Glassy State of Single Dendronized Polymer Chains

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ABSTRACT: We investigated the mechanical properties of single chains of dendronized polystyrenes with dendrons of generation 1 to 4 spin coated on the basal plane of graphite. A scanning force microscope was used both to image the chain relaxation upon annealing and to manipulate single chains directly. The two approaches show that conformations for higher dendron generations chains are inherently trapped at room temperature. This behavior is attributed to a glassy state of single dendronized polymer chains. Upon annealing, the chains relax and orient quite perfectly along the axes of the substrate.

1. Introduction

Dendrimers are regular and highly branched macromolecules with a globular shape. Their large size and surface makes them ideal for applications as containers (e.g., for drug delivery[1]), carriers (e.g., for gene transfection[2]), light-harvesters,[3] and building blocks for nanotechnology. Dendronized polymers[4,5] are a new class of comb polymers whose backbones carry dendrons (dendritic wedges) at each repeat unit (see Figure 1). In opposition to their great potential for applications[4,6] are considerable synthetic difficulties. Only recently a successful synthesis of a polystyrene with fourth generation dendrons at every repeat unit was reported.[7]

Thus far only a few experimental studies on dendronized polymers are published using, e.g., small-angle neutron scattering (SANS)[8,9] and scanning force microscopy (SFM).[6,7,10−14] Little is known about the mechanical properties of their single chains. It was found by SANS[8,9] that dendronized polymers of generation two can be described by the wormlike chain (WLC) model[15] which assumes purely elastic bending behavior and can be derived from the bending elasticity of a macroscopic rod.[16] Furthermore, the persistence length, which is a measure of chain stiffness in the WLC model, was found to increase with the generation number.[8,9] Qualitatively similar results were obtained for polymers with linear side chains.[17,18]

The trend of these findings cannot continue to arbitrarily high generation numbers as can be seen from a basic argument: unlike linear side chains, dendrons become more bulky with increasing molar mass. Since the distance between two consecutive dendrons along the polymer backbone is fixed, this leads to a tighter packing of the dendrons and possibly an increased overlap between neighboring dendrons. For high generation numbers chain bending therefore requires rearrangements in the dendritic shell. This links the flexibility of the whole polymer chain directly to the mobility of the dendrons, giving rise to effects such as viscoelasticity and plasticity which go beyond the WLC model.

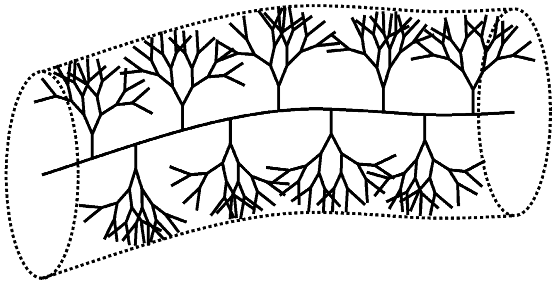

Figure 1. Schematic illustration of a fourth generation dendronized polymer.

These effects should be strongly solvent dependent. Despite the debate whether dendrons are back-folded or not,[19,20] theoretical,[21] numerical[22−24] and experimental[25−27] studies agree that the size of the dendron is dependent on the solvent quality and becomes smaller in a bad solvent. In a compact configuration, the contact between branches is enhanced and the free volume available for branch movement is reduced and consequently steric effects are increased. In the extreme, when dendrons are in the glassy state,[28,24] conformational changes of the polymer chain should be inhibited. Using the most widely accepted definition of the glass transition as a kinetic arrest upon cooling, one can describe the single molecule as being in the glassy state. This yet purely hypothetical state not only would be a new and interesting property of a new class of materials but also might be useful for applications. It would allow one to freeze the conformation of a polymer chain just by changing the temperature. For applications, it might be interesting to be able to switch between ductile and rigid behavior of single chains.

In this paper, we investigate the mechanical properties of dendronized polymers with the aim of verifying the existence of the glassy state. We use SFM as a tool for imaging and nanomanipulation of individual dendronized polystyrenes of generation one to four adsorbed onto graphite surfaces. We study the influence of temperature and solvent on chain conformation and flexibility.

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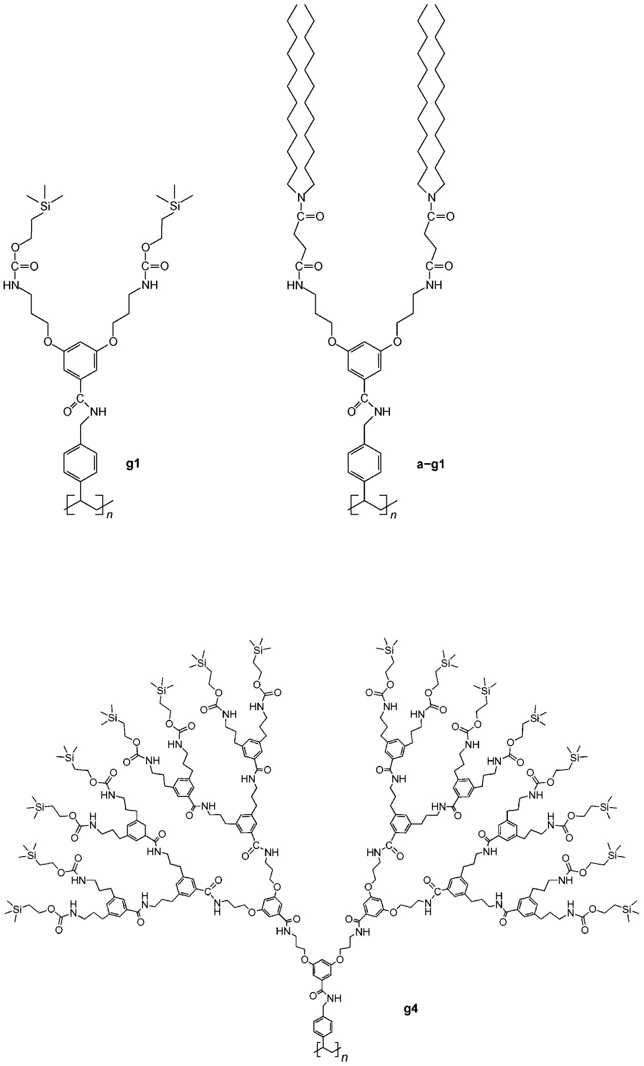

Figure 2. Molecular structure of the dendronized polymers **g1**, **a-g1**, and **g4**.

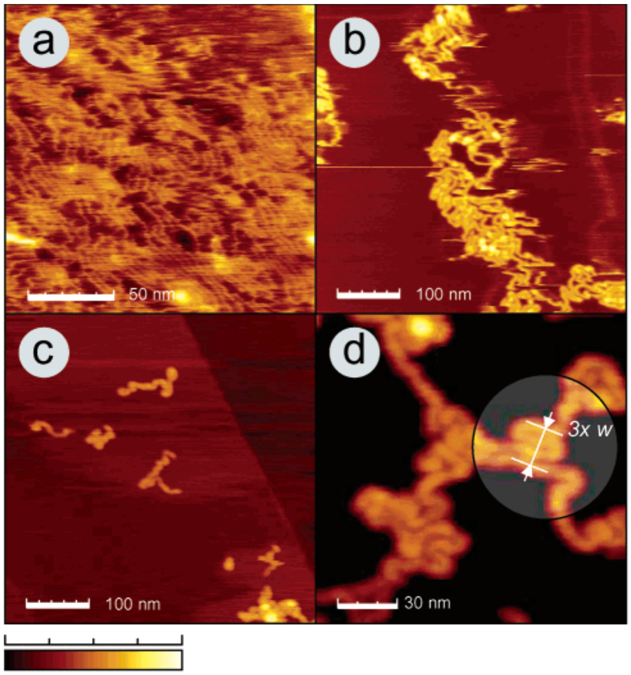

Figure 3. Typical SFM images of **g1** (a), **g2** (b), **g3** (c), and **g4** (d). The *z* range is 2, 4, 6, and 8 nm, respectively. Since **g1** and **g2** are rather mobile on the substrate, the images show artifacts caused by movement of molecules. In this case, stable imaging was only possible for aggregated chains. Molecular widths are determined by measuring the separation over several molecules as shown in the circle in part d.

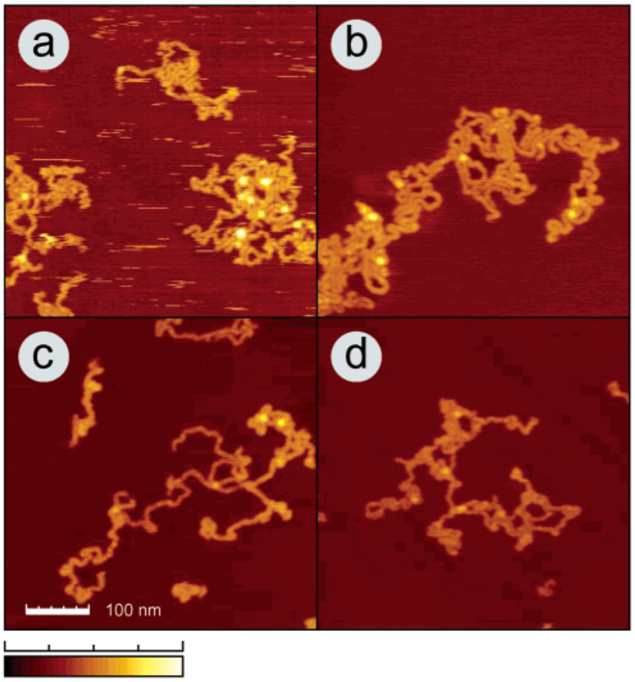

Figure 4. SFM images (a–d) of alkylated samples **a-g1** to **a-g4**. The *z* range is 4, 6, 8, and 10 nm for **a-g1** to **a-g4**, respectively.

2. Materials and Methods

Polymers **g2**–**g4** were prepared starting from **g1** (Figure 2) by sequential attachment of dendrons.[7] The efficiency of each dendronization step was controlled by UV markers, stating a total structure perfection of 97 ± 1% (for **g4**). The length distribution of the parent polymer **g1** was determined by analytical gel permeation chromatography (GPC) in THF vs polystyrene standard. The number-averaged molar mass was $M_n = 308\,000$ (corresponding to 460 repeat units) and the polydispersity PD ($=M_w/M_n$) = 1.8. To increase the adsorption energy to the basal plane of graphite, the homologous series of **g1** to **g4** was decorated with dodecyl chains (**a-g1** to **a-g4**), since it is known that alkanes interact rather strongly with graphite.[29,31]

The molecules were deposited by spin coating from dilute THF solutions onto freshly cleaved highly oriented pyrolytic graphite (HOPG) at 50 rps. The surface density of adsorbed molecules was varied from closed films to isolated molecules by varying the concentration of the spin coated solution between 10 and 100 mg/L. Annealing was carried out both in air and in solution. In the latter case the HOPG sample was removed from the sample puck, put in a closed flask, filled with the solvent, and treated at 60 °C.

Scanning force microscopy was carried out at room temperature in air, using a commercial instrument (Nanoscope IIIa, Digital Instruments, CA) and silicon cantilevers (Olympus) with a resonance frequency of about 300 kHz and a force constant of 42 N/m. All measurements were taken in the tapping mode. Image backgrounds were removed by fitting to first-order polynoms. No further image enhancement was applied. Nanomanipulation was performed in the lithography mode, moving the tip with 200 nm/s while applying a force of 1.6 μN to the substrate.[7] To investigate the orientation of the adsorbed molecules with respect to the substrate crystal axes, the same position was scanned twice, first with molecular resolution in the tapping mode and then with atomic resolution in the contact mode. To find exactly the same position on the sample, images were recorded in the tapping mode while

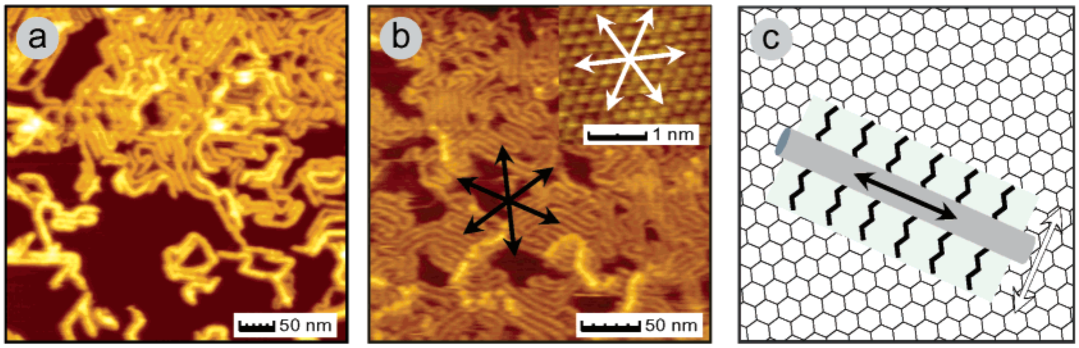

Figure 5. Orientation of chains and underlying graphite lattice: (a) oriented **a-g4**; (b) oriented **a-g1** and graphite lattice measured at the same positions, where the black and white rosettes are rotated by 90° showing that the polymers are oriented perpendicular to the zigzag axes; (c) schematic view of the orientation of the dendronized polymer backbone (gray) and the orientation of those alkyl side chains directly in contact with the surface.

Table 1. Measured Widths *w* and Apparent Heights *h* for All Investigated Molecules

molecule	*w* (nm)	*h* (nm)
g1	3.0 ± 0.3	0.74 ± 0.1
g2	3.8 ± 0.5	1.8 ± 0.1
g3	7.4 ± 0.6	2.1 ± 0.2
g4	7.3 ± 0.6	2.4 ± 0.2
a-g1	6.1 ± 0.3	1.2 ± 0.2
a-g2	6.8 ± 0.3	2.0 ± 0.2
a-g3	8.2 ± 0.3	2.5 ± 0.2
a-g4	8.8 ± 0.3	4.7 ± 0.3

stepwise zooming out to 80 μm scan size. After replacing the tip by a contact mode cantilever (force constant 0.4 N/m, Digital Instruments), it was stepwise zoomed in, using the graphite steps of the previous images as a guide.

3. Results and Discussion

Conformations of Adsorbed Molecules As Prepared. SFM images of single and clustered molecules of **g1** to **g4** and of **a-g1** to **a-g4** are shown in Figures 3 and 4. Some images show artifacts (horizontal stripes, fuzziness) indicating movement of molecules. Stable imaging for **g1** and **g2** was only possible for molecules which are packed in clusters, while isolated molecules could not be resolved. For **g3** and **g4**, on the other hand, the molecules appear quite stable, and diffusion of shorter fragments was observed only occasionally. The alkylated molecules appeared generally more stable compared to their nonalkylated analogues. By scanning a single molecule of **a-g2** several times and varying the time between successive images, we found that the molecular motion is much enhanced upon scanning; i.e., it is induced by the hammering of the SFM tip.

Additionally to isolated molecules, we found for most samples regions of dense molecular packing as shown for example in Figure 3d for **g4**. This packing can be attributed to an interplay between attractive (e.g., van der Waals forces and capillary forces upon drying) and repulsive forces (entropy loss of dendrons due to volume exclusion).[32,33] Measuring the separation over several molecules in an ordered array (see, e.g., the circled area in Figure 3d) allows the precise determination of the width *w* of a molecule, while the apparent width of an isolated molecule in a SFM image is broadened by the finite sized tip. Widths and heights for all molecules are given in Table 1.

In good solvents dendronized polymers are assumed to exhibit a circular cross section which was measured by SANS for **g1** and **g2** in methanol to be 3.8 and 4.9 nm, respectively.[8] These values are slightly larger than the widths obtained here, indicating that the dendrons at the surface may be not fully stretched out.

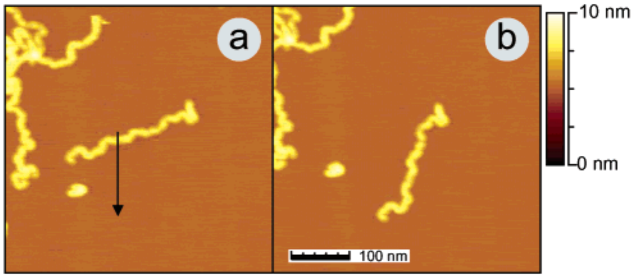

Figure 6. Nanomanipulation of a single **a-g4** molecule from image a to image b. The manipulation path is marked by the arrow. The lateral shape of the contour is clearly preserved. The images were presented before in a short communication.[7]

Mansfield[34] performed MD simulations of dendrimers at attracting surfaces. It was found that low generation dendrimers flatten at the interface in order to maximize the contact area. First generation dendronized polymers can thus be expected to be in a flattened conformation. The local shape of **g4**, on the other hand, should be nearly cylindrical following from a simple geometrical argument: Assuming that each repeat unit fills a cylindrical slice, where the thickness is given by the length of the repeat unit, and assuming a reasonable density of $\rho \simeq 1$ g mL^{-1}, one obtains a diameter of 8.2 nm. This value is in fair agreement to the width determined from ordered structures. In other words, **g4** and in a similar manner **a-g4** rather tightly fill the accessible space and therefore cannot be flattened much.

Heights of single molecules are usually underestimated in SFM measurements, possibly due to different deformation of substrate and molecule by the tip[35] and the peculiar role of the attractive force caused by a water meniscus between tip and sample.[36,37] Interestingly, heights were not constant along the contour of a single molecule as is shown later for a **g4** molecule. Typical height variations for **g4** are about 0.4 nm on a length of 20 nm.

We rule out chemical imperfections like missing dendrons as explanation, since each step in the synthesis was quantified by UV-markers, stating a chemical perfection of 97% for **g4**.[7] Instead, height variations might be explained by an irregular distribution of dendrons around the backbone.

Annealing. Dendronized polymers spin coated onto HOPG were annealed in THF at 60 °C for 30 min. As the SFM images show, molecules are not washed off by the treatment, but changed their conformation. Figure

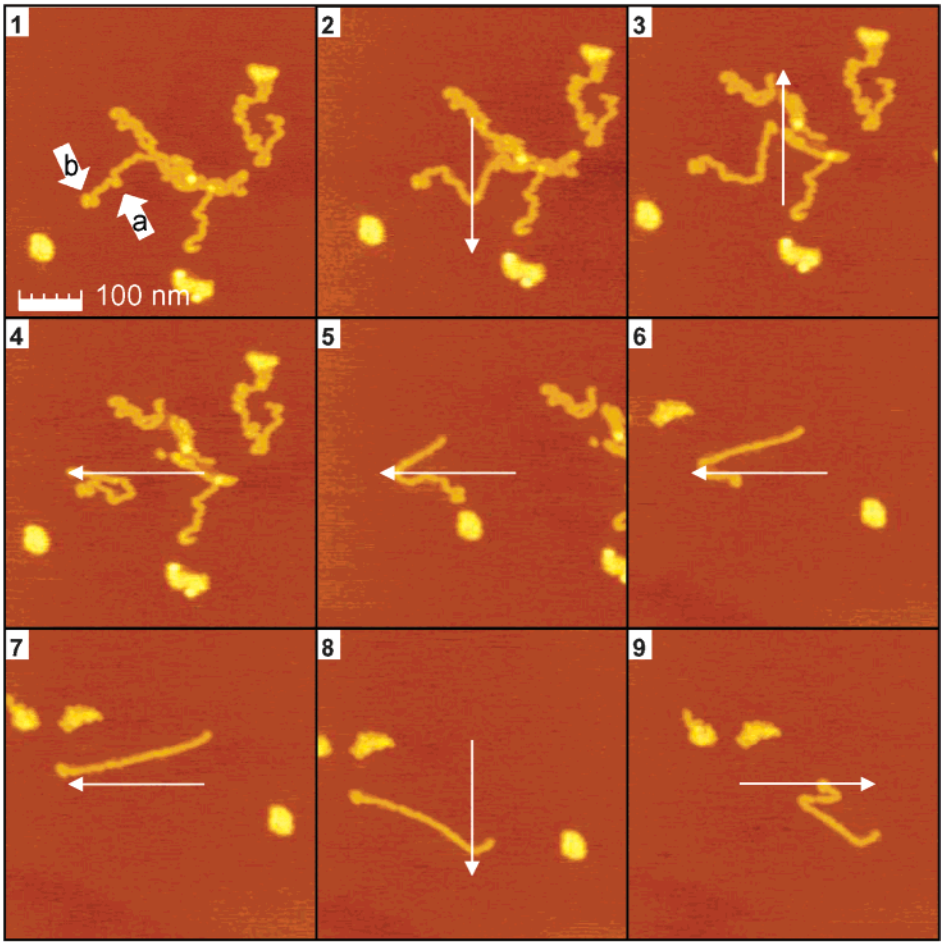

Figure 7. Manipulation sequence of a **g4** molecule. From 1 to 2 the hairpin (a) opens, whereas the "head" (b) does not change upon manipulation all the way from 1 to 9. Some of the images were presented before in a short communication.[7]

5a displays an image of **a-g4** after annealing. The molecules are aligned parallel to the substrate and bent at characteristic angles of 60 and 120° in order to follow the 3-fold symmetry of the substrate. The same annealing procedure was applied to **a-g4** samples in air, in water, and in THF at room temperature, but no ordering was observed. However, **a-g1** could be oriented by heating in air (see Figure 5b). For the nonalkylated molecules (**g1** to **g4**), we did not observe any orientation effect.

The inset of Figure 5b displays an image of the graphite lattice taken at the same position. The polymers are oriented perpendicular (with an uncertainty of ±2°) to the graphite zigzag axis. The observed backbone orientations are, therefore, consistent with the alkyl chains following the zigzag axis of the graphite substrate as sketched in Figure 5c. The backbone orientation differs by 30° from the one assumed in ref 30 for a related polymer.

Ordering of alkanes along the zigzag axis is known from STM studies[31] and the alignment of polymers with alkylated side groups has been observed before.[14,39] The driving force for the molecular orientation is, therefore, assumed to be the specific interaction of alkyl chains and the graphite surface. The observed irreversibility can be understood if the chains in air are trapped in their conformation on the time scale of the measurement. Besides this trapped state in air at room temperature, also a state must exist which allows full chain relaxation within 30 min.

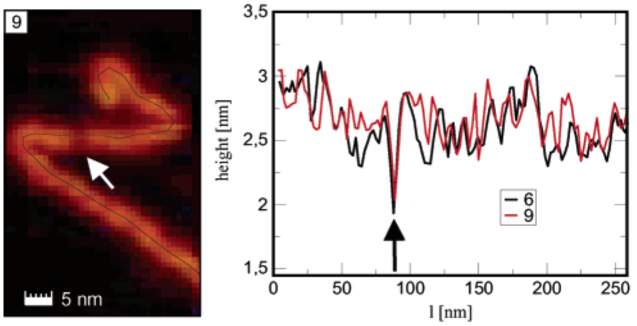

Figure 8. Height along the contour for the manipulated **g4** molecule, for images 6 and 9 from the sequence. Left: zoom of image 9 showing the line at which the height was recorded. The arrow marks a characteristic nick which can be found in all the images of this molecule. Right: height structure for images 6 and 9. The height scale starts from 0 at the substrate surface. Besides some noise, both curves show a clear correlation of characteristic features. The arrow gives the position of the nick.

In principle, the trapping can be caused either by the interaction to the substrate or be inherent to the molecules. Since the interaction and also the chain thickness is different between **a-g1** and **a-g4**, it is not possible to distinguish between both influences from only this experiment.

Manipulation of Single Molecules. The mechanical properties of macroscopic materials are commonly characterized by bending, stretching, sheer, or compression experiments. Similar experiments can be performed

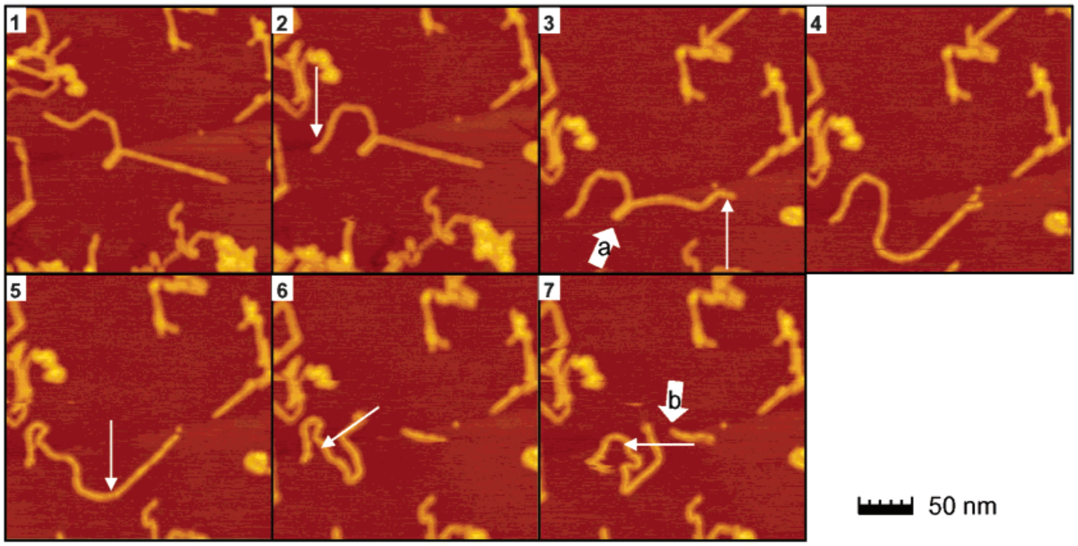

Figure 9. Manipulation sequence of an oriented **a-g3** molecule. The sample was annealed in THF as described in the text. Interesting is the opening of the hairpin (3 to 4, mark a) and the cutting (5 to 6, mark b). Image 3 was recorded twice with a time lag of 30 min, without a notable change of conformation.

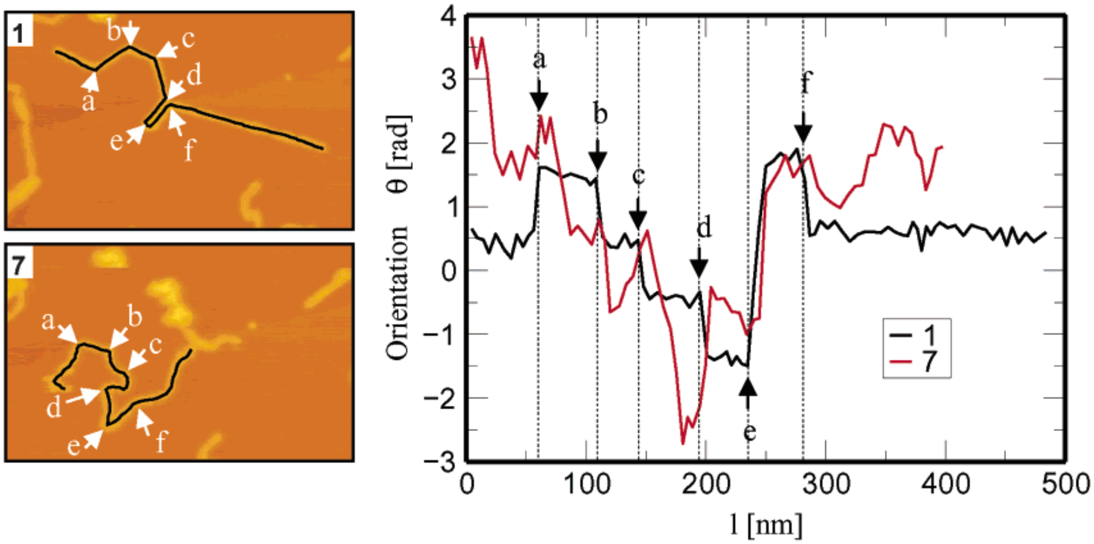

Figure 10. Orientation as a function of position along the contour for the manipulated **a-g3** molecule. Θ is the angle between the tangent in point *l* to the horizontal. In both images the kinks are at the same positions, marked a−f. At positions a and d the curvature changed sign.

by applying forces to single molecules using the tip of an SFM.[7,40] In Figure 6, a molecule of **a-g4** is shown before and after it is manipulated by moving the tip along the marked path in the left image.

Interestingly, the molecule moved as a whole and the molecular shape was preserved, except for one kink near the right-hand terminus. This experiment shows that it is not the immobility on the substrate causing the shape persistence. If the molecule would be trapped because of strong frictional forces to the substrate the chain would have been deformed upon manipulation because the pushing tip and the opposed frictional forces. Hence the trapping is an inherent property of the polymer chain.

Besides this shape persistence in 2D upon applying lateral forces, a persistence of the height structure can also be observed. In Figure 7, a series of images is presented describing the manipulation of a **g4** molecule. Unlike the alkylated analogue it gets deformed. The molecule unfolds its hairpin "a" in Figure 7 and changes its shape upon manipulation, similarly to a macroscopic wire. Only the hairpin "b" at the molecules' "head" does not open. In Figure 8, the height along the molecular backbone starting from the "head" is plotted for images 6 and 9 of the manipulation sequence. Despite the background noise, there is a clear correlation of characteristic features. The most distinctive feature observed in all these molecules' images is a characteristic nick which is marked with an arrow. Since dendrons are only connected at the backbone, in a liquid state they would be free to float and change conformation. The preservation of height features indicates that the dendron shell around the backbone is not liquidlike. Thus, also for **g4** a shape persistence can be stated, though laterally less distinct compared to **a-g4**.

Figure 9 displays a manipulation sequence of an **a-g3** macromolecule from an oriented sample. During the manipulation the molecule is stretched, bent, and finally compressed. Once manipulated, the chain segments lose their alignment with respect to the substrate axes. During the experiment no relaxation back to an oriented state was observed. Image 3 was recorded twice with a time lag of 30 min without any notable change in the conformation.

The analysis of the positions of kinks displayed in Figure 10 gives an interesting hint on the origin of the shape persistence. The segment orientation Θ relative to the horizontal is measured and plotted. The kinks appear to be at the same positions in both images, marked with letters a–f. At positions a and d the curvature changed sign. The appearance of kinks at the same positions is unlikely to be an accidental coincidence, but it is instead attributed to weak locations. The simplest explanation would be, that the molecule is thinner at these positions and therefore less rigid. However, there is no correlation between the height structure and the kink positions. Another explanation is that the weak positions are formed during drying and cooling.

The presented manipulation experiments show, that there is an inherent rigidity of at least **a-g3** and **a-g4** against lateral deformation. This result is in agreement with the idea of a glassy state of the dendrons which leads via the steric hindrance of neighboring dendrons to a freezing of the whole chain. From our experiments, it is not possible to exclude alternative explanations as for example the crystallization of terminal alkyl chains. Both explanations do lead to a shape persistence and additionally allow the interpretation of weak positions as inhomogeneities in the dendritic hull which are frozen in. However, the glassy state model is also consistent with the preservation of height features which was observed for the nonalkylated molecules **g3** and **g4**.

4. Summary and Conclusion

In summary, we presented experiments demonstrating that there is a shape persistence of dendronized polymer chains, and further experiments to clarify the physical origin. Particularly, we probed the shape persistence effect directly by nanomanipulating single polymer chains adsorbed onto graphite substrates at room temperature and in air. We found for all chains of higher generation (3 and 4) some shape persistence during dragging the chains across the surface. The effect appeared clearer for molecules which are decorated with alkyl chains, but was also observable for the nonalkylated chains. We showed by annealing experiments that the shape persistence further depends on the number of branching generations and on the solvent quality and attribute it to a single molecule glass state which is caused by the glassification of dendrons. A transition to the more mobile state is possible.

We believe that the switchable single polymer glass state is an interesting new property and might be useful for single molecule experiments as well as for applications. For example we have been able to image the surface of a thick layer of **a-g4** with submolecular resolution, allowing to identify the conformation of the single chains. The glassy state might be also useful when dendronized polymer chains are used as building blocks in nanotechnology applications, since it allows one to give single molecules a defined and stable shape.

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