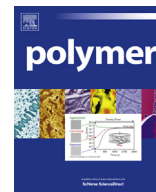




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## Recording stretching response of single polymer chains adsorbed on solid substrates

Lucie Grebikova<sup>a</sup>, Milad Radiom<sup>a</sup>, Plinio Maroni<sup>a</sup>, A. Dieter Schlüter<sup>b</sup>,  
Michal Borkovec<sup>a,\*</sup>

<sup>a</sup> Department of Inorganic and Analytical Chemistry, University of Geneva, Sciences II, 30 Quai Ernest-Ansermet, 1205 Geneva, Switzerland

<sup>b</sup> Department of Materials, Institute of Polymers, Swiss Federal Institute of Technology, ETH Zurich, HCI J 541, 8093 Zurich, Switzerland

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### ABSTRACT

Various techniques to measure the force-extension relationship of individual polymer chains with the atomic force microscope (AFM) are compared. Reliable stretching force profiles can be obtained with the nano-handling technique, which involves imaging of the measured individual polymer molecules prior and after the force experiment. Results originating from the classical pulling technique, which relies on dense adsorbed polymer layers, must be interpreted with care. Comparison with the nano-handling technique reveals that the stretching response of individual molecules can be obtained with the pulling technique, provided the adsorbed polymer layer is dilute. For denser adsorbed layers, such experiments may not reflect the correct stretching response. The discrepancies seem to be related to polymer–polymer interactions and entanglements within the adsorbed layer. AFM imaging of the adsorbed layers can provide an indication concerning the relevance of such entanglement effects. Similar caveats apply to fishing experiments, where polymers are adsorbed to the AFM tip and not to the substrate.

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### 1. Introduction

The atomic force microscope (AFM) has revolutionized our capabilities to image, probe, and manipulate nanoscopic objects on surfaces, especially for soft and polymeric materials. Among the different applications of this technique, which include single molecule imaging [1–3], measurements of forces and friction [4–7], the possibility to probe and manipulate single macromolecules seems most exciting [8–16].

Among these developments, the so-called single molecule force spectroscopy became a widely used tool to investigate the mechanical properties of single macromolecules, their interaction with surfaces, and chemical reaction kinetics on a single molecule level [10–26]. The technique relies on a configuration where the substrate and the tip are bridged with a single polymer molecule, and subsequent analysis of the measured force–distance curves, normally upon retraction, but eventually also upon approach. Two main classes of events can be normally observed, namely pulling and peeling. A pulling event resembles a spike in the force curve,

and ideally corresponds to the force-extension relationship of a single polymer molecule, which is firmly attached to the substrate and to the tip [5,12,20,27–29]. Such force profiles can be interpreted by the freely jointed and worm-like chain models including chain elasticity. Recently, such experiments were also carried out with two AFM-tips, which further provide time-dependent properties of a single polymer chain [23]. A peeling event is characterized with a plateau in the force curve, which reflects the force that is necessary to peel off the adsorbed molecule [30–36]. These forces reflect the affinity of the molecules to the surface, and can be related to the type of substrate and its charge. Peeling and pulling events also may occur in succession, and their relative occurrence can be sometimes tuned through the surface properties or its coverage [30,37]. A series of spikes resembling teeth of a saw is normally interpreted as the unwrapping of individual macromolecule domains, which are frequently observed for muscle proteins (e.g., tintin, tenascin) [11,38]. A series of peeling events, which resemble a staircase, are typically due to the peeling of several molecules from the surface, even though they could also be caused by a combination of sliding and peeling [31,32,37,39,40]. Frequently, however, several of these events occur in combination, and the respective force profiles have complex, random appearances, which are difficult to interpret. The focus of this article is to

\* Corresponding author.

E-mail address: [michal.borkovec@unige.ch](mailto:michal.borkovec@unige.ch) (M. Borkovec).

show how single-molecule stretching response can be obtained from pulling events, while peeling events will not be discussed further.

To generate a single bridging polymer molecule between the substrate and the tip, various techniques have been proposed, see Fig. 1a. The *nano-handling* technique identifies a single adsorbed polymer molecule on the surface by AFM-imaging, and this molecule is probed with the AFM tip through repeated approach-retraction cycles [12,30]. A bridging event is identified by its force response. The conformation of the adsorbed molecule can be again

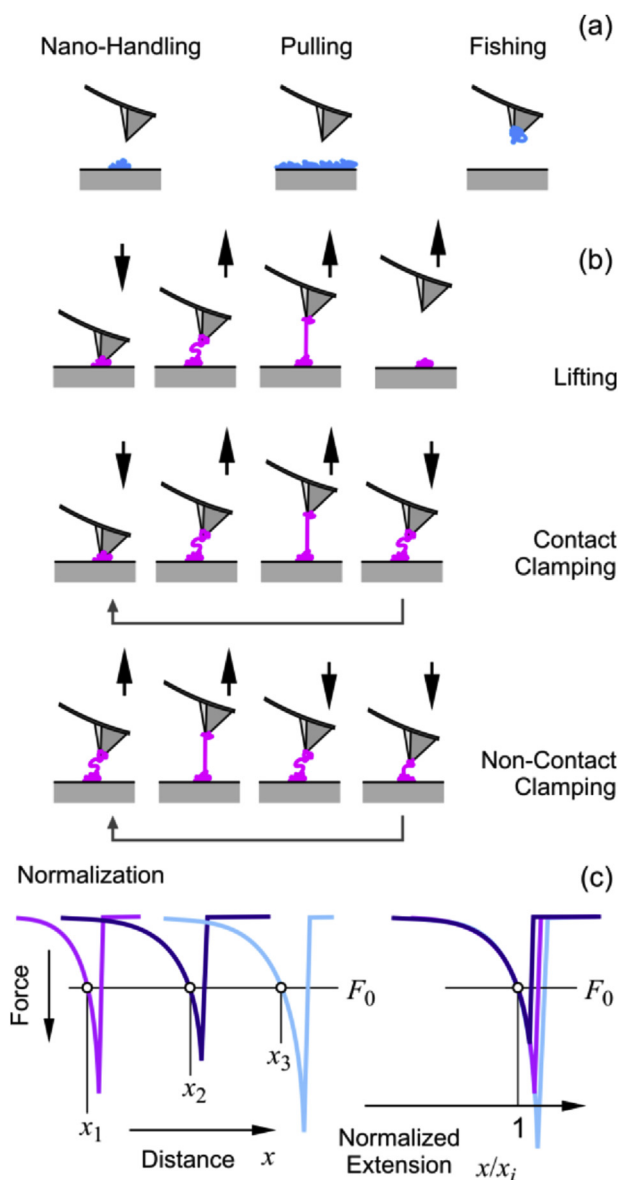
probed by imaging after the force experiment. This approach is similar to a technique proposed earlier [41,42]. The *pulling* technique is by far the simplest to realize and therefore the most popular [5,20]. This method relies on a substrate with an adsorbed polymeric layer, and this substrate is probed with repeated approach-retraction cycles. A bridging event is identified by spikes or plateaus in the force curve. The *fishing* technique is similar, but the polymers are adsorbed to the AFM tip [35,36,43,44].

For all these techniques, whether the polymers will be picked up in a given conformation, and whether they will be stretched or peeled, depends strongly on the solution conditions, the nature of the substrate and the tip, and their surface functionalization. When the affinity of the polymer to the substrate is strong, no events will occur, while when this affinity is weak, peeling events will be observed. Pulling events normally predominate when the affinity is intermediate.

Once a molecule has been picked up, the retraction part of the force curve reveals whether it is being peeled or pulled. The mechanical response of individual polymer molecules can be only extracted from pulling events. Such a response can be obtained in different ways, see Fig. 1b. The *lifting* mode relies on approach-retraction cycles between large separation distances and the contact region [5,20]. In this mode, each bridging polymer molecule detaches from the tip after each retraction. The *contact clamping* mode permits to access the reversibility of the stretching force response of an individual polymer [17,27,29,45]. Thereby, one retracts the tip from the surface only to the point that the polymer is being stretched, but without detaching it. The cycle is completed by approaching the tip again into contact. A hysteresis between the approach and retraction force curves indicates slow conformational transitions or refolding domains [46–48]. In the contact clamping mode, however, one cannot ascertain whether the same or a different polymer molecule is being extended within subsequent cycles. The *non-contact clamping* mode avoids this problem, since the tip is not approached to contact, whereby the polymer chain cannot be easily exchanged. Techniques involving combination of lateral and normal displacement of the tip were equally proposed, but they will not be pursued here [31,39].

Whether an observed pulling event originates from the stretching of a single or several polymer molecules is not necessarily obvious. Several tests were proposed that can be used to identify such events [12,35,41,49]. (1) When one uses the lifting mode, several pulling events may occur in succession upon retraction of the tip. Obviously, the last event likely corresponds to a single molecule. (2) Models of force-extension relationships suggest that the stretching force is only a function of the extension relative to the contour length. Therefore, the force profiles corresponding to single molecules will collapse upon a master curve, when plotted versus the normalized extension that corresponds to a given force, see Fig. 1c. (3) Performing fishing instead of pulling experiments will increase the probability to pick up a single molecule since the polymers are adsorbed on the tip only. (4) Most straightforward is to identify a single adsorbed polymer by imaging, and obviously, force extension experiments carried out in this configuration necessary involve single and isolated molecules only.

The aim of the present article is to demonstrate that not all these tests to identify the stretching response of a single molecule are trustworthy. Only (4) single molecule nano-handling seems reliable, but it may prove difficult to realize. On the other hand, the different tests including (1) last event, (2) master curve, and (3) fishing experiments, may prove unreliable and should be used with caution. We illustrate these facts with pulling experiments carried out with different polymers, and propose alternative tests to identify single molecule stretching response. The polymers used here include amino-functionalized dendronized polymers (DPs) of



**Fig. 1.** Probing the force response of single polymer molecules with the AFM. (a) Techniques used to pick up single polymer molecules. *Nano-handling* involves probing a single adsorbed polymer identified by imaging. *Pulling* lifts single molecules from an adsorbed polymer layer. *Fishing* uses polymers adsorbed to an AFM tip. (b) Available modes to stretch single polymer molecules. The *lifting* mode pulls molecules from contact to large distances after rupture. The *contact clamping* mode repeatedly stretches and relaxes an attached polymer molecule to its maximal extension but contacts the surface in between. The *non-contact clamping* mode also stretches and relaxes a polymer but avoids contacting the surface in between. (c) Identification of single molecule events by force normalization. Recording stretching events versus distance  $x$  and identification of distances  $x_i$  corresponding to the reference force  $F_0$  (left) and superposition of the force profiles versus normalized extension  $x/x_i$ .

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