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On the structure of polyamidoamine dendrimer monolayers

Valery N. Bliznyuk[a,b,*], **Frank Rinderspacher**†[a] **and Vladimir V. Tsukruk**[a]
[a]*College of Engineering and Applied Sciences, Western Michigan University, Kalamazoo, MI 49008, USA*
[b]*Institute of Semiconductor Physics, Ukrainian Academy of Science, Kiev 252650, Ukraine*
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Monolayers of polyamidoamine (PAMAM) dendrimers (generations 3.5 through 10) are prepared via electrostatic self-assembling from water solutions. Their thickness, morphology and mechanical stability are studied by scanning probe microscopy (SPM). A conformational state of dendritic macromolecules is discussed and compared to polymer scaling in the solution and recent molecular dynamics simulation results. The proposed model of molecular ordering assumes highly deformed (compressed along the surface normal) ellipsoidal shape for macromolecules in condensed monolayers. The molecular dimensions (thickness) versus molecular mass dependence is described by a scaling law with the exponent $\alpha = 0.28$ being in-between values typical for dendrimer solutions and for a globular state. © 1998 Elsevier Science Ltd. All rights reserved.

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Dendritic macromolecules with cascade, tree-like architecture, and hollows inside (dendrimers) are interesting objects which can be employed as well defined nanoparticles for many applications including biochemistry, surface chemistry, tribology, catalysis [1-8]. Dendrimers adopt a roughly spherical, globular shape in solution. Their cores are relatively loosely packed for most of the generations which allows them to trap guest molecules (selective encapsulation of drugs for targeted delivery). They can serve, after proper modification, chemical or biological nanocells (''microreactors'') with a controlled inter- and intamicellar environment. They have been recently shown to exhibit interesting transport properties at liquid–liquid interfaces [9] and introduce a number of interesting fundamental questions concerning conformational behavior of fractal macrochains at the interface. Such prospects attract a lot of research to the field. However, very limited data exist on dendrimer microstructures in the bulk state, and only a few studies are devoted to their behavior at the interfaces [10-14].

We demonstrate herein the possibility of forming a complete and homogeneous monolayer from dendritic molecules by electrostatic self-assembly on charged solid surfaces (see *Figure 1* for a general procedure) [15]. Polyamidoamine (PAMAM) dendrimers generations G3.5, G4 (Aldrich) and G3.5, G4, G5.5, G6, G9.5, G10 (Dendritech), are applied to fabricate self-assembled monolayers (SAMs) according to the procedure developed before [16-20]. Dendrimers of adjacent generations possess surface carboxylic (COONa for G3.5, G5.5, and G9.5) or amine (NH_2 for G4, G6, and G10) groups [21,22]. Some structural parameters of dendrimers under investigation are summarized in *Table 1*.

We varied pH for odd generations with carboxylic surface groups in the range 5.2–9.3 and for even generations with amine surface groups in the range of 2–4. We observed that the best adsorption results (completeness of surface coverage and stability of monolayer films) can be obtained below pH 3 for even generations and above pH 6 for odd generations. Scanning probe microscopy (SPM) topographical and friction contact modes (in water) and the tapping mode (in air) [23-25] were applied to study dendrimer films using a Dimension 3000 (Digital Instruments Inc.) microscope. Both the tapping mode in air and scanning in the water with a chemically modified tip allowed stable reproducible imaging of the soft dendrimer monolayers without visible damage. A detailed description of all experimental procedures used here can be found in Ref. 15.

Dendrimer monolayers at the early stages of the adsorption (short adsorption times) possess characteristic cell morphology frequently observed for tethered macromolecules at the initial stages of film formation (*Figure 2a*). However, complete films become very smooth and homogeneous with a slightly grainy surface morphology (*Figure 2b*). The monolayer microroughness detected by SPM (0.3–0.5 nm within $1.5 \times 1.5\ \mu m^2$) is slightly higher than the roughness of the supporting silicon substrates (RMS = 0.15 nm). This value indicates that grainy surface topography in *Figure 2b* and *c* is composed of areas with extremely small elevations (less than average diameter of polymer chain) and that dendritic monolayers indeed possess molecularly smooth surfaces. Friction force microscopy images confirm homogeneous surface composition of the dendrimer monolayers (*Figure 2d*). Dendrimer monolayers are relatively stable and are not damaged by multiple scanning in the tapping mode in air, which indicates a very low level of plastic deformation and high elasticity. These monolayers, however, cannot sustain shear stresses introduced by direct physical contact with the sharp SPM tip in the contact mode at a comparatively high normal load ($\gtrsim$ 30 nN). As demonstrated in *Figure 1c* and *d*, this results in plastic deformation of monolayers within a previously scanned area with the formation of the characteristic ''abrasion'' pattern typical for soft polymeric materials [26-28].

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[*] To whom correspondence should be addressed. Present address: Physics Department, University of California, Santa Cruz, CA 95064, U.S.A.

[†] Present address: Department of Plastics Engineering, University of Paderborn, Paderborn, 33098, Germany.

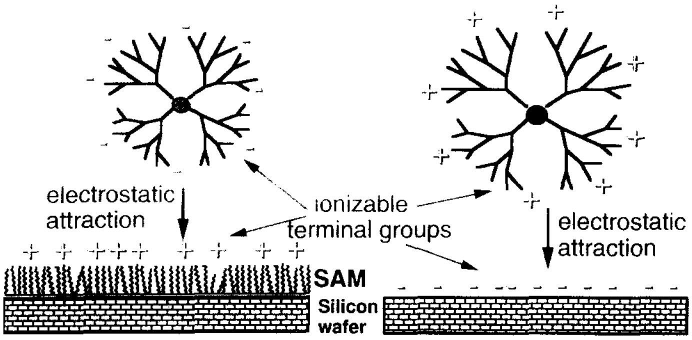

Figure 1 General scheme of electrostatic self-assembly of dendrimers. A negatively charged native silicon surface or positively charged surface of a self-assembled monolayer (SAM) of organic molecules 3-aminopropyltriethoxysilane are used for electrostatic adsorption of oppositely charged dendrimer molecules with terminal carboxylic (negative) or amine (positive) groups for odd or even dendrimer generations respectively. The terminal groups of both the substrate and adsorbate molecules are ionized by appropriate pH conditions (see more explanations in the text)

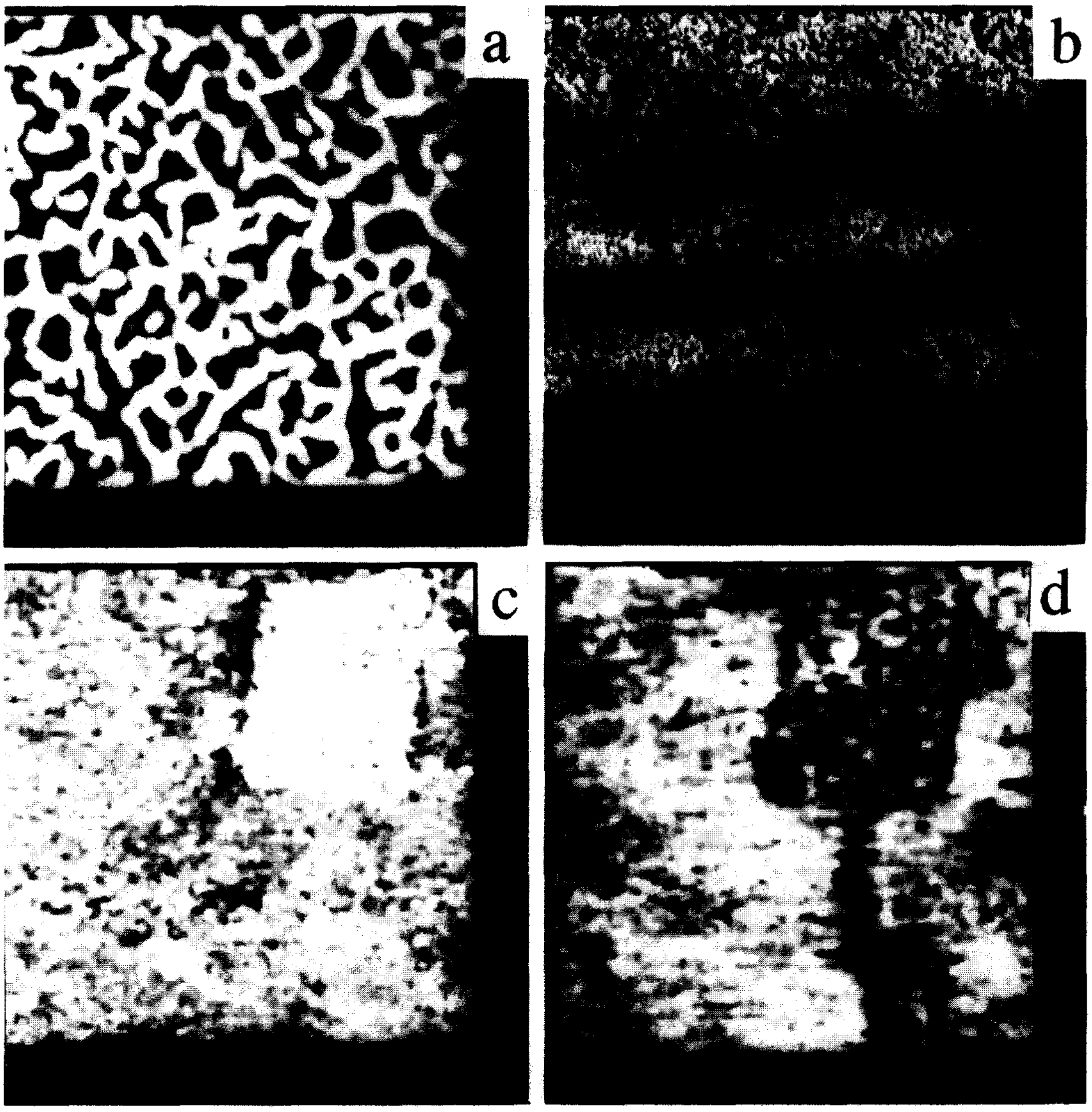

Figure 2 SPM images of PAMAM dendrimer self-assembled monolayers: (a) surface morphology of G10 dendrimer at early stages of monolayer formation, scan size 2 μm; (b) 3D view of complete G10 monolayer, scan size 12 μm; (c) surface morphology of G4 monolayer under water with a square track of damaged surface from previous scanning with higher forces, scan size is 5 μm; (d) friction force image of the same area. Images (a,b) were obtained in the tapping mode, in the air, 1 Hz scanning rate, forces about 1 nN; images (c,d) were obtained in the contact mode, under water, 2 Hz scanning rate, forces about 5 nN, surface damage is produced by scanning with a normal load higher 30 nN

The average thickness of monolayers determined from SPM images varies depending upon fabrication conditions but shows steady growth with the increase of a dendrimer generation number (*Table 1*). Thicknesses of monolayers obtained from X-ray reflectivity for some of the monolayers [15] are close to the monolayer thicknesses determined from SPM images (*Table 1*). Experimental data show that the thicknesses of all monolayers studied are

Table 1 Structural parameters of PAMAM dendrimer molecules and their SAMs

Generation (G)	Molecular weight [21] (M)	Number of functional groups	Surface charges*	Theoretical diameter [22] (nm)	Diameter in solution [22] (nm)	Monolayer thickness [15] X-ray (nm)	Monolayer thickness SPM† (nm)
3.5	12419	64	negative				0.9–1.0
4	14215	64	positive	6.56	4	1.8 ± 0.4	1.1–1.7
5.5	50865	256	negative				1.7–2.3
6	58048	256	positive	9.1	6.7	2.8 ± 0.5	1.8–2.4
9.5	819789	4096	negative				2.5–3.3
10	934720	4096	positive	14.3	12.4	5.6 ± 0.7	4.6–6.2
α‡				0.19	0.26	0.27	0.28

*After pH adjustment

†The range of monolayer thicknesses is shown for various fabrication conditions and surface locations

‡α is a scaling exponent, obtained by a linear fit of log D~log M plots

much smaller (by 60–70%) than the average diameters of dendritic macromolecules in a "contracted state" (*Table 1*) [21,22]. This thickness also is substantially lower than the short axis of asymmetrical (aspherical) dendrimers of low generation [29,30]. According to molecular dynamic simulations [31], the axial ratio (i.e., the ratio of the diameters along normal to the surface/parallel to the surface) of model dendrimers is close to 1 only for the high generations (G $\gtrsim$ 9) but can be close to 1:1.6 for G3.5–G4 generations.

We conclude, therefore, that the dendritic macromolecules are not only collapsed within monolayers but are uniaxially compressed along the surface normal. It is worth noting that structural state of charged dendrimers in compact, complete monolayers differs significantly from that observed for isolated islands of neutral dendrimers [10]. In these last cases, the observed thickness is usually very close to the expected dendrimer diameter.

The molecular dimension of dendrimers along the surface normal, D, follows closely the scaling law $D \propto M^{\alpha}$ observed for dendrimers in a solution with $\alpha \approx 0.27$ (*Table 1*). The super-branched structure of dendritic molecules which can be approximated by a thin spherical solid shell gives rise to values of α lower in comparison to values usual for linear polymer chains [32]. α approaches a globular state value (1/3) as a result of molecular condensation on the charged interface. The latter gives evidence of a more compact conformational state of dendrimer molecules in SAMs. On the other hand, similarity of the scaling law exponents for the solution state and the SAM state may indicate that the dendritic macromolecules adopt oblate ellipsoidal shape as a result of affine compression of their solid shells. Of course, the conformational behavior depends on the length and number of molecular branches (i.e., generation number) in this case. Neutron reflectivity experiments [11] might prove the proposed model.

Dendrimer spheres are "blown up" to an extent controlled by the strength of repulsive interactions of charged functional groups (pH conditions) in solution. Strong electrostatic interactions between soft dendritic macromolecules and charged substrates might be responsible for the observed conformational state in monolayers too. For instance, dramatic conformational changes, from a more compact coiled to a stretched state, have been observed during adsorption of non-branched polyionomers [33]. The electrostatic interactions can be complemented by short range Van der Waals, long range capillary forces, and ionic binding (e.g., formation of dimers or multiplets [34,35]). As known, capillary forces between soft spherical latex nanoparticles may lead to their complete smashing and surface spreading during the drying process [36]. We can speculate that similar behavior can take place for soft dendrimer nanoparticles because their glass transition temperatures are very close to room temperature [21].

Finally, molecular modeling of dendrimer adsorption predicts that such spreading of dendrimer macromolecules with "sticky" terminal groups should inevitably occur within dense monolayers at certain conditions [31]. These conditions are: relatively high molecular weight (generations G $\gtrsim$ 3), and high enough interaction strength between terminal functional groups of dendrimers and substrate surface. Certainly, dendrimers considered here fulfil these requirements. They represent a fairly good illustration of structural state of charged soft dendrimers within a dense monolayer, electrostatically self-assembled, and strongly tethered on the oppositely charged surface.

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