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Extracting a Single Polyethylene Oxide Chain from a Single Crystal by a Combination of Atomic Force Microscopy Imaging and Single-Molecule Force Spectroscopy: Toward the Investigation of Molecular Interactions in Their Condensed States

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S Supporting Information

ABSTRACT: A thiol-labeled single polyethylene oxide chain has been pulled out of its single crystal and the corresponding extraction force obtained quantitatively by a good combination of atomic force microscopy (AFM) imaging and AFM-based single-molecule force spectroscopy (SMFS). Our study extends the AFM-based SMFS to the investigation of polymer interactions in their condensed states (e.g., in polymer single crystals).

Research on the behavior of a single polymer chain during the crystallization process and the interchain interactions in polymer single crystals may shed light on the mechanism of polymer crystallization, eventually making it possible to direct polymer crystal engineering.[1] Because of the limitations of detection methods, such investigations have been impossible in the past. Atomic force microscopy (AFM)-based single-molecule force spectroscopy (SMFS) has been used extensively in both the materials and life sciences.[2,3] In the field of materials science, SMFS has been used successfully to investige the force-induced conformation transition of a single polymer chain, e.g., globule−coil[4] or chair−boat transition[5] in solution, where the molecules exist in a high elastic state. In addition, the effects of the primary structure,[6] such as the size of the side groups and tacticity, on the elastic properties of the corresponding polymer, as well as the adsorption behavior at solid−liquid interfaces,[3d,7] have been investigated systematically. To bridge the macroscopic and microscopic worlds effectively, it will be necessary to go one step further to investigate molecular interactions in their condensed states, which, along with the molecular nature, is an important factor in determining the properties of the bulk. However, due to the complexity of the system, to the best of our knowledge, such studies, especially in the field of materials science, have rarely been reported.[8]

As a proof-of-concept study, here we chose a polymer single crystal as a model system to investigate, for the first time, the molecular interactions of a single polyethylene oxide (PEO) chain within its single crystal by combining AFM imaging and SMFS. Our current study extends AFM-based SMFS to the investigation of molecular interactions in more complicated polymer systems (i.e., in polymer single crystals).

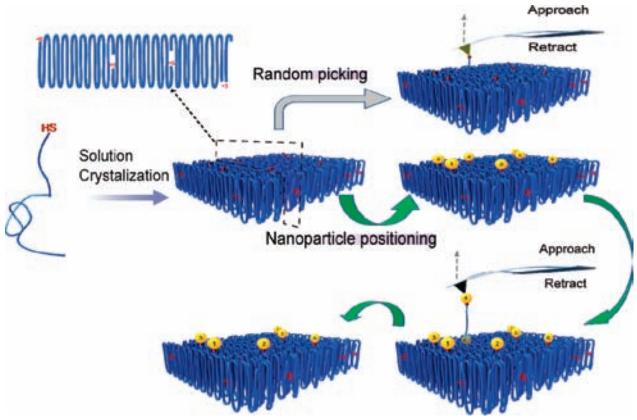

Figure 1. Schematic drawing of AFM-based SMFS experiment on PEO single crystals. In the random picking strategy, a gold-coated AFM tip is allowed to undergo random approach−contact−retract cycles to pick up the thiol end on the single-crystal surface. In the nanoparticle positioning strategy, the gold-nanoparticle-labeled thiol end is first positioned by AFM imaging before further tip contact and manipulation.

We have developed the following sample preparation method, which allows single polymers to be studied in their condensed state (i.e., in single crystals). Single crystals of thiol-terminated polyethylene oxide (HS-PEO-OCH_3, M_n = 48.5K, PDI = 1.05) were obtained through solution crystallization using a self-seeding method (see Supporting Information and Figure S1).[11−o] Due to the chain-folding nature of the polymer crystal, thiol-terminated ends were randomly distributed on both sides of the surface as well as within the crystal layer (see Figure1). One side of the crystal was then immobilized onto a silicon substrate via short cross-linkers (see Supporting Information), leaving the thiol ends on the opposite side of the single crystals exposed to be picked up directly by a gold-coated AFM tip (for random picking) or via a gold nanoparticle bridge (gold nanoparticle positioning, GNPP), as shown in Figure 1.

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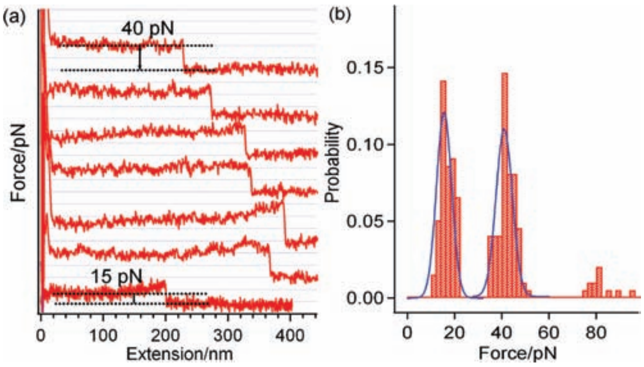

Figure 2. (a) Typical stretching curves obtained on HS-PEO-OCH$_3$ single crystals using the random picking method. (b) Force distribution of the corresponding force plateaus.

The random picking experiments were performed on selected single-crystal surfaces using gold-coated AFM tips. While the gold-coated AFM tip is in contact with the single-crystal surface, it is possible for the thiol terminals to become attached onto the tip via gold−thiol interactions. The corresponding PEO chain could subsequently be pulled out of the single crystal upon retraction of the AFM tip (top row in Figure 1). Different types of force−extension curves were obtained, as shown in Figure 2a. After a close look at the shapes of the curves, we found that the majority of the curves (86% of 1662 curves), especially in the middle region, showed plateaus. Statistical analysis on the average height of the force plateau produces a bimodal force distribution histogram (Figure 2b). A multipeak Gaussian fit gives the two most probable forces: 15 and 42 pN. We speculate that, in our current system, there are two possibilities that can cause the appearance of curves containing a plateau. The first one is the pulling of a PEO chain out of its single crystal. The second one is the desorption of a PEO chain,[7] which has been attached to the AFM tip, from the crystal surface.

To find out the origin of the two force plateaus, we performed a control experiment, doing the force−extension experiment on a pure PEO single-crystal surface (hydroxyl-group-terminated PEO, HO-PEO-OH, without thiol label) using a thiol−PEO-modified AFM tip. Force plateaus in the stretching curves were obtained, and the plateau force centers at about 15 pN, which is the same as the smaller plateau force in Figure 2b (see also the Supporting Information and Figure S2). In addition, it can be imagined that, during the random picking experiments on thiol-PEO single crystals as presented earlier, only after a PEO chain is attached to the AFM tip and extracted from the crystal will it have the chance to adsorb onto the crystal surface during subsequent tip−sample contact. Our results showed that the curves with a relatively lower height (~15 pN) did not appear until the curve with a higher plateau height (about ~42 pN) had been observed, which agrees well with our speculation. Moreover, the plateau force around 42 pN was found to increase with increasing stretching speed, while the 15 pN force plateau showed almost no pulling velocity dependence (see Figure S3 in the Supporting Information; more systematic studies are underway). All these results confirm that the 15 pN force histogram in Figure 2b should be ascribed mainly to the desorption force of PEO chains, which were linked to the tip, from the single-crystal surface.[7b−d] We would like then to attribute the force plateau of 42 pN to the pulling of a PEO chain out of its single crystal.

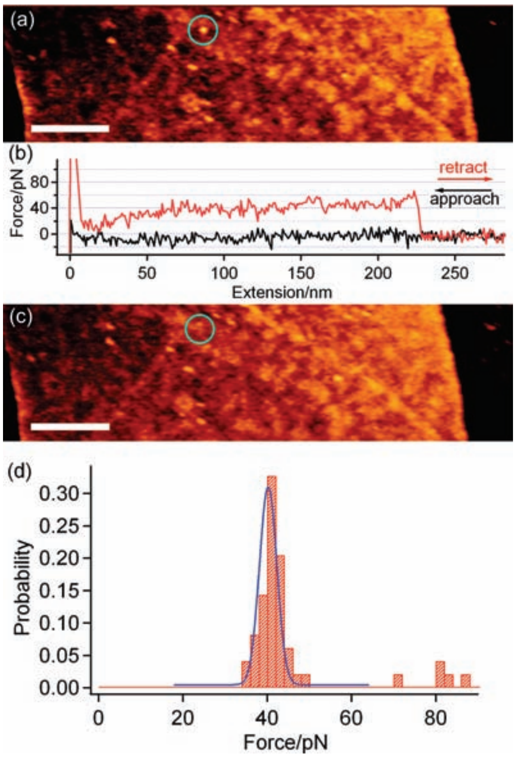

Figure 3. SMFS experiment on a gold-nanoparticle-labeled PEO single crystal (i.e., GNPP). (a) Part of the single crystal was imaged first to locate the GNP, and then the selected GNP, as marked by the blue circle, was picked up by an AFM tip. (b) The corresponding force−extension signal was recorded. (c) The same area of the single crystal was imaged again, and the corresponding GNP had disappeared. (d) Statistical analysis on the plateau forces produced a most probable force of 40 pN.

To further prove our hypothesis, we performed the pulling experiment using a more defined experimental design (i.e., the gold nanoparticle positioning, GNPP). The free thiol ends on the PEO single-crystal surface were first labeled by gold nanoparticles (GNPs)[1l,n] via thiol−gold chemistry (see Supporting Information, Figures S1c and S4, and Figure 3). The AFM tip was then positioned over the specific nanoparticle (e.g., the particle marked by the blue circle in Figure 3a), after which the corresponding PEO chain could be stretched via manipulation of the attached GNP. The absence of the specific GNP during subsequent AFM imaging (Figure 3c) is evidence that the force signal obtained during the manipulation of a GNP (Figure 3b) corresponds to the pulling of the PEO chain out of its single crystal. Similar to the previous random picking experiment, force plateaus were observed in the stretching curves, as can be seen in Figure 3b. The most probable height of the force plateau is ~40 pN by statistical analysis (Figure 3d), which is very close to the value estimated in the random picking experiment (42 pN) as discussed above. We believe that, in the vast majority of cases, only a single HS-PEO polymer chain is attached to each GNP for the following reasons: (1) Based on the well-accepted chain folding model, the probability for one GNP to interact simultaneously with two PEO chains was estimated to be 1−4%, and even much lower considering the non-integral folding[9] (for the detailed calculation, see the Supporting Information), let alone three or more PEO chains. (2) Our force distribution data in Figure 3d show a good Gaussian distribution, further confirming the single-molecule stretching process. In addition, a small population of plateau forces around 80 pN

(Figures 2b and 3d) may indicate the pulling of two PEO chains in parallel simultaneously out of a single crystal. Putting these facts together, we can conclude that to extract a single PEO chain from its single crystal will require an external force of $\sim$40 pN under our experimental conditions (at a pulling speed of 2 μm/s).

In both of the pulling strategies (random picking and nanoparticle positioning) mentioned above, the distributions of the extension lengths at the rupture points were found to be shorter and relatively broader as compared with the contour length and narrow molecular weight distribution of the PEO sample (PDI = 1.05, see Supporting Information, Figure S5). We attribute this difference mainly to the contribution of weak, nonspecific interactions (or weak chemisorption)[10] between the AFM tip and the sample (the HS group or GNP); for further discussions, please refer to the Supporting Information. In addition, the rising slopes (or tilted plateau) at shorter extension (e.g., the third curve from the top in Figure 2a and the curve in Figure 3b) or at longer extension, close to the rupture point region (e.g., the second and third curves from the bottom in Figure 2a), observed in some of the stretching curves (14% of 1662 curves) may due to the pulling of imperfectly folded fragments in the amorphous phase.[4,11] Such a pulling process may look like this: the pulling starts from an amorphous phase (producing the slope at shorter extension), followed by extraction of PEO fragments from the crystal phase (the plateau region), and then by entropic elastic stretching (the rising slope before rupture) before the link breaks.[4] In other words, the flatness of the force plateau may reflect the content of perfect (or imperfect) folding.

In summary, we have successfully extracted a single PEO chain from its single crystal and directly measured the interaction strength between folded polymer fragments to be around 40 pN (at a pulling speed of 2 μm/s) by a combination of AFM imaging and SMFS. Further study on the possible recrystallization behavior of the partially extracted PEO chain is under way. Our current study extends the usefulness of SMFS to the investigation of polymer interactions in their condensed states (e.g., in single crystals). We believe that the method established here can be used to study crystallization of various polymers at the single-molecule level.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Description of experimental methods and several control measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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