Quantifying the atomic-level mechanics of single long physisorbed molecular chains

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Individual in situ polymerized fluorene chains 10–100 nm long linked by C–C bonds are pulled vertically from an Au(111) substrate by the tip of a low-temperature atomic force microscope. The conformation of the selected chains is imaged before and after manipulation using scanning tunneling microscopy. The measured force gradient shows strong and periodic variations that correspond to the step-by-step detachment of individual fluorene repeat units. These variations persist at constant intensity until the entire polymer is completely removed from the surface. Calculations based on an extended Frenkel–Kontorova model reproduce the periodicity and magnitude of these features and allow us to relate them to the detachment force and desorption energy of the repeat units. The adsorbed part of the polymer slides easily along the surface during the pulling process, leading to only small oscillations as a result of the high stiffness of the fluorenes and of their length mismatch with respect to the substrate surface structure. A significant lateral force also is caused by the sequential detachment of individual units. The gained insight into the molecule–surface interactions during sliding and pulling should aid the design of mechanoresponsive nanosystems and devices.

force spectroscopy | conjugated polymers | adhesion | friction | nanomanipulation

Ever since the invention of the atomic force microscope (AFM) (1) and the first imaging applications, force spectroscopy has been applied to study the mechanical behavior of polymers (2); more complex chain-like biomolecules, e.g., DNA complementary strands (3); and proteins, subject to controlled extension (2) or applied force (4), mostly in solution and at room temperature. Reactive groups are chemically inserted at the ends and/or along each molecule to firmly bind some of them to suitably functionalized tips and sample surfaces. Irreversible jumps in curves of force vs. vertical separation may be associated in this way with the rupture of bonds or the unfolding of coiled subunits. If reproducible, the lowest peak in the histogram of the forces attained just before each jump is attributed to such an event in a single molecular chain or complementary pair. In the case of homogeneous polymers or protein segments, simulations based on two-state rate theory combined with a standard model of polymer nonlinear elasticity can reproduce such events, whereas reversible plateaus or continuous rises in the force may be associated with fast binding–rebinding processes or with large thermal fluctuations (2). Attention thus has focused on conformational changes strongly influenced by pulling speed or imposed force jumps (4) and also by external stimuli, e.g., optical excitation of inserted chromophores (5) or specific reactants or enzymes (6). Furthermore, mechanical forces recently were discovered by chemists as a unique stimulus to induce specific chemical reactions. In this so-called mechanochemistry, sonication typically is applied to polymer systems and is believed to result in a strong force acting on the weakest link in the chain, where the reaction takes place (7, 8). Regardless of the direct or indirect exposure to force, it is clear that the mechanics of polymer chains constrained in their surrounding environment is of utmost importance for a variety of biophysical and chemical processes as well as self-healing materials applications (9, 10).

A few pulling studies have been conducted on polyelectrolytes unspecifically adsorbed on self-assembled monolayers via tunable electrostatic interactions (11), including DNA (12). They merely revealed noisy force plateaus, interpreted as continuous partial desorption of single chains, terminated by a drop to zero upon complete detachment from the surface. Despite the undisputed merit of these studies, little is known about the mechanical behavior of single molecular chains pulled off a surface, both defined and characterized on the atomic scale, in the absence of significant thermal fluctuations and drifts. Measurements at low temperature reduce the diffusion of adsorbates and provide an opportunity to determine the energetic landscape of specific molecules interacting with a surface under controlled conditions. As demonstrated here, the sliding and detachment mechanisms of individual polymer repeat units can then be inferred from the analysis of pulling experiments. A detailed interpretation of our results, based on a modified Frenkel–Kontorova (FK) model (13), also is presented.

Single Polyfluorene Chains: Preparation and Experimental and Modeling Approaches

We present here an investigation of the aforementioned kind, using a homopolymer of substituted fluorene consisting of two phenyl rings fused by a central cyclopentadiene ring and two off-plane methyls at the apex. In contrast to solution chemistry, preparing an isolated, single, and long molecular chain on an atomically clean surface under clean ultrahigh vacuum (UHV) conditions is extremely challenging. Because of their large molecular

Significance

Mechanical properties of biopolymers such as DNA and proteins have been studied to understand the details of complex processes in living systems via systematic statistical analyses of repeated measurements. However, the mechanical behavior of a single molecular chain pulled off a surface has never been investigated with atomic-scale resolution. Herein, we present such a study on in situ polymerized fluorene chains by pulling individual chains with the tip of an atomic force microscope at 4.8 K. The measured variations of the force gradient provide detailed insights into the detachment process of fluorene units and the role of near-incommensurability with the substrate structure.

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weight, polymers cannot be deposited simply by using conventional thermal evaporation techniques. In situ polymerization of molecular precursors on a surface is, in contrast, an attractive way to achieve our goal (14). Polyfluorene molecular chains were synthesized on an Au(111) surface from dibromoterfluorene (DBTF) molecules. These molecules consist of three fluorene units carrying a Br atom at each end that dissociates at elevated temperature (490 K), thus allowing trimer radicals to diffuse and link. The well-defined 1D structure of the resulting chains (fluorenes linked by C–C bonds and alternatively tilted in opposite directions; see *inset* in Fig. 1*A*) opened the possibility of measuring electron transport through a free-standing segment connected to the substrate and to the tip of a scanning tunneling microscope (STM) in a controlled manner (15). Here, we measure the mechanical properties of such individual polymer chains vertically pulled by an AFM tip, using the same conducting tip to characterize the chains on the metal surface by STM before and after manipulation.

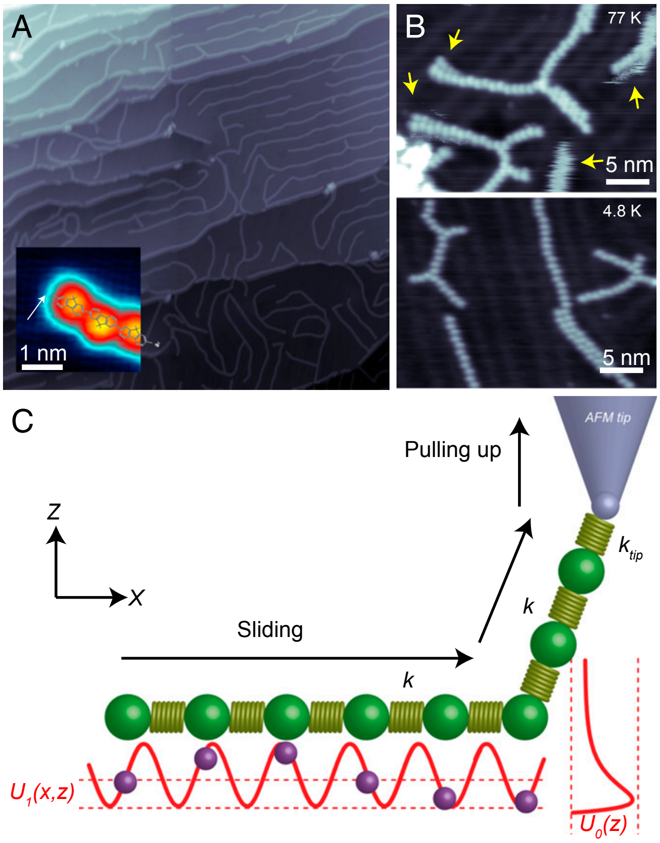

Fig. 1. (*A*) Overview STM image recorded after the polymerization of DBTF precursors to polyfluorene chains on an Au(111) surface (176×176 nm^2). (*Inset*) Zoomed-in STM image near one end of a molecular chain whose Br atom had dissociated upon annealing at 490 K. A schematic drawing of the DBTF molecule is superimposed. Each fluorene unit is imaged as a broad maximum caused by the upward-pointing methyl at the apex of the central pentagonal ring. (*B*) STM images obtained at 77 K (200 mV and 13 pA) and 4 K (100 mV and 20 pA) showing polyfluorene chains lying along as well as across the dark broader fcc stripes of the reconstructed substrate. (*C*) Schematic representation of the interactions acting while pulling up the molecular chain (see text).

All experiments were performed under UHV conditions with an Omicron AFM/STM equipped with a tuning-fork piezoelectric force sensor (16), operated at 4.8 K and 77 K. At 4.8 K, most of the molecular chains are physisorbed along fcc stripes of the herringbone reconstruction (Fig. 1*A*) (17). At 77 K, a few tilt defects causing local bends (15), as well as some motion of the polymer termini, were observed on the time scale of the STM imaging (Fig. 1*B*), thus indicating that activation barriers for untilting and lateral diffusion are small (*Supporting Information* and Figs. S1 and S2). Using a dynamic AFM at 4.8 K allows one to perform successive manipulations as well as to extract mechanical properties such as stiffness, pulling force, interaction potential, and interaction-induced additional energy dissipation (18). Because the oscillation amplitude of the probing tip is kept quite low (30 pm), the measured frequency shift Δf is proportional to the effective stiffness k_{ts} of the tip–sample interaction. The quantity of k_{ts} is defined as the gradient of the force acting on the tip along the vertical pulling direction z with respect to the z-displacement and is calculated as $k_{ts} = -2k_c\Delta f/f$, k_c being the stiffness of the force sensor and f its resonance frequency (16, 19, 20). However, in contrast to well-established dynamic AFM measurements of short-range chemical bonding between close tip apex and sample atoms (21–23) and controlled manipulation of the latter (24), the interpretation of the present measurements is more challenging. This is a result of the multiple bonding situation, with strong covalent bonds within the polymer, a weak interaction of each fluorene unit with the surface, and a relatively strong bond to the tip. The junction between chain and tip most probably involves a covalent Au–C bond (25), which should be weaker and longer, hence softer than a C–C bond. Such Au–C bonds form between gold electrodes and alkane or aromatic chains terminated by trimethyltin groups that are cleaved spontaneously in suitable solutions, as demonstrated by in situ single-molecule conductance measurements (25). In our case, the C-radicals left at the ends of in situ polymerized fluorene chains presumably can form Au–C bonds. Indeed, the probability of establishing the junction strongly depends on the tip positioning at the terminus of the last fluorene unit (15). Fig. 1*C* shows a schematic drawing of the experimental setup and a generic model that explains the salient features of our measurements. The bond of the tip apex to the pulled end of the molecular chain is represented by a spring of stiffness k_{tip}, and each fluorene unit is linked to its neighbors by springs of stiffness k. The polymer is physisorbed via weak van der Waals interactions mainly involving the downward-pointing methyl, as well as phenyl CH edge groups close to the Au(111) substrate. Furthermore, the remaining radical at the other chain end presumably interacts weakly with the substrate. Our goal is to detect fingerprint-like variations in the frequency shift Δf while pulling up individual molecular chains of different lengths and to interpret the experimental observations by means of simulations based on the sketched model using adsorption and corrugation potentials U_0 and U_1, described in further detail (see also *Supporting Information*).

Pulling Measurements

We first attempted to pull a polyfluorene chain about 20 nm long and consisting of 24 fluorene units (Fig. 2*A*). The tip apex (likely decorated by gold atoms picked up from the sample) was positioned precisely at the end of the molecular chain, indicated by the arrow, close enough to connect to the chain, as approaching the terminus increases the pulling efficiency (15). Whenever a strong bond to the tip is established, the sudden variation of the tip–sample interaction causes an abrupt Δf change in the AFM (26, 27). Then, the tip was retracted in the vertical z-direction while recording Δf. Fig. 2*B* shows the measured Δf curve up to a distance of 25 nm. The effective stiffness, calculated via Δf, is indicated on the scale on the right. An approximately periodic variation of Δf is observed clearly, with each period terminated by an abrupt jump (indicated by the broken lines) toward negative values affected by noise and sampling. In contrast to conductance measurements (15), the magnitude of the more reliable Δf maxima does not decay significantly with the length of the free-standing chain segment [see *Supporting Information* and Fig.

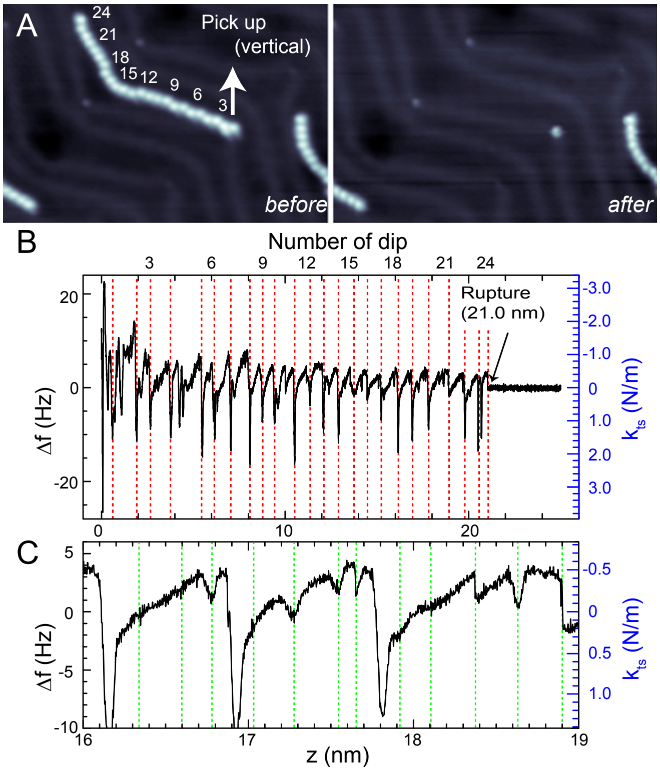

Fig. 2. (*A*) STM images of the same surface area before and after pulling off a molecular chain initially lying along an fcc stripe of the herringbone-reconstructed Au(111) substrate. (*B*) Frequency-shift trace measured while retracting the tip after contacting and pulling the chain at the end indicated by the arrow in *A*. (*C*) Magnification around $z = 17.5$ nm.

S3 for a longer chain (72.4 nm)] so that the mechanical behavior of the molecular chain is measurable readily until complete pull-off. In Fig. 2*B*, we observe 24 periods of Δf, which exactly correspond to the initial number of fluorene units on the surface. Furthermore, the mean distance between consecutive jumps is 0.91 ± 0.07 nm, which is close to the length of a fluorene unit (0.845 nm). These values are more accurate but agree with STM pulling experiments (15) and confirm that the molecular chain is stepwise lifted from the substrate surface unit by unit. In a closer observation of a single lifting event (Fig. 2*C*), we notice a minor modulation, with a periodicity close to the substrate lattice spacing parallel to the sliding direction along an fcc stripe (0.5 nm). At $z = 21$ nm, i.e., at a distance close to the length of the polyfluorene chain on the surface, the frequency shift suddenly levels off to $\Delta f = 0$. Indeed, the chain no longer is present in the STM image recorded after the pulling measurement (Fig. 2*A*). This means that the molecular chain was detached completely from the surface when the last abrupt change of Δf was detected.

To achieve a complete detachment sequence with well-defined periodicity, it is very important to choose an individual molecular chain lying along an fcc stripe of the herringbone structure. Interestingly, if the chain initially crosses some stripes and/or is partly bound along a substrate step, the tip–chain junction often ruptures during pulling (*Supporting Information* and Figs. S5 and S6). Once a chain is completely detached from the surface, it likely rolls up and connects to the tip in an uncontrollable manner, because no significant Δf change is observed if the tip subsequently approaches the surface. However, if the tip–molecule junction breaks before complete pull-off, the chain may be observed in a different configuration on the surface (*Supporting Information* and Figs. S4–S6). Because junction rupture occurred after many units were detached, and the stiffness of the free-standing segment scales with k were divided by the number of pulled-off units, we conclude that the stiffness of the tip–chain junction must be much weaker than that of a C–C bond.

Extended FK Model

The mechanical behavior of a molecular chain pulled along a crystal surface may be interpreted using the FK model (13). In the 1D FK model, the chain is approximated by a series of units connected by equivalent springs (with stiffness k and equilibrium length b); each unit interacts with the substrate via a sinusoidal potential of amplitude $U_1(x)$ and period a. Below a critical value of the dimensionless parameter U_1/ka^2, which depends on the ratio b/a, an infinite chain would continuously slide for a finite applied force F along x if b/a is an irrational number, because forces acting on units off minima and maxima of $U_1(x)$ would cancel out for any relative position of the chain. If b/a is rational, e.g., if periodic boundary conditions are applied, or in the realistic case of a finite chain, a finite depinning force F_c is required to initiate sliding, because the cancellation is incomplete and position dependent, as suggested in Fig. 1*C*. If F slightly exceeds F_c, nearly frictionless sliding (more precisely, a modulation of F about a zero average in the limit of vanishing pulling velocity) is possible if U_1/ka^2 is sufficiently low. In the present case, the scenario changes further in nontrivial ways, because the pulling force is applied to the last unit by a weaker spring and the tip is moved perpendicularly to the surface (in the z-direction) while the chain segment remaining on the surface slides along the surface (in the x-direction).

To clarify the mechanisms causing the observed variations of Δf during pulling polyfluorene chains, or of similar polymers consisting of rigid units connected by single bonds, and to quantify the experimental results further, we performed calculations based on the following model. In close analogy to the FK model, the polymer is approximated by a chain of harmonically coupled particles. In contrast to the FK model, we have chosen a more realistic interaction potential, introduced by Steele (28), to describe gas–atom solid interactions. In our case, each particle represents a fluorene unit, with the methyl side group close to the surface interacting with each gold atom of the sample via a 12-6 Lennard-Jones potential with well depth ε and steric diameter σ. As described by Steele, the interaction of each particle with a rigid crystal may be approximated by a truncated Fourier series, with position variables in the plane parallel to the surface. The assumption of an undeformed surface is reasonable in the case of alkanes adsorbed flat on Au(111), because measured adsorption energies are nearly proportional to the number of units (29), with small slopes consistent with physisorption and weak electron transfer (30). This also applies to conjugated arenes on the same surface (31). A detailed analytical description of the model is provided in *Supporting Information*.

Results of Simulations and Comparison with Experiments

Zero-temperature simulations of vertical pull-off were performed using damped Newtonian dynamics, assuming a particle mass and damping such that any excited vibrations rapidly died between successive detachment events (*Supporting Information*). Representative results are presented in Fig. 3 for a chain initially lying along a $[11\bar{2}]$ symmetry direction, i.e., along an fcc stripe (17). The sequential detachment of the units with a period coinciding with b is the most prominent feature, in very good agreement with the experimental data (Fig. 2). Both the normal force acting on the tip and its z-gradient jump whenever a molecular unit is detached. The measured force gradients are well reproduced if the parameter $\epsilon = 31$ meV is used. In this case, the averaged physisorption potential has a minimum of $-8.95\epsilon = 0.27$ eV. This value corresponds to the physisorption energy of one molecular unit and is reasonably close to a lower bound of 0.21 eV estimated for a tilted

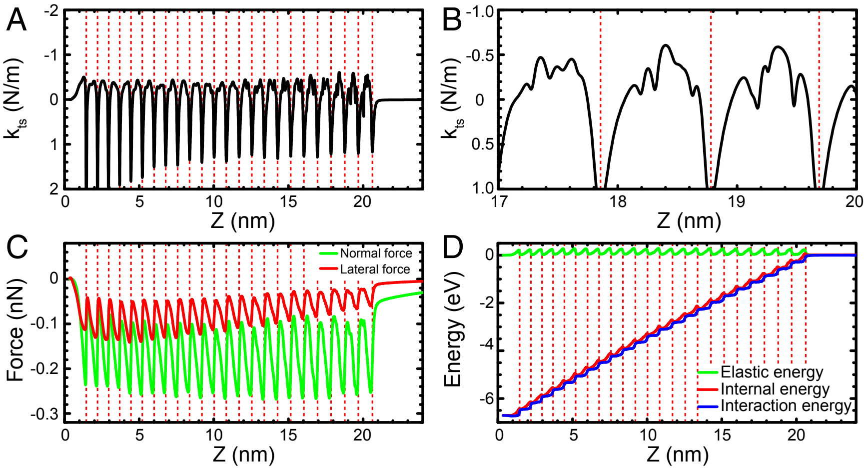

Fig. 3. (*A*) Calculated dependence of the normal force gradient vs. tip–surface distance *z*. (*B*) Magnified view showing superimposed modulation between three detachment events. (*C*) Normal and lateral forces vs. tip–surface distance *z*. (*D*) Interaction energy, elastic energy, and internal energy of the chain vs. tip–surface distance *z*. The chain consists of 24 units interacting with the (111) surface of an fcc gold crystal with interatomic spacing a = 0.288 nm. The parameters of the calculations were $\varepsilon = 0.005 \times 10^{-18}$ J, $b = 0.845$ nm, $k = 200$ N/m, $k_{tip} = 1$ N/m, $v_{tip} = 0.01$ nm/s, and $\sigma = 0.36$ nm (see text). Both force gradient and force variations are dominated by the successive detachment of individual molecular units. Each sharp jump is accompanied by an increase in the potential energy by 0.27eV, which equals the desorption energy of one molecular unit. The superposed modulation in *A* and *B* is a result of the frictionless sliding of the chain on the substrate, and reflects effects of the misfit between the monomer length b and the substrate periodicity along the sliding direction.

methylated fluorene (*Supporting Information*). The corresponding maximum vertical attractive force between the detached unit and the substrate is 0.25 nN. Similar to the experimental results, we also obtain a small continuous modulation related to the periodicity of the Au(111) substrate along the sliding direction (Fig. 3*B*). Being superimposed on the main variations, this modulation does not appear periodic but shows extrema or shoulders that gradually shift with respect to the main variation and reflect the misfit between the chain structure (b-periodicity) and the atomic lattice of the gold substrate. Note that in our measurements, even when the molecular chain moves along the straight part of an fcc stripe of the herringbone reconstruction, the modulation is more irregular, although the b-periodicity is maintained, as observed between the last 12 jumps preceding full detachment in Fig. 2*B*. This may arise from some wiggling of the chain perpendicular to the sliding direction.

A remarkable result of extensive simulations is that the normal force required to detach one unit after the other is nearly independent of the length of the chain and of the segment remaining on the surface, as long as the effective stiffness of the pulled-off segment is large compared with k_{tip}. This always is the case if the number of units is well below k/k_{tip}. The concomitant lateral forces along the sliding direction also show large variations, about one third of the normal force variation, and exhibit jumps to less attractive values at the same tip–sample separations (highlighted by the dashed lines) with a spacing very close to the chain period b in all panels of Fig. 3. Closer inspection reveals that the spacing between the dashed lines also slightly increases as pulling proceeds. This is consistent with the slowly decreasing net stiffness of the pulled-off segment. Both force components are determined primarily by the detachment of individual units, which correspond to fluorene monomers of length $b = 0.845$ nm. Indeed, the detachment of each unit involves motion in the full potential energy landscape, thus leading to both normal and lateral forces.

According to the standard FK model, the average lateral force exerted by the sliding segment should nearly vanish, whereas the attractive forces acting on the tip depicted in Fig. 3*C* obviously have finite averages. As z increases, the normal force exhibits nearly the same pattern, whereas lateral force variations gradually decrease. Indeed, although each detachment event generates nearly the same force on the currently lifted unit, the lateral component exerted on the tip is reduced because the lateral displacements of lifted units gradually decrease toward the last unit connected to the tip.

Another interesting result, apparent in Fig. 3*D*, is that the internal energy of the chain coincides with its interaction energy with the surface during slow sliding stages when all units move little while only the spring connecting the last one to the tip is extended significantly. This coincidence implies that the desorption energy per unit is given by the difference between adjacent internal energy plateaus. The first law of thermodynamics provides in principle a way to directly extract the desorption energy from experiment: the internal energy change is just the difference between the work done on the tip and the energy dissipated during fast variations. Whereas energy dissipation can be measured simultaneously with the frequency shift (5), the work cannot be calculated reliably by twice integrating $-2k_c\Delta f/f$ inward starting from a large enough z value, because the average normal force remains undetermined. This average is difficult to determine because the frequency detection circuit likely systematically lags during the rapid drops apparent in Fig. 2 *B* and *C*. A reliable determination is intrinsically problematic if the system jumps irreversibly between distinct configurations, each one associated with its own interaction energy hypersurface over finite, possibly overlapping z-range(s) (32). Such events also lead to concomitant jumps in the force, as observed when chains of atoms are pulled out of the surface of a metal (26) or insulator (33) upon close approach followed by retraction. Furthermore, energy dissipation inevitably arises in the range(s) in which two or more configurations are populated by thermal or instrumental noise, or by the imposed tip oscillation. Those difficulties were recognized in part in recent pull-off measurements on single molecules (rather than chains) (34). However, the proposed procedure of matching force and interaction energy curves computed from Δf on both sides of the range in which dissipation occurs ignores possible jumps. In our opinion, only variations of those quantities about unknown averages can be determined reliably (*Supporting Information*, especially Fig. S3 *B–E*). Direct force detection via the time-averaged deflection of an oscillating stiff cantilever (35) is an alternative method to determine the magnitude of released force during detachment of each unit. However, an accurate direct measurement of the normal force is practically impossible with the very stiff deflection sensors used in current low-temperature AFM setups. In contrast, direct force measurements using soft sensors are common in room-temperature studies of biomolecules (2–6), synthetic polymers (11, 12), and Au–single molecule contacts (36) in solution. The next step would be to combine advantages of both apparently disparate approaches to experimentally determine the desorption energy per monomer in future extensions of the present study.

Conclusions

We have manipulated single physisorbed molecular chains and investigated their mechanical behavior by pulling them from a reconstructed metal surface. An AFM is used and operated at low temperatures to suppress thermal effects. A periodic variation of the measured frequency shift proportional to the normal force gradient, interrupted by steep drops, then is observed together with a weak superimposed modulation. The period matches the length of each molecular unit, whereas the jumps are a result of the detachment of individual monomers. The modulation reflects the nearly frictionless motion on the surface expected for stiff-enough chains. The adsorption energy of a monomer is extracted by fitting the experimental data. Numerical calculations based on an extension of the FK model reproduce all experimental observations and also predict the underlying normal and lateral forces acting on the pulling tip, which are difficult to determine from the measured frequency shift and energy dissipation without questionable assumptions. Systematic studies of the mechanical properties of adsorbed polymers or conducting wires thus can be realized in a controlled manner on the molecular scale. The proposed model is remarkably simple but nevertheless is flexible enough to treat more complex heteropolymers by including separate interaction and deformation potentials for different units and/or adjusting parameters to account for specific interactions with naturally or intentionally structured substrates. Furthermore, as already demonstrated for synthetic polymers and biopolymers pinned at both ends and containing switchable units, effects of thermal fluctuations on their elastic properties and force-induced conformational changes (2, 37) may be described by few-state or potential models. Combinations of the above-mentioned extensions should provide a useful framework for describing the mechanochemistry (7, 8) of devices based on synthetic heteropolymers containing force-sensitive units deposited on templated substrates, with potential optoelectronic (38) or electromechanical applications.

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