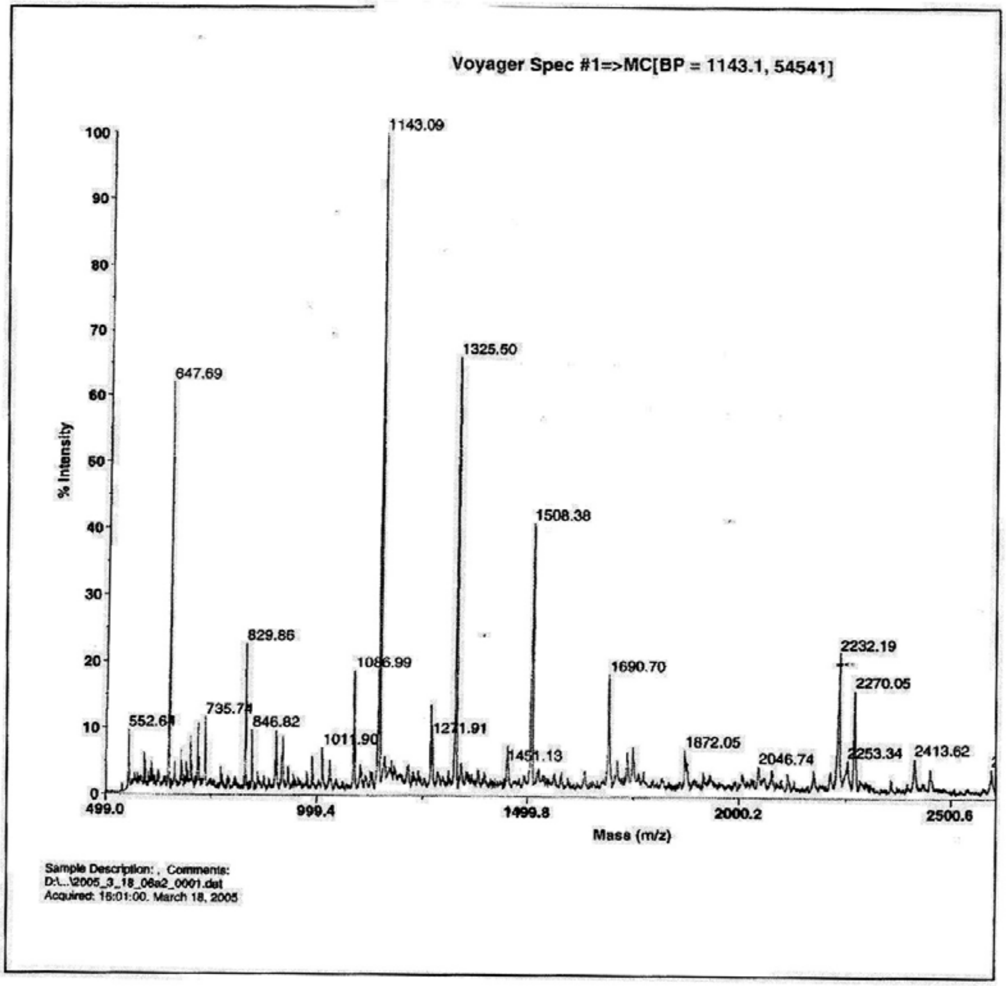

Figure 1. MALDI TOF MS spectrum of dendrimer **2a**

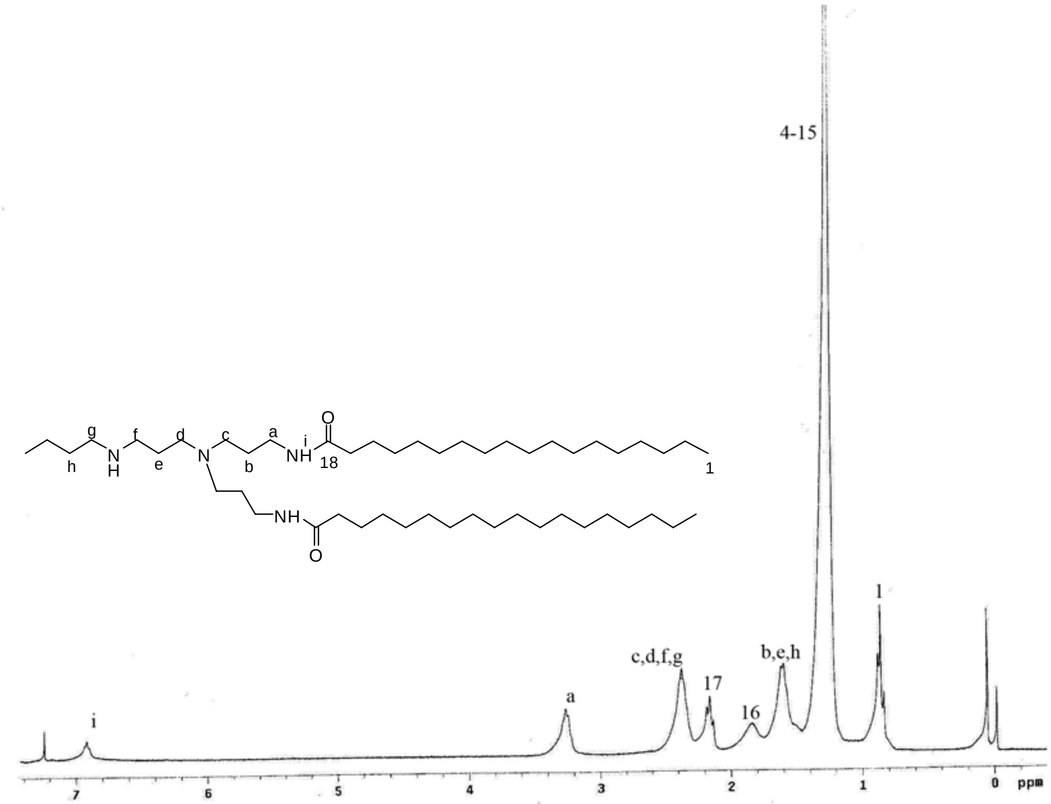

Figure 2. ^{1}H NMR spectrum of dendrimer **2b**

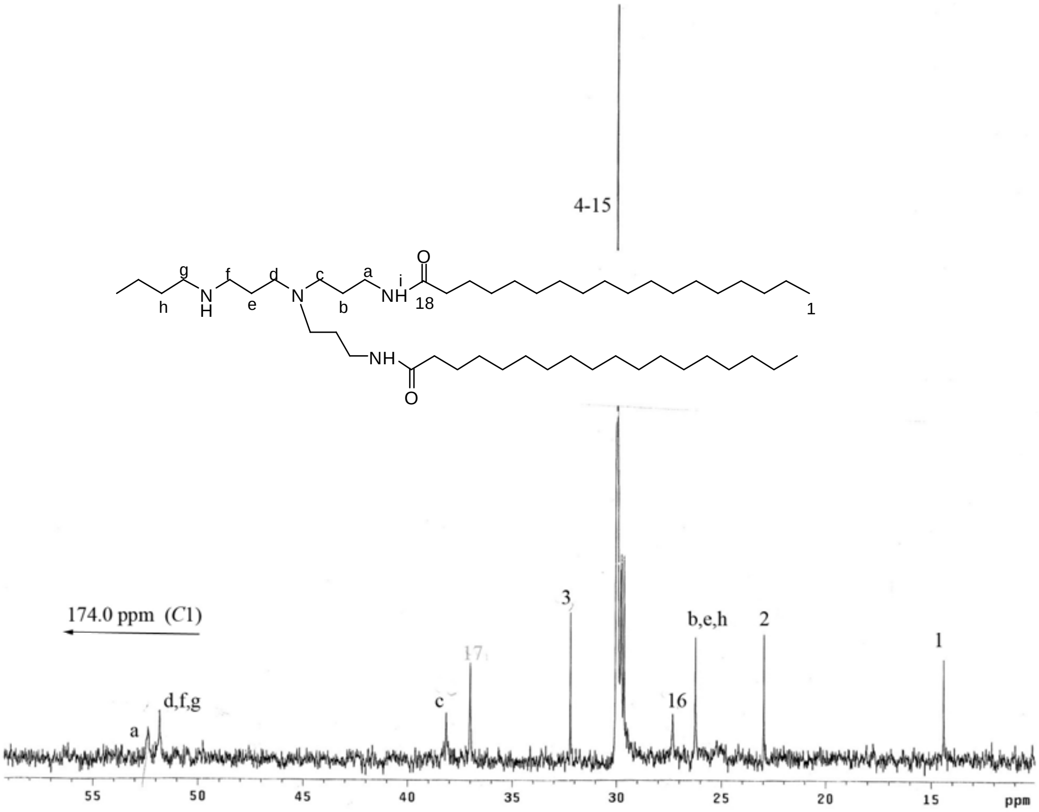

Figure 3. ^{13}C NMR spectrum of dendrimer **2b**

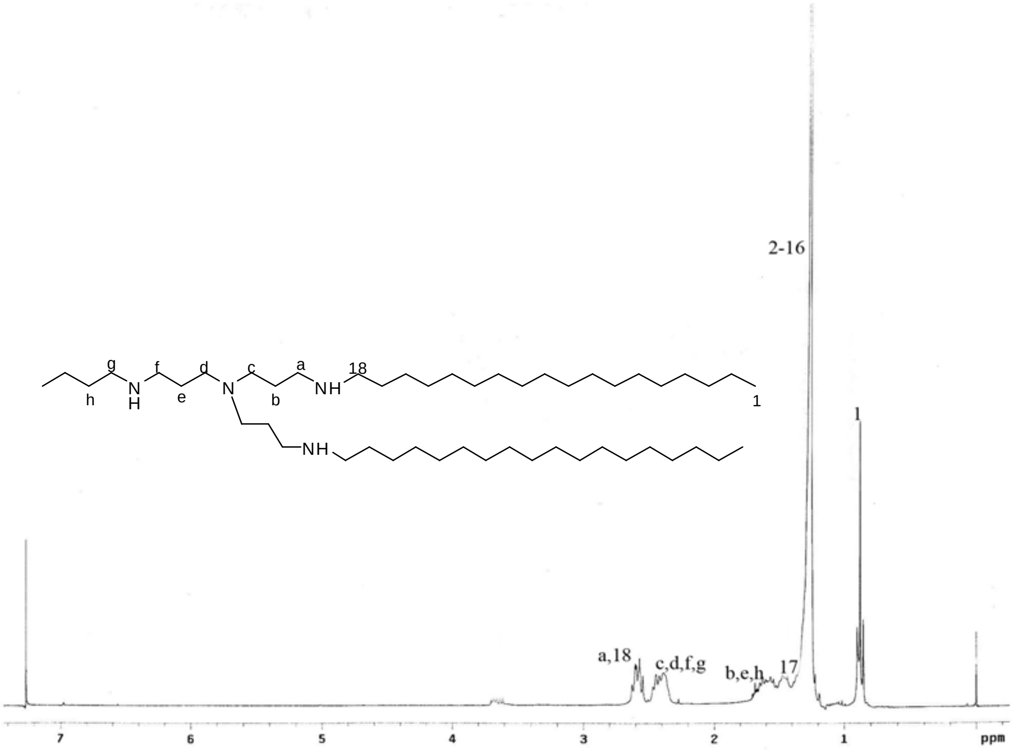

Figure 4. ^{1}H NMR spectrum of dendrimer **3b**

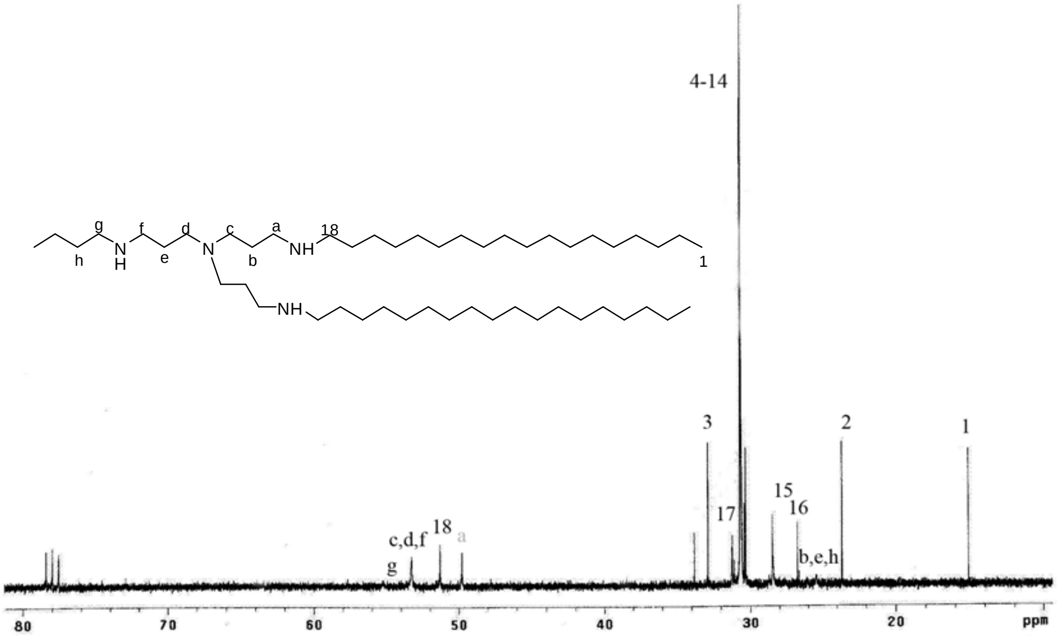

Figure 5. ^{13}C NMR spectrum of dendrimer **3b**

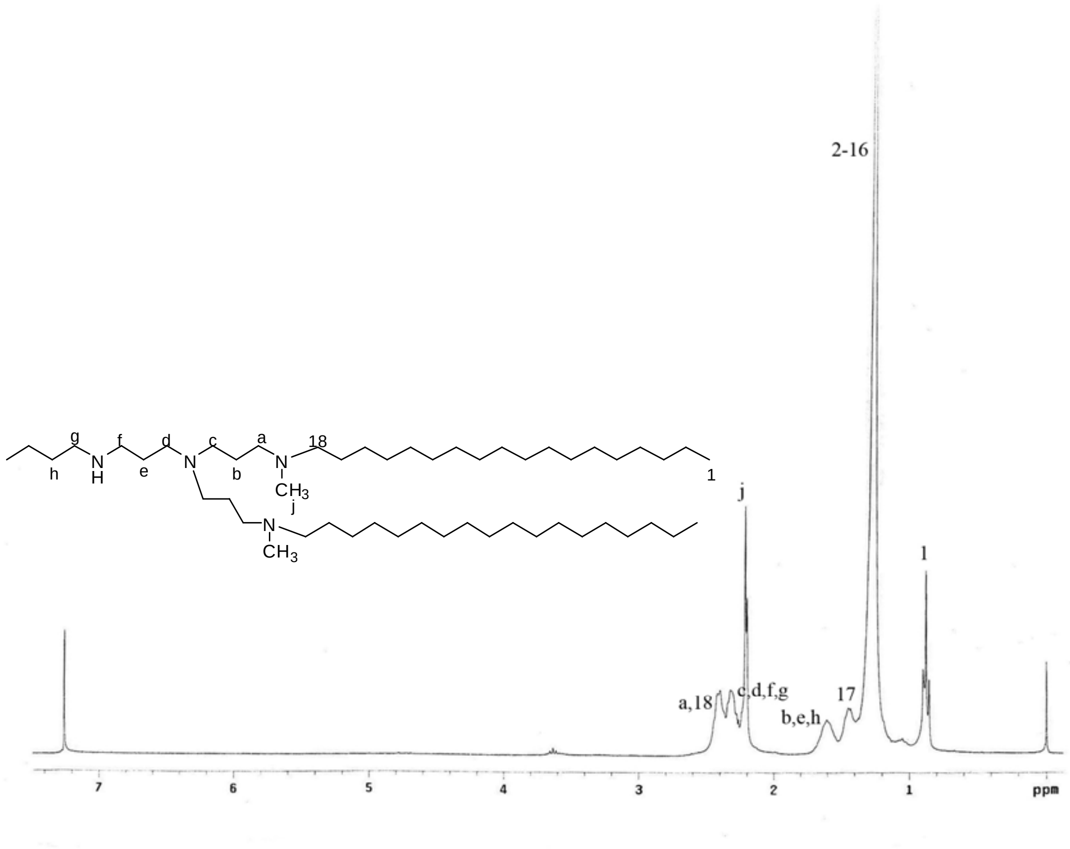

Figure 6. ^{1}H NMR spectrum of dendrimer **4b**

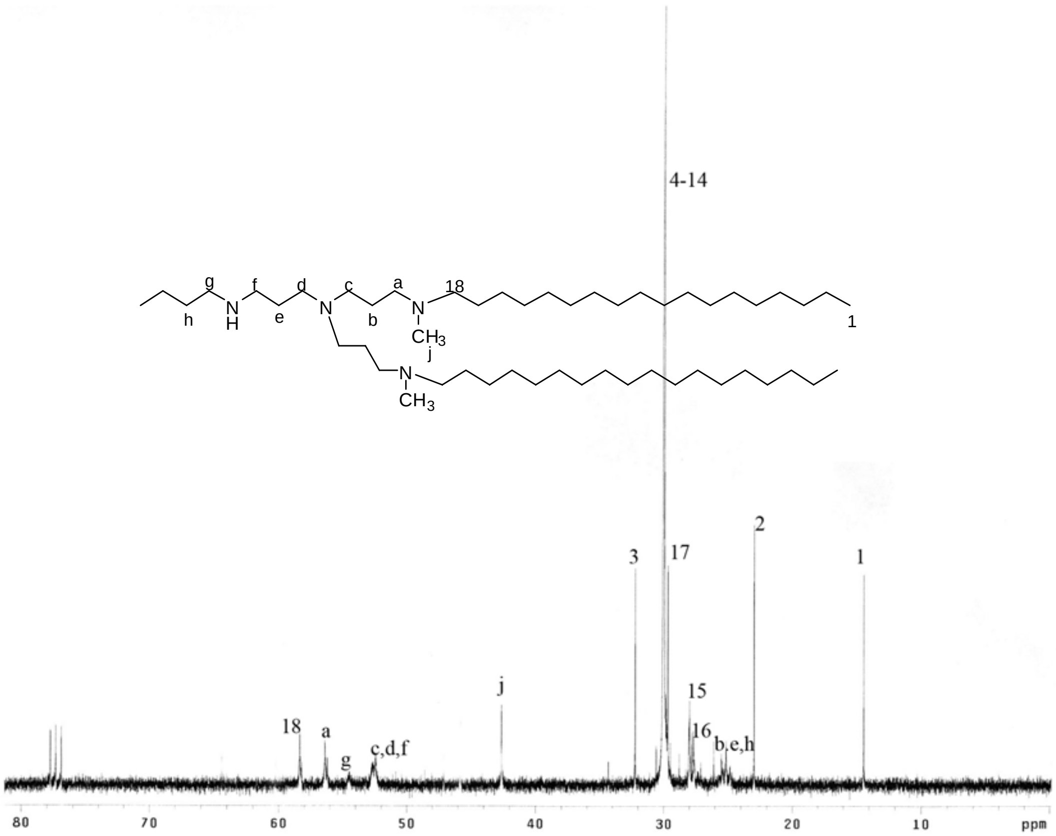

Figure 7. ^{13}C NMR spectrum of dendrimer **4b**

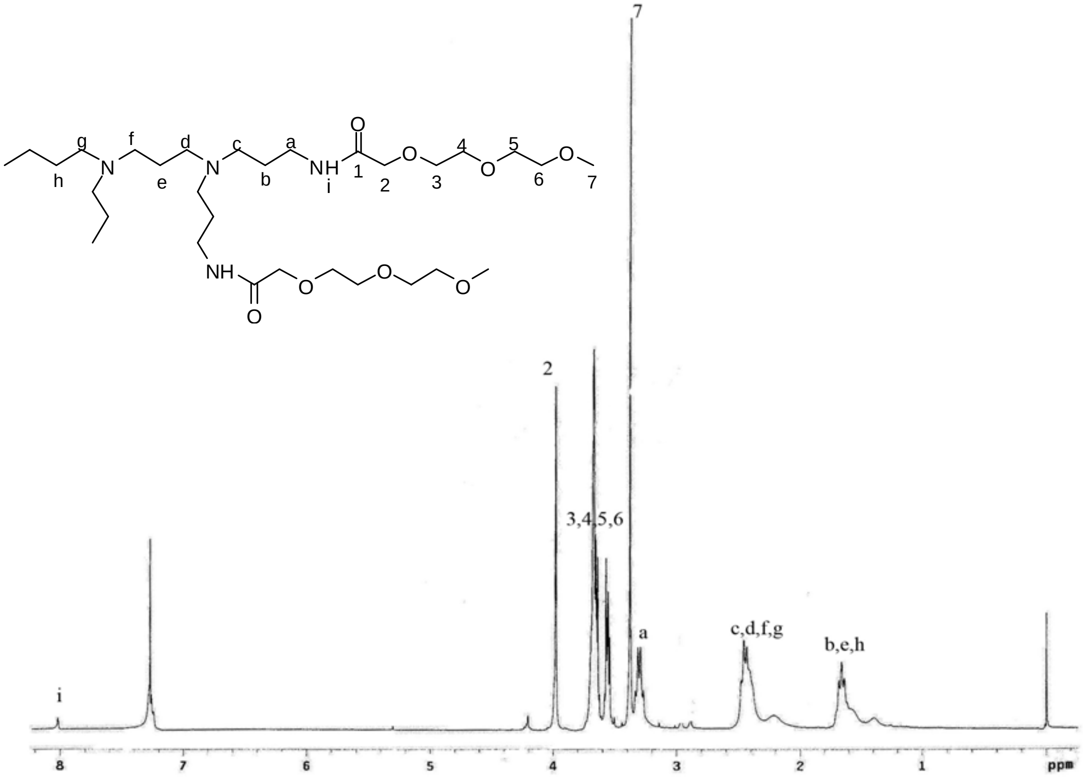

Figure 8. ^{1}H NMR spectrum of dendrimer **5**

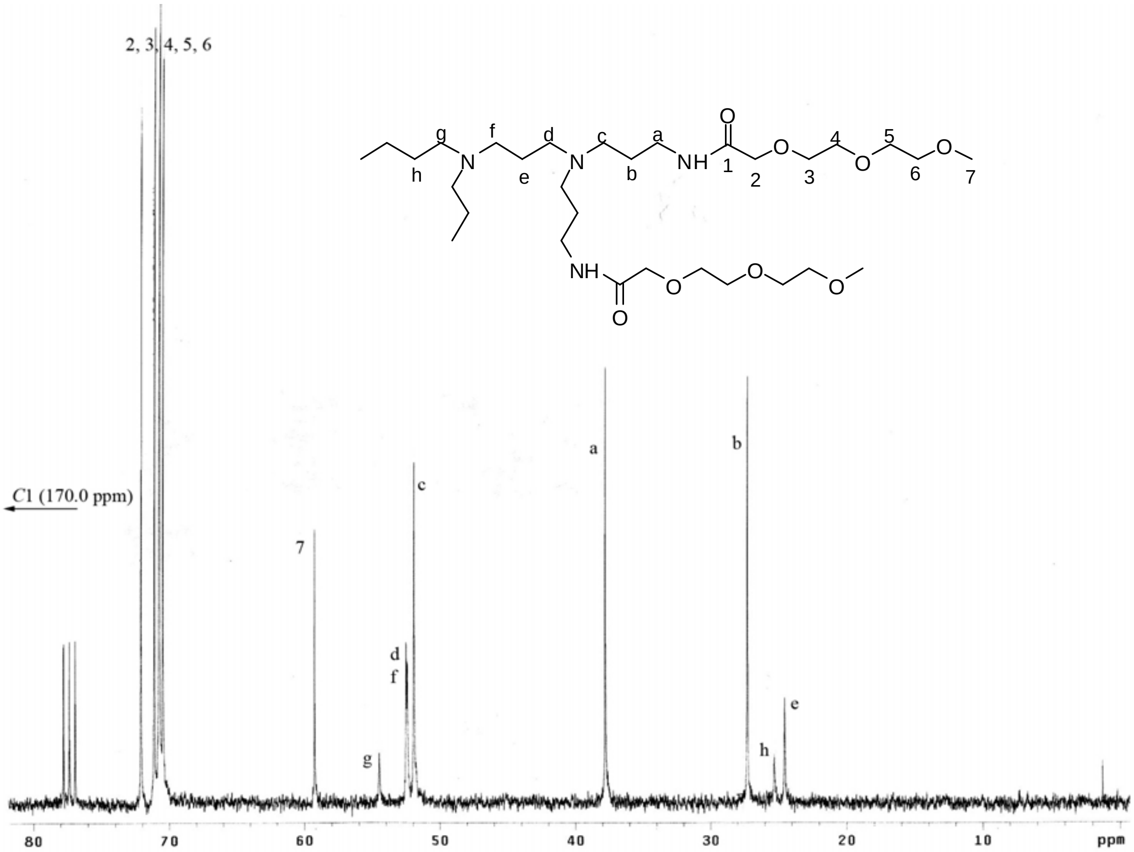

Figure 9. ^{13}C NMR spectrum of dendrimer **5**

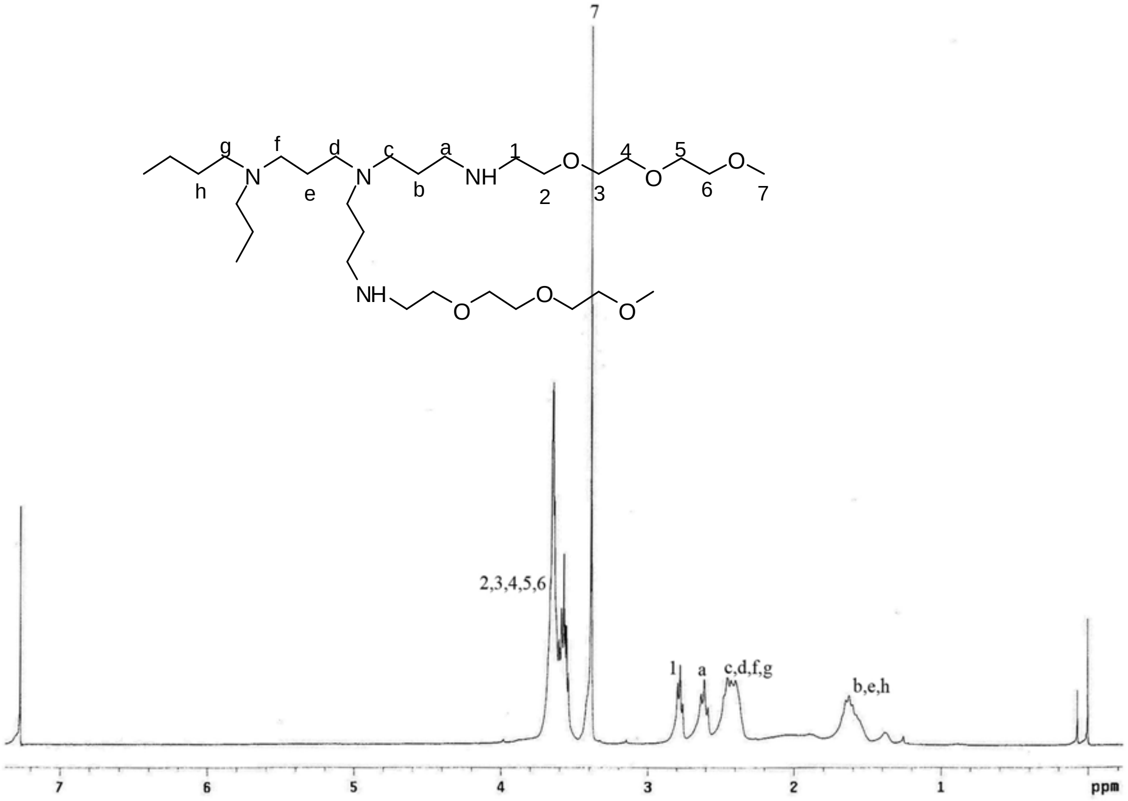

Figure 10. ^{1}H NMR spectrum of dendrimer **6**

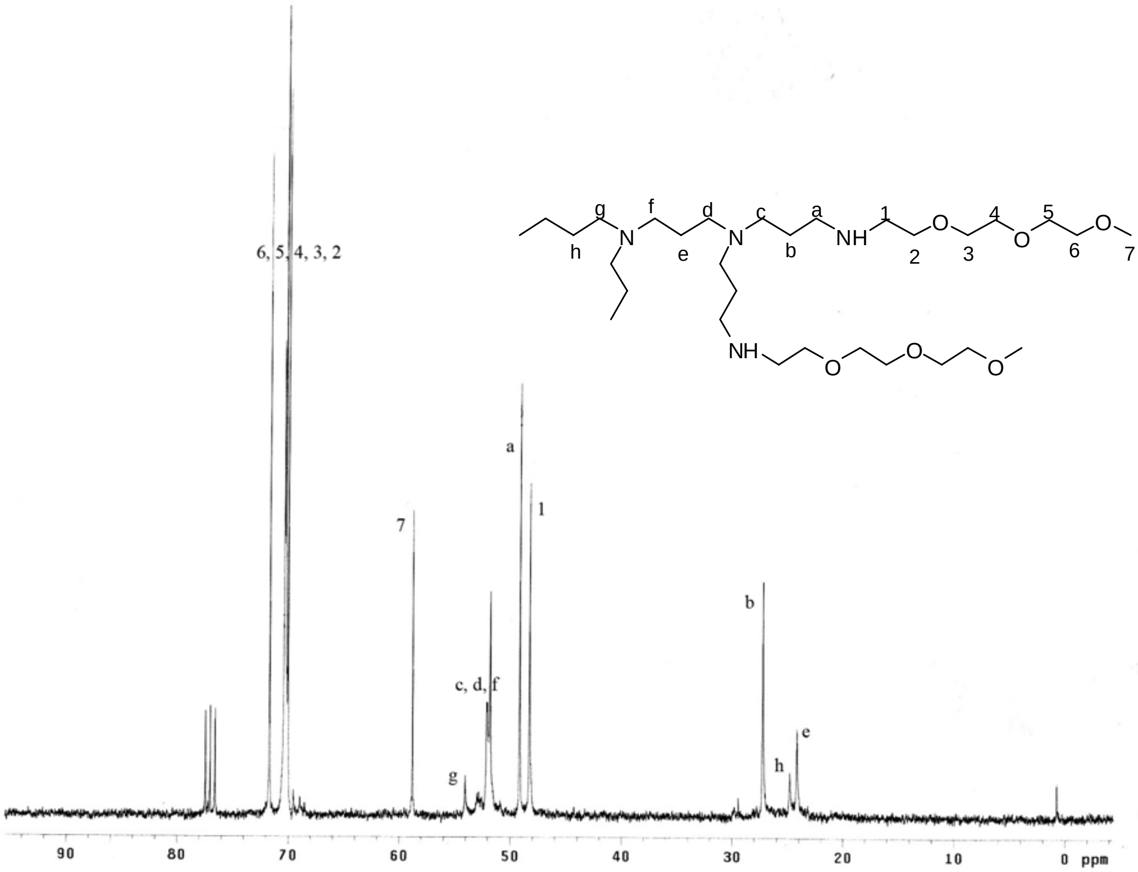

Figure 11. ^{13}C NMR spectrum of dendrimer **6**

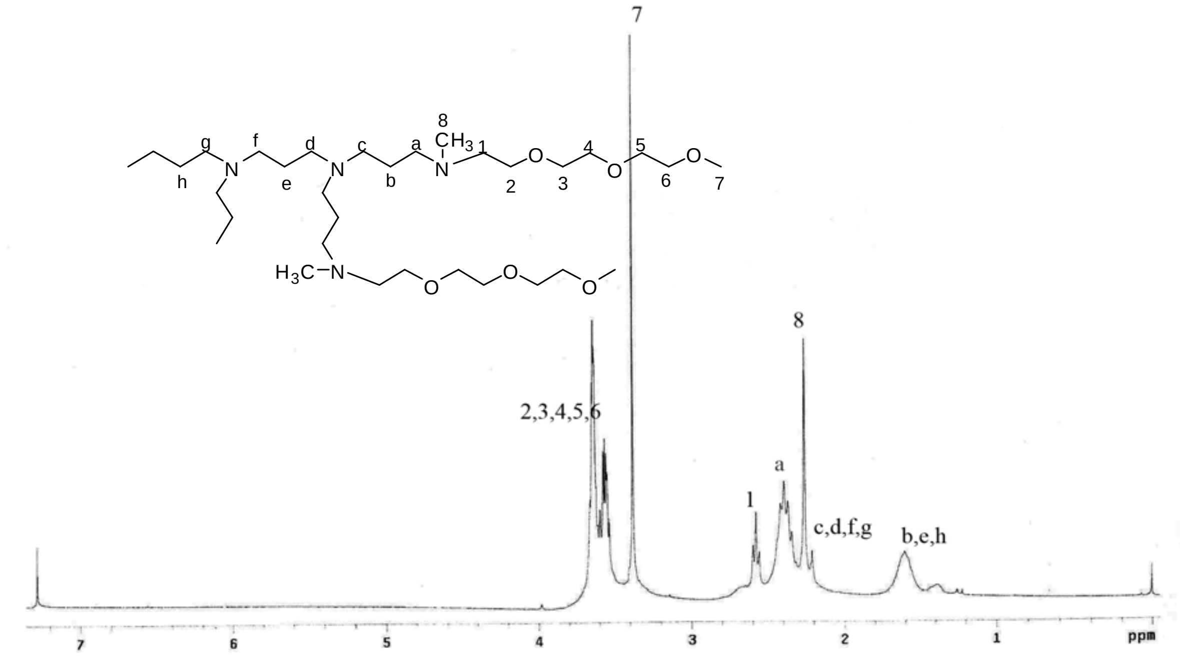

Figure 12. ^{1}H NMR spectrum of dendrimer **7**

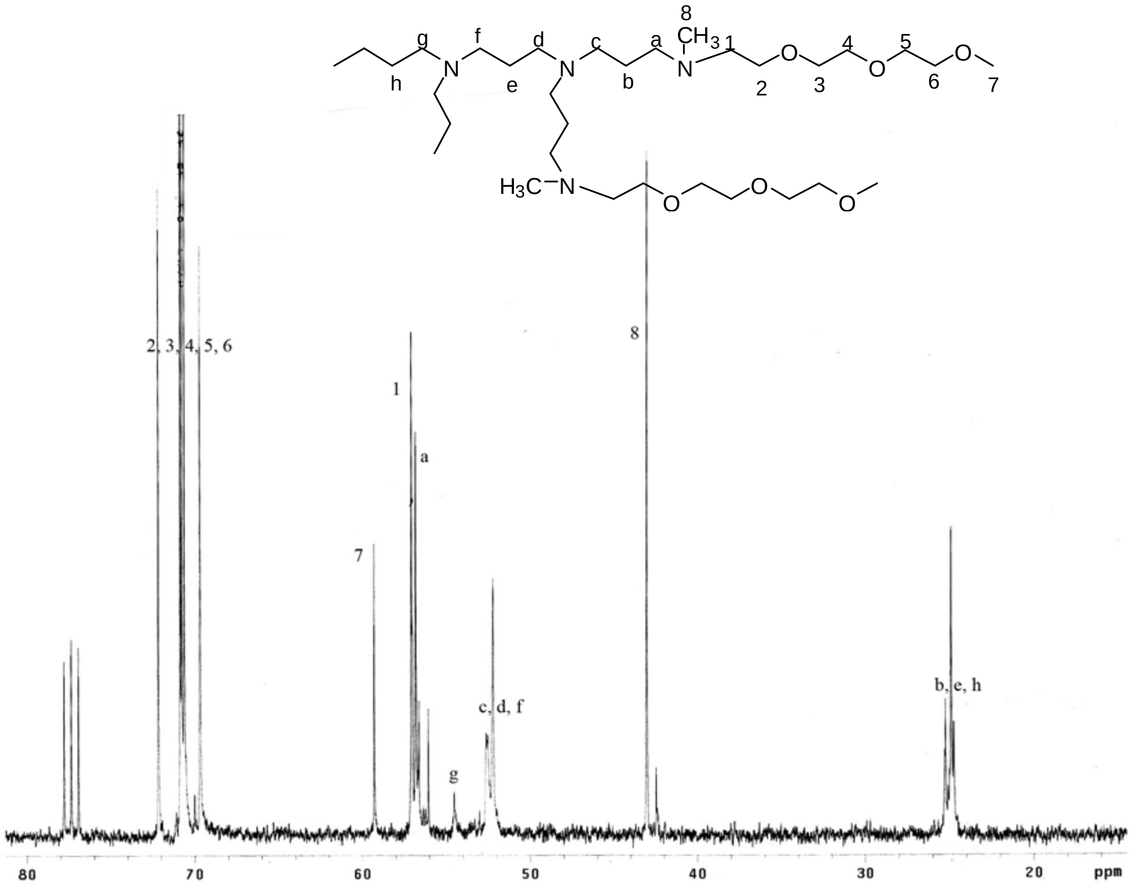

Figure 13. ^{13}C NMR spectrum of dendrimer **7**

VITA

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