Covalent Connection of Two Individual Polymer Chains on a Surface: An Elementary Step towards Molecular Nanoconstructions[**]

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Nano- and micrometer-sized objects can be manipulated in two and three dimensions by using a scanning force microscope (SFM) and optical tweezers, respectively.[1–4] Reactions

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in arrays of molecules immobilized on a surface have been accomplished in highly oriented monolayers[5] and at a single molecular level under ultrahigh-vacuum low-temperature conditions by using a scanning tunneling microscope (STM).[6] Recently, a chemical reaction between individual small molecules was performed with a STM under ultrahigh-vacuum conditions by using a "move-connect-prove" sequence.[7] If it were transferred to nanosized molecules under ambient conditions, this process could become a new key element for nanoscale science and technology. Dendronized polymers[8] are interesting candidates for molecular nanoconstructions, as they are considered to be nanocylinders with an interior and surface that can be engineered, and by which they may be functionalized. Examples include polymeric light emitters with an aggregation inhibitor,[9] and a synthetic light-harvesting antenna.[10] Herein, we describe the application of a move-connect-prove sequence under ambient conditions to two individual strands of dendronized polymers by using an SFM. The connection is achieved by UV irradiation and tested by challenging its mechanical stability.

Dendronized polymers have been synthesized with diameters of a few nm, lengths of up to several hundred nm, and equipped with 4, 8, or 16 peripheral amine groups at every repeat unit.[2,11] Amines are ideal anchor groups for modification reactions, as they couple preferentially with active esters or acid chlorides. Azides easily decompose thermally or photochemically into nitrenes (and elementary nitrogen), which are highly reactive, short-lived intermediates that undergo various addition and insertion reactions with the formation of covalent bonds.[12] The commercially available azide derivative, **2** (Figure 1) which has a succinidyl active ester group, was attached to the deprotected (positively charged) dendronized polymer **1a**[2] with eight amine groups per repeat unit (average degree of polymerization > 430). An orange solution of **2** (8.6 mg, 22 μmol) in DMSO (0.5 mL) was added dropwise in the dark to a clear solution of **1a** (4 mg, 12 μmol of amino groups) in dimethyl sulfoxide (DMSO, 0.5 mL). The resulting suspension was stirred for 20 h at 20 °C and subsequently dialyzed with DMSO for two days (benzoylated dialysis tubing from Sigma), and then freeze dried from DMSO to furnish **1b** (yield: 6.2 mg, 92 %; Figure 1). The complete removal of excess **2** was achieved by prolonged dialysis and proven by thin-layer chromatography. The IR spectrum of **1b** showed the expected azide stretch band at 2120 cm^{-1} and the UV/Vis spectrum exhibited $\lambda_{\max}$ (DMSO) = 476 nm. The coverage of the amine groups of **1b** with **2** was 95 % when determined by a reported procedure.[10] Polymer **1c** was obtained similarly by treating **1a** with the cinnamoyl chloride, **3** (Figure 1). Irradiation of a thin film of **1b** on a KBr plate with a standard Hg lamp led to the almost complete disappearance of the azide stretch band in the IR spectrum within 9 minutes.

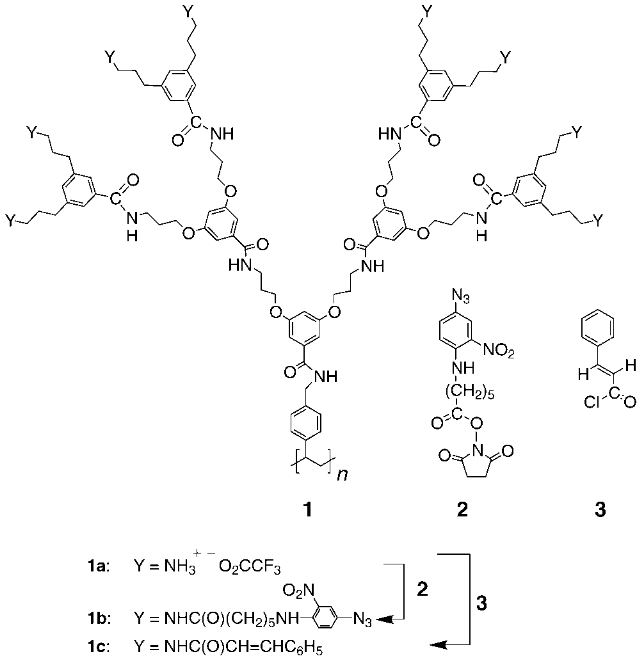

Figure 1. Synthesis of dendrimer derivatives.

For the SFM sample preparation, the procedure described above and a second procedure were applied. In the latter, methanol was used instead of DMSO, as methanol can be removed more easily from the employed highly oriented pyrolytic-graphite (HOPG) substrate, thereby simplifying stable SFM operation. At room temperature triethylamine in methanol ($1\times10^{-6}\ \text{mol}\,\text{mL}^{-1}$) was added to a polymer solution in a molar ratio of 1:1 with respect to the ammonium groups. After one hour, an equimolar solution of **2** ($c = 1\times10^{-6}\ \text{mol}\,\text{mL}^{-1}$ methanol) was added to the stirring reaction mixture to furnish **1b**. As the solubility of **1b** in methanol decreases because of the chemical modification of the azide active ester **2**, before precipitation of **1b** the solution was spin coated onto freshly cleaved HOPG at 50 rps to yield incomplete monolayers of individual polymer molecules.

For dragging the molecules across the surface (lateral manipulation) a home-built SFM based on the Multimode head and Nanoscope III controller (Digital Instruments, Santa Barbara, CA, USA) was used. The extended setup allows the movement of the SFM tip in the *xy* plane along a predefined trace with additional control of the normal forces between SFM tip and sample. Up to four channels of data (e.g., height and deflection of the SFM cantilever) can be recorded during the passing of the tip along the trace. This allows the right trace to be sought before dragging the molecule to the desired position. The spatial resolution for addressing a single molecule with this procedure is on the order of 5 nm. For the purpose of manipulation, the SFM can be gently switched from tapping to contact mode at predefined points while the tip is passing along the trace. From these points, the interaction between SFM tip and sample is enhanced, and thus can be used to drag a molecule across the surface.[2]

Figure 2 displays tapping-mode SFM images of **1b** on a graphite substrate. Figure 2a exhibits two individual molecules **1b**, both with their backbone extended essentially parallel to the substrate, thus revealing contour lengths on the order of 400 nm. Figure 2b shows the sample after the two molecules have been moved towards each other by using the procedure described above. After the irradiation of the whole sample in situ (while the SFM is scanning) for 3 minutes with

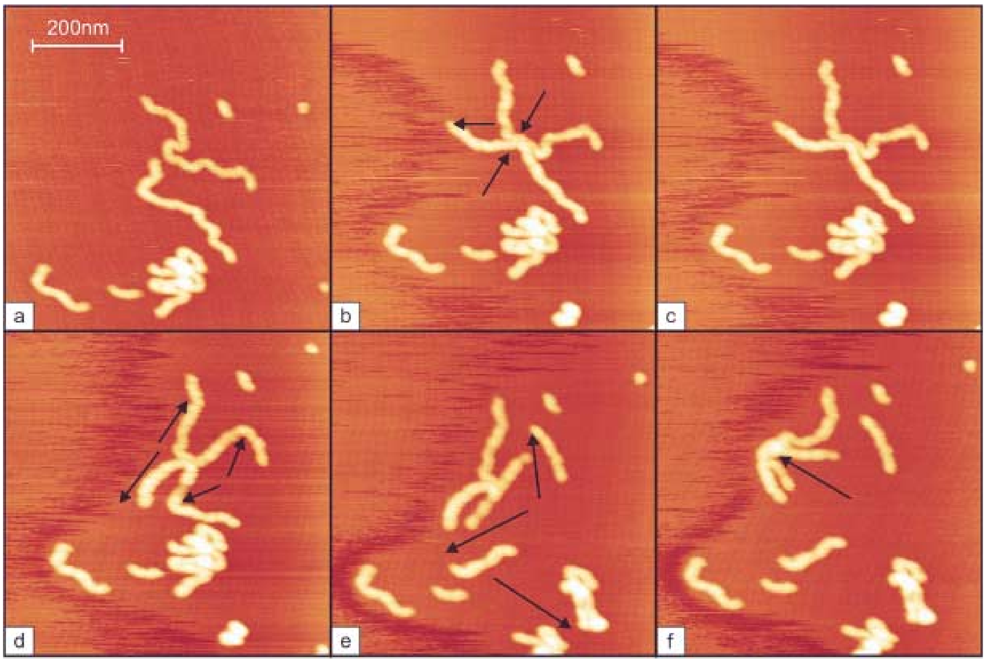

Figure 2. Tapping-mode SFM images of two individual dendronized polymers **1b**, moved towards each other ("move"; a→b), irradiated by UV light ("connect"; b→c), and challenged mechanically ("prove"; d,e,f). The arrows indicate the movement of the SFM tip during manipulation (an animated version of this sequence is provided as a video in the Supporting Information). In addition some smaller molecules and a molecular aggregate can be recognized.

the UV-C light of a high-pressure Hg lamp (Fluotest, Heraeus, $\lambda_{max} = 220$ nm), no change of the image was observed (Figure 2c). To test whether the irradiation caused a stable (covalent) linking of the two adjacent molecules, we challenged the mechanical stability of the junction by pulling on each of the four chain ends with the SFM tip; the junction did not break (Figure 2d). When the molecular chains were moved through the two points of strongest bending, the molecular chains were cut at the position of impact rather than on the newly formed junction (Figure 2e), thus indicating the junction is stronger than the main chain. This can be understood, as the number of covalent bonds in the junction could be more than 100, which estimates a contact length on the order of 20 nm. When the whole molecule was dragged across the surface (Figure 2f) the junction did not break. The experiment was reproduced several times and other topologies, including a full circle, were fabricated. As a control, the same experiment was repeated several times without irradiation, and on each occasion it was easy to pull the molecules apart again. We conclude that there is no covalent connection between the newly formed molecule and the underlying HOPG because the molecule can be manipulated after irradiation. This can be understood because cycloaddition of nitrene to a graphite double layer leads to a separation between the top and the top-1 layer which lowers the dispersion interaction and direct orbital overlap between the two and is therefore energetically unfavorable. Preliminary results show that the connection can also be achieved with the cinnamic ester modified polymer **1c**.

The work presented herein demonstrates that two individual polymer chains on a surface can be manipulated until they attain a predetermined relative position in which they can be covalently connected. This is the first application of a move-connect-prove sequence under ambient conditions and opens possibilities for generating and covalently fixing structurally defined, nanosized functional units of macromolecules. The same sequence could be used to connect unaltered macromolecules if azide terminated commercially available spherical dendrimers instead of dendronized polymers were used as a "glue" between two nano-objects such as nanotubes and DNA, the only condition being that they can be manipulated and imaged with the SFM. For instance carbon nanotubes (CNT) have an increased reactivity arising from the high surface curvature with respect to the inert basal plane of HOPG. It was shown that single-wall CNT can be easily attacked by [2+1] cycloaddition of nitrenes.[13] The method described herein is a means to synthesize single macromolecules with novel homo and hybrid structures (e.g., in the shape of an X, Y, O, or 8), which by conventional synthesis are not accessible.

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