Chapter 7

End-Grafted Chains in Good-Solvent Conditions: Single Chain Entropic Force, Rupture of a Single Bond and Brush Elasticity

In this chapter, we investigate the polymer elastic properties in good solvent conditions. As a model system we chose the poly(methacrylic acid) PMAA which is water soluble. Using mixed monolayers (to attain low polymer grafting densities), we covalently attached individual and well separated polymer chains to a SFM tip and a substrate. Taking reverse force-distance curves, we observed sharp attractive forces in the nanonewton range. These forces are associated with the rupture of covalent bonds and polymer elasticity. For a polymer alone end-grafted monolayer (relatively high grafting densities), the forward force-distance curves show the distinctive repulsive force associated with polymer brushlike configurations. During the reverse force-distance curve we observed long range attractive forces. We show that these forces appear because of the stretching of individual chains or parts of chains that have adhered to the tip, probably due to physisorption.

7.1 Introduction

Traditionally, the SFA (Surface Force Apparatus) has been used to study polymer properties in good solvent conditions and in confined geometries [1]. Few studies have employed the SFM technique to study the polymer chains in this regime. O’Shea et al. [2] observed brushlike behavior of the block copolymer PEO/PS physisorbed on mica when xylene (selective solvent for PEO/PS) was used as a solvent. Overney et al. [3] used the SFM as “a local probe for elastohydrodynamic lubrication” on a system of end-grafted PS chains.
in toluene. Measurements of the single chain entropic elasticity\(^1\) with SFM have been limited to rather large biological molecules like DNA strands [5] or polysaccharides [6].

Our first objective was to directly observe the stretching and fracture of a single chain. We used poly(methacrylic acid) that contains a terminal thiol group at both ends (HS-PMAA-SH) and it chemisorbs onto gold substrates via a gold thiolate bond forming both “loops” (both ends grafted on the same surface) and “tails” (one end grafted on the surface) [7]. It is expected that the polymer chains have the swollen “mushroom” conformation under water in sufficiently low grafting densities. To attain low grafting densities a 12-mercaptop-1-dodecanole was used to reduce the number of possible grafting sites. The method of mixed solutions (thiol-terminated short molecules and polymer) has an advantage compared with the method of low incubation times in polymer (only) solutions: because of the drastic reduction of surface sites, there should be higher probability of acquiring tails (one thiol end free) than loops. This is a prerequisite in order to tether and stretch a single chain by its end links. The tip used was gold coated. For this particular experiment, we employed an original device, the “molecular tensile tester” (MTT) [11].

Our second objective is to show the response of a polymer brush on forward and reverse Fd-curves. As we have already mentioned similar experiments (force profiles) have been performed with SFA. The main difference from SFA experiments is that in SFM configuration the area of contact is smaller (due to small dimensions of the tip). We used poly(methacrylic acid) that contains a terminal thiol group only at one end (PMAA-SH), chemisorbed on gold substrates from polymer solutions.

### 7.2 Molecular Tensile Tester (MTT)

Experiments on mixed monolayer (HS-PMAA\(_{100}\)-SH and 12-mercaptop-1-dodecanole) were done using an instrument [11] based on magnetic levitation.

An inherent disadvantage of conventional SFM’s, owing to the finite stiffness of the cantilever used, is the inability for sensitive force-distance measurements close to molecular contact. Magnetic levitation offers a new possibility to overcome this essential drawback.

A schematic diagram of the device is depicted in fig. 7.1a. The tip is mounted on a small magnet and placed in a magnetic field produced by a coil. The magnetic force that is exerted on the magnet is proportional to the current that passes through the coil. The intensity of the current is controlled by a feedback system (servo loop) and an optical device, which monitors continuously the real position of the magnet, in such a way that equilibrium is accomplished all the time. Thus, if a perturbation pulls the magnet downwards, the control system increases the intensity of the levitation current. Reversely, if an applied force pushes the magnet upwards, the control circuitry decreases the current.

\(^1\)Bustamante et al. [4] measured the DNA elasticity by applying a magnetic field to a single DNA macromolecule attached by one of its ends to a glass slide and by the other to a tiny (3 \(\mu m\)) magnetic bead.
Figure 7.1: a) Simplified schematic drawing of the experimental set-up b) Forward force-distance curve between a tungsten tip and a mica surface. The attractive part of the force is fitted with the law \( F = -\frac{HR}{6D^2} \) which describes the van der Waals force between a sphere of radius \( R_t \) and a plane at distance \( D \); \( H \) is the material-dependent Hamaker constant.
In this way, the magnet remains at the same position in space and the intensity of the levitation current is a measure of the forces exerted on the tip by the surface.

This surface is placed just below the tip and is ascended slowly by means of a piezoelectric crystal. As soon as the force becomes repulsive and rises above a given threshold, the movement of the piezo is reversed, and the surface withdraws from the tip. During this movement, the position of the magnet (i.e. of the tip) and the applied force on the tip are monitored simultaneously. The force profile that is obtained constitutes a force-distance curve (Fd curve) which provides information about the magnitude and functional dependence of the forces and the elastic and plastic properties of the sample.

Due to feedback, this device does not suffer from instability in the presence of attractive forces, and it allows quantitative and direct measurement of interactions between the tip and the surface down to atomic contact. In (fig. 7.1b) a forward force-distance curve between a tungsten tip and a mica surface is shown. The attractive part of the force is fitted with the law \( F = -\frac{HR}{6D^2} \) which describes the van der Waals force between a sphere of radius \( R \) and a plane at distance \( D \); \( H \) is the material-dependent Hamaker constant.

### 7.3 Experimental Part

#### 7.3.1 Materials

12-mercapto-1-dodecanol (HS-[CH\(_2\)]\(_{12}\)-OH) was synthesized according to methods described in the literature [8]. Thiol-terminated poly(methacrylic acid) was prepared according to the manner reported in ref. [9]. Deionized water used as a solvent. The molecular weight and the molecular weight distribution of the polymer were determined by gel permeation chromatography (GPC) and light scattering. Molecular weight data for the polymers used, are given in table 7.1.

<table>
<thead>
<tr>
<th>polymer</th>
<th>( M_w )</th>
<th>( M_w/M_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS-PMAA(_{100})-SH</td>
<td>9 000</td>
<td>2</td>
</tr>
<tr>
<td>PMAA(_{800})-SH</td>
<td>66 200</td>
<td>2</td>
</tr>
</tbody>
</table>

\((\alpha)\) The subscript refers to the approximate degree of polymerization.

#### 7.3.2 Monolayer Preparation

All the samples were prepared by exposing gold substrates (prepared as described in the subsection 3.2.2) to a water solution of the desired composition of the components. The polymer concentration was 1 mg/ml. HS-PMAA\(_{100}\)-SH and 12-mercapto-1-dodecanole was used for the mixed monolayer (\( x_{PMAA} = 0.85 \)). The mixed monolayer was formed on a gold-coated tungsten tip. PMAA\(_{800}\)-SH alone was used for the brush formation. The
polymer concentration in the solution was kept well below the critical overlap concentration \( c^* \) [10]. After an incubation time of 24 h the gold substrates were removed and rinsed exhaustively with deionized water.

XPS (X-ray Photoelectron Spectroscopy) measurements verified the formation of the PMAA monolayers.

### 7.3.3 Scanning Force Microscopy

In the experiment with the mixed monolayers (HS-PMAA\(_{100}\)-SH and 12-mercapto-1-dodecanole): The surface approaches and withdraws by steps of 0.0866 nm every 1 ms. A tungsten wire was used as a tip. It was first chemically etched and then gold-coated (radius of curvature \( \approx 500 \text{ nm} \)).

Experiments on the PMAA brush (polymer-only samples) were performed with the usual SFM (Topometrix Explorer). Commercially available Si\(_3\)N\(_4\) (V-shaped, force constants 0.032 N/m) cantilevers were used. Force-distance curves (force profiles) were conducted at 0.1 \( \mu \text{m/s} \).

All experiments have been performed under deionized water (PMAA molecules water soluble).

### 7.4 Theoretical Background

#### 7.4.1 Single Chain Elasticity

The stretching of a polymer chain induces a restoring force. This force is entropic in origin, ultimately a consequence of the Brownian impulses acting on the polymer that tend to keep it coiled. The force appears because the number of possible conformations with the given end-to-end distance \( R \) decreases with stretching [10, 12].

We consider an ideal chain in its equilibrium shape. The probability distribution of its end-to-end vector \( R \) is approximately Gaussian:

\[
P(R) \propto \exp\left[\frac{-3R^2}{2Nb^2}\right]
\]

Where \( b \) is the Kuhn statistical length. Thus, the partition function for an end-to-end vector \( R \) is \( Z(R) = CP(R) \), where \( C \) is the normalizing factor and it is independent of \( R \). The free energy of the ideal polymer chain is \( \mathcal{A}(R) = -kT \ln Z(R) = \text{const} + \frac{3kT R^2}{2L} \), where \( k \) is the Boltzman constant, \( T \) is the temperature and \( L \) is the length of the totally stretched chain (length at full extension).

We consider now that the ideal chain is weakly stretched by an external force \( F \) applied to its end links. In equilibrium, the force \( \mathbf{F} \) is counterbalanced by the elastic force \( \mathbf{F}_{el} \) of the chain, \( \mathbf{F} = \mathbf{F}_{el} \). Let the mean end-to-end vector be \( R \) as a result of stretching. Then, \( \mathbf{F}_{el} = -\frac{\partial \mathcal{A}(R)}{\partial R} \), and therefore
\[ F = \frac{3kT}{Lb}R \]  

(7.2)

The force is proportional to the displacement and opposite to the stretching force. Thus, one concludes that an ideal polymer chain obeys the Hooke law.

The Gaussian probability distribution is valid for not-too-large values of \( R \). However, if one uses the freely jointed model the elasticity of a single polymer can be described quite accurately at all extensions.

![Figure 7.2: Normalized end-to-end distance \( R/L \) of a freely jointed chain as a function of the normalized stretching force \( Fb/kT \).](image)

Following the same procedure but using now the the partition function of a freely jointed chain stretched by its ends, the entropic force is inferred to be

\[ F = \frac{kT}{b}L'(\frac{R}{L}) \]  

(7.3)  

where \( L' \) is the inverse Langevin function \( (L(x) = \coth x - \frac{1}{x}) \). Thus, the end-to-end distance \( R \) of a freely jointed chain as a function of stretching force is (Fig. 7.2)

\[ R = L(\coth \frac{Fb}{kT} - \frac{kT}{Fb}) \]  

(7.4)

At the asymptotic limit of \( Fb \gg kT \) (high stretching), equation 7.3 takes the form

\[ F = \frac{kT}{b}(1 - \frac{R}{L})^{-1} \]  

(7.5)
Hence, the value of $R$ (extension) approaches saturation corresponding to total chain extension $L$. This means that close to total extension the force will increase (in absolute value) steeply since the chain cannot be extended further than its total length. Practically, at some point the force will be so large that the chain will break. It is to be expected that this force will be equal to the rupture force of a single bond (either at the backbone chain or the tethers).

### 7.4.2 Brush Repulsive Pressure

It is well known that polymers attached by one end to an interface at relatively high coverage stretch away from the interface to avoid overlapping, forming a polymer brush [13]. The thickness $L_0$ of a brush in good-solvent conditions has been given by Alexander [14] as

$$L_0 = \sigma^{1/2} R_F^{5/3},$$

where $\sigma$ is the grafting density. If two brush-bearing surfaces are closer than $2L_0$ from each other there is a repulsive pressure $P$ between them given by Alexander-de Gennes theory [15, 16] as

$$P(D) \approx \frac{kT}{d^3} \left[ \left( \frac{2L_0}{D} \right)^{9/4} - \left( \frac{D}{2L_0} \right)^{3/4} \right]$$

(7.6)

where $d$ is the mean distance between the grafting points of the chains and $D$ is the distance between the surfaces. The first bracketed term accounts for the osmotic repulsion due to increasing polymer concentration as the surfaces are pushed together. The second bracketed term represents the decrease in elastic energy of the chains as they are compressed. For $D/(2L_0)$ in the range 0.2 to 0.9 the above pressure is approximately exponential and is given by

$$P(D) \approx \frac{100kT}{d^3} \exp\left(-\pi D/L_0\right)$$

(7.7)

This approximation essentially neglects the strong osmotic repulsive forces resulting from the compression of the chains at low $D$. This occurs anyway in a SFM experiment since the tip displaces laterally some of the polymer chains if the repulsive forces become too strong.

The Alexander-de Gennes theory assumes no interpenetration of the polymer brushes. Thus, we can rewrite the above expression for the compression of a polymer brush on a single wall by substituting $2D$ for $D$ and dividing the right-hand side by 2. Hence,

$$P(D) \approx \frac{50kT}{d^3} \exp\left(-2\pi D/L_0\right)$$

(7.8)
7.5 Results and discussion

7.5.1 Single Chain Elasticity and Rupture of a Single Bond

Fig. 7.3 shows a forward-reverse force-distance curve of a treated tip (gold+ HS-PMAA$_{100}$-SH and 12-mercapto-1-dodecanol) and a bare gold substrate taken by the MTT. While the substrate approaches the tip some of the grafted polymer chains (to the tip) tether also to the substrate via a gold thiolate bond. Approaching further towards the grafted layer the polymers are compressed and a repulsive load force is experienced by the tip. The substrate may be moved further in the forward direction until a predetermined loading force is achieved. The direction of the substrate movement is then reversed and the loading force is continuously decreased and finally one enters the adhesive regime where a spatially extensive attractive force is exerted on the tip (adhesive force due to the gold substrate since the chains have been displaced laterally). On further removal from the tip surface we observe 4 steep attractive forces due to stretching of 4 individual bridged polymer chains. At one point the exerted force exceeds the bond strength and the chains break (probably at the relatively weaker gold thiolate bonds).

The sequential and random breaking of the bonds can be explained by the polydispersity of the chains and the roughness of both the substrate and the tip. We believe that the attractive peaks occur relatively close$^2$ to the substrate ($\approx 15$ nm) for the same reasons. It is known that chemically etched tips have large radii of curvature and suffer from morphological irregularities. We have to note that the occurrence of such curves with attractive events is the exception and not the rule. Most of the curves showed no abrupt attractive peaks. This is to be expected since there is a finite and low probability for the covalent bond to occur$^3$. Although the jump to contact is averted, the force resolution is relatively poor because the feedback corresponds to a high effective spring constant and subsequently the force determination is less sensitive.

The attractive peaks are at about 3.5 nN. We can evaluate the rupture force by dividing the experimentally determined bond energies $E_b$ by a length $a$ representative of the range of the force $F$, $F = E_b/a$. Taking $a = 0.15$ nm (since we have a short-range force), for a C-C bond ($E_b \approx 80$ kcal) we have $F_{C-C} \approx 4$ nN and for a Au-S bond ($E \approx 40$ kcal [17]), we get $F_{Au-S} \approx 2$ nN. Since the noise is about 1 nN and our estimation is approximate, it is not clear which bond breaks.

In fig. 7.4 we compare one of the four attractive peaks of the figure 7.3 to the theoretical force necessary to elongate a freely jointed chain of full length $L = 30$ nm with a Kuhn length $b$ twice as long as one monomer unit ($\approx 0.6$ nm). We can see that the steep increase

$^2$The full length of a PMAA chain with polymerization index $N = 100$ is expected to be around 30 nm.

$^3$We note that we did experiments on mixed monolayers with thiol-terminated PMAA from one end only (PMAA-SH). No attractive forces, associated with bond rupture, were observed. Furthermore, measurements on only SH-PMAA-SH monolayers failed also to produce polymer bridging from their ends. This indicates that if no alkanethiol (which reduces the available grafting sites) is used, the formation of loops is favoured.
Figure 7.3: (a) The gold substrate approaches the tip; no force is detected. (b) Substrate-tip contact; repulsive force. (c) Adhesion due to the gold substrate; long-range attractive force. (d), (e) Stretching and rupture of single polymer chains; steep attractive forces. The four attractive peaks correspond to rupture of 4 covalent bonds. We have drawn the theoretical entropic force for a freely jointed chain with $b = 0.6$ nm and $L = 30$ nm.
of the force is predicted quite accurately by equation\(^4\) 7.4. As the end-to-end separation approaches saturation (full polymer length \(L\)), it becomes harder and harder to further stretch the chain. Presumably the breaking of the connection occurs at the weaker bond.

We fit the attractive peaks with a Morse-type force function

\[
F_{\text{Morse}} = -\frac{\partial}{\partial r} V_{\text{Morse}} = 2\beta D_e \left[ \exp[-2\beta(r - r_0)] - \exp[-\beta(r - r_0)] \right]
\]  

(7.9)

where \(D_e\) is the dissociation energy, \(\beta\) is called Morse \(\beta\) parameter, \(r - r_0\) is the deviation from equilibrium distance. We found \(D_e = 0.7\) aJ and \(\beta = 0.9 \times 10^{10}\) m\(^{-1}\). \(D_e\) is in the range of the dissociation energy for a typical covalent bond while for \(\beta\) there is a deviation of 50% to 100% (for a typical covalent bond, \(\beta\) is around 1.5 to \(2 \times 10^{10}\) m\(^{-1}\)); it is clear that we measured a relatively long interaction length. This might indicate that the breaking occurs at the Au-S bond since it is known that covalent bonds involving metals are of longer range \[19\]. However, the long interaction length could also be attributed to 1) the partial superposition of the single chain elasticity; 2) the finite response of the servoloop; 3) the poor definition of zero force since the noise is about 1nN (due to high effective spring constant).

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\(^4\)Although this equation has been derived for an ideal chain, it is expected to hold also for a -real chain in a good solvent- at high extensions, since in this case its average monomer density decreases leading to a weakening of the excluded volume effect \[10, 18\].
7.5. Results and discussion

7.5.2 Brush Elasticity

Two types of force profiles were observed on a PMAA$_{800}$-SH monolayer. Fig. 7.5a shows the first one. During the forward movement, we observe the gradual increasing of the loading force due to the low compressive elasticity of the brush. No adhesive force is observed because in this case the brush steric repulsion screens the interaction with the surface. During the reverse movement, there is negligible adhesion and the polymer brush is decompressed in a largely reversible way.

Fig. 7.5b shows that a simple exponential does describe the SFM data in the regime of intermediate compression of the brush.

Equation 7.8 connects the pressure $P$ that a surface exerts on a brush with the distance $D$. The surface energy $E(D)$ per unit area is related to the force per unit area as

$$E(D) = \int_{D_0}^{D} F(D') dD'$$

thus,

$$E(D) \approx \frac{50L_0kT}{\pi d^3} \exp(-2\pi D/L_0)$$

Our experimental data is plotted in terms of the force $F(D)$ which in the Derjaguin approximation is related to the $E(D)$, $F(D) = 2\pi R_t E(D)$. Hence eq.7.11 is written

![Figure 7.5: (a) First type of force profile observed over a polymer brush. Notice the absence of hysteresis. (b) Logarithmic plot of the forward Fd curve.](image-url)
\[ F(D) \approx \frac{100R_tL_0kT}{d^3} \exp(-2\pi D/L_0) \]  

(7.12)

We can directly check this equation on our data. We fitted several force profiles with the last equation and we obtained \( L_0 \approx 100 \text{ nm} \) and \( d = 16 \text{ nm} \). Apparently, the value of \( L_0 \) is too large. The value of \( d \) corresponds to a mass coverage of about 0.5 mg/m\(^2\) which is rather small. Therefore, we conclude that the Alexander-de Gennes theory describes poorly our data. The discrepancy probably arises from the fact that since our probe is small and spherical, a large proportion of the chains lie near the edge and therefore are expected to bend than to compress. A more appropriate theory must take into account the spherical shape of the tip and the bending of the chains.

Figure 7.6: (a) Second type of force curve observed over a polymer brush. The continuous lines correspond to the theoretical prediction for stretching of individual chains or parts of a chain. (b) Zoom on one of the attractive forces. Note the resemblance with the theoretical curve of fig. 6.2.

The second type of force profiles is shown in fig. 7.6a. The forward Fd curve is essentially the same: gradual increase of the loading force due to gradual compression of the brush. However, during the reverse Fd curve we observe some long-range attractive forces. The full length of one chain should be around 240 nm (since \( N = 800 \) and \( a = 0.3 \text{ nm} \)). All attractive forces occur within a range of 0 to about 200 nm. Their magnitude is in the range of 0.1 to 0.5 nN. Forces in this range can be attributed to monomer physisorption to a surface. Since we observe gradual increase in the first derivative of these forces we attribute them on parts of chains, individual chains and/or small clusters of chains that were adhered to the tip and subsequently stretched during the reverse
movement. The continuous lines correspond to entropic force for a single polymer chain with full length approximately equal to the distance between the contact point \((D = 0)\) and the minimum of each attractive force\(^5\). We have assumed that \(b = 0.6 \, \text{nm}\).

In fig. 7.6b we zoom on an attractive peak (dashed rectangular in fig. 7.6a). For this plot the variables have been reversed \((y = D\) and \(x = F\)) and the absolute value of the force has been used. The experimental curve fits well with the theoretical formula 7.4 that describes the stretching of a single chain.

### 7.6 Conclusions

We investigated the elastic properties of PMAA chains in good solvent conditions. We chemically tethered individual polymer chains to a SFM tip and a gold substrate. By stretching these chains, the rupture of single covalent bonds was directly observed. Taking force profiles on a polymer brush we monitored its compression and the elastic force of single polymer chains. We found that Alexander-de Gennes theory is partly inadequate to describe brush compression via a SFM tip probably due to spherical shape of the tip and chains bending at the edge of the tip-apex. The single chain elastic force was found to agree with the entropic force predicted by the freely jointed chain model.

### References


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\(^5\)Actually, the agreement is better if we use full length that is 1 – 3 nm longer. This is to be expected since the adhesion is rather low and the polymer unstick from the tip not so close to the full length.


