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.

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...
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. 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 occurring 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 structures (AFM observation) into consideration, the semicircle structure is occurring 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.\(^6\) 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.\(^7,8\) 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 pyrolytic 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 (\( M_c^-; 3.9 \times 10^5 \)) 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
bulged on the top. Therefore, the helicity of the observed structures is right-handed. The observed helical pitch in the AFM images was determined to be about $44.2 \pm 4.2$ 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. 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. In the case of C, the end-termini of the polymer chains are crossing each other, while in D, the end-termini are not 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 polylines 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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Notes and references