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SHORT COMMUNICATION

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Characterization of aliphatic and aromatic polyester hyperbranched dendrimers by AFM imaging

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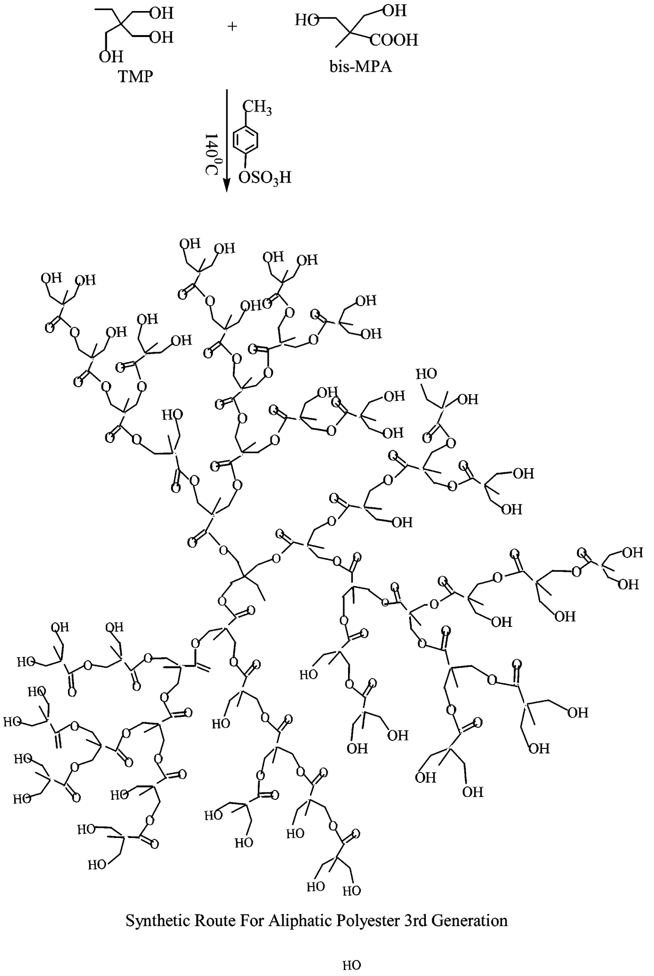
Abstract The aggregates of aliphatic (AL-PE) and aromatic polyester (AR-PE) hyperbranched dendrimers were imaged by tapping mode atomic force microscopy (AFM). The second and third generations of AL-PE dendrimers were adsorbed on mica in large aggregates of 150- and 166-nm diameters with little heights (ca. 1–2 nm). The origin of such flattened aggregates is attributed to their favorable adsorption on mica in view of the presence of –OH surface groups. AR-PE did not show such flattened aggregates instead small aggregates of 63 nm were observed in an organized manner beaving a cavity in the center of each aggregate. The organized aggregates of AR-PE with smaller dimension than AL-PE are ascribed to less favorable adsorption of the latter on mica in view of its stronger hydrophobicity.

Keywords Aliphatic and aromatic polyester dendrimers · AFM · Aggregates · Cavity formation

Introduction

Dendritic molecules belong to a truly special area of polymer science [1–6]. They are distinct among the various classes of polymers in that they can be prepared as discrete, highly pure, monodisperse molecules. The globular geometry of dendritic molecules affords interesting properties, such as unusually low viscosities in comparison to linear polymers at high molecular weights, and high solubility [6]. The dendrimer name reflects the ordered, branching tree like architecture, and are recognized as promising nanoscale building blocks for both super and supramolecular assemblies [3]. Dendrimers are produced in an iterative sequence of reaction steps in which each additional iteration leads to a higher generation material [2]. Due to their specific shape and size, dendrimers are used as substrate for the attachment of antibodies, contrast agents, radionuclides etc. for use in various biological/medical and chemical applications [7–11]. In view of these potential applications, there is a need for analytical technique that could answer a number of fundamental questions concerning dendrimer characteristics and properties such as their dimensions, uniformity of size and shape, and degree of rigidity, etc. Atomic force microscopy (AFM) offers this possibility, since it provides high-resolution imaging and measurement of surface topography and properties on the molecular scale [12–17]. It has been shown to be very useful in gaining insight into the properties of nanostructures. Recently, significant progress has been made to characterize molecular parameters of various generations of poly (amido amine) dendrimers (PAMAM). A most systematic work has been reported by Li et al. [18] regarding the visualization and characterization of PAMAM by AFM. They have evaluated the molecular weights of various generations of PAMAM from 5G to 10G, which agree well with the theoretical values. Apart from this, some studies [19–21] have reported the formation of dendritic films made up of compressed macromolecules, and self-assembled films developed through layer by layer deposition technique [22]. Even the visualization of 4G to 8G PAMAM on a Au (III) substrate has also been reported [23].

All these studies are mainly related to PAMAM dendrimers while there are few reports [24, 25] related to the AFM studies of hyperbranched dendrimers. The hyperbranched dendrimers have quite distinct properties from the regular ball shaped dendrimers. We, here, report the characterization and visualization of hyperbranched aliphatic and aromatic polyester dendrimers on mica surface and have discussed some unique features of their aggregation on surfaces.



Synthetic Route For Aliphatic Polyester 3rd Generation

Scheme I

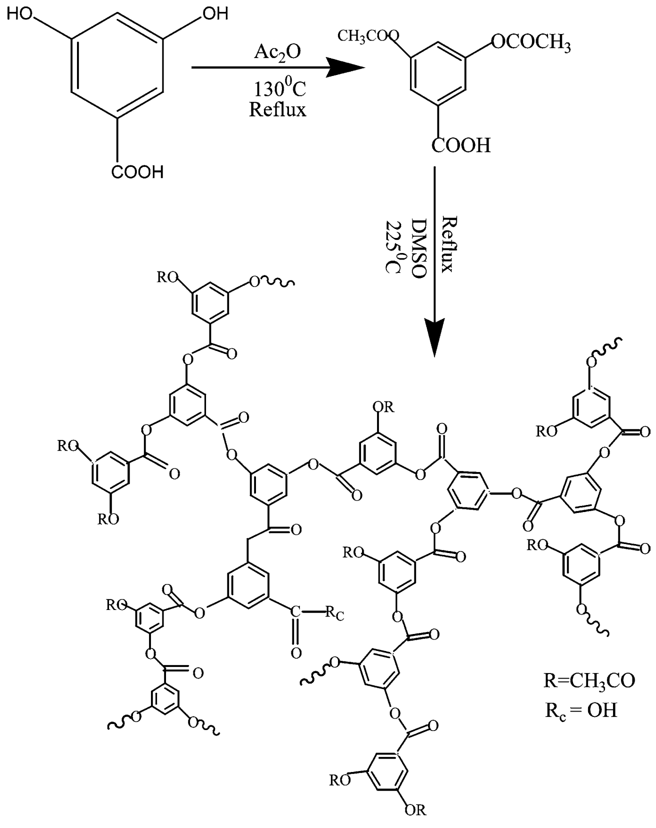
Experimental

2, 2-bis(hydroxymethyl)propionic acid (bis-MPA), 2-ethyl-2-(hydroxymethyl)-1, 3-propanediol (TMP), para-toluenesulphonic acid (*p*-TSA), 3, 5-dihydroxybenzoic acid, acetic anhydride, and diphenyl ether, all from Lancaster Synthesis, England, were used as received.

Aliphatic polyester (AL-PE) (second and third generations) and aromatic polyester (AR-PE) hyperbranched dendrimers were synthesized (schemes I and II, respectively) as reported in the literature [26, 27] and fully characterized by IR, ^{1}H NMR, ^{13}C NMR, and mass spectroscopy before use.

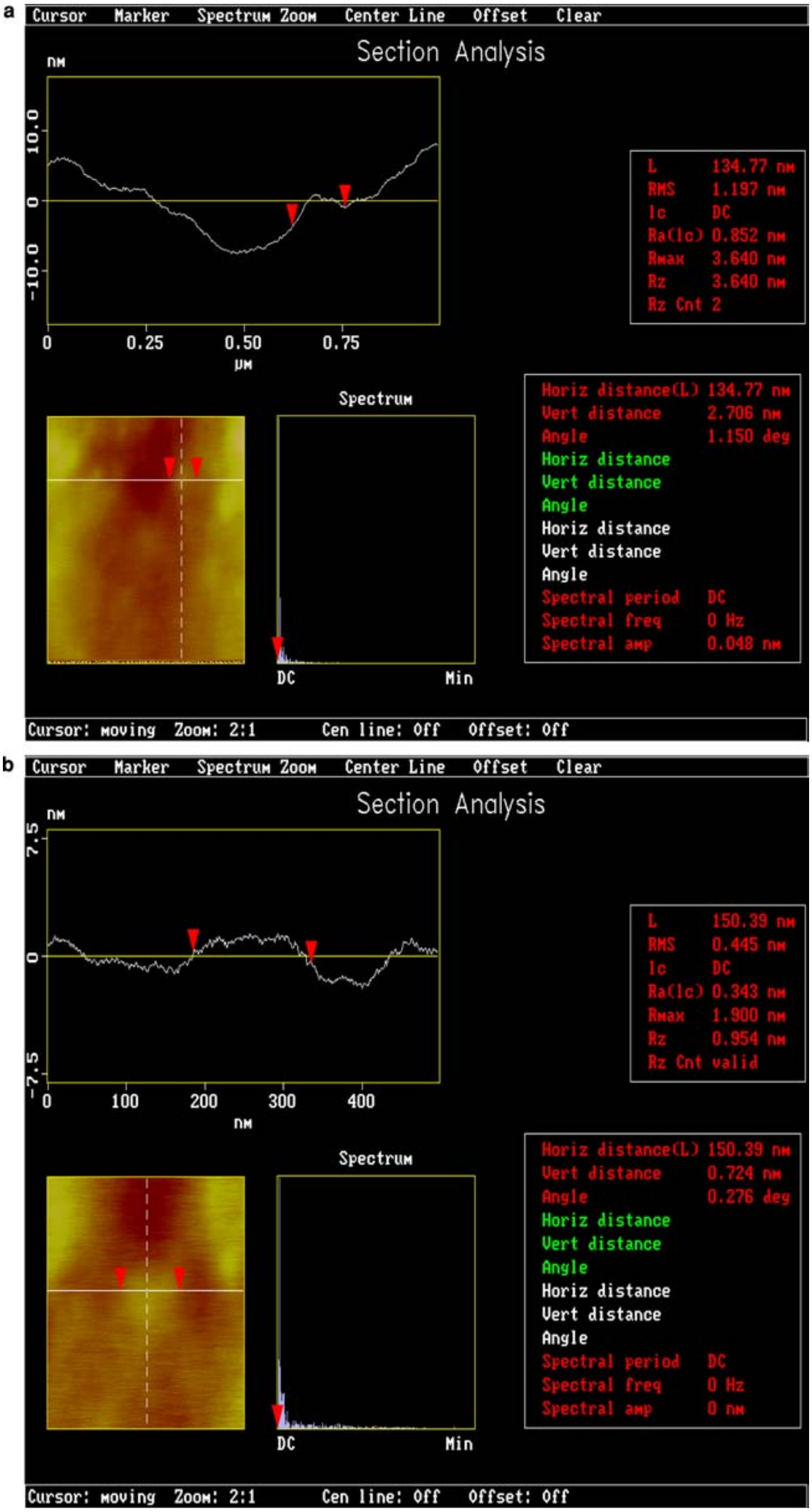
AFM measurements

Atomic force microscopy observations were carried out using tapping mode operation with a Nanoscope III Multimode scanning probe microscope from Digital Instruments (Santa Barbara, CA, USA) using a "D" vertical engage scanner. Silicon micro-cantilever (SI-DF40, manufacturer specifications: spring constant



Synthetic Route For Aromatic Polyester

Scheme II



L 134.77 nm
RMS 1.197 nm
Ic DC
Ra(Ic) 0.852 nm
Rmax 3.640 nm
Rz 3.640 nm
Rz Cnt 2

Horiz distance(L) 134.77 nm
Vert distance 2.706 nm
Angle 1.150 deg
Horiz distance
Vert distance
Angle
Horiz distance
Vert distance
Angle
Spectral period DC
Spectral freq 0 Hz
Spectral amp 0.048 nm

Cursor: moving Zoom: 2:1 Cen line: Off Offset: Off

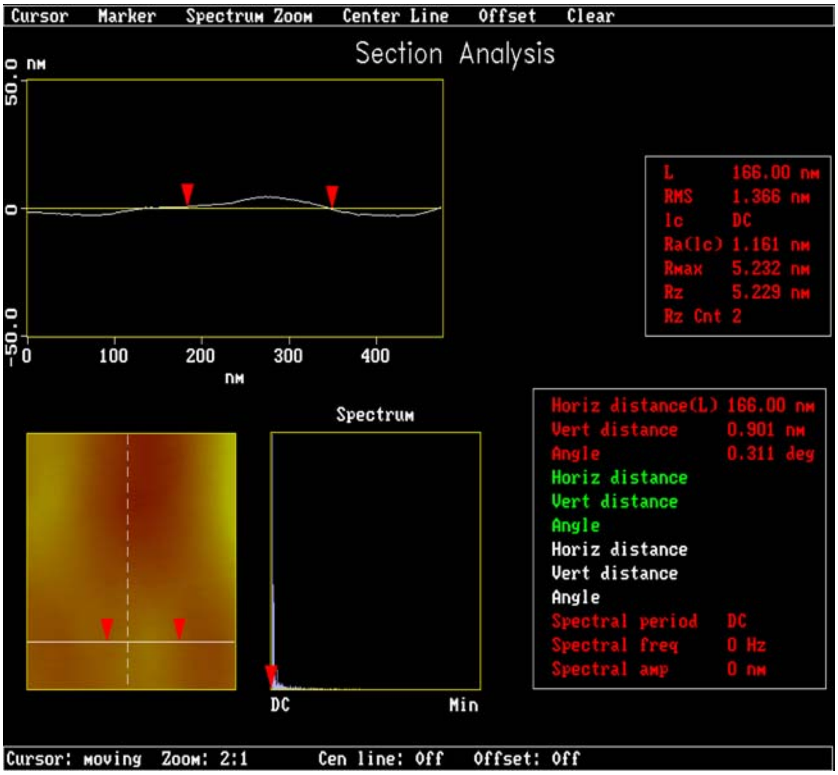
L 150.39 nm
RMS 0.445 nm
Ic DC
Ra(Ic) 0.343 nm
Rmax 1.900 nm
Rz 0.954 nm
Rz Cnt valid

Horiz distance(L) 150.39 nm
Vert distance 0.724 nm
Angle 0.276 deg
Horiz distance
Vert distance
Angle
Horiz distance
Vert distance
Angle
Spectral period DC
Spectral freq 0 Hz
Spectral amp 0 nm

Cursor: moving Zoom: 2:1 Cen line: Off Offset: Off

Fig. 1 Tapping mode AFM images of 2G AL-PE on mica surface: **a** section analysis of the height image; and **b** section analysis obtained from an another topographic image with a scan size of 500×500 nm

42 Nm^{-1}, resonance frequency 250–390 KHz) obtained from Seiko Instrument Inc. (Japan) was used for imaging. All images were flattened and dendrimer height and width dimensions (x, y, and z) were measured by random cross section analysis in the x–y plane of surface.



```
L          166.00 nm
RMS        1.366 nm
lc         DC
Ra(lc)     1.161 nm
Rmax       5.232 nm
Rz         5.229 nm
Rz Cnt     2

Horiz distance(L) 166.00 nm
Vert distance     0.901 nm
Angle             0.311 deg
Horiz distance
Vert distance
Angle
Horiz distance
Vert distance
Angle
Spectral period   DC
Spectral freq     0 Hz
Spectral amp      0 nm

Cursor: moving  Zoom: 2:1     Cen line: Off  Offset: Off
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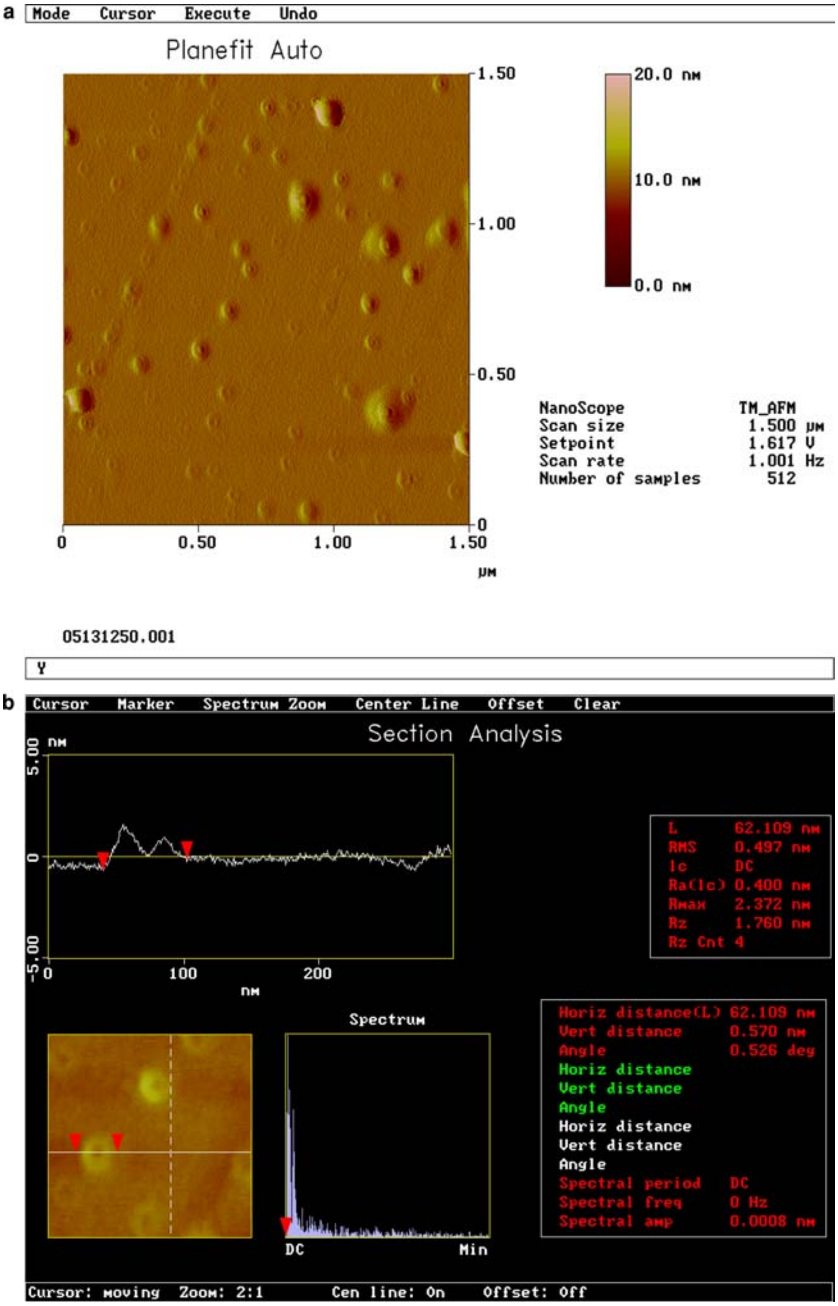
Fig. 2 Tapping mode AFM images of 3G AL-PE on mica surface showing section analysis obtained from another topographic image with a scan size of 500×500 nm

Results and discussion

The present AL-PE dendrimers are sparingly soluble while AR-PE dendrimer are insoluble in water, therefore, their 0.1% w/w solutions were made in methanol and tetrahydrofuran, respectively. Both solutions were spin coated (at the rate of 500 rpm) on clean mica surfaces and AFM images were taken under tapping mode conditions. Figure 1a, b shows surface topology of 2G AL-PE with large patches of different sizes. A section analysis has suggested the presence of somewhat smaller aggregates, which comes out to be around 134 nm. A section analysis indicates the presence of aggregates of 134 and 150 nm with height of around 2.7 and 0.7 nm, respectively. As far as the diameter of these dendrimers is concerned, the height is too small which indicates that the aggregates are quite spread over mica. It is to be mentioned here that decrease in the concentration from 0.1% w/w to 0.001% w/w did not produce any image of individual dendrimers. Similarly, Fig. 2 demonstrates the topography of 3G AL-PE with some patchy structures. A section analysis demonstrates a quite flat aggregate with dimension equal to 166 nm and height of 0.9 nm. This much increase in the size (i.e., 14%) can obviously be related to a similar increase in the molecular weight (i.e., 17%) from 969 (2G AL-PE) to 1,171 (3G AL-PE). Li et al. [18] have estimated the sizes of various generations of PAMAM ranging from G5 to G10. They pointed out that the measured diameters are always larger than the heights, indicating that the dendrimers are no longer spherical but dome shaped when deposited on a mica surface. Furthermore, several studies have reported [21, 23] that the measured diameters of dendrimer molecules by AFM are much larger than the theoretical values, which indicates their flattened structures on the surfaces. Some explanations have been put forth [18] to explain this deformation. The dendrimer macromolecules are open and soft material rather than rigid and due to this reason they tend to deform on surfaces. The electrostatic interactions between the negatively charged mica surface and the surface groups of dendrimer may further tighten the adsorption of dendritic species. Such deformations are even more expected in the case of present 2G and 3G AL-PE in view of their hyperbranched nature which should have more open structures. Hence, they are expected to be more prone to intercalate with each other rather than closed PAMAM macromolecules giving rise to very small height in each case as demonstrated by Figs. 1 and 2.

Figure 3 shows the AFM images of AR-PE dendrimer, which is again a hyperbranched dendrimer. More clear images can be seen for this dendrimer. Figure 3a demonstrates the topography of AR-PE adsorbed on mica. AR-PE macromolecules are relatively



```
NanoScope              TM_AFM
Scan size               1.500 µm
Setpoint                1.617 V
Scan rate               1.001 Hz
Number of samples         512
```

```
L         62.109 nm
RMS       0.497 nm
lc        DC
Ra(lc)    0.400 nm
Rmax      2.372 nm
Rz        1.760 nm
Rz Cnt    4
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```
Horiz distance(L)  62.109 nm
Vert distance      0.570 nm
Angle              0.526 deg
Horiz distance
Vert distance
Angle
Horiz distance
Vert distance
Angle
Spectral period    DC
Spectral freq      0 Hz
Spectral amp       0.0008 nm
```

Fig. 3 Tapping mode AFM images of AR-PE on mica surface: **a** amplitude image with a scan size of 1.5×1.5 µm; **b** section analysis of the latter height image

in less associated states than AL-PE. Enlarged topography can be seen in Fig. 3b. These images indicate the presence of a clear cavity in the center of each aggregated assembly represented by a dark area. Recently, Sui et al. [28] have also observed similar cavities of hydrophobic nature with 10–20 µm diameter for amphiphilic polymerizable PAMAM dendrimers at air/water interface with the help of Brewster angle microscopy. They have attributed the appearance of these dark holes to the self-assembling pattern of amphiphilic PAMAM. A section analysis of AR-PE (Fig. 3b) measures the sizes of small aggregates equal to 63 nm. The presence of a clear cavity with approximate size of 15 nm is also shown by this section analysis. A large difference between the size of the cavities reported by Sui et al. [28] and by AR-PE could be due to the difference in the self-assembling nature of amphiphilic PAMAM and that of AR-PE (scheme II). These findings can be compared with monolayers formed by analogous alkyl substituted polyphenylene dendrimers on graphite surface reported by Loi and Butt [24]. They observed similar cores in the monolayers consisting of twisted interlocked benzene rings and an external shell of alkyl chains. These structures are present in the form of granular and homogeneous, and nanorod patterns. We do not see any such pattern in our present AR-PE samples which might be attributed to the absence of long alkyl chains in AR-PE dendrimers. All above results of Fig. 3 and those of related works point to one common conclusion that polyaromatic dendrimers produce self aggregated small or large (depending upon the concentration) organized assemblies with well-defined patterns on surfaces. Such patterns identify themselves as different from those demonstrated by aliphatic polyester. Hence, the surface adsorption is more favorable in the case of AL-PE rather than AR-PE in view of the more hydrophilic nature of AL-PE due to the presence of surface –OH groups (scheme I). A favorable surface adsorption renders self assembled aggregates less feasible. That is why the aggregates of AL-PE are less organized and more spread over than AR-PE.

Conclusions

The following conclusions can be drawn from this study:

1. Both AL-PE and AR-PE hyperbranched dendrimers exist in the form of aggregates, which are much larger in the former case.
2. The larger aggregates with much smaller height in the case of AL-PE have been attributed to the favorable adsorption on mica surface in view of their hydrophilic nature due to the presence of surface—OH groups.
3. Smaller but much organized aggregates are formed in the case of AR-PE which also demonstrates cavity formation in each aggregate.

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