Switching in molecular shapes: main chain length driven rod–circle transition of isolated helical polysilanes†

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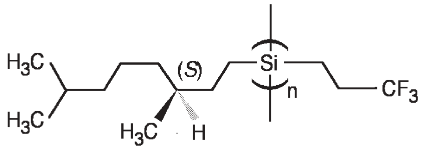
Unique conformations such as rod, semicircle, and circle structures of isolated semi-flexible helical polysilanes were observed by atomic force microscopy (AFM); the chain topology was significantly related to the chain length (molecular weight) on the surfaces.



Scheme 1 Structure of fluoroalkyl-containing helical polysilane, **FPS**.

Although recent progress in experimental and theoretical studies of polymer science allows us to create various unique polymer structures in solution, liquid-crystal, and solid states, comprehending an alteration in topology at the single polymer chain level is the ultimate goal for the development of polymer-based nanomaterials for functionalities such as solubility, flexibility, stability, and electronic properties.[1]

More recently, nano-scaled circle architecture composed of organic/inorganic materials has attracted much attention because it is expected to provide a superior device performance due to the lack of defects in the end-terminus part, which strongly affects energy loss.[2] In the field of synthetic chemistry, several groups have succeeded in the construction of structurally controlled circles of semiconducting organic molecules and polymers.[3] In addition to the synthetic approach, it has also been reported that based on theoretical considerations, the circle-like structure can be formed by exploiting the relationship between the persistence length and its chain length (molecular weight).[4–6] Sano and coworkers, for example, have demonstrated that single walled carbon nanotubes (SWNTs) having reactive end-termini with more than 2-fold persistence length easily formed a complete-closed ring structure.[4] Yoshikawa and co-workers have reported that the topology of single high molecular weight (giant) DNA can be changed from a coil to a globular conformation, including a doughnut-shaped toroidal structure, by external stimulus.[5] Furukawa and coworkers have successfully observed that long semi-flexible polysilane chains immobilized on a substrate form not only toroids but also an octopus-like structure composed of several entangled polymer chains.[6]

We have succeeded by means of atomic force microscopy (AFM) in detecting for the first time that the topology of an isolated helical polysilane chain bearing a fluoroalkyl side group (Scheme 1, **FPS**) changes from a rod to a circle structure depending on the main chain length. Fluoroalkylated helical polysilane is an ideal model molecule with different lengths, which as a one-dimensional, semi-flexible semiconductor, has exhibited unique properties that have contributed to intramolecular C–F···Si interactions, and consequently, possesses relatively high rigidity compared to non-fluoroalkyl-containing polysilane.[7]

Fig. 1 exemplifies typical AFM images of **FPS** on mica surfaces. In these images, three different kinds of topology, namely, rod, semicircle, and circle structures, were clearly distinguished and

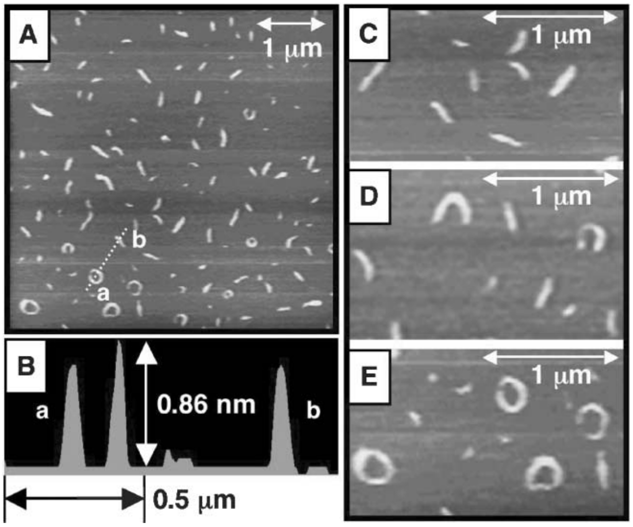


Fig. 1 Typical AFM images of isolated **FPS** chains on mica surfaces in large area (A); cross section profile of line a–b in A (B); rod-like structure (C); rod-like and semicircle structures (D); and rod-like, semicircle, and circle structures (E).

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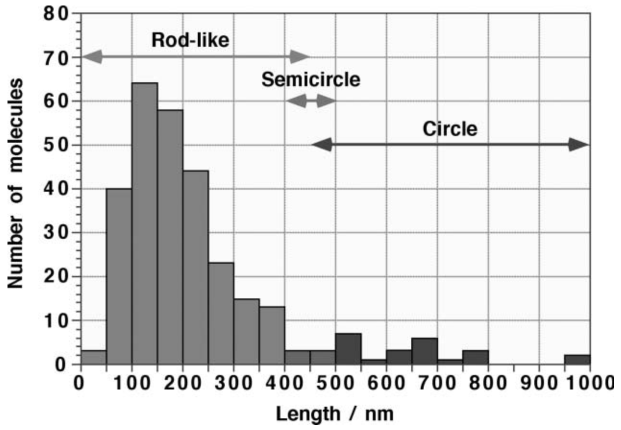

Fig. 2 Contour length distribution of **FPS** estimated from AFM images.

these structures coexisted. Fig. 1C, D, and E show AFM images of rod, semicircle, and circle structures respectively, in a relatively narrow area. The average height of both the rod and circle structures is approximately 0.86 nm and almost uniform, which corresponds to the real height of adsorbates. Although the average widths were determined to be approximately 100 nm, from cross-section profiles shown in Fig. 1B, due to a tip broadening effect,[8] these values are also uniform in all observed structures. It is obvious that all the observed rod, semicircle, and circle structures are not aggregated forms but isolated single polymer chains.

Furthermore, we measured the weight-average contour length (L_w) and number-average contour length (L_n) from about 300 randomly selected molecules. The L_n was obtained from AFM images. The averaged L_w and L_n from AFM observations were 314 and 177 nm, respectively. The distribution of L_n is shown in Fig. 2. In the region of shorter lengths in Fig. 2, only rod-like structures were observed (Fig. 1C). This is essentially consistent with previous results that showed that **FPS** possesses a stable semi-rigid helical conformation owing to an intramolecular C–F···Si interaction in the solution system.[7] However, it should be emphasized here that chain topology eventually transformed from rods to circle structures as main chain length increased on the surfaces. In particular, we observed semicircle structures in the very narrow region of medium length (400–500 nm) in Fig. 2, thereby showing that topological switching between rod and circle structures is occuring due to the discontinuous transition phenomenon. The distribution of end-to-end distance also exhibited a discrete decrease as contour length increased (see ESI†). Taking the transition phenomenon from rod to circle structures (AFM observation) into consideration, the semicircle structure appears to be an intermediate state in the rod–circle topological transition. Therefore, the semicircle structure is presumably not stable even on the surfaces, resulting in its existence only within a very narrow range. Here, we assume the contour length of the semicircle structure as critical length L_c which lies in the range between 400 and 500 nm on the surfaces. If the contour length L is shorter than L_c, the chain shape adopts a rod-like form, while a circle-like structure will be formed if L is longer than L_c. Yoshikawa and coworkers have reported similar behavior in that the coil–globule transition in DNA chains is due to a discrete first order transition.[5] They have also demonstrated that the coil and globule can coexist in the process of nucleation and growth even in a solution system.

It has been reported that the driving force for the formation of circle architectures composed of associated forms, such as porphyrin derivatives with long alkyl chains and poly(phenylene-ethynylene) bearing dendrons as the side chain group, is ascribable to kinetic factors such as the evaporation process of solvents and the effect of bubbles.[9,10] It is noted that the chain dynamics are realized not in the solution system but on the surfaces. Although these structures cannot be formed in the solution system due to thermal fluctuation, the mechanism of topology switching of single polymer chains is different from that of associated forms. The dominant driving force of topology switching would originate from a degree of freedom wherein the topology of a single polymer chain depends greatly on the chain length on the surfaces. The proper adsorbate–substrate interaction, which should not be too weak nor too strong, enables the detection of topology switching.

In fact, we have also investigated such behavior on highly oriented pyrolitic graphite (HOPG) surfaces. In the case of HOPG, no such chain alteration was observed regardless of the molecular weight. A much stronger interaction between the hydrophobic polymer and the hydrophobic substrate might inhibit the chain mobility for topology switching on the surfaces. Additionally, we have confirmed similar behavior for another polysilane of high molecular weight fraction (M_w: 3.9 × 10^5) bearing no fluoroalkyl side group (see ESI†) on the mica surfaces. This result also significantly supports the importance of the chain length (molecular weight) effect of conformational transitions.

We also confirmed the higher-order helical conformation in a circle structure from a high resolution AFM image, as shown in Fig. 3. Each bright spot and its cross-section profile clearly indicates that the polymer chain has a helical structure (Fig. 3A, 3B, and 3C). From the cross section profile in Fig. 3D, we can see that the local conformation of R_2 is flat on the bottom but R_1 is

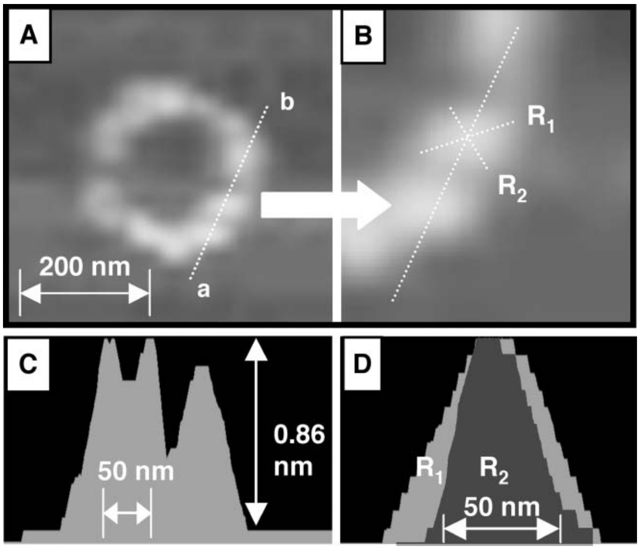

Fig. 3 High resolution AFM image of the circle structure of **FPS** (A); high zoom image of A (B); cross section profile of line a–b in A (C); and cross section profiles of segments R_1 and R_2 (D). The greater width of R_1 in the profile indicates that the polymer chain posesses a right-handed helical structure.

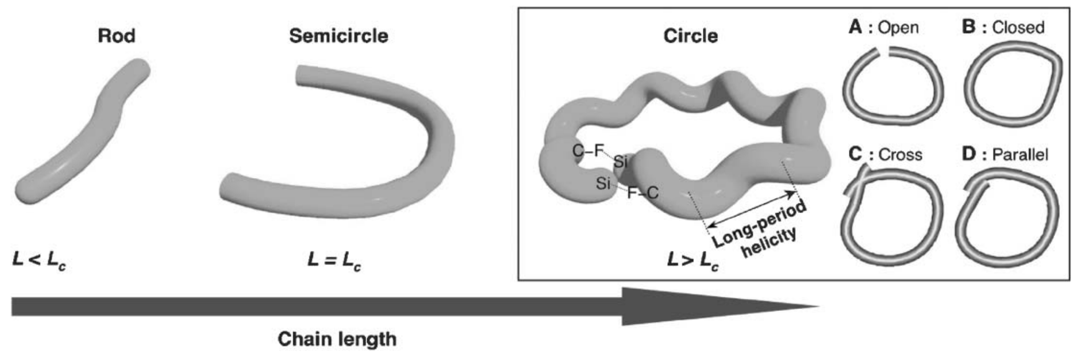

Fig. 4 Schematic representation of morphology switching of single polymer chain with chain length dependence based on AFM observations. L_c indicates the critical length of semicircle structure as an intermediate state between rod and circle structure. In circle structure, (A), (B), (C), and (D) indicate proposed models, open, closed, cross, and parallel, respectively.

bulged on the top.[11] Therefore, the helicity of the observed structures is right-handed. The observed helical pitch in the AFM images was determined to be about 44.2 ± 4.2 nm, although it was much longer than that expected from the 7/3 helical structure model (0.45 nm). This might be attributed to not only a tip broadening effect but also the intramolecular C–F···Si interaction, leading to long-period macromolecular right-handed helicity.[12] As for the rod and semicircle structures, however, we did not observe such a helical conformation. Significant long chains might be required to configure the long-period helicity.

In several AFM images and their cross-section profiles, the height and width were frequently different at the right and left or up and down points in the circle structure (*e.g.* Fig. 1B). Proposed structural models regarding the circle structure are shown in Fig. 4. Imperfect open-circle structures with a narrow end-to-end gap were frequently observed, as illustrated in Fig. 4 (open circle A). In the case of B, it is thought that the intramolecular C–F···Si interaction allows it to form and stabilize a perfect closed-circle structure because the fluorine atoms on the side chains may attach to the Si atoms on the main chain close to the end groups. Besides this effect, a Si–O–Si bond may be formed between the end-termini *via* hydrolysis of the Si–H end group by water adsorbed on the mica surfaces.[13] In the case of C, the end-termini of the polymer chain are crossing each other, while in D, the end-termini are not crossing but are parallel to each other. These structural models can be the precursors of toroidal structures. In fact, much longer polymer chains frequently formed toroid-like structures (see ESI†).

In summary, we have been the first to successfully detect in three different kinds of chain topologies; rod, semicircle, and circle structures by means of AFM. High resolution AFM images also reveal that longer polymer chains tend to adopt circle structures that have long-period helicity. These characteristics of chain alteration depend remarkably on the chain length (molecular weight), which add to the development of polymer science. To understand the switching mechanism with regard to topology in detail, we will be using other polysilanes to investigate not only the relationship between other substrates and chain topology with various molecular weights but also the identification of end-termini in the circle structure. In addition to synthetic methodology, direct observation of the conformation of conjugated polymers at single chain level is crucial.

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