

Adsorption and Self-Organization of Dendrimers at Water–Solid Interfaces

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Abstract: Adsorption of poly(amido amine) (PAMAM) dendrimers at water–silica interfaces and the resulting self-organization on this type of substrate is discussed. Investigations with optical reflectivity and atomic force microscopy (AFM) reveal that dendrimers form monolayers of low coverage on such surfaces with liquid-like structure. The nearest neighbor separation distance in these layers is dictated by screened Coulomb repulsion forces between the adsorbing dendrimers. This effect rationalizes the strong increase of the adsorbed amount with the ionic strength and pH. These layers are stable for high dendrimer generations, while they can become unstable for lower generations.

Keywords: Adsorption · Atomic force microscopy · Dendrimer · Reflectivity · Water–silica interface

1. Introduction

Since the synthesis of poly(amido amine) (PAMAM) dendrimers was described in 1985 by Tomalia,^[1] dendritic molecules continue to fascinate chemists. Dendrimers are synthesized in a stepwise fashion around a core, whereby each step leads to a new generation (Fig. 1). In the case of PAMAM dendrimers, generations up to G10 are known. These macromolecules have unusual properties, for example, their internal structure,^[2] solution viscosity,^[3] or acid-base behavior.^[4] At the same time, promising applications as light-harvesting antennas,^[5] nanoreactors,^[6,7] or non-viral gene vectors^[8] are emerging.

Interfacial phenomena involving dendrimers have received only moderate attention so far.^[9,10] Dendrimers interact strongly with interfaces, and the resulting adsorbed films are promising for surface-based sensors or surface nanopatterning.^[11,12] While some authors have investigated dendrimer adsorption at the air–liquid interface,^[13,14] others have focused on their interaction with water–solid interfaces.^[12,15–20]

The archetypal adsorption of PAMAM dendrimers to the water–silica interface is discussed here.

2. Structure of Adsorbed Dendrimer Layers

PAMAM dendrimers adsorb strongly at the water–silica interface. The water–

silica interface develops a negative charge due to the dissociation of the silanol groups, whereby the magnitude of the surface charge density increases with pH.^[21,22] PAMAM dendrimers develop a positive charge in solution due to the dissociation of their primary and tertiary amino groups.^[23] As a consequence, PAMAM dendrimers are strongly attracted to the water–silica interface by electrostatic interactions.

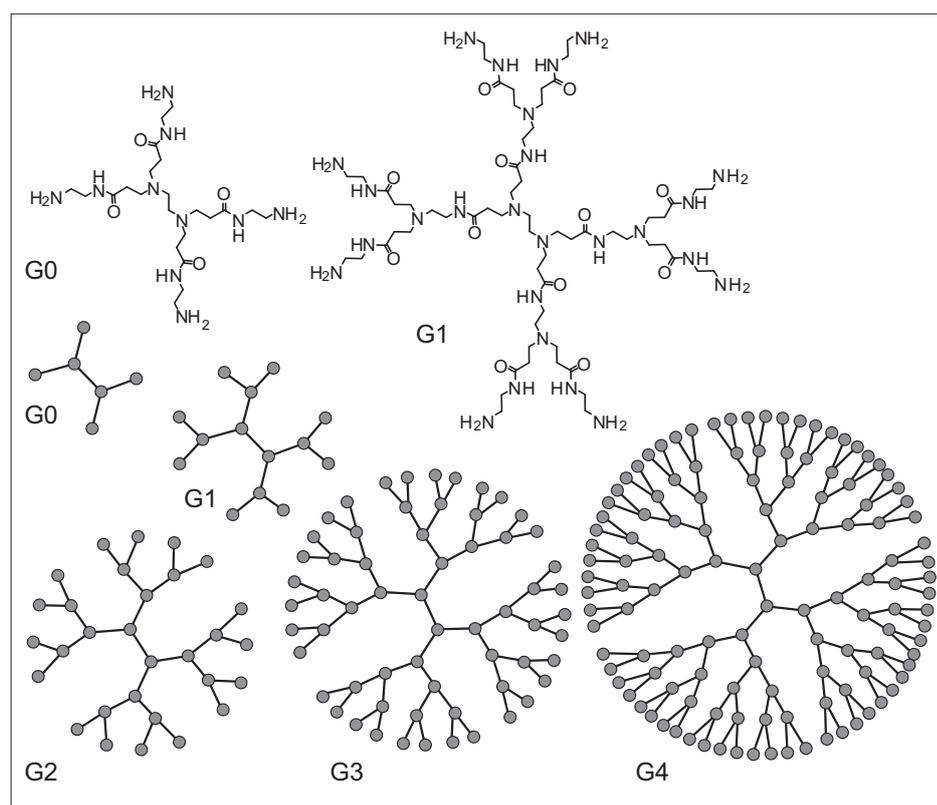


Fig. 1. Structure of poly(amido amine) dendrimers (PAMAM) of increasing generations. The largest G10 dendrimers have a molecular mass of about 935 kg/mol and a diameter of 13.5 nm.

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However, dispersion interactions and hydrogen bonding are expected to contribute to these attractive forces as well.^[19,24]

Dendrimer adsorption can be probed with atomic force microscopy (AFM) at the single molecule level. Typical images for G10 adsorbed on silica at pH 4 are shown for three different ionic strengths adjusted with KCl (Fig. 2a). The dendrimers adsorb individually in a loose monolayer, which becomes progressively dense with increasing ionic strength. From such images, one can directly estimate the adsorbed mass by counting, and this quantity increases with increasing ionic strength. One further observes that the surface arrangement of the dendrimers is not completely random, but rather liquid-like. This spontaneous structuring of the layer is evidenced by the peak in the pair-distribution function (Fig. 2b).^[19,25] This peak shows that nearest neighbors can be found at a rather well-defined distance, which decreases with increasing ionic strength. The reason for this characteristic behavior will be discussed further below.

From such AFM images, one can equally deduce that dendrimers flatten upon adsorption strongly, and that their diameter in the adsorbed state is 3–4 times larger than their height.^[19,25] The deformation occurs due to the softness of the dendrimers and their strong attraction to the surface.

3. Formation and Stability of Adsorbed Layers

While AFM images give detailed information about the structure of the adsorbed layers, the overall adsorbed mass can be determined more easily *in situ* by optical surface-sensitive techniques. The optical response is converted into the adsorbed mass by a thin-layer model, and the correctness of the procedure has been verified by AFM.^[20] Such optical techniques further provide direct information on the formation kinetics and stability of such layers.

Typical results of dendrimer adsorption on silica as obtained by optical reflectivity are shown in Fig. 3. The experiment starts by equilibration of a clean silica surface in contact with the electrolyte in question, and by a subsequent injection of a dendrimer solution in the same electrolyte. Due to the attractive dendrimer–surface interactions, one observes a rapid build-up of the adsorbed layer, which basically is controlled by convective transport to the surface and diffusion through the stagnant layer. This initial rapid adsorption is followed by a slower saturation process, leading to an adsorption plateau. The adsorbed mass at the saturation plateau strongly depends on the dendrimer generation and

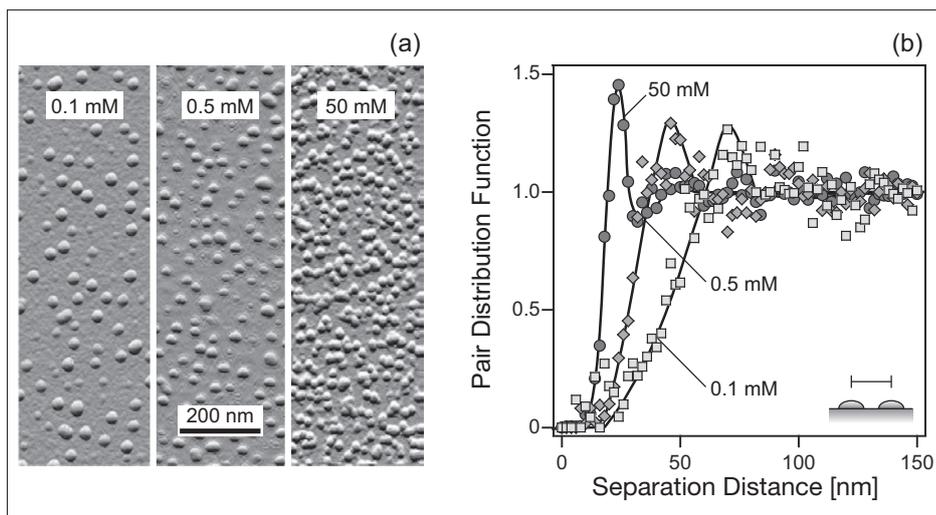


Fig. 2. Adsorbed PAMAM G10 dendrimer monolayer on silica. (a) AFM amplitude images in air obtained by adsorption from solution at a dendrimer concentration of 3 mg/L at pH 4 and different ionic strengths. (b) Pair distribution function at different salt levels. The peak indicates the liquid-like structure of the layer. The inset indicates the separation distance between two adsorbed dendrimers.

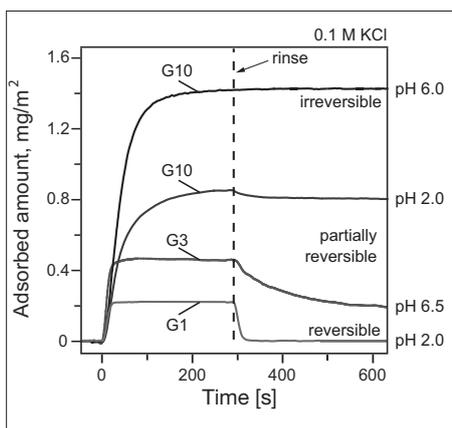


Fig. 3. Formation and stability of adsorbed layers of PAMAM dendrimers on silica studied by reflectometry. The stability of the layers is assessed by monitoring the decrease of adsorbed mass upon rinsing with dendrimer-free solution.

solution conditions. For the same solution conditions, the adsorbed mass increases with increasing generation. This trend can be explained by the facts that the surface coverage remains approximately constant, and that the dendrimer size increases with increasing generation. However, one also observes that the saturation mass increases with increasing pH. The latter trend will be discussed below.

The stability of the adsorbed layer can also be investigated by reflectometry in a straightforward fashion. The simplest approach is to rinse the dendrimer-coated surface with the original electrolyte solution without dendrimers.^[24] Fig. 3 reveals several characteristic features concerning the layer stability and of the eventual desorption process. No desorption is observed

for G10, and therefore the adsorbed film is stable under these conditions. On the other hand, one observes full desorption for G1, indicating that the film is unstable. The intermediate behavior features a two-step desorption process, which suggest a partial stability of the adsorbed film. Initially, a fraction of the adsorbed dendrimers desorbs rapidly, but the onset of an intermediate plateau indicates a stable remaining fraction. One finds fully stable adsorbed films for high generations, high pH, and low salt concentrations, while in opposite situations the adsorbed films become unstable. The stable films reflect strong attractive dendrimer–surface interactions, and the latter are especially important for high generations due to the large contact area. Since these attractive forces are mainly electrostatic in origin, one can understand why they weaken with increasing ionic strength and decreasing pH. At higher ionic strength, the electrostatic screening becomes more important, while at lower pH, the surface develops a lower charge. We suspect that progressive flattening of the dendrimers on the surface promotes the formation of the highly stable films. A similar behavior was equally suggested based on computer simulations.^[26]

4. Random Sequential Adsorption (RSA)

Adsorption of higher generation dendrimers can be rationalized in terms of the random sequential adsorption (RSA) model. This model was initially proposed to explain the irreversible adsorption of proteins,^[27–29] and later it was used to describe deposition of colloidal particles on

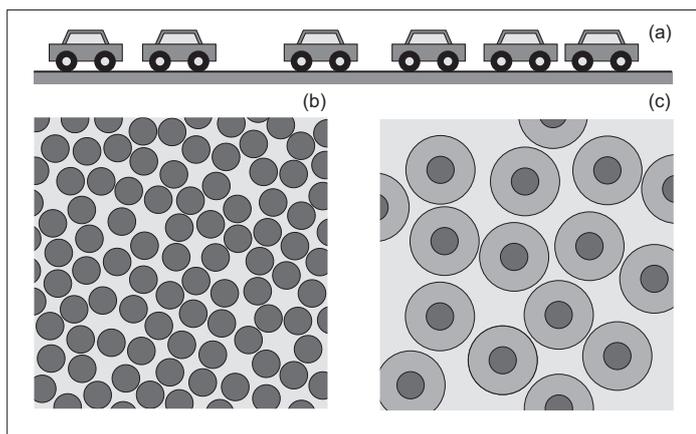


Fig. 4. Random sequential adsorption (RSA) model. (a) Classical car parking problem with a jamming limit corresponding to a coverage of 0.75. (b) Adsorption of disks with a jamming-limit coverage of 0.55. (c) When the dendrimers repel through electrical double layers, the jamming coverage is determined by the thickness of the diffuse layer (light grey circles), while the actual coverage turns out to be substantially smaller (dark grey circles).

solid substrates with success.^[30–32] The essence of the RSA model can be best visualized in one dimension (Fig. 4a).^[29] Imagine cars parking along a street without any marked parking spots. As long as the street is empty, cars will be park randomly, but as their number increases, the newly arriving cars must find their spot aside those already parked. When the street becomes crowded, one repeatedly finds cars parked such that no others can fit even though their spacing might be noticeable. This car parking problem can be solved exactly and at the so-called jamming limit one finds that 75% of the available space is occupied. The same question can be studied in two dimensions with hard disks, which are randomly placed on a sticky surface. Once in place, the disks are assumed to be irreversibly bound. As one continues to fill the surface, the jamming occurs close to a coverage of 55% (Fig. 4b).

The coverage observed in the AFM image shown in Fig. 2a is much smaller than the jamming limit, especially at low ionic strength. This discrepancy can be explained through the existence of electrostatic repulsive forces between the dendrimers, as the adsorption process will involve no configurations with an energy exceeding substantially the thermal energy. Since the charged dendrimers interact with a screened Coulomb potential, they will not approach closer than a distance which is comparable to the thickness of the diffuse layer (*i.e.* Debye length). Otherwise, their interaction energy will exceed the thermal energy. To apply the RSA model to describe the adsorption of charged dendrimers, one must only reinterpret the size of the disks to take into account the thickness of the diffuse layer. For this reason, the actual surface coverage turns out to be relatively small in spite of the fact that the system is

strongly interacting (Fig. 4c). By the same token, the nearest neighbor separation of the adsorbed dendrimers defines the position of the peak of the pair correlation function (Fig. 2b). An analogous picture has been put forward for the deposition of charged colloidal particles.^[30–32]

We refer to this approximation as the two-body RSA model, since a two-body screened Coulomb potential is used to describe the interaction between the adsorbing dendrimers. The comparison of this two-body RSA model with experimental data is shown in Fig. 5. One observes good agreement with the data at pH 4. In particular, the model describes the increase of the adsorbed amount with increasing ionic strength very well. This increase is due to the progressive shrinkage of the diffuse layer, which reduces the nearest neighbor separation and increases the maximum coverage.

With increasing pH, however, the adsorbed amount increases and this increase cannot be rationalized within the simple two-body RSA model. This phenomenon can be explained as follows. With increasing pH, the charge of silica increases, and an increasing number of counter ions accumulates in its diffuse layer. When dendrimers are adsorbing at the surface, they interact laterally through this diffuse layer. However, the ion concentration in this layer is higher than in the bulk, which leads to additional screening and a smaller nearest neighbor separation. This effect can be quantified by evaluating a three-body interaction potential between two dendrimers in the presence of the surface.^[20] The

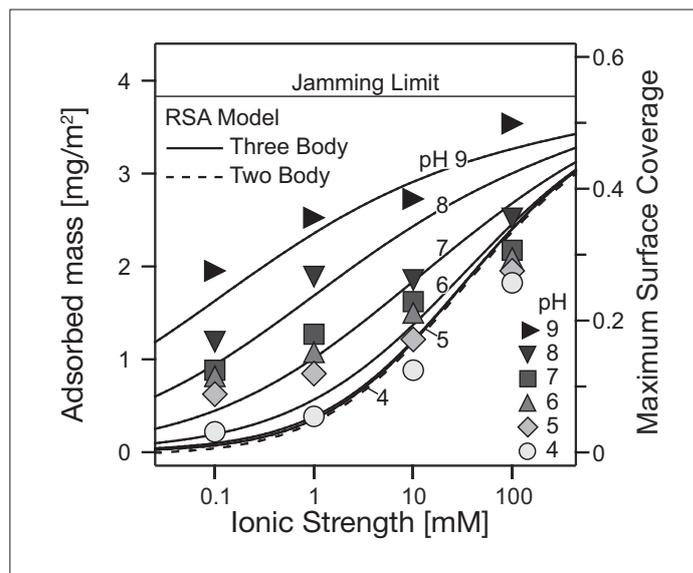


Fig. 5. Adsorbed mass and coverage of G10 PAMAM dendrimers on silica as a function of the ionic strength and for different pH values. Experimental data determined by reflectometry (symbols) are compared to the predictions of the RSA model (lines). The two-body interaction potential describes the data at low pH where the charge of silica is low, while a three-body interaction potential is needed to describe the pH dependence.

results of such a three-body RSA model are shown in Fig. 5. The good agreement of this model with experiments suggests the correctness of the proposed mechanism. For a weakly charged surface, this effect is absent and for this reason the classical two-body RSA model is recovered. Such good agreement is only obtained for high-generation dendrimers. For lower generations, additional effects come into play, such as, surface mobility or specific ion effects. However, these phenomena have not been explored so far.

5. Conclusion and Outlook

Recent progress in the understanding of the formation and stability of adsorbed layers of PAMAM dendrimers on silica substrates has been presented. Optical reflectivity and AFM imaging reveal that dendrimers form saturated liquid-like layers of low coverage. These self-organized monolayers feature a well-defined nearest neighbor distance, which is determined by screened Coulomb repulsion between the adsorbing dendrimers. This effect rationalizes the strong increase of the adsorbed amount with the ionic strength and pH. For high dendrimer generations, these layers are stable in dendrimer-free solutions. For low generations, however, these layers become unstable and desorb either partially or entirely, especially at low pH and high ionic strength.

Such self-organized adsorbed layers may have several applications. Most

directly, they provide a simple means to pattern surfaces on the nanometer scale, quite similar to colloidal lithography used on larger length scales.^[33] The adsorbed dendrimers could be equally used as chemical reactors, for example, to synthesize metal nanoparticles at predefined spots on the surface as is being carried out in the bulk.^[7]

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