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Microcontact printed poly(amidoamine) dendrimer monolayers on silicon oxide surface

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Abstract

Patterning of silicon substrates with poly(amidoamine) generation 5 (PAMAM-G5) dendrimers using soft lithographic microcontact printing (μCP) is presented. μCP is shown to yield monolayers of dendrimers patterned with high level of definition over μm^2 to mm^2 areas. The patterns are stable over a period of weeks, which is attributed to the suppressed diffusion of partially charged G5 PAMAM on oxidized silicon. However, the dendrimers studied were shown to be relatively weakly bound to the substrate when subjected to lateral stresses. In aqueous conditions most of the dendrimers desorbed from the substrate.

Keywords: AFM; Dendrimer; PAMAM; Microcontact printing

1. Introduction

Dendrimers are a unique class of synthetic, nearly monodisperse polymers, which encompass hyperbranched, tree-like, covalent structures with precisely defined molecular architectures [1–4]. Their dimensions range from one to several nanometers and they exhibit increasing sizes with increasing degree of molecular branching (hereafter referred to as generation). A characteristic feature of dendrimers is the presence of well-defined, controllable functional groups at their molecular "surface" (dendrimer periphery), which determine their chemical properties, and provide synthetic versatility. Due to their exact molecular size and well-defined architecture, dendrimers have been frequently used as building blocks in bottom–up macromolecular nanotechnology. Poly(amidoamine) (PAMAM) dendrimers feature among the most commonly used, and best studied hyperbranched structures, based on ethylenediamine core [5], exhibiting various surface groups. For example "generation 5" (G5) PAMAM dendrimers have 128 accessible terminal primary amines available for derivatization. Although the synthesis and solution properties of dendrimers have been studied in depth, the knowledge of the structural and physicochemical properties of dendrimers at interfaces is still limited. Nevertheless, owing to their unique properties, dendrimers have found applications in

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a broad range of fields including medicinal chemistry [6], catalysis [7], and photonics [8].

During the last decade many investigations were concerned with fabrication and properties of dendrimer surface structures [9]. For the preparation of dendrimer monolayers or multilayer films, layer by layer assembly [10,11], self assembly [12], covalent linking [13,14], spin coating [15,16], soft lithography [14,17–22] and dip pen nanolithography [14,23,24] were used.

Among possible fabrication methods microcontact printing (μCP) is one of the simplest, most robust and inexpensive methods to obtain sub-50 nm dendrimer patterns over large areas [25]. However, only few studies of μCP of dendrimers were reported in the literature to date [14,17–20,22,26]. Depending on the μCP conditions, formation of monolayers [14,18,22,26], multilayered structures [17], and thin films [19] were reported. Recently, sub-50 nm patterns of dendrimers on silicon [18] and palladium [22] were achieved. The feasibility of the μCP technique to pattern stable PAMAM dendrimer monolayers on silicon substrates on larger length-scales, however, was not given considerable attention. Also the time dependent stability of the patterns in air and in liquids was not addressed.

In addition to controlled fabrication of surface patterns with dendrimers, the resulting interfaces must be well characterized, preferably with a resolution down to the diameter of the individual hyperbranched particles. Atomic force microscopy [27] (AFM) was shown to be very useful to investigate the morphology of the dendrimer assemblies at the solid–air, solid–liquid, and liquid–air interfaces. AFM images revealed the extent of dendrimer packing, aggregate formation, or the quality of monolayers [28]. AFM related experiments allowed one to elucidate the structural deformations (if any) of dendrimers deposited on various surfaces. To this end, studies of single core-shell tecto(dendrimers) on mica [16], single PAMAM (G4 and G8) on Au [29], (G5-G10) on mica [30,31] and HOPG substrates [31] were performed.

In the context of possible applications, high level of definition of the printed patterns and absence of diffusion of the dendrimeric ''ink'' on the silicon substrates can be advantageous for some chip-based analytical technologies. If e.g. G5-PAMAM dendrimers are used, part of the available amine terminal groups can interact with the silicon substrate, nevertheless, there would be still a substantial amount of NH_2 groups left for further functionalization with e.g. biomacromolecules. The usefulness of such patterns in various applications mentioned is mainly limited by the pattern stability in aqueous environments.

In this communication, we show that microcontact printing (μCP) is a relatively easy and straightforward technique to fabricate large area (μm^2 to cm^2), amino-functionalized G5-PAMAM dendrimer monolayer patterns on silicon oxide substrate. We demonstrate that AFM can be successfully used to characterize, and modify these patterns. The dendrimers adopt a flattened conformation at the surface indicating favorable interactions with the silicon oxide. Unlike for dendrimers of lower generation, G5-PAMAM patterns display a remarkable stability over a period of several weeks when stored in ambient conditions. However, when subjected to lateral stresses, the dendrimers can be ''moved'' across the surface indicating that the interactions between the dendrimer terminal amine units and the silicon oxide substrate are relatively weak. In water environment most of the dendrimers desorb from the substrate. Covalent coupling of the dendrimers to the substrates is needed for further functionalization and applications in aqueous media.

2. Experimental section

Methanolic solutions of PAMAM dendrimers of G5 (5 wt%) were obtained from Aldrich and used as received. Absolute methanol was obtained from Biosolve (The Netherlands). Silicon substrates were cut from a 4-inch silicon wafer into a $1 \times 1\ cm^2$ pieces. The substrates were cleaned by immersing in a freshly prepared Piranha solution (solution containing 70% of concentrated sulfuric acid and 30% of hydrogen peroxide) for 5 min, and rinsed with high purity Milli-Q water (Millipore Milli-Q water). Cleaned substrates were stored in an ethanolic solution. When needed for experiments, the substrates were rinsed several times with ethanol, dried in a stream of N_2 and used immediately for dendrimer deposition. PDMS stamps were fabricated by pouring a 10:1 mixture of Sylgard 184A and Sylgard 184B precursors (Sylgard 184, Dow Corning) over a cleaned and pre-patterned silicon master. The PDMS stamps were cured for 24 h at 60 °C. Cured stamps were peeled off from the master for subsequent use in μCP. Microcontact printing of dendrimers was performed according to the procedure reported in [26]. The PDMS stamps were dipped