

Supporting Information

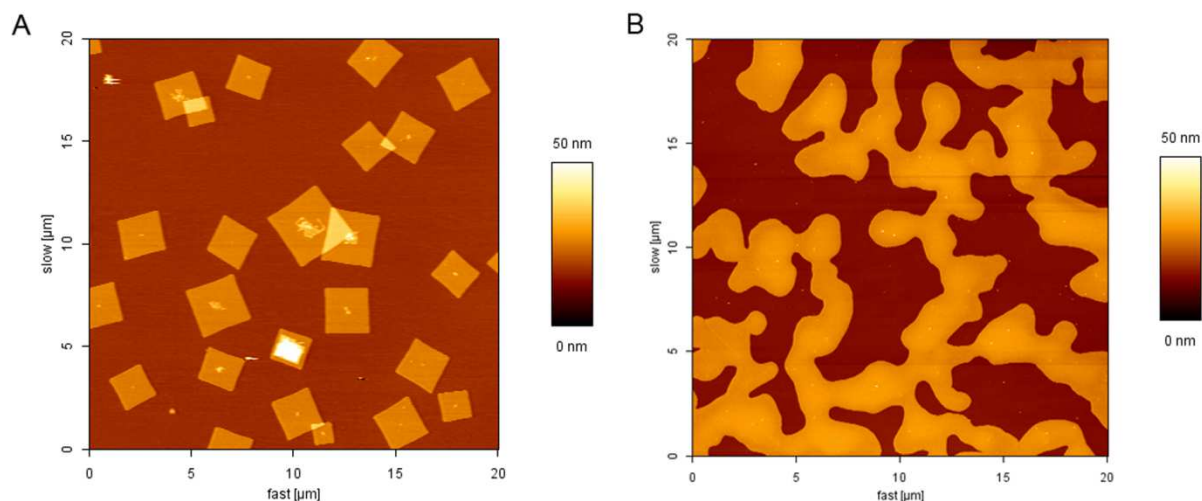
Exploring the folding pattern of a polymer chain in a single crystal by combining single-molecule force spectroscopy and steered molecular dynamics simulations

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Sample Preparation. For the single crystal obtained from solution, PEO single crystals were prepared from dilute solution by self-seeding method which was adapted from the previous work by Li et al.¹ 1 mg PEO (48.5k) was dissolved in 10 g amyl acetate at 60 °C for 10min. The hot solution was then transferred to a water bath of rather low temperature (5 °C for 4h). Then the polymer solution was heated to the seeding temperature (47 °C) with a heating rate of 10 °C/min and held at this temperature for 10 min to form stabilized and uniform nuclei. Subsequently, the solution was brought to crystallization temperature (38 °C) and crystallized for 2 hrs (48.5k). For the single crystal obtained from melt, different patterns, such as dendrite, seaweed and compact structure have been deeply studied.²⁻⁵ Thin PEO films were first heated to 80 °C for 10 min to melt completely. Then, the samples were cooled to crystallization temperature (40 °C) for 12h.

AFM Images

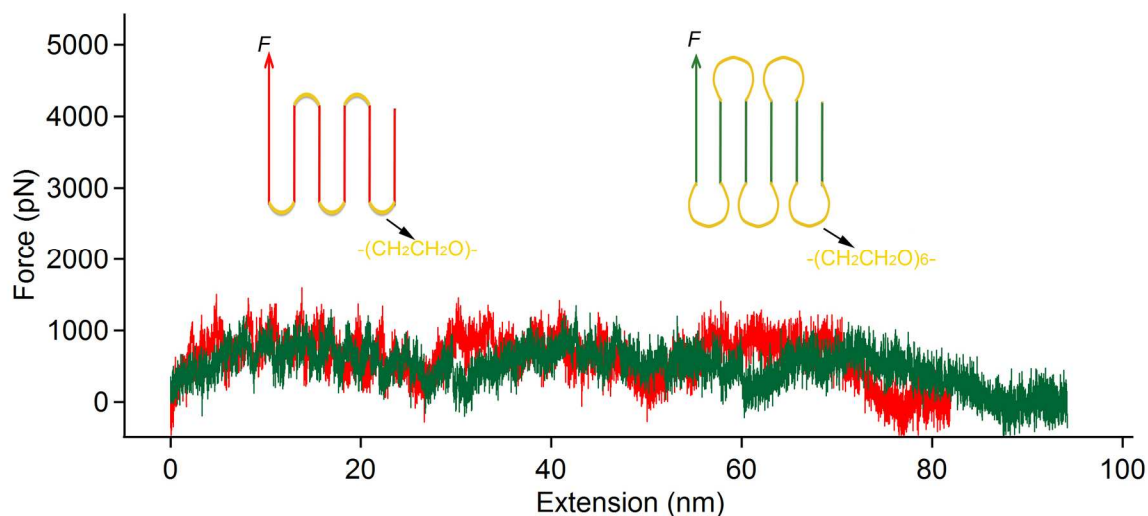
Figure S1. AFM images of HS-PEO-OCH₃ (Mn=48.5K) single crystals grown from dilute solution (A) and melt (B).



SMD Simulations

1) Supporting Figure

Figure S2. SMD simulation on the effect of loop size on the gaps between adjacent peaks. Three folds of PEO fragments with one (red curve) and six (green curve) repeat units in the amorphous loops were pulled out of its single crystal, respectively.



2) Supporting Movie

The movie (PEOmovie.wmv) shows the pulling of three PEO folds with six repeat units of PEO in each of the amorphous loops from the crystal (i.e., the process of the green trace shown above).

The highlighted blue and red atoms within those armophous loops, which can be used to guide the eyes, stand for carbon and oxygen, respectively.

References

- (1) Li, B.; Li, C. Y. Immobilizing Au nanoparticles with polymer single crystals, patterning and asymmetric functionalization. *J. Am. Chem. Soc.* **2007**, *129*, 12–13.
- (2) Meakin, P. *Fractals, Scaling and Growth Far from Equilibrium*; Cambridge University Press: Cambridge, 1997.
- (3) Langer, J. S. Instabilities and pattern formation in crystal growth. *Rev. Mod. Phys.* **1980**, *52*, 1–28.
- (4) Zhai, X. M.; Wang, W.; Zhang, G. L.; He, B. L. Crystal pattern formation and transitions of PEO monolayers on solid substrates from nonequilibrium to near equilibrium. *Macromolecules* **2006**, *39*, 324–329.
- (5) Reiter, G.; Sommer, J.-U. Crystallization of absorbed polymer monolayers. *Phys. Rev. Lett.* **2001**, *86*, 3771–3774.