Electronic Supplementary Information (ESI) for

Switching in Molecular Shapes: Main Chain Length Driven Rod-Circle Transition of Isolated Helical Polysilane

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Experimental Section

Gel Permeation Chromatography (GPC)

The weight-average molecular weight of polymer (Mw) and number-average molecular weight of polymer (Mn) were estimated using gel permeation chromatography (Shimadzu 10A instruments, PLgel 10µm mixed-B as a column and HPLC-grade tetrahydrofuran as eluent) at 40°C, based on a calibration with polystyrene standards. The molecular weight obtained from GPC is generally different from absolute molecular weight obtained by light scattering measurement.

The Mw of FPS and poly{(S)-3,7-dimethyloctyl-3-methylbutylsilane} PS are 3.3 x 105 (PDI: 3.06) and 3.9 x 105 (PDI: 3.02), respectively.

AFM observation

AFM experiments were conducted using a SPA-3800N microscope with SPA-400 scanner (Seiko Instruments Inc., Japan) equipped with Si-DF20 tips in ambient conditions. Polymers were dissolved in isooctane (the concentration range of 2.0 – 2.5 µg/mL). The solution was then deposited on mica under nitrogen flow (flow rate: approximately 1L/min.). All images were obtained by cyclic contact mode in air and the drive frequencies were typically set at 110-150 kHz. All images were collected with the maximum available number of pixels (512). To ensure accurate counting of polymers, several images were collected from different areas of the same sample. We measured the weight-average contour length (Lw) and number-average contour length (Ln) from about 300 randomly selected molecules. The Ln is observed contour length from AFM images. The Lw was estimated by using the following the equation:

\[ L_w = (n_1 * L_1 + n_2 * L_2 + ...)/(n_1 * L_1 + n_2 * L_2 + ... ) \]
We estimated end-to-end distances of the approximately 100 randomly selected polymer chains from observed AFM images. The distribution of the end-to-end distance showed a discrete decrease as contour length increased, although the distance linearly increased to around 160 nm (in the region of red circle) with narrow distribution as shown in Fig. S1. The distribution observed in the region of rod structure is also indicative that polymer chains have a tendency to change their conformation from rod to bent structure as chain length increases. Furthermore, in the range of 400 ~ 500 nm, all the structures (rod, semicircle, and circle) were observed. These results also support the fact that morphological switching behavior between rod and circle structure is a discontinuous transition phenomenon on the surfaces. In the region of circle structure (blue circle), most of the observed structures were closed-circle except for trroidal structures, but some structures possessed very small end-to-end gap with the small range of around 20 nm. This clearly shows the existence of imperfect open-circle structures. This imperfect ring might be promising for device application because end-to-end gap can be utilized as nano-gap electrode. We also observed the other circle structure which has no end-to-end gap, perfect ring. The reason why the structure was formed on the surfaces that the intramolecular C–F⋯Si interaction may allows it to form and stabilize the perfect closed-circle structures. Furthermore, it is also thought that Si–O–Si bond may be formed between the end-termini via hydrolysis of Si–H end group by water adsorbed on mica surfaces (We have reported that end termini of polysilane was assigned as Si–H by FT-IR and 2D-NMR; A. Saxena, K. Okoshi, M. Fujiki, M. Naito, G. Guo, T. Hagihara, and M. Ishikawa, *Macromolecules*, 2004, 36, 367.).
**Fig. S2** shows typical AFM images of poly((S)-3,7-dimethyloctyl-3-methylbutylsilane) PS on mica surfaces. In **Fig. S2A**, rod, semicircle, and circle structures were observed, the same as in the case of FPS. Because the average height and width of the rod and circle structures were almost uniform, all the observed rod, semicircle, and circle structures were not aggregated forms but almost all of them were isolated single polymer chains. In addition to these structures, however, some toroidal structures were clearly observed, shown in **Fig. S2B** (marked by arrow). Much longer polymer chains probably form a toroidal structure more easily. What should be emphasized is that we have observed the topology switching of another polysilane which has a different chemical structure to FPS. These results also significantly support the effect of chain length (molecular weight) dependency. In this case, however, we did not observe the long-period helicity, such as shown in **Fig. 3**, at all in circle structures. The only difference regarding these results might be related to the intramolecular interaction, namely, that intramolecular C–F···Si interaction of FPS presumably stabilizes the formation of long-period helicity in circle structure, while PS forms the circle and toroid structures but without helicity.

**Fig. S2** Chemical structure of Poly((S)-3,7-dimethyloctyl-3-methylbutylsilane) PS and AFM images of adsorbed structures on the mica surfaces.