Molecular visualization of brush-like macromolecules on surfaces: molecular conformation and spreading dynamics

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ABSTRACT

FRANK CHEN SUN: Molecular visualization of brush-like macromolecules on surfaces: molecular conformation and spreading dynamics

(Under the direction of Sergei S. Sheiko)

Polymer molecules change their conformation in response to variations of the substrate’s surface energy, vapor pressure of the surrounding environment, and under lateral compression. As such, visualization of brush-like macromolecules as they change their conformation on substrates opens intriguing opportunities for quantitative studies of various interfacial phenomena with molecular (sub-100 nm) resolution. Atomic force microscopy was used to study the conformational switching due to variations in the surface energy, molecular swelling and collapse in asymmetric polymer mixtures, pressure gradient and frictional coefficient within a spreading film, and adsorption-induced scission of covalent bonds. The responsiveness of the molecular brushes allowed us to use them as miniature probes to measure both the pressure gradient and frictional coefficient on the substrate. In addition to conformational changes, we discovered that brush-like macromolecules undergo scission of the covalent bonds that make up their backbone due to physical interaction with the substrate. This significantly expands the range of future applications of branched macromolecules as environmental sensors, mechanical actuators, and reaction accelerators. The process of adsorption-induced bond scission is of first order kinetics and the corresponding rate constant was determined.
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TABLE OF CONTENTS

LIST OF TABLES --------------------------------------------------------------------- vi
LIST OF FIGURES --------------------------------------------------------------------- vii
LIST OF ABBREVIATIONS AND SYMBOLS ----------------------------------------------- x

CHAPTERS

1. INTRODUCTION ------------------------------------------ 1
   1.1. Conformation of Branched Macromolecules on Surfaces 2
   1.2. Spreading of Polymer Melts 7
   1.3. Molecular Visualization 11
   1.4. Experimental Challenges and Rationalizations 13

2. Highlighted Accomplishments-------------------------------- 18

3. Experimental Methods --------------------------------------- 22
   3.1. Materials ---------------------------------------------- 22
         3.1.1. Brush-like Macromolecules 22
   3.2. Sample Preparation ------------------------------------- 24
         3.2.1. Spin-casting of Dilute Solutions 24
         3.2.2. Spreading of Drops 24
         3.2.3. Atomically Flat Substrates 25
   3.3. Experimental Techniques 26
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Molecular characteristics of PBA brush molecules</td>
<td>36</td>
</tr>
<tr>
<td>2.</td>
<td>Surface tensions and interaction energies of varying mixtures of methanol and water</td>
<td>39</td>
</tr>
<tr>
<td>3.</td>
<td>AFM data on molecular dimensions of PBA brushes deposited on a surface of varying mixtures of methanol and water</td>
<td>45</td>
</tr>
<tr>
<td>4.</td>
<td>Time dependence of the film length at different relative humidity (RH)</td>
<td>65</td>
</tr>
<tr>
<td>5.</td>
<td>Properties of the precursor films in different spreading experiments</td>
<td>65</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Brush-like macromolecule (cartoon)</td>
<td>2</td>
</tr>
<tr>
<td>2.</td>
<td>Persistence length of the brush versus side-chain length</td>
<td>3</td>
</tr>
<tr>
<td>3.</td>
<td>Adsorption of a brush from solution (cartoon)</td>
<td>4</td>
</tr>
<tr>
<td>4.</td>
<td>Conformational diagram of brushes with regard to spreading energy and grafting density</td>
<td>5</td>
</tr>
<tr>
<td>5.</td>
<td>Extension of the backbone due to adsorption to the surface (cartoon)</td>
<td>6</td>
</tr>
<tr>
<td>6.</td>
<td>Four different surface conformations for brushes (cartoon)</td>
<td>7</td>
</tr>
<tr>
<td>7.</td>
<td>Spreading of a drop (cartoon)</td>
<td>9</td>
</tr>
<tr>
<td>8.</td>
<td>Examples of different branched macromolecules</td>
<td>11</td>
</tr>
<tr>
<td>9.</td>
<td>Diagram of linear (1-D) and radial (2-D) flow</td>
<td>13</td>
</tr>
<tr>
<td>10.</td>
<td>Example of drops deposited to simulate linear and radial flow</td>
<td>14</td>
</tr>
<tr>
<td>11.</td>
<td>Synthesis of the linear macroinitiator</td>
<td>23</td>
</tr>
<tr>
<td>12.</td>
<td>Visualization of molecules within the precursor film</td>
<td>25</td>
</tr>
<tr>
<td>13.</td>
<td>Schematic of the atomic force microscopy tip and forces</td>
<td>28</td>
</tr>
<tr>
<td>14.</td>
<td>Schematic of tapping mode Atomic Force Microscopy</td>
<td>29</td>
</tr>
<tr>
<td>15.</td>
<td>Diagram of the Langmuir-Blodgett Trough</td>
<td>32</td>
</tr>
<tr>
<td>16.</td>
<td>Schematic of software analysis of a worm-like chain</td>
<td>33</td>
</tr>
<tr>
<td>17.</td>
<td>Compression and expansion isotherms for PBA on different mixtures of methanol</td>
<td>40</td>
</tr>
<tr>
<td>18.</td>
<td>AFM images of conformational changes due to variations of the surface energy of the substrate</td>
<td>43</td>
</tr>
<tr>
<td>19.</td>
<td>Variation of the molecular dimensions of the brushes</td>
<td>44</td>
</tr>
<tr>
<td>No.</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Histogram of the length distributions measured by AFM</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Conformational transition from rod-like to globule (cartoon)</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Brush molecules embedded in a melt of linear chains (cartoon)</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>AFM images of brush molecules embedded in a number of different molecular weights of linear PBA</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>Dependence of the square root of the mean-square radius of gyration of the PBA brush on the degree of polymerization of the surrounding linear PBA chains</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>Three conformational regimes of a brush embedded in a melt of linear chains</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>Spreading of a melt of brushes (cartoon and schematic)</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>Monitoring conformational changes of brushes within the spreading precursor film</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>Measuring film pressure within the spreading precursor film</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>Calibration of the pressure sensors on different surface energies</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Dependence of the side-chain length on the persistence length of the brush</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>Distribution of wetting-induced tensile force</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>Visualization and measurement of the scission process</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>Computer simulation of the scission process</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>Scission process on different surfaces</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>AFM studies of nanoparticles formed by intramolecular collapse</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>Counting of the number of arms for amphiphilic multiarm star polymers</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>AFM studies of dendronized polystyrene</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>AFM studies of dendronized polyferrocenylsilanes</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>AFM studies of single helical polyguanidine chains on graphite</td>
<td></td>
</tr>
</tbody>
</table>
40. AFM studies of single helical polyguanidine chains on silicon -------------- ------95
41. AFM studies of stretched single helical polyguanidine------------------------ ------96
42. Brushes embedded in the precursor film of a spreading linear polymer ---- -----98
43. Brushes undergoing the scission process while 
flowing across the surface --------------------------------------------------------- ------99
44. Effect of variations in the surface energy on the rate of the scission -------- ---- 101
# LIST OF ABBREVIATIONS AND SYMBOLS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>PBA</td>
<td>Poly (n-butyl acrylate)</td>
</tr>
<tr>
<td>$L_n$</td>
<td>Number average contour length per monomeric unit of the backbone</td>
</tr>
<tr>
<td>$N_n$</td>
<td>Number average of monomeric units in the backbone</td>
</tr>
<tr>
<td>$l$</td>
<td>Average contour length of the backbone</td>
</tr>
<tr>
<td>$\mu$m</td>
<td>Micrometers</td>
</tr>
<tr>
<td>pN</td>
<td>Piconewtons</td>
</tr>
<tr>
<td>$l_p$</td>
<td>Persistence length</td>
</tr>
<tr>
<td>$n$</td>
<td>Degree of polymerization of the side-chains of the brush</td>
</tr>
<tr>
<td>$N$</td>
<td>Degree of polymerization of the backbone</td>
</tr>
<tr>
<td>$\phi_a$</td>
<td>Fraction of adsorbed side-chains</td>
</tr>
<tr>
<td>$\phi_d$</td>
<td>Fraction of desorbed side-chains</td>
</tr>
<tr>
<td>$\phi_l$</td>
<td>Fraction of adsorbed side-chains on the left side</td>
</tr>
<tr>
<td>$\phi_r$</td>
<td>Fraction of adsorbed side-chains on the right side</td>
</tr>
<tr>
<td>$S$</td>
<td>Spreading parameter</td>
</tr>
<tr>
<td>$f_\perp$</td>
<td>Force perpendicular to the backbone</td>
</tr>
<tr>
<td>$f_\parallel$</td>
<td>Force parallel to the backbone</td>
</tr>
<tr>
<td>$d$</td>
<td>Width of the brush</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Width between side-chains of the brush</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>$h$</td>
<td>Measured height of the brush</td>
</tr>
</tbody>
</table>
V  Flow velocity
pl  Picoliters
mm  Millimeters
°C  Degrees Celsius
RH  Relative Humidity
HOPG  Highly ordered pyrolytic graphite
DP  Degree of polymerization
NB  Degree of polymerization of surrounding matrix polymer
N  Degree of polymerization of the side-chains (melt study)
NA  Degree of polymerization of the backbone (melt study)
Tg  Glass transition temperature
ATRP  Atom Transfer Radical Polymerization
HEMA-TMS  2-(trimethylsilyloxy) ethyl methacrylate
PBPEM Poly (2-(2-bromopropionyloxy) ethyl methacrylate)
CRP  Controlled Radical Processes
RAFT  Reversible Addition–Fragmentation Chain Transfer
Å  Angstroms
SiO4  Silicon tetroxide
Fd  Repulsive forces due to surface deformation indentation
Fa  Attractive van der Waals forces
Fw  Surface Tension wetting forces
Fc  Forces that cause deflection of the cantilever
A0  Free cantilever amplitude
Asp  Amplitude set by operator
Π  Surface pressure
γ  Surface tension in absence of a monolayer
γ_l  Surface tension of the liquid-air interface
γ_ls  Surface tension of the liquid-solid interface
GPC  Gel Permeation Chromatography
MALLS  Multi-Angle Laser Light-Scattering Detector
SLS  Static Light Scattering
γ_s^p  Contribution of dipole-dipole interactions to the surface tension
γ_s^d  Contribution of dispersion forces
γ_{water}^d  Contribution of polar interactions in pure water
W_{sl}  Work of adhesion
W_s^d  Contribution of dispersion forces
W_{water}^p  Contribution of polar (non-dispersion) between water and polymer
PDI  Polydispersity Index
R_S  Square-root of the mean-square radius of gyration
R  Total radius of the film
R_0  Total radius of the drop
t  time
Σ  Area occupied by an individual molecule
A  Total number of covalent bonds remaining
A_0  Initial number of covalent bonds before scission
k  Rate constant of the scission process
1. Introduction

There is great interest in the structure and flow properties of molecularly thin polymer films, as they are at the heart of many practical applications such as coatings, composites, microfluidics, and lubrication.\textsuperscript{1-24} In some applications, these properties ensure even surface coverage; while in others, molecular flows act as new tools for surface patterning\textsuperscript{25-27} and performing biochemical assays on microchips. The spreading behavior is well studied for thick films.\textsuperscript{28-35} However, there are still many unanswered questions for monomolecular films.\textsuperscript{36-46} Due to the intimate coupling of flow properties to surface-confined molecular conformation and dynamics in monomolecular films, molecular mechanism of spreading, driving forces, and rate-determining dissipation mechanisms remain largely unknown. As such we have set out to investigate the response of molecular conformation to the substrate attraction and to the wetting-induced flow. This response will provide unique information both on the molecular mechanism and dynamics of spreading.

Experimental studies of spreading are significantly hindered by the lack of experimental techniques that have enough sensitivity and resolution to study flow on molecular length scales. To investigate the flow on these length scales, we decided to use Atomic Force Microscopy (AFM) along with “AFM-visible” macromolecules to monitor and probe flow properties on sub-100 nm length scales. In addition to visualization, the brush-like macromolecules are advantageous for this study due to their ability to change
conformation in response to variations in the surrounding environment and interaction with the substrate.

1.1 Conformation of Branched Macromolecules on Surfaces

The branched macromolecules being studied in this work are better known as cylindrical brush polymers or molecular bottle-brushes. They are linear polymers with many densely grafted side chains (Figure 1). The architecture of cylindrical brush polymers can be varied by being densely or loosely grafted, having flexible or stiff side chains, being comprised of homopolymers or copolymers. These chemical variables affect the properties of a brush, but it is the relatively dense grafting that has the greatest effect on their structure and properties. The polymers that were studied in this work feature 100% grafting, i.e. every monomeric unit of the backbone has a side chain grafted to it.

![Figure 1.](image-url) **Figure 1.** Brush-like macromolecules are composed of linear side chains tethered to a polymer chain. This molecular design allows synthetic control of the side chain length, length of backbone, and grafting density.

Due to the high grafting density, the side chains repel each other prompting the backbone to stretch its conformation from a coil-like to an extended chain (Figure 2a). The steric repulsion significantly increases upon adsorption of molecular brushes onto a substrate as the surface confinement further reduces the configurational space available for the side chains. Figure 2b shows an AFM micrograph of monolayers of poly (n-butyl...
acrylate) (pBA) brushes with long side chains that have a degree of polymerization of 15 pBA units. The number average contour length \( L_n \) per monomeric unit of the backbone was measured to be \( l = L_n / N_n = 0.23 \pm 0.02\,\text{nm} \), which is close to \( l_0=0.25 \,\text{nm} \), the length of the tetrahedral C-C-C section. This indicates that the backbone is locally extended adopting a nearly all-trans conformation. The steric repulsion between the side chains also causes global straightening of the backbone reflected in the increase of the persistence length with increasing side chain length. Depending on the side-chain length, the persistence length ranges from 10-5000 nm (Figure 2c), which covers the persistence length of DNA (~50 nm) and approaches that of F-actin (~10 \( \mu \text{m} \)). To extend the chain a substantial amount of tensile force is required. For example, complete extension of a polymer chain requires forces on the order of 100 pN.\(^47\) We show that this tensile force can be capable of rupturing the covalent bonds of the backbone of the molecule (Chapter 7).

**Figure 2.** (a) Schematics of molecular brushes within a dense monolayer. Backbones with a ridge of desorbed side chains provide the height contrast, while adsorbed side chains determine the spacing between the molecules. (b) Atomic force microscopy was used to visualize conformation of pBA brush-like macromolecules on mica. The light threads in the height images correspond to the backbone and the areas between threads are covered by side chains, which cannot be visualized at this scale. (c) Persistence length of the adsorbed macromolecules increases with degree of polymerization of the side chains as \( l_p \sim n^{2.7} \).
In addition to the high grafting density, interaction of side chains with the substrate breaks the symmetry of the molecule. Unlike for regular linear chains, adsorption of cylindrical brushes results in the formation of two partitions (Figure 3): (i) side chains split into adsorbed and desorbed side chains and (ii) side chains that are segregated on the left and right sides of the backbone. This partitioning results in fundamental changes in a diagram of conformational states, which includes a set of well-defined conformations depending on the fraction of adsorbed side chains and left/right asymmetry.

**Figure 3.** Change in conformation during adsorption of brush-like macromolecules on to a surface. The symmetry of the brush molecule is broken when adsorbed on to a surface and can be divided into two partitions. One partition being the adsorbed side chains ($\phi_a$) and the other partition being the desorbed side chains ($\phi_d$). The brush can also be portioned again with side chains on the left ($\phi_l$) and right ($\phi_r$) of the backbone.

Let us first consider a symmetric brush with a 50/50 distribution of side chains adsorbed on the left ($\phi_l$) and on the right ($\phi_r$). In this case, the conformation is solely determined by the fraction of adsorbed chains. Depending on the interaction with the substrate one can distinguish three well-defined conformations: ribbon-like, hemicylindrical, and globule conformation. The ribbon-like conformation exists when all side chains are tightly adsorbed to the substrate (strong adsorption) (top, center of Figure 4). This conformation is energetically favored, as the side chains reduce the systems interfacial energy by increasing the number of contacts between itself and the surface.
This large number of surface contacts leads to an over crowding of side chains on the surface, which extends both the side chains and the backbone leading to the increase of the persistence length. The hemi-cylindrical or ribbon-cap conformation (left, center of Figure 4) exists when the fraction of adsorbed side chains ($\phi_a$) is much less then the fraction of desorbed side chains ($\phi_d$). This conformation is energetically favored, as the desorbed side chains become less extended compared to their adsorbed counterparts. There is also an intermediate regime which features a coexistence of the ribbon-like and hemi-cylindrical or cap conformation (lower left corner of Figure 4). A cap of desorbed side chains emerges on top of the ribbon at a moderate strength of adsorption when the energy loss due to the extension of adsorbed side chains becomes comparable to the energy gain due to adsorption. The persistence length of the molecule decreases with desorption of the side chains as the backbone becomes more flexible. However, the molecules remain rod-like since their conformation is stabilized by those side chains that remain adsorbed on the substrate.

Figure 4. How the spreading parameter (S) and the grafting density affect the conformation of an adsorbed brush-like macromolecule. In our experiments we are dealing with 100% grafted brushes and can see that the brush will transition from a ribbon conformation to a cap-like conformation with decreasing S.
The stabilization of the rod-like conformation is an interesting issue as it concerns the global conformation of molecular brushes. While, the extended conformation is promoted by adsorbed side chains due to strong steric repulsion between them. However, the desorbed side chains can both stabilize and destabilize the backbone. If the side chains are in a good solvent, then the excluded volume repulsion will cause additional extension of the backbone (Figure 5). However, if desorbed side chains are in a poor solvent state (e.g. melt) they tend to coagulate into a spherical drop to minimize the surface energy. This dewetting transition causes axial contraction of molecular brushes followed by a transition to a globular conformation.

![Figure 5](image)

**Figure 5.** Spreading of side chains causes extension of the backbone, while desorption causes coagulation into globule. The side chains cause tension to be created perpendicular and parallel to the backbone. The tension that is perpendicular is shared over all of the side chains while the tension parallel is focused solely upon the backbone of the molecule.

Now we will explore the situation when distribution of side chains is $\phi_r \neq \phi_l$. With one side of the brush having a larger fraction of side chains curvature is induced in the backbone to accommodate the uneven distribution of the side chains (Figure 6B). This effect is referred to as spontaneous curvature due to a stronger repulsion that occurs at a denser grafted side of the backbone.
Figure 6. Brush-like macromolecules on surfaces may adopt four distinct global conformations. A) ribbon-like, B) spontaneous curvature, C) globule, D) hemicylindrical.

Through the use of atomic force microscopy one is able to obtain all of the molecular dimensions including contour length, local curvature, radius of gyration and end-to-end distance. This gives us direct information about both local conformation (determined by extension and flexibility of the backbone) and global conformation (determined by interaction of separated monomeric units). In addition, one can also measure height dimensions and evaluate the thickness of the ribbon of adsorbed side chains and the height of the cap of desorbed chains. This allows quantitative measurements of the fraction of adsorbed side chains, which is a key parameter in determining molecular conformation. Being able to probe our molecules with this kind of precision truly allows us to study the conformational changes that will occur due to varying surface energies or surface pressure. These phenomena will be discussed further in the following Chapters 4 and 6.

1.2 Spreading of Polymers on Surfaces

We know that our macromolecules will undergo various types of conformational changes in response to interfacial interactions at the substrate. These interactions are an
integral part of the film pressure found in flowing films. This two-dimensional gradient of pressure is what drives the flow in thin films; i.e. the pressure progressively decreases with distance away from the drop. Therefore, one can imagine that such macromolecules will also change their conformation within flowing films.

Spreading of liquids on solid surfaces occurs through the formation of a thin (usually monolayer thick) precursor film in front of the macroscopic drop (Figure 7). As stated earlier, the spreading behavior is well studied for thick films; however the molecular mechanism of spreading and the parameters that control the kinetics of flow at the surface is incomplete and controversial. The spreading of molecularly thin films encompasses a number of interesting physical phenomena ranging from diffusion and mixing, to deformation of individual molecules, and manipulation of flow by external fields. However, in thin films there are still many unanswered questions due to the intimate coupling of the driving and frictional forces to surface-confined molecular conformation and dynamics. How do we assess the driving and friction forces that are controlled by the molecular interactions between the fluid and the solid surface? What is the origin of molecular diffusion within flowing monolayers, which enables ordering and mixing of large macromolecules? How do the natural surface heterogeneities (both topographical and chemical) affect the flow rate and flow pattern? How does one separately characterize the linear velocity and mass flux? And finally, what is the effect of flow on molecular conformation and visa versa?
Figure 7. Spreading starts with the formation of a monolayer thick precursor film in front of the macroscopic drop. The macroscopic drop then spreads on top of the precursor film. The precursor film however is perfect for our studies, as it is only a monolayer thick and allows for molecular visualization.

To begin to answer these questions one must remember that the behavior of polymer chains at interfaces differs significantly from that in the bulk. Their conformation and dynamics are strongly influenced by attractive interactions with the surface. On homogeneous substrates the diffusion coefficient of isolated chains of various lengths $N$ scales as $D \sim N^{-1}$ as has been recently confirmed for DNA molecules on lipid membranes. However, if the surface contains impenetrable obstacles or pinning sites one expects a stronger dependence on the chain length. Recently, Granick et al have demonstrated the $D \sim N^{-3/2}$ dependence for diffusion of polymer chains on a solid substrate. For single molecules, this dependence is surprising and may indicate the profound effect of the substrate heterogeneities.

Similar issues as to the chain length dependence of the diffusion coefficient were addressed in monolayers under flow. In some systems, the flow rate was found to be independent of the chain length, which was ascribed to plug flow on homogeneous substrates. Yet, in other systems, a strong dependence on the chain length is observed. This has been attributed to reptation through a network of substrate-pinned molecular
Continuum hydrodynamic theories have been developed to describe the flow of thin films driven by the capillary forces and disjoining pressure. While these theories work well for relatively thick films (with a thickness of order 10 nm), their use for thin films is ambiguous. First, the contribution of the molecular conformation to the disjoining pressure is largely unknown. Second, vigorous discussions continue with respect to the role of different dissipation channels and the molecular mechanism of flow. However, the lack of experimental data for the motion of fluids on the molecular scale leads to considerable ambiguities in the interpretation of the flow behavior of liquid monolayers.

Typically, optical ellipsometry and, more recently, phase-modulated microscopy are used to monitor motion of thin films. However, due to the low resolution, optical techniques fail to answer questions on the molecular mechanism of flow. Methods that can be used for molecular visualization are limited. Fluorescence microscopy was successfully used to study various molecular-scale phenomena. While the analysis of molecular conformation and dynamics is reliable for long and stiff molecules, optical techniques are inaccurate in the case of short and flexible chains, whose overall size and local curvature are below the optical resolution limit.

The unique advantage of AFM is that it allows visualization of molecules in great detail including the contour length and the local curvature. This is possible because AFM is able to probe length scales that are under the resolution of optical techniques. However, the impact of molecular visualization becomes even more significant when the molecules are compressible. The response of the molecular conformation to flow provides
independent measures for the local pressure gradient and friction coefficient that exists within spreading films.

1.3 Molecular Visualization

In recent years, AFM has been successfully used for the visualization of both natural\textsuperscript{72-83} and synthetic\textsuperscript{84-127} molecules. The role of molecular visualization has grown to be especially profound with the synthesis of complex molecules\textsuperscript{128-137} whose structures are difficult to confirm using conventional characterization techniques such as nuclear magnetic resonance and light scattering. This is especially true for molecules that are branched, heterogeneous, and polydisperse. Here, AFM images provide unambiguous proof of the molecular architecture along with accurate analysis of size, conformation, and ordering of molecules on surfaces.\textsuperscript{138-140} During the last few years, the research activity of our group has been focused on visualization of small, individual, and flexible molecules within liquid films.\textsuperscript{141-146}

\textbf{Figure 8.} AFM height images of different branched macromolecules: (a) semi-flexible pBA brushes with the degree of polymerization of the side chains n=9 and backbone N=4000. (b) Four-arm pBA brush molecules. (c) Star-like molecules with 16 p(BMA-b-EO) chains. (d) Spherical molecules of carbosilane dendrimers were clearly resolved by AFM using specially designed ultrasharp AFM tips with a radius of 3 nm.
Figure 8 shows four prominent examples of “fluid molecules” that we have visualized by AFM. In Figure 8a, one can see comb-like polymers with short pBA side chains. At room temperature the material is a viscous liquid with a glass transition temperature of $T_g=-50^\circ C$ and zero-shear viscosity $\eta_0=8340$ Pa·s. Figure 8b shows another brush-like architecture, i.e. four-arm polymer brushes. Figure 8c demonstrates 16-arm star-like macromolecules wherein we were able to resolve every individual arm of p(BMA-b-EO) and thus characterize the arm-length distribution separately from the overall size. To visualize the individual molecules of carbosilane dendrimers of different generations from 5 to 9 whose diameter ranges from 6 to 9 in Figure 8d, special AFM tips were used that have atomically sharp needles on top of a regular Si-tip.

The model properties of molecular brushes are associated with densely grafted side chains that aid in the visualization process in five ways. First, adsorbed side chains separate the molecular backbones: depending on the side-chain length and the grafting density, the intermolecular distance varies from 5 to 100 nm. Second, due to the high grafting density there is a fraction of side chains that aggregate along the backbone above the substrate plane. The ridge of the desorbed side chains with a height of $h\approx1$ nm provides topographic contrast. Third, the repulsion of the adsorbed side chains increases the stiffness of the backbone. Depending on the side chain length, the apparent persistence length ranges from 10-5000 nm enabling measurements of molecular curvature. Fourth, the number of monomeric contacts with the substrate (per unit length of the backbone) increases with the side chain length and the grafting density. This reduces the mobility of adsorbed molecules and aides in their temporal resolution. Fifth,
the brush-like architecture allows tuning the interaction between the monolayer and substrate through the chemical structure of the side chains.

1.4 Experimental Challenges and Rationalizations

While brush-like macromolecules hold great potential to unlocking the mysteries that surround the spreading of molecularly thin films, there are many difficult challenges that surround the experiments. This is caused by several factors, the first of which is involves the deposition of polymer melt for drop studies. For spreading studies, we would like to be able to reproduce the same size drop (~ radius of 100 µm). The size of the drop is dependent upon the sharpness of the object used to apply the drop, and the initial size of the contact area between the drop and the surface. We were able to control this using a nano-positioning stage with x, y, and z-axis control. This allowed us to have finer control over the contact area between the drop and the surface.

![Image](linear_flow.png)

**Figure 9.** In linear flows, the pressure gradient does not depend on the distance \( x \) from the reservoir, i.e. it has the same value all over the film. In radial flows (e.g. spreading drops), the pressure gradient decreases with distance \( r \).

In addition, the spreading behavior depends on the flow geometry (Figure 9). In one-dimensional flows which are relevant to short precursor films, the pressure decreases
almost linearly with distance meaning the pressure gradient is constant along the film. This directly follows the following equation wherein the flow velocity is the same all over the film and equal to velocity of the film edge, i.e. \( V(x) = V \). Therefore, in short films one expects the distance-independent pressure gradient \( -\frac{\partial \Pi}{\partial r} = \zeta \cdot V \). However, the situation is noticeably different in long films due to the radial decrease of the flow velocity within the film \( V(r) = \frac{R}{r} V \), resulting in \( 1/r \) dependence of the pressure gradient.

In order to verify the effect of geometry on the variation of molecular conformation, spreading of drops of different shapes will be investigated (Figure 10). The radial flow geometry can be realized through spreading of tiny liquid drops with a volume \( \sim 100 \text{ pl} \) and radius \( \sim 50 \text{ µm} \) deposited on a solid substrate in a clean environment under controlled temperature and relative humidity. The linear flow can be generated by preparing hemi-cylindrical drops that preferentially spread in the direction perpendicular to the cylinder axis (Figure. 10). Both systems spontaneously generate a monomolecular precursor film with a length up to 1 mm.

**Figure 10.** Microscopic drops of PBA melt of different shapes were deposited using a nano-manipulator and an extra-sharp needle. Hemi-cylindrical (left) hemispherical (right) drops demonstrate linear (1-D) and radial (2-D) spreading, respectively. The arrows indicate the spreading directions.
The second set of difficulties involves control over the spreading rate of the drop, which is directly dependent upon the relative humidity surrounding the drop. The relative humidity, which is a measure of the amount of water vapor in a gaseous mixture of air and water, is very temperature dependent. The amount of relative humidity is very important as it controls the amount of water on our mica surface. This water layer acts as a lubricating layer for our spreading experiments. To remove the possibility of temperature changing our relative humidity, experiments were carried out in an oven set at a constant 25 °C. Different levels of relative humidity were obtained by using saturated salt solutions inside custom designed chambers, which is a well known technique for control the relative humidity. Through these experiments, we would learn that our polymer would not spread on mica at a relative humidity that was less than ~ 88%. We have always wanted to be able to do these experiments in-situ, but have not been able to due because they require such high levels of relative humidity to induce spreading, so all experiments were done ex-situ. The ex-situ experiments were done by exposing our samples to a certain relative humidity level for a selected period of time. However, in-situ experiments can be done on highly ordered pyrolytic graphite (HOPG), since the polymer will spread on the surface at room temperature under ambient conditions. HOPG unfortunately is hydrophobic, so we cannot use different levels of relative humidity to affect the spreading rate.

Now to calibrate our molecular pressure sensors for our spreading experiments control over the substrate surface energy was needed. Modifying solid substrates to have very well-defined surface energies is difficult. Thus to do these experiments we decided to use the Langmuir-Blodgett trough. The subphase for these experiments is most
commonly pure water, which has a surface tension of 72 mN/m. Our first experiments were done by mixing in different fractions of methanol into the water subphase to alter the surface energy. The surface energy of our mixtures was checked using a tensiometer. However we found that the methanol was evaporating faster than the water from our subphase and thus overtime the surface energy of our subphase was changing. This was acceptable for our conformational experiments as the time scale we were working on the subphase was stable. When we switched to doing experiments on mixed subphases that required longer exposure, the solvent mixed into the subphase was switched from methanol to propanol. The switch to propanol was made because it had a closer evaporation rate to that of water.

With the sample preparation difficulties solved, the remaining problems were with the analysis of these samples. Molecular visualization of brushes with long side chains is a fairly simple task. However as the side chain length is reduced the brushes become more flexible and the cap, which is usually recognizable, shrinks in size making the brushes harder to visualize. To increase our resolution sharper atomic force microscopy tips can be used. The tips also have a more flexible cantilever, which is more sensitive to the smaller height variations.

In the proposed research, molecular visualization will be used to characterize the conformation of molecules within liquid monolayers providing accurate measurements of the contour length, fractal dimensionality, persistence length, and radius of gyration. The unique advantage of visualization experiments is that one obtains the molecular dimensions in direct space affording more opportunities for statistical analysis. However, the impact of molecular visualization becomes even more significant when the molecules
are compressible. The response of the molecular conformation to flow provides independent measures for the local pressure gradient and friction coefficient. In addition, pictorial resolution allows fractionation of the visualized molecules by size, branching topology, and chemical composition as well as sorting out the irrelevant species.
2. Highlighted Accomplishments

The experimental research was conducted in collaboration with the synthetic group of K. Matyjaszewski at the Carnegie Mellon University (CMU) and two theoretical groups of M. Rubinstein at the University of North Carolina (UNC), and A.V. Dobrynin group at the University of Connecticut at Storrs (UConn). Well defined macromolecular brushes used in this research were synthesized by Kathryn L. Beers and Hyung-il Lee (CMU). The experimental findings were tested against theoretical predictions for conformation of brush-like macromolecules on surfaces made by Michael Rubinstein (UNC) and Andrey V. Dobrynin (UConn).

Switching conformation. \(^1\) We demonstrated that cylindrical brush molecules switch their conformation in response to variations in the surface energy of the substrate. It was determined that the cylindrical brush molecules abruptly change conformations from ribbon-like to globular upon decrease of the surface energy of the substrate (see Chapter 4 for more detail). We were able to observe the coexistence of the rod-like and globular molecules, which is consistent with the predicted first-order of this conformational phase transition. In addition, we showed that prior to the phase transition brush molecules undergo axial contract of the backbone which offers interesting opportunities for designing miniature molecular actuators and sensors.

Asymmetric mixtures.² In addition to the effect of the surface energy, we studied the conformation of brush molecules imbedded in a matrix of linear chains. Through molecular visualization, we explored the effect the molecular weight of a matrix of linear polymer chains on the conformation of the brush molecules. Swelling of a brush molecule was shown to depend not only on the degree of polymerization (DP) of the surrounding linear chains, \( N_B \), but also affected by the DP of brush’s side-chains, \( N \), which determines the structural asymmetry of the mixed species. The swelling region were observed to be confined between \( N_B \cong N^2 \) and \( N_B \cong N_A/N \), where \( N_A \) is the degree of polymerization of the brush backbone. (see Chapter 5 for more detail). Our experimental findings confirmed the theoretical generalization of the Flory theorem for structurally asymmetric mixtures by Dobrynin and Rubinstein.

Molecular pressure sensors.³ The ability to visualize the shape-responsive macromolecules in motion provided exceptional opportunities for studying the mechanism of fluid transport on nanometer length scales. The visualized variations of molecular conformation due to flow-induced extension of liquid films allowed quantitative measurements of both the pressure gradient and frictional coefficient within the spreading film (see Chapter 6 for more detail). In addition to single-component monolayers, the flow-responsive macromolecules were imbedded in monolayers of linear chains to probe the local film pressure. The brush molecules were shown to change their


³ Xu, H.; Sun, F.; Shirvanyants, D.G.; Beers, K.L.; Matyjaszewski, M.; Rubinstein, M.; Sheiko, S.S. “Molecular Pressure Sensors.” Accepted to Advanced Materials.
conformation during flow indicating that they are sensing the pressure gradient. This suggests that molecular brushes can be used as miniature pressure sensors in other systems.

**Adsorption-induced scission of covalent bonds.** In addition to conformational changes, interaction with the substrate induces tension in covalent bonds of branched macromolecules. We discovered a remarkable phenomenon that molecular brushes with long side chains undergo scission of the backbone covalent bonds, as a result of adsorption onto a substrate. The macromolecule’s self-destruction occurs because its side chains stretch the polymer backbone as the macromolecule struggles to reconfigure and maximize the number of contacts with the substrate. Using molecular visualization, it was confirmed that the process is of first order kinetics and the corresponding rate constant was determined (see Chapter 7 for more detail). The rate constant was shown to strongly depend on the surface energy of the substrate and on the side-chain length. In addition, this research has also led to the preliminary observations of molecular fracture during spreading in response to variations of the film pressure with the flowing film.

**Molecular characterization.** The role of molecular visualization has grown to be especially valuable with the synthesis of complex molecules whose structures are difficult to confirm using conventional characterization techniques such as nuclear magnetic resonance, light scattering, and size-exclusion chromatography. This is especially true for designer macromolecules that are branched, heterogeneous, and

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polydisperse. In addition to confirming synthetic strategies, molecular visualization enables accurate measurements of molecular weight, size, and conformation. Through molecular visualization one obtains molecular dimensions in direct space affording more opportunities for statistical analysis. Moreover, the pictorial resolution enables fractionation of the visualized molecules by size, branching topology, and chemical composition as well as sorting out the irrelevant species. A broad variety of designer macromolecules have been analyzed that were synthesized in the following groups: 5-9 Geoffrey W. Coates at Cornell University, Harm-Anton Klok at the École Polytechnique Fédérale de Lausanne, Ian Manners at the University of Bristol, and Bruce M. Novak at North Carolina State University (see Chapter 9 for more detail). Through these experimental studies it has been shown that atomic force microscopy is able to provide proof of the molecular architecture along with analysis of the size and conformation of molecules.

5 Cherian, AE.; Sun, F.C.; Sheiko, S.S., Coates, G.W. Submitted to J. Am. Chem. Soc.

6 Tang, Hong-Zhi; Garland, Eva R.; Novak, Bruce M.; He, Jiangtao; Polavarapu, Prasad L.; Sun, Frank Chen; Sheiko, S.S. Macromolecules 2007, 40, 3575.


3. Experimental Methods

3.1 Materials

The visualizable molecules that will be used are brush-like macromolecules with a flexible backbone surrounded by a dense shell of side chains. The side chains are what create the space between molecules allowing for individual molecules to be easily visualized. Many different brush-like macromolecules were made for these experiments. The length of the backbone and side chains were varied, but the monomer that made up the side chains for these experiments was poly (n-butyl acrylate) (PBA). Since the brushes are made from PBA and have a glass transition temperature of -50ºC (T_g) they are fluid at room temperature. This is important as it allows the molecule to be sensitive to environmental changes due to its fluid nature and not frozen if the molecule were above T_g.

3.1.1 Brush-like Macromolecules

The brushes are thus made using atomic transfer radical polymerization (ATRP), which was pioneered by our collaborator Krzysztof Matyjaszewski.\textsuperscript{149} The first step in the synthesis of the brush macromolecules is in the preparation of a linear macronitiator. Typically an ATRP macronitiator is prepared by polymerization of a monomer with a protected functional group, such as 2-(trimethyisilyloxy) ethyl methacrylate (HEMA-TMS). The next step is to cleave off the TMS protecting group and esterification with 2-bromopropionyl bromide to yield poly (2-(2-bromopropionoxy) ethyl methacrylate)
The following Figure 11 is a schematic of the approach described above on how to synthesize the multifunctional macroinitiator. After the macroinitiator is prepared various monomers can be attached to the backbone via ATRP from each repeat unit by a grafting from mechanism.\textsuperscript{151}

![Figure 11. Typical synthesis approach of the linear macroinitiator for brush synthesis.\textsuperscript{152}](image)

Using this method macroinitiators with a backbone length from 50 to over 6,000 monomer units can be prepared by controlled radical processes (CRP), the later by reversible addition–fragmentation chain transfer (RAFT). This RAFT prepared backbone is the molecule that is used in the adsorption induced scission study, while the other
molecules that were used in conformational studies were prepared by ATRP. The side chains of the brushes are then added on using ATRP and have ranged from 20 to 200 monomer units by grafting from reactions.

3.2 Sample Preparation

Samples for molecular visualization experiments were prepared by spin-casting, the Langmuir-Blodgett technique (this method will be discussed in Section 3.3.2), and the spreading of drops. There are pros and cons to each technique.

3.2.1 Spin-casting of Dilute Solutions

Spin-casting is a routine and rapid method to prepare uniform films including ultra-thin films and finely dispersed macromolecules. The most common method used when spin coating materials is to start with a dilute polymer solution. The target substrate, which is then covered in the solution, is rotated at speeds between 2,000 to 4,000 revolutions per minute. The solvent then rapidly evaporates to leave a very smooth and high quality film of pure polymer. However, this method does not allow one to control the exact thickness and deposition rate of the molecules on the surface. The process can also induce orientation of the adsorbed macromolecules.

3.2.2 Spreading of Drops

Another method that was used to produce our monolayers for AFM analysis was through the spreading of drops of polymer melt. Small drops (volume ~100 pl and radius ~50 µm) of polymer melt were deposited on the surface of mica using a needle and a
three-axis nano-positioning stage. The drops were then spread on a solid substrate in a clean environment under controlled temperature and relative humidity (RH). The RH was controlled using various salt solutions from 88% to 99% RH. The drops first spread by generating a molecularly thin precursor film (Figure 12). This molecularly thin precursor film is the area of most interest to us.

What is of major importance is that these molecular bottle-brushes are also pressure-responsive and that they change shape upon lateral compression on a substrate (Figure 12). Their shape change is due to the fact that side chains desorb from the surface under lateral compression causing a coiling of the backbone. This response to compression allows us to determine the pressure gradient and frictional coefficient within the spreading film. This result is discussed more detail in Chapter 6.

![Figure 12](image_url)

**Figure 12.** Visualization of the individual molecules within the spreading precursor film. The molecular area per molecule can be seen increasing as we travel from the drop along the flow direction.

### 3.2.3 Atomically Flat Substrates

In general, for the analysis of nanoscale objects the smaller and smaller the object you would like to visualize is the flatter and smoother you need your substrate to be. Otherwise your molecules will wind up being perturbed by the surface of your substrate.
In other words, the size of the particle should be greater than the topographical features of the substrate. Thus the two main substrates that experiments were done on were mica and highly ordered pyrolytic graphite (HOPG). Both mica and HOPG can be described as consisting of a lamellar structure that is composed of stacked planes. The lamellar structures have much stronger forces within the lateral planes than between the planes. This distribution of force explains why both of these samples can be cleaved easily to expose fresh surfaces. Muscovite mica is a layered silicate mineral made up of ca. 10 Å thick silicate sheets bound together by potassium ions. The surfaces are molecularly flat, and, for that reason, mica sheets are extensively used as the substrate in AFM studies. Another key factor is that mica is hydrophilic, which allows for our spreading experiments to be done under high levels of relative humidity. HOPG when cleaved will also produce nearly atomically flat surfaces. The key difference for our experiments between mica and HOPG is that HOPG is completely non-polar and is thus hydrophobic. It can be see in Chapter 6 the importance of using HOPG as the friction coefficient between itself and the polymer brushes is significantly less. This allows the polymer brushes to spread over time without the influence of relative humidity. Both are ideal substrates for doing AFM since they are easily renewable and produce nearly atomically flat surfaces with well-defined structures.

3.3 Experimental Techniques

Molecular visualization was accomplished through the use of atomic force microscopy. This technique allows imaging of individual molecules both as single
species and within dense monolayers. It also allows tracking macromolecules as they diffuse and spread on surfaces.

3.3.1 Atomic Force Microscopy

Atomic force microscopy was invented by Binnig, Quate, and Gerber in 1986, and is one of the foremost tools for imaging, measuring, and manipulating matter on the nanoscale. AFM is part of a microscopy group referred to generally as scanning probe microscopy. The most important difference between AFM and other forms of non-optical microscopy is that it is able to image samples under ambient room conditions. The samples do not have to be placed under destructive artificial conditions, such as drying, sputter coated with metal, vacuum, or freezing. In many cases, AFM allows measurements which are difficult or impossible through other techniques, e.g. conformational analysis and probing of individual macromolecules at the sub-10 nm scale.

In AFM the sample is first adsorbed onto a solid substrate. For the majority of the experiments in this work the solid substrate used was mica. A sample is then analyzed with a sharp tip (with radius of curvature on the order of nanometers) that is mounted on a flexible cantilever, which scans across the sample substrate and probes the interactions between the tip and the substrate. When the tip is brought into close proximity of our sample surface, forces between the tip and the sample lead to deflection of the cantilever. A discussion of the true nature of these forces will not be discussed here. However, regardless of the nature of these forces the deflection of the cantilever is measured using a laser spot that is focused onto the top of the cantilever and reflects back into an array of
photodiodes. How this deflection is interpreted is important to the two main modes of operation of an AFM.

The first mode being contact mode is when the tip is brought into permanent contact with the substrate. A feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample as the tip is dragged along the surface (Figure 13). By measuring the deflection of the cantilever, one is able to map out the height profile of the sample. This allows one to directly determine the size and shape of the features on the surface. In contact mode, one can also measure lateral tip-sample forces to study the friction on different surfaces. While friction measurements are a valuable asset of AFM, the permanent contact between the tip and surface generates shear deformation at the sample surface, which may lead to modification and even damage of soft polymers and thus represents a serious limitation of contact AFM.

**Figure 13.** (a) AFM probe (cantilever with a sharp tip at the end) scans across the substrate surface to measure its topography. (b) In the contact area, one observes deformation of the sample due to the tip indentation and formation of the meniscus due to condensation of the surrounding vapors (usually water). As such, the AFM tip experience a combination of repulsive forces $F_d$ due to surface deformation indentation and attractive van der Waals forces $F_a$ and surface tension wetting forces $F_w$. These forces cause deflection of the cantilever $F_c=F_w+F_a-F_d$, which is measured by the position sensitive detector.
In the second mode of operation known most commonly as tapping mode, the cantilever is oscillated at or close to its resonance frequency (Figure 14). As the oscillating tip is brought closer to the surface, oscillation amplitude, phase, and resonance frequency are modified by the tip-sample interaction forces. By monitoring the variations in the amplitude, they can be transformed into the height profile of the surface features. In tapping mode the AFM tip is only in intermittent contact with the surface, which eliminates lateral forces. This enables the characterization of softer and weakly adhered samples that would be altered by the tip in contact mode.

**Figure 14.** (a) Schematic description of tapping mode AFM when scanning a heterogeneous sample which includes variations in both topography and chemical composition. (b) Schematic description of amplitude and phase detection in the tapping mode. The change in cantilever amplitude from $A_0$ (amplitude of free-oscillating probe) to $A_{sp}$ (set-point amplitude selected by the operator) is used for the feedback mechanism which tracks surface topography. The phase shift, which is larger on viscous, i.e. energy dissipative materials, provides material contrast.

The resolution of AFM is a complex issue which includes many different phenomena, though it is ultimately determined by the force-distance dependence between the tip and the substrate i.e. the greater the slope of the force-distance curve the higher the resolution. Another key factor to resolution in AFM revolves around the radius of curvature of the tip. Typically, the commercial Si probes used in these experiments have
a radius of about 10 nm. However ultra-sharp probes have been developed that have tips with a radius of curvature of approximately 1 nm.

The main use of the AFM in this research is the visualization of the conformation of individual polymer brush molecules through the use of tapping mode.

3.3.2 Langmuir-Blodgett Technique

One of the methods used to prepare samples for AFM analysis is the Langmuir-Blodgett Technique. Langmuir-Blodgett films are a combination of the work done by Irving Langmuir on floating monolayers on water\textsuperscript{166} and Katherine Blodgett on sequential monolayer transfer.\textsuperscript{167} Films that are a few molecular layers in thickness to films that are monomolecular in thickness can be produced with this technique. Organic thin films can also be deposited on solid substrates by other techniques such as thermal evaporation, sputtering, electrodeposition, molecular beam epitaxy, adsorption from solution, self-assembly, etc…\textsuperscript{168} The advantage the Langmuir-Blodgett technique has over these other techniques is that it enables (1) the precise control of the films thickness, (2) homogeneous deposition of the film over large areas, (3) the possibility of making multilayer structures with varying layer composition, and (4) the ability to deposit films onto any kind of solid substrate.\textsuperscript{169,170}

The first step in producing a Langmuir-Blodgett film is to select a molecule that is in insoluble with water. The molecule should then be dissolved in a volatile solvent that is insoluble and will spread across the surface of water. The solvent most commonly used in these experiments was chloroform. The solution is placed onto the surface of water drop-wise using a syringe where it spreads quickly to cover the surface area of the trough.
The purpose of using a volatile solvent is that as the solvent evaporates it leaves the molecules on the surface of the water.

At first when the area of the trough is greater than the area covered by the molecules, often there is space between adjacent molecules thus making their intermolecular interactions weak. The best way to describe the molecules is that they are in a two-dimensional gas phase. To create the Langmuir Film, a barrier system is used to reduce the amount of available surface area. As the area between the molecules is reduced, the molecules begin to exert a repulsive effect on one another. This repulsive effect is referred to as surface pressure ($\Pi$), and is given by the following relationship as:

$$\Pi = \gamma - \gamma_o,$$

where $\gamma$ is the surface tension in absence of a monolayer and $\gamma_o = \gamma_l + \gamma_s$ is the surface tension with the monolayer which includes the liquid-air and liquid-substrate interfacial energies. Reducing the area available to the monolayer film through the movement of the barriers allows us to study the conformation of our molecules under different amounts of film pressure.

After a desired pressure is achieved the monolayer needs to be transferred onto a solid substrate to be studied (Figure 15). The transfer process is accomplished by dipping a solid substrate up through the monolayer. The solid substrate most commonly used in these experiments is mica. The instrument compensates for the removal of film onto the solid substrate by adjusting the barriers to keep a constant film pressure during the dipping process. If desired multiple layers can be deposited by passing the substrate through the film an additional number of times.
In this work, the Langmuir-Blodgett technique was used for many different purposes. These include: 1) the preparation of dense monolayers with a defined molecular density, 2) characterization of the molecular weight, 3) analysis of the effect of the pressure and surface energy on the conformation of our brush polymers. To study the effects of surface energy a pure water surface was not always the subphase used for our experiments and will be discussed in more detail in Chapter 4 and 7.

3.4 Image Analysis

To analyze our AFM images and obtain details about the molecules dimensions, a graduate student in our group, David Shirvanyants, has developed computer software to aid us in this task. The developed software is designed to identify individual molecules on a surface and record coordinates of their contour. The recorded coordinates allow quantitative analysis of the contour length, local curvature, radius of gyration and end-to-end distance. The developed software allows for the quantitative analysis of the...
conformation of individual molecules including the contour length, and local curvature, along with positional and orientational correlations of molecules within a dense film.

**Figure 16.** AFM image of a wormlike chain. The solid line shows the backbone, while the dashed line is the shortest route between the ends calculated by the software.
4. Conformational Switching in Response to the Energy of Interaction with the Substrate

Abstract

Cylindrical brush molecules adsorbed on a surface change the contour length and then switch conformation from rod-like to globular upon decrease of the surface energy of the substrate. The conformational changes result from partial desorption of poly(\(n\)-butyl acrylate) side chains as the surface pressure drops from 23.7 to 3.1 mJ/m\(^2\) and the energy of interaction between the side chains and the substrate decreases from 89.7 mJ/m\(^2\) to 69.1 mJ/m\(^2\). At the lowest value of the interaction energy, one observes a coexistence of rod-like and globular molecules. This result is in agreement with the theoretical prediction of the rod-globule transition of surface confined brush molecules as a conformational phase transition of the first order.

Introduction

Shape responsive molecules can be designed based on the so-called molecular bottlebrushes\(^{172,173}\). For these molecules, the conformation is largely controlled by the densely grafted side chains. In solution, steric repulsion between the side chains results in a worm-like conformation of cylindrically shaped molecules, in which the persistence length increases with the side chain length and the grafting density.\(^{174-178}\) On a surface, the conformation depends on the fraction of adsorbed side chains.\(^{179-181}\) Adsorption of side chains causes extension of the backbone due to steric repulsion of the chains, while
desorption and attraction of desorbed side chains promotes a change in conformation from worm-like to globular. Adsorbed side chains reduce the systems interfacial energy by increasing the number of contacts with the surface; however, this occurs at the expense of the entropy which decreases due to extension of the side chains as well as the backbone. Recently, we have shown that this enthalpy-entropy interplay leads to a rod-globule conformational transition upon desorption of side chains caused by lateral compression of a water supported monolayer. This transition was shown to be a conformational phase transition of the first order. Additional experiments were carried out to show that this transition is pure molecular in nature, as it was also observed for single molecules. In one of the previous papers, we predicted that a similar transition can occur upon decreasing the surface energy of the substrate.

Here we report on the axial contraction followed by rod-globule transition of cylindrical brushes in response to the decrease in the energy of interaction between brush molecules and the underlying substrate. The interaction energy was varied by changing the substrate composition via mixing water (higher surface energy) and methanol (lower surface energy). As the interaction energy dropped from 89.7 mJ/m² on the pure water to 69.1 mJ/m² on the 79/21 wt./wt.% water/methanol mixture, brush molecules with poly(n-butyl acrylate) side chains demonstrated a transition from a rod-like to a globular conformation. These results support our recent studies of the rod-globule transition caused by exposing brush molecules to vapors of ethanol. In the transition region, one also observes a coexistence of the globular and the rod-like conformations. The coexistence of two conformations is in agreement with the theoretical prediction of the first order phase transition.
Experimental Section

Materials. Cylindrical brushes with poly(n-butyl acrylate) (PBA) side chains were prepared by the grafting of n-butyl acrylate (nBA) from a poly(2-(2-bromopropionyloxy)ethyl methacrylate) (pBPEM) macroinitiator using atom transfer radical polymerization (ATRP).\textsuperscript{184-188} Using this synthetic technique one can prepare brush molecules with a well-defined degree of polymerization of the main chain and uniform distribution of the side chains along the backbone.\textsuperscript{8,189,190} In this work, we studied only one type of brushes for which the degree of polymerization of the backbone was measured to be N=567 and the degree of polymerization of the side chains to be n=35 (Table 1).

Table 1. Molecular characteristics of PBA brush molecules.

<table>
<thead>
<tr>
<th>n</th>
<th>m\textsubscript{n}^{a)}x10^6</th>
<th>N \textsuperscript{b)}</th>
<th>M\textsubscript{n}\textsuperscript{c)}x10^6</th>
<th>M\textsubscript{h}\textsuperscript{d)}x10^6</th>
<th>n\textsubscript{n}\textsuperscript{e)}</th>
</tr>
</thead>
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<td>15</td>
<td>567±35</td>
<td>2.7±0.15</td>
<td>2.5±0.22</td>
<td>35±3</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a)} number average molecular weight of the macroinitiator (backbone).
\textsuperscript{b)} number average degree of polymerization of the backbone \( N = \frac{m_n}{m_0} \), where \( m_0=265 \) – molecular weight of BPEM monomeric unit.
\textsuperscript{c)} number average molecular weight determined by MALLS-GPC, \( dn/dc=0.068 \).
\textsuperscript{d)} number average molecular weight determined by the AFM-LB method.
\textsuperscript{e)} the number average degree of polymerization of the side chains was determined as \( n_n=(M_n-m_n)/N_nM_0 \), where \( M_n \) –number average molecular weight of the PBA brush measured by MALLS-GPC, \( m_n \) –number average molecular weight of the main chain determined by MALLS-GPC of the macroinitiator, and \( M_0=128 \) – molecular weight of BA monomeric unit.

Characterization. Average molecular weights and molecular weight distribution were measured by gel permeation chromatography (GPC) equipped with Waters microstyragel columns (pore size 10\textsuperscript{5}, 10\textsuperscript{4}, 10\textsuperscript{3} Å) and three detection systems: a
differential refractometer (Waters Model 410), multi-angle laser light-scattering (MALLS) detector (Wyatt, DAWN EOS), and a differential viscometer (WGE Dr. Bures, \(\eta\)-1001). The 90° detector was calibrated using toluene. All other detectors were normalized to the 90° signal. The refractive index increment \(dn/dc\) was determined with an Otsuka Photal RM-102 differential refractometer. Static light scattering (SLS) measurements were done using a Brookhaven Goniometer equipped with a Coherent argon laser using the 514 nm line, an operating power of 20-100mW, and an angle range of 15-155°. Solutions were made with a concentration range from \(10^{-4}\) to \(10^{-2}\) g/ml in THF that had been filtered using 0.2\(\mu\)m NALGENE PTFE filters.

**Sample Preparation.** Monolayers of brush molecules were prepared by the Langmuir-Blodgett technique using a KSV-5000 instrument filled with double-distilled water (Milli-Q). Compressed monolayers were transferred onto a mica substrate at 25°C and a transfer speed of 1.0 mm/min. During transfer, the pressure was kept constant. A transfer ratio of 0.98 was determined separately by using a larger substrate at the same transfer speed. A value close to unity indicates that the transfer did not cause significant changes in the mass density of the water-supported monolayer.

**Measurements.** AFM images were collected using a Multimode Atomic Force Microscope (Veeco Metrology Group) equipped with a Nanoscope IIIa control station in tapping mode. We used Si cantilevers (Mikromasch-USA) with a resonance frequency of about 140 kHz and a spring constant of about 5 N/m. The radius of the probe was less than 10 nm. To ensure accurate counting of visualized molecules, several images were
collected from the same sample but in different areas, using different scan sizes and scan directions. For every sample an average of 300 molecules were counted. The counting was performed using a custom software program for analysis of digital images. The program identifies the molecular contour and determines the contour length, the end-to-end distance, and the curvature distribution.

**Results and Discussion**

To create a change in the interaction energy between PBA brushes and the subphase used in the Langmuir-Blodgett technique, methanol was mixed into the traditional water subphase. Methanol was chosen because of its low surface energy ($\gamma = 23$ mN/m at 25°C) and because it is completely miscible with water ($\gamma = 72$ mN/m at 25°C). By increasing the percentage of methanol in the water subphase the interaction energy as well as the surface tension of the mixture decreased. The mixtures along with the corresponding surface and interaction energies are depicted in Table 2.
Table 2. Surface tensions and interaction energies of varying mixtures of methanol and water.

<table>
<thead>
<tr>
<th>percentage of methanol</th>
<th>$\gamma_s^a$, mN/m</th>
<th>$\gamma_s^p$, mN/m</th>
<th>$\phi^c$</th>
<th>$\pi^d$, mN/m</th>
<th>$W_{sl}^e$, mJ/m²</th>
<th>$W_p^f$, mJ/m²</th>
<th>$\phi^g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>70.3</td>
<td>50</td>
<td>0</td>
<td>23.7</td>
<td>89.7</td>
<td>38</td>
<td>0</td>
</tr>
<tr>
<td>5%</td>
<td>60.8</td>
<td>40</td>
<td>0.20</td>
<td>15.9</td>
<td>81.9</td>
<td>31</td>
<td>0.19</td>
</tr>
<tr>
<td>10%</td>
<td>55.3</td>
<td>35</td>
<td>0.30</td>
<td>11.2</td>
<td>77.2</td>
<td>26</td>
<td>0.32</td>
</tr>
<tr>
<td>15%</td>
<td>51.1</td>
<td>31</td>
<td>0.38</td>
<td>6.8</td>
<td>72.8</td>
<td>21</td>
<td>0.45</td>
</tr>
<tr>
<td>20%</td>
<td>48.8</td>
<td>29</td>
<td>0.42</td>
<td>3.9</td>
<td>69.9</td>
<td>19</td>
<td>0.50</td>
</tr>
<tr>
<td>21%</td>
<td>47.2</td>
<td>27</td>
<td>0.46</td>
<td>3.1</td>
<td>69.1</td>
<td>18</td>
<td>0.53</td>
</tr>
<tr>
<td>22%</td>
<td>46.7</td>
<td>26.5</td>
<td>0.47</td>
<td>2.7</td>
<td>68.7</td>
<td>17</td>
<td>0.55</td>
</tr>
</tbody>
</table>

a) surface tension of the subphase according to percentage of methanol in water (± 0.2 mN/m).
b) contribution of dipole-dipole interactions to the surface tension of the subphase $\gamma_s^p \equiv \gamma_s - \gamma_s^d$, where $\gamma_s^d = 20 \pm 2$ mN/m is the contribution of dispersion forces.
c) the fraction of methanol at the free surface of the subphase was calculated as $\phi \equiv 1 - \frac{\gamma_s^p}{\gamma_{water}^p}$, where $\gamma_{water}^p = 50 \pm 2$ mN/m is the contribution of polar interactions in pure water.
d) surface pressure from the isotherms measured at high compressions, i.e. for thick films.
e) the interaction energy (or work of adhesion) $W_{sl} = \pi + 2\gamma_l$ was determined for thick PBA films at large compressions, using $\gamma_l = 33$ mN/m - the surface tension of PBA and $\pi$ - the surface pressure measured for thick films at high degrees of compression.
f) contribution of polar interactions to the interaction energy $W_{sl}^p \equiv W_{sl} - W_s^d$, where $W_s^d \equiv 2\sqrt{\gamma_s^d \cdot \gamma_l^d}$ is the contribution of dispersion forces and $\gamma_l^d \equiv \gamma_l = 33$ mN/m – surface tension of PBA at 25ºC.
g) the fraction of methanol at the free surface was calculated as $\phi \equiv 1 - \frac{W_{sl}^p}{W_{water}^p}$, where $W_{water}^p \equiv 38$ mJ/m² is the contribution of polar (non-dispersion) interactions between PBA and water molecules.

The Langmuir Blodgett experiments were all run under the same experimental conditions except for variations in the subphase. The surface pressure-molecular area isotherms from those experiments are shown in Figure 17. The isotherms all have the same main features in that each has two distinct plateaus that occur at the same critical
molecular areas. The only difference between the curves is the location of the pressure onset and the maximum pressure achieved. In fact, the curves obtained on water/methanol mixtures can be collapsed onto the water curve by shifting the curves along the \( \pi \)-axis.

**Figure 17.** Compression-expansion isotherm for PBA brushes at different percentages of methanol mixed in water: A–0% (no methanol), B–5%, C–10%, D–20%, E–21%, F–22%. Squares (■) on the isotherms show the area per molecule and pressure at transfer. Decreasing the surface energy has a profound affect on the maximum pressure achieved during compression.

The difference in the curves can be clearly seen that with changing surface energy one gets a decrease in the overall surface pressure \( \pi = \gamma_s - \gamma_f \), where \( \gamma_s \) and \( \gamma_f \) are the surface energies of the subphase and the free energy of the film (per unit area), respectively. For thick films, i.e. at large degrees of compression, the free energy of the film is mainly determined by the surface energy of the film and the interfacial energy, i.e. one can write \( \gamma_f \approx \gamma_i + \gamma_{sl} \), where \( \gamma_i \) is the surface energy of the poly(n-butyl acrylate) film (liquid at room temperature) and \( \gamma_{sl} \) is the interfacial energy at the film-subphase.
interface. One can also determine the interaction energy or the work of adhesion between PBA and a water/methanol substrate as $W_{sl} = \pi + 2\gamma_l$. Table 2 summarizes the surface tensions $\gamma_s$ and the interaction energies $W_{sl}$ calculated for different subphases at large compressions where the surface pressure levels off. Both the surface tension and the interaction energy reduce with larger fraction of methanol. This indicates that the interaction between the PBA film and the water/methanol subphase is largely determined by the strong dipole-dipole interactions between the polar acrylate units and water molecules. The number of acrylate/water contacts decreases upon addition of methanol to the subphase.

In the first approximation assuming that contributions of different types of interactions are additive, the interaction energy is a sum of dispersion forces and non-dispersion (polar and hydrogen bonding) interactions, i.e. $W_{sl} = W_{sl}^d + W_{sl}^p$. The dispersion contribution can be calculated as $W_{sl}^d \equiv 2\sqrt{\gamma_s^d \cdot \gamma_l^d}$, where $\gamma_s^d$ and $\gamma_l^d$ are the dispersion force contributions of the surface tensions of the water/methanol subphase and the PBA liquid, respectively. Using literature data $\gamma_s^d = 20 \pm 2$ mN/m for water/methanol and $\gamma_l^d \approx 33$ mN/m for PBA, one can calculate the contribution of non-dispersion (polar and H-bonding) interactions in excess of dispersion force interactions as $W_{sl}^p \equiv W_{sl} - 2\sqrt{\gamma_s^d \cdot \gamma_l^d}$. In the same way, one can also calculate the contribution of polar interactions to the surface tension of the water/methanol subphase, i.e. $\gamma_s^p \equiv \gamma_s - \gamma_s^d$, where $\gamma_s^d = 20 \pm 2$ mN/m is the contribution of dispersion forces. The obtained values are summarized in Table 2. Note that both the $\gamma_s^p$ and $W_{sl}^p$ decrease with fraction of
methanol in a similar fashion. From these data, one can roughly estimate the fraction of methanol molecules at the free surface of the subphase which differs from the percentage of methanol in bulk solution (Table 2). The addition of methanol results in depletion of water molecules at the free surface. This corroborates our conclusion that non-dispersion interactions between PBA side chains and water molecules dominate the interfacial interactions in these systems.

The first plateau region is of greatest interest in this experiment because it is the location of the rod-globule transition. Thus in the experiment different subphases with different fractions of methanol were examined until the phase transition region occurred. For each different subphase, a monolayer of PBA brush molecules was transferred on mica at a low pressure of about 0.5 mN/m. The LB monolayers were examined by AFM. The AFM technique was vital to this experiment as it allowed visualization of the changes in individual molecules because of variation of surface energy. Figure 18 shows a series of AFM micrographs obtained for different fractions of methanol in water. The white threads in the images correspond to the backbone, whereas extended side chains cover the areas between the threads. As the fraction of methanol is increased, the molecules change their conformation.
Figure 18. AFM micrographs (cropped from 2 x 2 µm² images) of monolayers of PBA brushes transferred on mica at different percentages of methanol in water: A–0% (no methanol), B–5%, C–10%, D–20%, E–21%, F–22%. One can see the obvious change in conformation as the fraction of methanol is increased. Multiple images of each sample were analyzed to obtain molecular dimensions of the PBA brushes.

One can discriminate two types of conformational changes. First, the average contour length of the brush molecules decreases. Second, at a certain fraction of methanol the rod-like molecules undergo a transition to a globular conformation. While it is hard to see from the figure, the distance between molecules does not change significantly before collapse into a globule. The intermolecular distances and the lengths of brush molecules can be independently measured by AFM. The obtained results are summarized in Table 3 and plotted in Figure 19 which shows variations in the length and the distance between molecules upon adding methanol to the water subphase.
Figure 19. Variation of molecular dimensions of the polymer brushes as a function of surface tension: (■) distance between backbones and (●) number average contour length $L_n$. The lines on the Figure are only to show the trend in the data and have no quantitative meaning. The plots show that the average length of the molecules decreases, but the distance between molecules virtually remains the same after the addition of methanol to the subphase.

The lines in the figure are only there to guide the reader and to show that there is a small decrease in the distance as methanol is added to the subphase, while the length changes significantly. After the initial decrease in the distance, it nearly remains constant at 44 nm after more methanol is introduced into the subphase. The length of brush molecules demonstrates an opposite behavior. The length decreases only slightly at small fractions of methanol, while it drops significantly when more methanol is added into the water subphase. In total, the length shrinks by a factor of 1.5 as the surface pressure decreases from 23.7 to 3.1 mN/m. Note that on pure water the molecular backbone is almost fully extended, since the length per monomeric unit $l_m = \frac{L_n}{N_n}$ is equal to $0.23\pm0.02$ nm (Table 3), which is close to the length $l_0 \approx 0.24$ nm of a monomeric unit in
an all-trans polymer chain. The observed length variation is in agreement with theory. As the energy of interaction with the substrate is decreased the number of side chains that detach from the surface and collapse onto the backbone becomes greater. With less side chains in contact with the surface, the backbone is no longer forced into extension but can relax and more curvature can be seen as in Figure 18D. The area per molecules was also determined by AFM and is solely dependent upon the length of the molecules, as the distance between molecules remains constant (Table 3). These rod-like molecules could thus be thought of as molecular springs or actuators whose length is sensitive to changes in pressure but also to the surface energy of the material that they are on.

Table 3. AFM data on molecular dimensions of PBA brushes deposited on a surface of varying mixtures of methanol and water.

<table>
<thead>
<tr>
<th>fraction of methanol</th>
<th>$D^a$, nm</th>
<th>$L_m^b$, nm</th>
<th>PDI$^c$</th>
<th>$A_{AFM}^d$, nm$^2$</th>
<th>$A_T^e$, nm$^2$</th>
<th>$l_m$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>51±2.0</td>
<td>128</td>
<td>1.13</td>
<td>6595</td>
<td>6249</td>
<td>0.23</td>
</tr>
<tr>
<td>5%</td>
<td>47±2.0</td>
<td>122</td>
<td>1.15</td>
<td>6009</td>
<td>5906</td>
<td>0.22</td>
</tr>
<tr>
<td>10%</td>
<td>44±2.3</td>
<td>114</td>
<td>1.16</td>
<td>5382</td>
<td>5344</td>
<td>0.20</td>
</tr>
<tr>
<td>15%</td>
<td>43±3.1</td>
<td>111</td>
<td>1.19</td>
<td>5116</td>
<td>5194</td>
<td>0.19</td>
</tr>
<tr>
<td>20%</td>
<td>44.5±1.4</td>
<td>96</td>
<td>1.15</td>
<td>4480</td>
<td>4602</td>
<td>0.17</td>
</tr>
<tr>
<td>21%</td>
<td>44±4.8</td>
<td>82</td>
<td>1.07</td>
<td>4140</td>
<td>4495</td>
<td>0.14</td>
</tr>
<tr>
<td>22%</td>
<td>N/A$^f$</td>
<td>N/A$^f$</td>
<td>N/A$^f$</td>
<td>4100</td>
<td>4179</td>
<td>N/A$^f$</td>
</tr>
</tbody>
</table>

$^a$) number average distance between brush molecules.
$^b$) number average contour length of brush molecules.
$^c$) length polydispersity index PDI=$L_w/L_m$ of brush molecules.
$^d$) number average area per brush molecule ($\pm$ 200 nm$^2$).
$^e$) number average area per brush molecule measured during the LB transfer.
$^f$) the values could not be determined due to coalescence of molecules.

Qualitative changes in conformation were observed as the surface pressure of the film decreased to 3.1 mN/m and the interaction energy decreased to 69.1 mJ/m$^2$ for a
mixture of 21% methanol in water. At this value of the interaction energy, poly($n$-butyl acrylate) brushes demonstrate a transition from a rod-like to a globular conformation. Moreover, Figure 18E shows a coexistence of two conformations, i.e. rods and globules at the same temperature and the same surface pressure. The coexistence can be demonstrated by constructing a histogram of the length distributions for different fractions of methanol as seen in the AFM micrographs (Figure 20). One can see that with increasing percentages of methanol the histogram shifts further to the left because of decreasing average length. However at 21%, the size distribution reveals two peaks corresponding to the two different species. The peaks are blurred together because the difference in linear dimensions between the rods and globules in the transition region is small.

![Figure 20](image)

**Figure 20.** Histograms of the length distribution measured by AFM: Water (— — —), 10% (●●●), 20% (—■—), 21% (——). The length distribution shifts to the left and becomes narrower as the fraction of methanol is increased. At 21% there are two separate peaks showing the coexistence of the rod and globule phases.

In the next mixture observed all of the rods have completely collapsed into globules at 22% methanol in water. Thus the rod-globular transition is very sensitive to
the surface energy of the subphase. One can see in Figure 18F, the small globules and much larger ones that form when small globules coalesce together. Further samples show even greater coalescence of molecules into larger globules.

The following illustration (Figure 21) depicts the pathway for the conformational changes for the rod-globule transition. In Figure 21A, the side chains of the molecule are adsorbed on the water subphase where the adsorbed side chains cause extension of the backbone. As described earlier the adsorbed side chains reduce the systems interfacial energy by increasing the contacts with the surface. Upon decrease of the interaction energy by the addition of methanol as depicted in Figure 21B some of the side chains detach from the surface and coil up upon the backbone. As some side chains leave the surface, other side chains that remain adsorbed on the substrate begin to coil to gain back some of the entropy lost by extension. At this stage the backbone remains extended showing only weak changes in the average contour length of brush molecules. As the PBA/water interaction is further decreased by addition of more methanol, more side chains detach from the surface but the distance between molecules remains constant because the backbone starts to contract as depicted in Figure 21C. The contraction is also favored by attraction and aggregation of desorbed side chains. Note that on this stage the molecules remain rod-like since their conformation is stabilized by those side chains that remain adsorbed on the substrate. Finally, as shown in Figure 21D, by further increasing the methanol fraction, the rod-globule transition occurs in which the desorbed side chains aggregate into a globule while the desorbed side chains form a circular corona around.
Figure 21. Illustration of the rod-globule transition upon decreasing the interaction energy: A) side chains are adsorbed to the surface and backbone is extended, B) side chains begin to detach and collapse on the backbone; those side chains that remain adsorbed on substrate get more space to coil and reduce their extension, C) further desorption of side chains allows the backbone to contract from its extended state, D) aggregation of desorbed side chains causes the molecule to go from rod-like to globular.

Conclusion

Cylindrical brush molecules do indeed switch conformations from rod-like to globular upon decrease of the surface energy of the substrate. These types of molecules can serve a dual purpose as they can act as pressure sensors, but also react in response to changes in the surface energy of a substrate they are spread upon. AFM measurements allowed for the observations of these conformational changes. By AFM, we were able to observe the coexistence of the rod-like and globular molecules. Thus agreeing with theory that the coexistence of two conformations indicates that the rod-globule transition of surface confined brush molecules is a phase transition of the first order.
5. Verification of the Flory Theorem for Structurally Asymmetric Mixtures

Abstract

The generalization of the Flory theorem for structurally asymmetric mixtures was derived and tested by direct visualization of conformational transformations of brush-like macromolecules embedded in a melt of linear chains. Swelling of a brush molecule was shown to be controlled not only by the degree of polymerization (DP) of the surrounding linear chains, $N_B$, but also by the DP of the brush’s side-chains, $N$, which determines the structural asymmetry of the mixed species. The boundaries of the swelling region were established by scaling analysis as $N^2 < N_B < N_A/N$, where $N_A$ is the degree of polymerization of the brush backbone. Experiment and theory demonstrated good agreement.

Introduction

Polymer solutions are unique physical systems in which the interactions between macromolecules become screened as polymer concentration increases. In polymeric melts, where the interactions are completely screened, macromolecules behave as almost ideal chains obeying random walk statistics. The ideality of polymer chains in a melt was first established over fifty years ago by Flory and became latter known as the Flory theorem. There is a very interesting consequence of the Flory theorem related to the swelling behavior of polymer chains in a polydisperse melt. A “guest” molecule with the degree of polymerization $N_A$ embedded into a melt of chemically identical polymer chains with the degree of polymerization $N_B$ starts swelling when $N_A > N_B^{2(4-d)}$, where $d$ is
the space dimensionality. For 3-D ($d=3$) and 2-D ($d=2$) mixtures, shorter macromolecules tend to penetrate and swell the guest macromolecule when $N_A > N_B^2$ and $N_A > N_B$, respectively. Experimental studies on both 3-D and 2-D binary mixtures confirmed swelling of longer chains in a melt of shorter chains.\(^{194-198}\)

The recent developments in nanocomposite materials pose new challenges in determining the controlling factors for the stability and conformation of polymeric mixtures that contain molecular species with different architectures.\(^{199-201}\) Mixtures of linear polymers with dendrimers, branch polymers, nanoparticles, carbon nanotubes, and clay platelets are used to create novel nanocomposite materials. Since the structures of these molecules are significantly different from those of linear polymer chains, this makes applicability of the classical Flory theorem to these mixtures questionable. In this letter, we show that one can modify the Flory approach to describe mixtures of structurally different species. We use atomic force microscopy (AFM) to monitor conformations of well-defined brush-like macromolecules\(^{202-204}\) with a degree of polymerization (DP) of the backbone $N_A$ and DP of side chains $N$ embedded into a monolayer of linear chains that have a degree of polymerization $N_B$ (Figure 22). The experiments clearly show that molecular brushes swell as the DP of the surrounding linear chains, $N_B$, decreases. The intriguing finding of this study is that the swelling behavior not only depends on the length of the linear chains ($N_B$) but it is also affected by the length of the brush’s side-chains ($N$) that define the structural asymmetry of the mixed species. To explain these findings, the Flory theorem of polymer melts was reformulated to account for the structural asymmetry and to establish the boundaries of the swelling regime.
Experimental Section

The brush-like macromolecules used in this study consist of a long flexible backbone ($N_A=1580$) with densely grafted poly($n$-butylacrylate) (pBA) side chains ($N=10$). These macromolecules were synthesized by atom transfer radical polymerization. For the polymeric solvent/matrix to be chemically identical to the molecular brushes, we used melts of linear pBA chains. A series of well-defined linear pBA’s with degree of polymerization ranging from 10 to 9000 and monomer molecular weight $M_0=128$ were purchased from Polymer Source Inc.

Sample Preparation and Characterization

The brush-like macromolecules used in this study consist of a long flexible backbone ($N_A=1580$) with densely grafted poly($n$-butylacrylate) (pBA) side chains ($N=10$). These macromolecules were synthesized by atom transfer radical polymerization. For the polymeric solvent/matrix to be chemically identical to the molecular brushes, we used melts of linear pBA chains. A series of well-defined linear
pBA’s with degree of polymerization ranging from 10 to 9000 and monomer molecular weight $M_0=128$ g/mole were purchased from Polymer Source Inc.

Monolayers of pBA brushes dispersed in linear pBA chains were prepared by the Langmuir-Blodgett technique. To obtain these dispersions, the brush molecules were first mixed with matrix polymers at a ratio of 10/90 wt./wt.% in chloroform, a common solvent for both the brush and linear polymers. The solution was then deposited onto the water surface of a Langmuir trough. After allowing 30 minutes for system equilibration, the water-supported monolayers were transferred onto a solid substrate (mica) at a constant pressure of 0.5 mN/m and a transfer ratio of 0.98. The transfer pressure $\pi=0.5$ mN/m corresponds to 10% compression of a dense pBA monolayer. This leads to desorption of 10% of the side chains, which in turns causes decrease in the persistence length of the brush. To ensure that all samples have the same fraction of desorbed side chains, all monolayers were transferred at the same 0.5 mN/m pressure and the same 10% compression ratio. The transferred samples were studied by AFM with the aim of visualization of individual brush molecules. The samples were imaged in Tapping-mode using a Multimode AFM (Veeco Metrology group) and silicon cantilevers from Mikromasch USA with a resonance frequency of about 160 kHz, spring constants of 5.0 N/m, and a tip radius being smaller than 10 nm.

**Results and Discussion**

Figure 23 depicts a sequence of conformations of brush-like macromolecules sparsely dispersed in a matrix of linear pBA chains. The height contrast results from the partial desorption of the side chains that segregate around the backbone of the brush and
form a ridge of approximately 0.5 nm in height. The side chains that remain adsorbed to the substrate are not distinguishable from the surrounding melt of linear pBA chains. Upon increasing $N_B$, brush macromolecules undergo conformational transformations from swollen coils in a melt of short chains (Figure 23 a,b) to a compact coil in a melt of longer chains (Figure 23 g,h). Note that in 2-D systems, the ideal coil conformation corresponds to a dense packing of the polymer chain. There is also a crossover region between the two pure regimes (Figure 23 c-f).

**Figure 23.** Height AFM images of individual brush molecules embedded into monolayers of linear pBA chains having different degrees of polymerization: a - $N_B=11$, b - $N_B=24$, c - $N_B=102$, d - $N_B=214$, e - $N_B=322$, f - $N_B=602$, g - $N_B=1766$, and h - $N_B=8813$.

Molecular conformations were analyzed using a custom-designed software program which allowed automatic detection of individual molecules and measurements
of their contour length, radius of gyration, and curvature distribution. The determined molecular dimensions are accurate since the persistence length of brush macromolecules (~100 nm) is larger than the radius of an AFM tip (~10 nm). In addition, the molecular resolution is facilitated by adsorbed side chains that separate the neighboring backbones by a distance of 20±2 nm. Clear resolution of the individual molecules enabled visual fractionation of isolated molecules and molecular clusters. The latter were manually excluded from a set of detected species prior to the conformational analysis. Figure 24a depicts the square-root of the mean-square radius of gyration of the section of the brush backbone, $R_S$, as a function of the number of monomers in the section, $N_S$, measured in two different matrixes, i.e. $N_B=11$ and $N_B=1766$. Both plots display two conformational regimes. For the short chain sections ($N_S<200$), their size $R_S$ scales linearly with $N_S$, i.e. the short sections of the backbone adopt a rod-like conformation. At the larger length scales, the size of the chain section approaches the power law $R_S \approx bN_S^\alpha$ with $\alpha=0.69\pm0.03$ for $N_B=11$ and $\alpha=0.48\pm0.04$ for $N_B=1766$. The value of the former exponent is close to $\alpha=0.75$, which is characteristic for the 2-D self-avoiding walk, while the value of the second exponent is close to $\alpha=0.5$, which is typical for a 2-D globule. The analysis of similar plots for the mixtures of the brush molecules with linear chains of different degree of polymerizations, $N_B$, shows that the exponent $\alpha$ gradually decreases from 0.75 to 0.5 with increasing values of $N_B$. This is in agreement with the conformational transformations of the brush macromolecules shown in Fig. 23.

Figure 24b combines measurements of the root mean-square radius of gyration of the pBA brushes for different degrees of polymerization of the pBA linear chains. The radius of gyration was averaged for ca. 300 brush molecules with a similar contour length
which gave a standard error of mean below 10%. Note that the swelling stops at much
greater chains ($N_B \gg 1$), unlike linear chains that are expected to continue swelling down
to $N_B \approx 1$. Therefore, the location of the crossover region notably differs from those of
structurally symmetric melts.

**Figure 24.** (a) The square-root of the mean-square radius of gyration of a section of the
backbone of brush macromolecules $R_S = \sqrt{\langle R_S^2 \rangle}$ as a function of the polymerization
degree of the section $N_S$ was measured for two matrixes of linear chains with $N_B=11$ (■) and
$N_B=1766$ (●). (b) Dependence of the square root of the mean-square radius of
gyration of the pBA brush on the degree of polymerization of linear pBAs chains for
different degrees of polymerization of the backbone.

To understand the physical mechanism of the observed swelling behavior we have
developed a scaling model of brush-like macromolecules in a melt of linear chains. An
adsorbed brush molecule is considered as a ribbon with a width of $D \cong bN$ and a contour length of $L_0=bN_A$, where $b$ is the monomer size (Figure 22). Since we are dealing with an extremely dense brush, wherein every monomeric unit of the backbone contains one side chain, we assume that the linear chains do not interpenetrate the side chains. The penetration is sterically unfavorable because the tightly adsorbed side chains represent a dense 1-D brush aligned perpendicular to the main chain backbone. Thus, the effect of the linear chains on the swelling behavior of molecular brushes is solely associated with the entropy of mixing of these chains with a brush. A test molecule occupies only the fraction of the area $\varphi R_A^2$, where $\varphi=L_0 D/R_A^2=b^2 N_A N/R_A^2$ is the volume fraction of monomers belonging to a brush inside area $R_A^2$, which leaves an area $(1-\varphi)R_A^2$ accessible for the linear chains. The entropic contribution to the free energy due to placement of the linear chains with the degree of polymerization $N_B$ over the area $R_A^2$ is equal to:

$$
\frac{F_{\text{mix}}}{k_BT} \approx \frac{R_A^2 (1-\varphi)}{b^2} \ln (1-\varphi) \approx \frac{N_A^2 N}{N_B} + \frac{b^2 (N_A N)^2}{2N_B R_A^2} \quad (1)
$$

Note that only the last term in the right hand side of Eq. 1 depends on the size of the brush molecule $R_A$. Here and below we use a scaling analysis and neglect all numerical prefactors on the order of unity. The Flory free energy of a guest molecule mixed with the linear chains can be written as a sum of the free energy of mixing (Eq. 1) and of the test molecule’s elastic free energy. The elastic free energy term accounts for the change of the conformational entropy as the guest macromolecule swells from the ideal size

$$
R_A^0 \approx \left( L_p L_0 \right)^{1/2} \approx b N_A^{1/2} N^{3/2} \quad (2)
$$
where \( L_p \cong bN^3 \) is the persistence length of an adsorbed brush macromolecule, which is a ribbon with a width of \( D \cong bN \). \(^{207}\) Thus, the total free energy of the molecular brush dispersed in a melt of linear chains is

\[
\frac{F}{k_B T} \approx \left( \frac{R_A}{R_A^0} \right)^2 + \frac{b^2 (N_A N)^2}{N_B R_A^2}
\]

(3)

The equilibrium size of the probe molecule is obtained by minimizing Eq. 2 with respect to the size \( R_A \) as

\[
R_A \approx bN_A^{3/4} N^{5/4} N_B^{-1/4}
\]

(4)

which is valid for intermediate values of the matrix chain’s degrees of polymerization, \( N_B \). For very long linear chains, the intrabrush interactions are almost completely screened. In this case, the test macromolecule contracts and its size eventually approaches the ideal size \( R_A \approx R_A^0 \). This takes place at \( N_B \approx N_A / N \). This upper boundary for the swelling regime is a surprising result because it points out that linear chains sense a brush macromolecule as a linear chain composed of \( N_A / N \) effective monomeric units. In other words, the ribbon-like brush with a width of \( bN \) and contour length \( bN_A \) can be viewed as a chain of \( N_A / N \) monomeric units each with linear size \( bN \) and having \( N^2 \) original monomers.
Figure 25. Three conformational regimes of a brush-like macromolecule embedded in a melt of linear chains with a degree of polymerization, $N_B$. The upper boundary of the swollen chain regime, $N_B=N^2$, is determined by the degree of polymerization of the side chains (N), while the lower boundary of the ideal chain regime, $N_B=N_A/N$, also depends on the degree of polymerization of the brush’s backbone ($N_A$).

As the degree of polymerization of the linear chains, $N_B$, decreases the brush molecule swells. The brush becomes completely swollen with size

$$R_A^{sw} \approx L_p \left( \frac{bN_A}{L_p} \right)^{3/4} \approx b(NN_A)^{3/4}$$

(5)

at $N_B \approx N^2$ for which $R_A \approx R_A^{sw}$. For $N_B < N^2$, the equilibrium size does not depend on the length of the surrounding linear chains. In Figure 25, we summarize different swelling regimes as a function of the degree of polymerization of the solvent, $N_B$. It is important to point out that the interval of the intermediate $N_B$ values, $N^2<N_B<N_A/N$, only exists when the number of monomers forming the brush backbone $N_A$ is larger than $N^3$. The latter corresponds to the persistence length of brush-like macromolecules under conditions of strong adsorption.

The dependence of a chain size on the system parameters in three conformational regimes depicted in Figure 4 can be approximated by a simple crossover formula
with the fixed exponent $\beta=3$ and three adjustable numerical constants $A_1$, $A_2$, and $A_3$. The constants are introduced to adjust the molecular size and the location of the crossover region, respectively. For long linear chains ($N_B > N_A/N$), the formula approaches the ideal size of a polymer brush $R_A^0 = A_1 A_3^{1/12} b N_A^{1/2} N^{3/2}$ (Eq. 2). For a melt of short linear chains ($N_B < N^2$), this expression reduces to the size of a completely swollen molecule $R_A^{sw} = A_1 b(NN_A)^{3/4}$. For different sizes of brush-like macromolecules, Eq. 6 accurately describes all three conformational regimes with a single set of three adjustable parameters $A_1=0.33\pm0.01$, $A_2=0.36\pm0.08$, and $A_3=0.47\pm0.03$ (Figure 3b). It is important to emphasize that for different brushes, both limiting values for the radius of gyration ($R_A^0$ and $R_A^{sw}$) can be accurately fitted with the same set of adjustable parameters. Overall, experiment and theory demonstrated good agreement confirming the dependence of the size of a brush-like macromolecule on the degree of polymerization of the surrounding linear chains forming a two-dimensional melt.

One can easily generalize the analysis presented above to the case of a test macromolecule with thickness $D$, contour length $L_0$ and having a persistence length $L_p$ immersed into a melt of the linear chains with the degree of polymerization $N_B$ by rewriting Eqs. 1-3 in terms of chain parameters $D$, $L_0$, $L_p$ and space dimensionality $d$. Such test chains begin to shrink when the volume occupied by the host chains $b^d N_B$ becomes larger than the volume occupied by an effective monomer $D^d$ of the guest molecule, $b^d N_B > D^d$. Above this crossover value, the matrix chains screen intrachain

$$R_A = A_1 L_p \left( \frac{N_A}{N^3} \right)^{1/4} \left( 1 + A_2 N_B / N^2 \right)^{\beta} + A_3 \left( \frac{N^3}{N_A} \right)^{1/4\beta}$$

(6)
repulsive interactions between the monomers of the test macromolecule, which is manifested by the decrease of the size of the test molecule with increasing degree of polymerization of the linear chains \( N_B \) as 

\[
R_A \approx \left( \frac{L_0^4 L_p D^{2d-2}}{N_B b^d} \right)^{\frac{1}{d+2}} \sim N_B^{-1/(d+2)}.
\]

The shrinking continues until the size of the test molecule becomes comparable with its ideal size, \( R_A^0 \approx (L_p L_0)^{1/2} \). This occurs when the degree of polymerization of the linear chains \( N_B \) is on the order of 

\[
L_0^{(4-d)/2} D^{2d-2} / (L_p^{d/2} b^d).
\]

The generalized Flory theorem for mixtures of structurally asymmetric macromolecules can be formulated as follows: “Test macromolecules with thickness \( D \), contour length \( L_0 \) and a persistence length \( L_p \) dispersed in a melt of linear chains with the degree of polymerization \( N_B \) will remain in their ideal (Gaussian) conformations until the degree of polymerization of the linear chains \( N_B \) exceeds 

\[
L_0^{(4-d)/2} D^{2d-2} / (L_p^{d/2} b^d).
\]

Shorter linear chains will then fill the volume of the test macromolecules causing their swelling. This swelling continues until the excluded volume occupied by the linear chain \( b^d N_B \) becomes comparable with the volume of the effective monomer \( D^d \) of the test macromolecule.”
Chapter 6. Molecular Pressure Sensors

Flow properties of molecularly thin films are at the foundation of many practical applications such as lithography, microfluidics, coatings, and lubrication. Further advances in these fields depend on understanding the mechanisms that control the kinetics of flow. However, one of the problems in flowing monolayers is the independent characterization of the driving and frictional forces that are intimately coupled through the molecular interactions between the fluid and the substrate. In this regard, the visualization of compressible macromolecules during flow provides an exceptional opportunity to study these forces. Here we report on the monitoring of brush-like macromolecules as they change their shape in response to variations in the film pressure during flow. After appropriate calibration, these molecular sensors can be used to gauge both the pressure gradient and the friction coefficient at the substrate. We anticipate the utilization of such miniature sensors for probing flow properties on nanometer length scales.

The design of the pressure-responsive macromolecules is based on brush-like polymer architectures comprised of a flexible backbone surrounded by a dense shell of side chains (Figure 26a). The characteristic property of these macromolecules is their ability to change shape upon lateral compression on a substrate. If the film pressure increases, the number of side chains adsorbed to the surface decreases allowing the backbone to coil. This causes the macromolecules to become more compact and occupy less area on the substrate. Therefore, the area per molecule can be used as a pressure
sensitive parameter to gauge the variations of film pressure within flowing monolayers. Molecular brushes (Figure 26a) with the same degree of polymerization of a poly(2-hydroxyethyl methacrylate) backbone \( (n=570 \pm 50) \) and different degrees of polymerization of poly\((n\)-butyl acrylate\) (pBA) side chains \( (n=35 \pm 5 \text{ and } n=51 \pm 5) \) were synthesized by atom transfer radical polymerization.\(^{226-227}\) At room temperature, the materials are fluid melts that spontaneously spread when placed on higher surface energy substrates such as mica and graphite.\(^10\) Small drops of molecular brushes (volume ~1nl, radius ~100\(\mu\)m) were deposited on a substrate inside an environmental chamber under controlled temperature \( (T=25^\circ\text{C}) \) and relative humidity \( (\text{RH}=30-99\%) \). Like many other fluids, the drops first spread by generating a molecularly thin precursor film moving ahead of the macroscopic drop (Figure 26b).\(^{229}\) Using an atomic force microscope (Multimode, Nanoscope 3A Veeco Metrology Group), we monitored the spreading process over a broad range of length scales ranging from the motion of the film front all the way down to the movements of the individual molecules within the film.\(^{230}\)

\(^{10}\) The glass transition of PBA brushes is \( T_g = 50^\circ\text{C} \). At room temperature \( (T = 25^\circ\text{C}) \), PBA brushes are in the melt state characterized by the zero-shear viscosity \( \eta_0 = 8340 \text{ Pa}\cdot\text{s} \) and the surface tension \( \gamma = 33 \text{ mN/m} \).
Figure 26. Spreading of a melt of brush-like macromolecules. a, The so-called molecular bottlebrushes are comprised of a flexible backbone surrounded by a dense shell of poly(n-butyl acrylate) side chains. b, Atomic force microscopy (AFM) was used to monitor spreading of a drop of a polymer melt on a solid substrate (mica or graphite). The spreading begins with a molecularly thin precursor film that emerges from the drop, which acts a reservoir for the film. The total radius of the film (R) is a sum of the length of the precursor film (L) measured by AFM and the radius of the drop (R₀). c, The time (t) dependence of the film length observed on mica at a relative humidity (RH=99%). The length approximately follows the law \((R - R₀)^2 \approx D t\), where \(D\) is the spreading rate. For longer films \((R >> R₀)\), the spreading kinetics is described by \(F(R) = R^2 (\ln(R/R₀) - \frac{1}{2}) + \frac{R²}{2} = D t\) (inset), wherein the logarithmic term accounts for the radial growth and the resulting deviation of the data points from the linear dependence (dashed line). The more accurate equation gives a spreading rate of \(D=980 \, \mu m/s^2\).

Figure 26c shows the time dependence of the film length \(L = R - R₀\) observed on mica at a high relative humidity (RH=99%), where \(R₀=63 \, \mu m\) is the initial drop radius
and $R$ is the total radius of the film at time $t$ (Table 4). The length follows the well-known law, observed for different types of simple and complex fluids, $(R - R_0)^2 \cong Dt$, where $D$ is the spreading rate having the dimension of a diffusion coefficient.\textsuperscript{231,232} The slight deviation of the data points from the linear time dependence (dashed line in Figure 26c) is due to the radial spreading, which becomes significant for long films ($R > R_0$). In this case, the spreading kinetics is described by $R^2 (\ln \frac{R}{R_0} - \frac{1}{2}) + \frac{R_0^2}{2} = Dt$, wherein the logarithmic term accounts for the radial growth. As shown in Figure 26c (inset), the above equation allows a better fit of the experimental data and provides more accurate values for the spreading rate $D$. Table 5 summarizes the $D$ values obtained for a series of drops at different conditions including variations in RH, the substrate type, and the molecular weight. As can be seen, the spreading rate most strongly depends on the humidity of the surrounding environment and on the substrate type. The spreading rate on mica decreases by more than three orders of magnitude from 980 $\mu$m$^2$/s to 0.23 $\mu$m$^2$/s when the RH decreases from 99% to 95%. When the RH is below 85%, the spreading effectively stops. Unlike the hydrophilic mica, the flow on graphite does not depend on the humidity showing a spreading rate of $D = 3.9 \times 10^{-3}$ $\mu$m$^2$/sec. The table also shows that the spreading rate does not depend on the molecular weight, which is consistent with the plug-flow mechanism for the spreading of polymer precursor films.\textsuperscript{233-235} The plug flow is also consistent with the minor contribution of molecular diffusion within spreading monolayers.
Table 4. Time dependence of the film length at different relative humidity (RH).

<table>
<thead>
<tr>
<th># a)</th>
<th>N b)</th>
<th>RH (%) c)</th>
<th>t (min) d)</th>
<th>R₀ (µm) e)</th>
<th>R (µm) f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35</td>
<td>99</td>
<td>10</td>
<td>63</td>
<td>638</td>
</tr>
<tr>
<td>2</td>
<td>35</td>
<td>97</td>
<td>10</td>
<td>40</td>
<td>126</td>
</tr>
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<td>95</td>
<td>10</td>
<td>52</td>
<td>59</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>99</td>
<td>10</td>
<td>38</td>
<td>359</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>30</td>
<td>900</td>
<td>150</td>
<td>162</td>
</tr>
</tbody>
</table>

a) experiments #1-3: spreading of pBA brushes with n=35±5 (Mₙ=2.7×10⁶ g/mol) on mica substrate at different relative humidities; experiment #4: spreading of pBA brushes with longer side chains (n=51±5, Mₙ=3.8×10⁶ g/mol) on mica substrate at RH=99%; experiment #5: spreading of pBA brushes with n=35±5 on highly oriented pyrolytic graphite at RH=30%. b) degree of polymerization of the side chains of brush molecules. c) relative humidity within the chamber. d) time allowed for spreading process e) the initial radius of the drop does not change significantly during the spreading process. f) radius of the precursor film at time t, R(t)=R₀+L(t).

Table 5. Properties of the precursor films in different spreading experiments.

<table>
<thead>
<tr>
<th># a)</th>
<th>D x 10¹⁰ b)</th>
<th>ζ x 10⁻⁷ c)</th>
<th>ΔΠ_total d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.8±1.5</td>
<td>4.6±1.4</td>
<td>22.7±2.3</td>
</tr>
<tr>
<td></td>
<td>0.17±0.02</td>
<td>273±61</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(23±1) x 10⁻⁴</td>
<td>(2.0±0.3) x 10⁻⁴</td>
<td>23.2±1.6</td>
</tr>
<tr>
<td>3</td>
<td>10²</td>
<td>10⁴</td>
<td>22.5±1.6</td>
</tr>
<tr>
<td>4</td>
<td>10.2±1.4</td>
<td>4.6±1.4</td>
<td>23.6±1.6</td>
</tr>
<tr>
<td>5</td>
<td>3.9±0.2 x 10⁻⁵</td>
<td>(9.8±1.6) x 10⁻⁵</td>
<td>19.2±2.5</td>
</tr>
</tbody>
</table>

a) see Table 4. b) spreading rate in m²/s determined by fitting the experimental data points by (R – R₀)² ≅ Dt for short films and by R² ln(R/R₀) = 2Dt/R₀² for longer films. c) coefficient of friction between the flowing monolayer and the underlying substrate. d) pressure reduction over the film length: ΔΠ_total = Π(R₀) - Π(R).

In addition to the ability to monitor the position of the contact line, molecular visualization provides information about conformational changes caused by flow. Figure 27 displays the key finding of this study, that the flowing macromolecules change their
conformation with increasing distance from the fluid reservoir, i.e. drop. Close to the drop, the molecules are more coiled; while near the film edge, the molecules become more extended and occupy a larger area per molecule. The observed variation in the molecular area $\Sigma(r)$ reflects the decrease of the two-dimensional film pressure $\Pi(r)$ along the flow direction. In addition, the conformational changes contain information about the friction coefficient at the substrate, since the pressure gradient is locally balanced by the frictional force as

$$-\frac{\partial \Pi(r)}{\partial r} = \zeta \cdot V(r)$$

(7),

where $\zeta$ is the friction coefficient per unit area and $V(r)$ is the velocity of the film at a distance $r$ from the edge of the macroscopic drop.

**Figure 27.** Monitoring conformational changes of brush-like macromolecules within the spreading precursor film. The AFM height micrographs show that the macromolecules become more extended with increasing distance ($r$) from the drop centre and occupy a larger area per molecule ($\Sigma$) during spreading on mica at RH=99%. The area variation $\Sigma(r)$ is ascribed to the corresponding variation in the two-dimensional film pressure $\Pi(r)$,
which decreases along the flow direction. The numbers at the AFM micrographs approximately correspond to the marked positions along the precursor film where the images were captured.

To determine the pressure gradient within the spreading film, i.e. to substitute $\Sigma(r)$ in Figure 27 with $\Pi(r)$, we measured film pressure as a function of molecular area $\Pi(\Sigma)$, which corresponds to the thickness dependence of the disjoining pressure, the driving force of spreading. The pressure was measured during compression of monolayers of brush molecules on a liquid substrate using a Langmuir trough and the Wilhelmy plate method. Note that the substrates used for the $\Pi(\Sigma)$ measurements are different from those used in the spreading experiments. Therefore, we separately studied the substrate effect by compressing brush monolayers on various liquids that are non-solvents for poly($n$-butyl acrylate) such as water, methanol, ethanol, glycerol, dimethylformamide, and ethylene glycol (Figure 29). Figure 28a shows the pressure-area isotherms measured on the surface of different mixtures of water and methanol. In these isotherms, the molecular area was additionally verified through molecular visualization of LB‐transferred monolayers by AFM (Figure 28a) as $\Sigma = \frac{A \cdot T}{\Gamma}$, where $\Gamma$ is the number of molecules within a given area $A$ of a solid substrate and $T = 0.98 \pm 0.02$ is the measured transfer ratio.\textsuperscript{144} Even though the isotherms were measured on different substrates, they can be superimposed by shifting them along the $\Pi$-axis (see inset in Figure 28a). The superposition of the curves gives a calibration curve $\Delta \Pi(\Sigma)$, i.e. relative film pressure versus molecular area. While the absolute pressure varied significantly, the slope of the curves exhibited less variations for all liquid substrates used in this study (Figure 29). As will be shown below, the change in the pressure across the film and not the absolute film
pressure is what is necessary to measure the pressure gradient and the interfacial friction coefficient of a spreading monolayer.

Figure 28. Measuring film pressure within the spreading precursor film. a, The molecular area dependence on the film pressure provides calibration of the brush-like macromolecules to be used as pressure sensors. The pressure-area isotherms were measured on the surface of different mixtures of water and methanol. The numbers above the curves correspond to the weight percentage of methanol in the subphase. Height AFM micrographs show the molecular structure of the monolayers transferred from the water substrate at different degrees of compression (1-3). (inset) The isotherms measured on the different substrates were superimposed by shifting them along the Π-axis. The superposition of the curves gives a calibration curve ΔΠ(Σ) for the relative film pressure versus molecular area. b, The distance dependences of the film pressure ΔΠ(r) were measured for precursor films of different lengths. From the slopes of these curves one determines the pressure gradient. In short films (◊) (RH=95%, spreading time t=10
min), the pressure decreases almost linearly with distance, which demonstrates that the pressure gradient is constant along the film. In longer films $(R \gg R_0)$ measured at RH=99% for $t=10$ min ($\circ$) and $t=30$ min ($\square$), the pressure demonstrates logarithmic decay due to the radial decrease of the flow velocity within the film. The inset shows the logarithmic decrease $\Delta \Pi = (0.072-0.0098) \ln(r)$ for a film measured at RH=99% for $t=10$ min, where $r$ is in meters.

The obtained calibration curve was applied to the $\Sigma(r)$ curve in Figure 27 to plot the variation of pressure within the precursor film. Figure 28b shows the distance dependence of the relative film pressure $\Delta \Pi(r)$ measured for precursor films of different lengths corresponding to different spreading times and spreading rates. In short films (diamond symbols), the pressure decreases almost linearly with distance, which demonstrates that the pressure gradient is constant along the film. This is consistent with linear, or one-dimensional, plug flow, wherein the flow velocity $V(r)$ is the same all over the film and equal to velocity of the film edge, i.e. $V(r) = \hat{R}$. Therefore, from Eq. 7, in short films one obtains the $r$-independent pressure gradient $-\frac{\partial \Pi}{\partial r} = \zeta \cdot \hat{R}$. However, the situation is different in long films due to the radial decrease of the flow velocity within the film $V(r) = \frac{R}{r} \hat{R}$, which results in $\frac{1}{r}$ dependence of the pressure gradient. After integration of Eq. 7, one obtains logarithmic decrease of the film pressure (inset in Figure 28b). The agreement between the experimental data points and Eq. 7 confirms the plug-flow model which has been previously suggested based on slow molecular diffusion within flowing monolayers.

The slope of the curves in Figure 29b gives the friction coefficient between the flowing monolayer and the underlying substrate. The obtained data are summarized in Table 5 for different spreading systems. It is important to note that even though the
pressure gradients were different within the films of different lengths captured at various stages of the spreading process, the calculated friction coefficient for these films was nearly the same. This demonstrates the relevance of the developed pressure sensors.

There are three important observations in Table 4. First, the kinetics of spreading on hydrophilic substrates such as mica does not depend on the molecular weight of the brush molecules (experiments 1 and 4). Second, the samples measured at different RH’s show nearly identical pressure drop over the film length $\Delta \Pi_{\text{total}} = \Pi(R_0) - \Pi(R)$, but vastly different friction coefficients (experiments 1, 2, 3). Third, on a hydrophobic substrate like graphite, the spreading rate does not depend on the humidity while both the friction coefficient and the $\Delta \Pi_{\text{total}}$ notably change compared to mica (experiment 5). These observations suggest that the precursor film on mica slides on top of a thin layer of condensed water confined between the film and the mica substrate. On the hydrophilic mica, the friction decreases with the thickness of the condensed water layer, while the pressure drop does not change significantly since it is largely determined by the same polymer-water surface interactions. On the hydrophobic graphite, the lack of the water layer results in RH-independent spreading rate and significant alteration of both driving and frictional forces. Furthermore, the friction coefficient on graphite $\zeta \cong 9.8 \times 10^{12} \text{ N} \cdot \text{s/m}^3$ favourably agrees with the lower limit of the molecular friction coefficient $\zeta_{\text{mol}} \geq \frac{k_B T}{D_{\text{therm}}} \cong 0.041 \pm 0.013 \frac{N \cdot \text{s}}{m}$ from the molecular diffusion measurements, which gives the friction coefficient per unit area $\zeta \cong \frac{\zeta_{\text{mol}}}{\Sigma} \geq 5.5 \times 10^{12} \text{ N} \cdot \text{s/m}^3$. The good agreement between the spreading and diffusion experiments on graphite additionally validates the measured pressure gradients.
The reported method has several limitations. First, the method relies on visualization of individual molecules. Therefore, it will not work for molecules that cannot be individually recognized and for macromolecules that overlap. Second, molecules need to be visualized during spreading. Currently, conventional AFMs capture images at a rate of ~0.1 frames/sec. This limits application of the method to substrates with a relatively high friction coefficient such as graphite and mica at RH<95%. Increase of the humidity leads to significant increase of the spreading rate of up to \(10^3\) µm²/s. This requires a scanning rate of ~10 frames/sec to monitor flow-induced conformational changes in real time. Recently developments in AFM techniques may enable ultrafast imaging in the near future through the use of higher frequency cantilevers and electronic enhancement of the cantilever’s quality factor. The third limitation is imposed by the necessity to visualize changes in the molecular area. Brush-like and star-like macromolecules are particularly suitable to sensor application due to their ability to significantly change conformation through desorption of polymer arms. Finally, limitations are imposed by the calibration technique based on compression of brush monolayers on the surface of various fluids. Strictly speaking, this calibration is accurate only for the spreading on the same liquid substrates. The calibration remains appropriate for spreading on solid substrates covered by a liquid layer, e.g. mica covered by condensed water. Using this calibration procedure for other types of substrates is less accurate. As demonstrated in Figure 29, the slope in the pressure-area isotherms for different liquid substrates demonstrates standard deviation of 20% from the average value measured for the same interval of molecular areas. Therefore, using water for calibration of spreading of pBA brushes on a non-water substrate may generate an error in
calculation of the friction coefficient of at least 20%. However, this error is much less compared to experimental variations of the friction coefficient due to minuscule changes in the relative humidity of the surrounding environment. Table 5 demonstrates that the friction coefficient increases by four orders of magnitude due to ~5% variation in the relative humidity, while the surface energy of the water-covered mica does not change much with humidity. In addition, water covers a broader range of film pressure, which makes the calibration on water more useful than on other liquids.

Figure 29. Calibration of the pressure sensor. Pressure-area isotherms were measured for monolayers of poly(n-butylacrylate) brush-like macromolecules on various substrates: (1) water, (2) glycerol, (3) ethylene glycol, (4) dimethylformamide, (5) methanol, and (6) ethanol. While the absolute pressure varies significantly, the slope of the curves is similar for all liquid substrates and varies at \( \frac{\partial \Pi}{\partial \Sigma} = 1.3 \pm 0.4 \text{ N/m}^3 \). The latter was used to calibrate the molecular area and determine the pressure gradient within the spreading precursor film.

Experimental
**Polymer characterization.** Average molecular weights and molecular weight distribution of brush-like macromolecules were measured by gel permeation chromatography (GPC) equipped with Waters microstyragel columns (pore size $10^5$, $10^4$, $10^3$ Å) and three detection systems: a differential refractometer (Waters Model 410), multi-angle laser light-scattering (MALLS) detector (Wyatt, DAWN EOS), and a differential viscometer (WGE Dr. Bures, $\eta$-1001). In addition, we used a newly developed approached based on combination of AFM and Langmuir-Blodget techniques. This combination of methods ensured relative experimental errors in determining the polymerization degrees of the backbone and side chains below 5% and 10%, respectively Langmuir-Blodget monolayers. To study the kinetics of the scission process, brush-like macromolecules with pBA side chains were adsorbed onto a surface of a water/propanol (99.8/0.2 wt./wt/%) substrate. Propanol was chosen for its low surface energy and nearly equivalent vapor pressure to water. This was necessary for long incubation times so that any subphase evaporation would lead to a minimal change in the surface energy. The evaporation of the subphase was closely monitored and controlled in an environmental chamber. For AFM analysis, the monolayer films were transferred onto a mica substrate at a controlled transfer ratio of 0.98using the Langmuir-Blodget technique. The surface tension of the substrate and the corresponding spreading parameter were measured by the Wilhelmy plate method.

**Atomic force microscopy.** Topographic images of individual molecules were collected using an atomic force microscope (Veeco Metrology Group) in tapping mode. We used silicon cantilevers (Mikromasch-USA) with a resonance frequency of about 140
kHz and a spring constant of about 5 N/m. The radius of the probe was less than 10 nm. The analysis of digital images was performed using a custom software program. The program identifies the molecular contour and is capable of determining the contour length, the end-to-end distance, and the curvature distribution, required for evaluation of the persistence length. For every sample, about ten images of about 300 molecules, i.e. total three thousand molecules were measured to assure a relative standard error below 4 % and an experimental error below 5 % of the persistence length (Figure 27), contour length, and polydispersity index (Figure 28) measurements.
7. Adsorption-induced scission of carbon-carbon bonds

The molecular foundation of life is based on a simple principle: covalent carbon-carbon bonds are hard to break. Their strength is evident in the hardness of diamonds and tensile strength of polymeric fibers. Various types of mechanical stimuli have been applied to extend and eventually rupture polymer chains. These include extensional flow, ultrasonic irradiation, receding meniscus, and single-chain stretching by nanoprobes. However, it has not been demonstrated that such large forces can be spontaneously generated inside macromolecules, without any external stimuli, and induce scission of their covalent bonds. Here we present evidence that relatively weak van der Waals interaction forces can locally conspire to destroy brush-like macromolecules upon adsorption onto a substrate. The macromolecule’s self-destruction occurs because its side chains stretch the polymer backbone as the macromolecule struggles to reconfigure and maximize the number of contacts with the substrate. By engaging in this intramolecular tug-of-war, the macromolecule opts to incur the large cost of breaking covalent bonds in order to reduce the overall free energy of the system. Our findings call into question the generally accepted belief that the primary structure of macromolecules synthesized in solution remains intact after deposition onto a substrate.

A series of brush-like macromolecules with the same degree of polymerization of a poly(2-hydroxyethyl methacrylate) backbone (N=2000±100) and different degrees of polymerization of poly(n-butyl acrylate) (pBA) side chains (n=12, 130, and 140) were synthesized by atom transfer radical polymerization. Due to the high grafting density,
the side chains repel each other prompting the backbone to stretch its conformation from a coil-like to an extended chain. The steric repulsion becomes significantly enhanced upon adsorption of molecular brushes onto a substrate as the surface-confinement further reduces the configurational space available for the side chains. On attractive substrates, this leads to significant extension of the polymer backbone revealing strong dependence on the side-chain length. Figure 30 shows two AFM micrographs of monolayers of pBA brushes with short (Figure 30a) and long (Figure 30b) side chains. In the former case, the number average contour length $L_n$ per monomeric unit of the backbone was measured to be $l = L_n / N_n = 0.23 \pm 0.02 \text{nm}$, which is close to $l_0=0.25 \text{ nm}$, the length of the tetrahedral C-C-C section. This indicates that even when the side chains are relatively short ($n=12$), the backbone is already locally extended adopting a nearly all-trans conformation. As the side chains become longer (Figure 30b) and the steric repulsion between them increases, one observes global straightening of the backbone reflected in the increase of the persistence length (Figure 30c).

Figure 30. Atomic force microscopy was used to visualize conformation of pBA brush-like macromolecules on mica. The light threads in the height images correspond to the backbone and the areas between threads are covered by side chains, which cannot be visualized at this scale. With increasing side-chain length, molecules change from (a) flexible for $n=12$ to (b) rod-like conformation for $n=130$, where $n$ is the number average degree of polymerization of the pBA side chain. (c) The persistence length, $l_p$, of the
surface-adsorbed macromolecules was determined from the statistical analysis of the backbone curvature. It is found to increase with the side chain length as $l_p \sim n^{2.7}$.

Obviously, the chain extension requires a substantial amount of tensile force, which will be estimated using simple spreading arguments (Figure 31). Just like in normal liquids, the polymeric side chains desire to spread and cover the higher energy substrate. Unlike conventional liquid drops however, the spreading of the side chains is constrained by their connection to the backbone allowing for each individual side chain to adsorb to the surface only in the direct vicinity of the backbone. This causes the backbone to extend generating more space on the substrate for additional side chains to adsorb. In addition, one needs to realize that even after the polymer backbone becomes fully elongated, there is still a large fraction of desorbed side chains that struggle to get into contact with the substrate causing the polymer backbone to extend beyond its physical limit. Furthermore, a major fraction of the wetting-induced tensile force is concentrated at the backbone, which is the main constraint for the macromolecule’s spreading. The tensile force along the backbone can be estimated as $f \approx S \cdot d$, where $S$ is the spreading coefficient and $d$ is the width of adsorbed brush macromolecules (Figure 31). For estimation purposes, we consider only the dominant term in $S$, i.e. the difference between the surface free energies of a solid-gas, liquid-gas, and solid-liquid-gas interfaces ($S = \gamma_s - \gamma_l - \gamma_{sl}$). Previous measurements for the substrates that were used in this study, found the spreading coefficient to be about $S = 23 \pm 3$ mN/m on graphite and $S = 21 \pm 3$ mN/m water/propanol mixtures. Therefore, a brush macromolecule with short side chains ($n=12$) and a width of $d=11$ nm, is capable of generating a force of approximately 220 pN on either of these two substrates. This exceeds the typical range of
tensile forces 10-100 pN measured by other techniques for the stretching individual polymer chains.47

Figure 31. After adsorption onto an attractive substrate, a brush-like macromolecule spreads on the substrate surface in order to increase the number of monomeric contacts with the substrate. The brush-like architecture imposes constraints on the spreading of the macromolecule causing an anisotropic process, which leads to extension of the backbone. The wetting-induced tensile force \( f \approx S \cdot d \) is concentrated at the covalently linked backbone, where \( S \) is the spreading coefficient and \( d \) is the width of the brush.

Note that the force value is proportional to the molecule’s width and also depends on the surface energy of the substrate. Therefore, in order to generate a force value larger than 2 nN and challenge the strength of covalent bonds in the backbone, we synthesized pBA brushes with longer side chains (\( n=140 \)) that would lead to a width of \( d=130 \) nm and a tensile force of about 2.7 nN. The molecules were adsorbed onto different solid and liquid substrates such as mica, graphite, silicon wafers, as well as water/propanol mixtures. While molecules on solid substrates could be directly imaged by AFM, the liquid-supported films were first transferred onto a solid substrate using the Langmuir-Blodget (LB) technique and then scanned by AFM. Figure 32a shows a series of AFM images obtained for different incubation times on the water/propanol (99.8/0.2 wt./wt.%) substrate having a surface energy of 69 mN/m. As the time spent on the substrate
increases, one sees that the molecules are getting progressively shorter while the number of species per unit area correspondingly increases. This is consistent with chain scission (Figure 32b) and suggests a constant cumulative length of molecules per unit mass of the material. The cumulative length was measured as $\Lambda = \sum \frac{L_i \times n_i}{\sigma \times A}$, where $n_i$ is the number of molecules of length $L_i$ within a substrate area $A$ and $\sigma$ is the LB-controlled mass per unit area of the monolayer. As shown in Figure 32c, the cumulative length remains approximately the same ($\Lambda = 9.6 \pm 0.5 \mu m/fg$) at different exposure times corroborating the chain scission. Similar observations were made on other solid and liquid substrates to demonstrate that the chain scission does not depend on the chemical specificity of the substrate (Figure 34). However, in our experiments, we gave a preference towards liquid substrates that allow gradual variation of the surface energy by mixing two different liquids and also facilitate rapid equilibration of the monolayer structure. Both factors ensure reproducibility of the kinetics study discussed below.

**Figure 32.** (a) Height AFM images of the brush-like macromolecules with long side chains ($n=140$) were measured at different exposure times to the water/propanol (99.8/0.2 wt./wt.%) substrate. (b) The molecules get shorter with greater exposure time to the substrate which is attributed to spontaneous scission of the polymer backbone. From the
molecular images one obtains (c) the time dependence of the cumulative length, 
\[ \Lambda = \sum_{i} \frac{L_i \times n_i}{\sigma \times A}, \]
along with (d) the number average contour length, 
\[ L_n = \frac{\sum L_i \times n_i}{\sum n_i} \]
and polydispersity index of the system, 
\[ \text{PDI} = \frac{L_w}{L_n}. \]
The cumulative length was measured within an area of 
\[ A = 25 \mu m^2 \] at a constant mass density of 
\[ \sigma = 0.08 \mu g/cm^2 \] controlled by the Langmuir-Blodget technique. The cumulative length was found to stay approximately the same during the scission process at a value of 
\[ \Lambda = 9.6 \pm 0.5 \mu m/fg \] of material. The experimentally measured time dependence of the contour length (●) is fitted with the equation 
\[ L = \frac{1}{L_0} \left( 1 - e^{-kt} \right), \]
where 
\[ L_0 = 500 \text{ nm} \]
is the initial number-average contour length measured by AFM at \( t=0 \) and 
\[ L_\infty = 40 \pm 3 \text{ nm} \]
is the length of the shortest molecules observed during the scission process. The obtained equation was used to fit the experimental data using \( k \) as a fitting parameter resulting in 
\[ k = 2.3 \times 10^{-5} \text{ sec}^{-1}. \]
The fact that we did not observe molecules shorter than 40 nm even at very long exposure times makes perfect sense because brush molecules at a short backbone adopt star-like morphologies (see the last cartoon in the series in Figure 32b), wherein the side chains

Figure 32d shows the rapid decay of the average molecular length with increasing exposure time of the brush-like macromolecules to the water/propanol substrate. In order to analyze the kinetics of the scission process we assume that the bond scission occurs as a first order reaction: 
\[ A = A_0 e^{-kt}, \]
where \( A \) is the total number of covalent bonds in all backbones within a unit area of the substrate, \( A_0 \) is the initial number of bonds at \( t=0 \), and 
\( k \) is the rate constant. Assuming that the cumulative length is conserved, one obtains the number average contour length 
\[ L = \frac{1}{L_0} \left( 1 + \frac{k}{L_\infty} t \right), \]
where 
\[ L_0 = 500 \text{ nm} \]
is the initial number-average contour length measured by AFM at \( t=0 \) and 
\[ L_\infty = 40 \pm 3 \text{ nm} \]
is the length of the shortest molecules observed during the scission process. The obtained equation was used to fit the experimental data using \( k \) as a fitting parameter resulting in 
\[ k = 2.3 \times 10^{-5} \text{ sec}^{-1}. \]
have more space to spread out, easing some tension at the backbone and thus preventing further scission.

The scission process seems to be completely random suggesting the uniform distribution of the tension along the backbone. This was proved by directly analyzing and using computer modeling to simulate the length distribution of the reaction products, i.e. fractured molecules. As shown in Figure 32d, the polydispersity index \( PDI = L_w / L_n \) initially increases and then decays as the system moves towards monomeric units. This is consistent with random scission: at the beginning the random cleavage of the backbone C-C bonds results in larger length polydispersity, while at later stages the system gradually approaches the monodisperse monomeric units. The simulation was done using a computer model wherein the probability \( P \) of bond scission occurring at any point along the backbone, except the ends, is the same (Figure 33a). Solid lines in Figure 33b depict length distributions obtained at different durations of the computer-simulated scission process. As can be seen, the obtained distribution functions compare favourably with the corresponding length distributions measured by AFM (see dots in Figure 33b) and results in good agreement between the modelled and experimentally measured polydispersity index (Figure 32d). Thus, the analysis of the length distribution confirms that the scission of the polymer backbone in surface-deposited molecular brushes is a random process that obeys the first-order kinetics.
Figure 33. (a) A computer model was designed to simulate the random scission process, wherein the scission probability $P$ is set constant along the most of the backbone, except the ends. At the ends, $P$ decays linearly to zero from $x_2=120$ nm to $x_1=40$ nm. This ensures the scission process stops at the experimentally observed $L_\infty=40$ nm. (b) Length distributions obtained by computer simulation (solid lines) demonstrate good agreement with the corresponding distributions obtained by AFM (data points). The distributions are presented as the weight fraction of polymer chains of a certain number average contour length with a resolution of 50 nm. It is important to note, that the initial distribution function at $t=0$ of the computer simulation is the same as in the AFM experiment.

Experiments are also being conducted to verify the effects of the substrate surface energy and the side-chain length on scission. The preliminary findings show that the backbone scission is very sensitive to small variations in both parameters. If the surface energy of the substrate is decreased by adding more propanol into the water/propanol substrate, the molecules with long side chains ($n=140$) that readily break on 99.8/0.2 wt./wt.% substrate ($\gamma=69$ mN/m) remain intact on the substrates having a surface energy below 60 mN/m. Sharp retardation of the scission process was also observed upon
shortening of the side chains. If brush molecules with the same backbone but shorter length side chains (n=130 instead of n=140) are deposited on the same substrate, i.e. 99.8/0.2 wt./wt.% water/propanol mixture, they become indefinitely stable. By stable it is meant that within a reasonable experimental times (e.g. days), we have not observed any noticeable shortening of pBA brush-like molecules with n=130. However, these molecules are found to break on graphite which has a slightly higher surface energy (Figure 34).

**Figure 34.** (a) On the surface of highly-oriented pyrolytic graphite, PBA brush-like macromolecules with long side chains (n=130) were found to slowly break with time at ambient conditions. (b) PBA brush-like macromolecules with even longer side chains (n=140) break instantaneously on mica. Even though the scission-causes undulations that are clearly visible in the prepared sample (left), one needs to expose the sample to water vapour to reduce friction at the substrate and thus allow the sliding of the scission products away from each other (right). Since in both experiments we do not control the surface coverage, the cumulative length per unit mass of the material can not be compared.
The essential feature of the bond scission observed here is that it occurs spontaneously upon adsorption onto a substrate. This distinguishes it from other chain-breaking experiments wherein an extramolecular force was applied to induce the chain scission. It is remarkable that the relatively weak van der Waals interaction forces with the substrate can compound and break the molecular skeleton. One can envision other types of branched macromolecules whose primary structure is at risk of the intramolecular tug-of-war game when adsorbed to a substrate. Thus, with the current pursuit of new macro- and supramolecular materials that are specifically tailored for various surface applications, the surface-induced scission of covalent bonds will need to be considered when designing complex molecular architectures.

**Experimental Methods**

To determine the kinetics of the scission process, brush-like macromolecules with pBA side chains were adsorbed onto a surface of a water/propanol (99.8/0.2 wt./wt/%) substrate. Propanol was chosen for its low surface energy and nearly equivalent vapor pressure to water. This was necessary for long incubation times so that any subphase evaporation would lead to a minimal change in the surface energy. The evaporation of the subphase was closely monitored and controlled in an environmental chamber. For AFM analysis, the monolayer films were transferred onto a solid substrate (mica) using the Langmuir-Blodget technique. A transfer ratio of 0.98 was controlled to ensure that mass was conserved during transfer of the film.

Topographic images of individual molecules were collected using a Multimode Atomic Force Microscope (Veeco Metrology Group) in tapping mode. We used silicon cantilevers (Mikromasch-USA) with a resonance frequency of about 140 kHz and a
spring constant of about 5 N/m. The radius of the probe was less than 10 nm. To ensure accurate length measurements of the visualized molecules, several images were collected from the same sample in different areas, using different scan sizes and scan directions. For every sample an average of three thousand molecules were measured. The measurements were performed using a custom software program for the analysis of digital images. The program identifies the molecular contour and is capable of determining the contour length, the end-to-end distance, and the curvature distribution, required for evaluation of the persistence length.
8. Molecular Characterization

Modern technologies and materials rely on our ability to design macromolecules which adopt a particular conformation and execute predetermined functions. However, designer macromolecules often demonstrate complex structure, which may include multiple branching, heterogeneous chemical composition, and specific functional groups. The role of molecular visualization has grown to be especially valuable with the synthesis of these complex molecules whose structures are difficult to confirm using conventional characterization techniques such as nuclear magnetic resonance (NMR), light scattering, and size-exclusion chromatography (SEC). This is especially true for molecules that are branched, heterogeneous, and polydisperse. Molecules have been analyzed for the following groups: Geoffrey W. Coates at Cornell University, Harm-Anton Klok at the École Polytechnique Fédérale de Lausanne, Ian Manners at the University of Bristol, and Bruce M. Novak at North Carolina State University. Through these experimental studies it has been shown that atomic force microscopy (AFM) is able to provide proof of the molecular architecture along with analysis of the size and conformation of molecules.

8.1 Following Reaction Progress by Atomic Force Microscopy: Formation of Nanoparticles by Intramolecular Cross-linking

Formation of molecular nanoparticles was confirmed by Atomic Force Microscopy (AFM) through visualization of individual molecules at different stages of

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11 Cherian, A.E.; Sun, F.C.; Sheiko, S.S.; Coates, G.W. Submitted to Journal of American Chemical Society
crosslinking. Figure 35a-d shows height images of samples 1-3 and 5 prepared by spincasting from a dilute solution in 1,2,4-trichlorobenzene on a mica substrate. The uncrosslinked sample in Figure 35a reveals extended molecules that adsorb as either isolated species or clusters of overlapped chains. The number average length of the isolated molecules was measured to be $L_n = 58 \pm 7$ nm. This is about 3 times shorter than $L_0 = 176$ nm, the length of a fully extended polymer chain with a number average degree of polymerization of $N_n = 370$, and indicates a coiled microconformation of the polymer chain. In the course of the crosslinking reaction, molecules became more compact, occupying a smaller area (Figure 35b-d). The majority of the crosslinked molecules were visualized as isolated particles, providing further support, along with the GPC data, for predominate intramolecular crosslinking under dilute conditions.

To characterize the change in elasticity of the molecular particles, we measured the number average particle area ($\Sigma$) and determined the extension ratio $\lambda = \Sigma / \Sigma_1$, where $\Sigma_1 = 24$ nm$^2$ (the area occupied by a solid spherical particle with $M_n = 54,100$ g/mol and dry volume ($V = 90$ nm$^3$). Figure 35e shows that the extension ratio decreases with crosslinking, while the volume of the particles remains nearly constant. Furthermore, the square of the extension ratio ($\lambda^2$) exhibits linear dependence on the degree of crosslinking. Extrapolation of the line to $x = 0$ gives $\lambda^2 = 102 \pm 3$ and $\Sigma = 242 \pm 7$ nm$^2$, which is consistent with the calculated area of a flat molecular disk ($\Sigma_0 = V / h = 90$ nm$^3 / 0.4$ nm = 225 nm$^2$).

In order to understand the observed linear dependence we considered a crosslinked molecule as an affine network which was deformed due to attraction to the substrate. Deformation of the network $\lambda = \Sigma / \Sigma_1$ can be determined by minimization of the
particle’s free energy $F = F_c + F_s + F_{vdw}$ including three contributions. The first term, $F_c = n k T (2\lambda + 1/\lambda^2 - 3)/2$, is the free energy change due to substrate-caused deformation of the molecule, where $n$ is the number of network strands per molecule. The second contribution is the energy decrease due to spreading on the substrate, $F_s = (\gamma_s - \gamma_p - \gamma_{sp}) \Sigma$, where $\gamma_s$, $\gamma_p$, $\gamma_{sp}$ are the surface energies of the substrate, polymer, and polymer-substrate interfaces, respectively. The third term represents the long range van der Waals interactions between the particles and the substrate, $F_{vdw} \approx -A \Sigma / 12 \pi h^2$, where $A$ is the Hamaker constant and $h$ is the particle thickness. Minimization of the total free energy for $\lambda > 1$ and $V = \Sigma h$ gives $\lambda^2 = (S \Sigma_1 - nkT) / 3A$, which helps to explain the linear dependence $\lambda^2(x)$, since the number of network strands is linearly proportional to the fraction of crosslinked vinyl groups, $n \sim x$.\textsuperscript{12}

\textsuperscript{12} Even though the assumption of an affine network demonstrates good agreement with experiment, we do not claim that the molecules are affine networks. One should consider other types network topologies including multiple loops that are typical for intramolecular cross-linking and do not contribute to the network elasticity.
Figure 35. AFM height images of the nanoparticles: (a) 0% vinyls cross-linked, (b) 42%, (c) 59%, (d) 76%. (e) The plot presents the square of the extension ratio $\lambda = \Sigma / \Sigma_1$ and the particle volume $V \equiv \Sigma h$ as a function of the percentage of crosslinked vinyl groups. The hollow square symbol corresponds to $\lambda = \Sigma_0 / \Sigma_1$ of the uncrosslinked molecule.

8.2 Water-Soluble, Unimolecular Containers Based on Amphiphilic Multiarm Star Block Copolymers$^{13}$

Direct proof for the branched architecture of the star block copolymers was obtained from atomic force microscopy (AFM) experiments on monomolecular films. As a representative example, an AFM image of H40-PBMA58-$b$-PPEGMA40 on mica is shown in Figure 36. The AFM image clearly shows the individual arms of the star polymers and allows for the determination of the exact number of arms per molecule. Figure 36b shows the arm-number distribution obtained after analysis of more than 1000 molecules. The average number of arms is 16, which is only slightly lower than the

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number determined by alcoholysis of the H40-PBMA \textsubscript{x} precursors. Interestingly, the arm number distribution is not continuous but reveals maxima at 8, 12, 16, 20, and 24 arms. These results can be rationalized by considering that the macroinitiator that has been used for the ATRP is a pseudo-fourth-generation, structurally heterogeneous polymer (Chart 1). Because of the 4-fold symmetry of the macroinitiator, star polymers containing a multiple number of 4 arms can be generated from a number of isomeric initiators, which explains the observed relatively high abundance of 8-, 12-, 16-, 20-, and 24-arm star polymers.

Figure 36. (a) Atomic force microscopy height micrograph of H40-PBMA\textsubscript{58} \textsubscript{b}-PPEGMA\textsubscript{40}. (b) Distribution of the number of arms, as evaluated from AFM images, for H40-PBMA\textsubscript{58} \textsubscript{b}-PPEGMA\textsubscript{40}.
8.3 L-Lysine Dendronized Polystyrene\textsuperscript{14}

In an attempt to obtain additional insight into the structure of the dendronized polymers, AFM experiments were performed on thin films, which were spin-cast from DMF on mica substrates. Obtaining high resolution images of the samples proved difficult and took significant effort; however, using ultrasharp tips, single molecule resolution could be achieved. So far, only images from dendronized polymers based on macromonomers 6\textit{a} and 7\textit{a} could be obtained. Figure 37 shows images obtained from dendronized polymers prepared by polymerization of 6\textit{a} at concentrations of 0.1 and 0.5 mol/L and 7\textit{a} at 0.1 mol/L. The image with the highest resolution is Figure 37c, which shows rodlike objects. Analysis of an ensemble of 100 molecules in Figure 37c revealed an average length of 15 ± 7 nm and an average diameter of 6.6 ±1.3 nm. The length of the rods is close to that expected for an extended backbone conformation assuming a length of 0.25 nm per styrene repeat unit and a degree of polymerization of ~90. Although the resolution is not as good as in Figure 37c, the images in Figure 37b and Figure 37d reveal short rodlike objects and globular structures, respectively. Since the samples imaged in Figure 37b and Figure 37d have degrees of polymerization of ~50 and ~5, which is much smaller than that of the sample shown in Figure 37c, this illustrates the effect of the degree of polymerization on the single molecule structure of these peptide dendronized polymers.

Figure 37. (a) TEM micrograph of an ultrasharp Hi’Res AFM tip with a radius <3 nm. (b-e) AFM images of dendronized polymers obtained by polymerization of macromonomer 6a at a concentration of 0.1 mol/L (b), macromonomer 6a at a concentration of 0.5 mol/L (c, e), and macromonomer 7a (d). Samples were prepared by spin-casting onto mica substrates.

8.4 Synthesis, Characterization, and AFM Studies of Dendronized Polyferroacenylsilanes

We also investigated the conformation of the chains of PFSD1 and PFS-D1-Ph. DLS measurements for PFS-D1-Ph in cyclohexane showed a hydrodynamic radius of 37 nm. The cyclohexane solution of PFS-D1-Ph was spin-cast on a fresh cleaved mica substrate and then studied by AFM. We observed dendronized polymer chains as an elongated bar shape. The lengths of the observed chains were 38-76 nm. The height of the observed polymer chain was ca. 1.5 nm (Figure 38C). The elongated conformation of PFS-D1-Ph could be a result of dominant intramolecular hydrogen bonding between the amide groups of the dendrons. However, the large distance between two neighboring

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dendrons (ca. 6.4 Å) on the PFS backbone may prevent a PFS-D1-Ph chain from being folded into a dense stiff structure assisted by the close packing of the liquid crystalline dendrons. PFS-D1 did not reveal any defined conformations by AFM experiments.

Figure 38A shows the AFM images observed from the dendronized PFSs on a mica substrate. We observed spherical objects from PFS-D1 dispersed on a mica substrate but only in a low population. We did not observe any ordered state of dendronized PFS on a mica substrate by AFM experiments due probably to low concentration of polymer solutions used for the sample preparation and the lack of the rigidity of the conformation of dendronized PFSs indicated by weak liquid crystal formation.

![AFM images of fractionated and unfractionated dendronized polymers.](image)

**Figure 38.** AFM images of fractionated and unfractionated dendronized polymers. The sample specimens were prepared by spin-casting the solutions of polymers on a freshly
cleaved mica substrate. (A) **PFS-D1** (fractionated, $M_w$ 121 000 g/mol, CHCl$_3$ solution). (B) **PFS-D1-TEG** (fractionated, $M_w$ 140 000 g/mol, cyclohexane solution). (C) **PFS-D1 Ph** (unfractionated, $M_w$ 110 000 g/mol, cyclohexane solution). The elongated objects in the circles in (C) indicate the polymer chains of 38 nm long (left) and 75 nm long (right).

### 8.5 Direct Observation of Single Helical Polyguanidine Chains

Visual conformations of the large helical polyguanidine, poly-2-2, were undertaken on various substrates including graphite, mica, and alkylated silicon wafer. These three substrates show how the interaction between the substrate and the poly-2-2 directly affects the surface conformation of the polymers. Depending on the substrate used, epitaxial alignment of the polymer chains along with intra- and intermolecular crystallization is seen. Samples were prepared by spin-coating dilute chloroform solutions at room temperature or 50 °C.

Figure 39A shows the AFM image of poly-2-2 on graphite. Poly-2-2 appears to form a network, making it very hard to discern the end of one polymer from another. Helical polyguanidines lay in such sharp angles due to the alkyl groups interacting with the graphite substrate leading to the epitaxial alignment of the polymers. Single helical polymer chains were found to range in size from 400 nm to greater than 1 μm in size.

Figure 39B shows a closer view of one of the junctions between two polymer chains. The polymer chains do not only join together at their ends; sometimes they also appear to crystallize together in the middle of the polymer chains. When two or more polymer chains join together, a thickening of the contact region can be seen (circled).

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Figure 39. AFM images (A: a general view; B: a closer view) of poly-2-2 on graphite spin-coated from a dilute chloroform solution at room temperature. Large white blobs in the images are most likely clusters of molecules that did not adsorb to the graphite surface. The single helical polymers are highlighted with white threads to help differentiate these molecules. The area circled shows where the molecules begin to crystallize with one another to form a network.

Figure 40A shows the AFM height images of poly-2-2 on mica. The polymers were spin-coated at a higher temperature of +50 °C to separate the polymer chains and prevent them from crystallizing together in solution. However, the helical polymers still form a network on mica. The structure of the network is different from that on graphite. First, there is no epitaxial alignment of the polymer chains. Second, the ends of the helical polymer chains and the junction points between some polymer chains appear to be thicker due to the intra- and intermolecular crystallization. Figure 40B is a closer view of single polymer chains on mica. The end of the helical polymer chain is thicker than the rest of the molecule (circled). This is probably due to the polymer chain crystallizing with itself instead of crystallizing with other molecules into a network structure. The length of this molecule is _1.3 _m. Also circled is a polymer chain that seems to have completely crystallized upon itself, adopting a conformation of a shorter thicker rod instead of a very long chain.
Figure 40. AFM images (A: a general view; B: a closer view) of poly-2-2 on mica spin-coated from a chloroform dilute solution at 50 °C.

Figure 41A shows the AFM images of poly-2-2 that was spincoated on an alkylated silicon wafer. Again, it can be seen that the polymer is still crystallizing with itself and other molecules. However, the polymer chains are much more curved and bent than those imaged on the mica surface. The crystallization of the ends into rodlike objects is apparent as well as a greater amount of intermolecular crystallization not at the ends. Polymers in this image are clearly very long, but it is impossible to discern what part of the network is from which polymer chain. The polymer chains also have been stretched out, which can occur during the spin-coating process. Figure 41B is an image of the stretched out molecules. From this image, the much thicker ends of the molecules are still observed; however, the areas between the ends of the polymer are just single polymer chains. Circled is a section that is a single polymer chain and not a collection of two or more polymer chains crystallized together. This section of the helical polymer chain is ~3 μm in length.
Figure 41. AFM images (A: a general view; B: stretched out molecules) of poly-2-2 on an alkylated silicon wafer spin-coated from a chloroform dilute solution at 50 °C.
Chapter 9. Uncompleted Studies

While the accomplished research has laid the foundation for further studies on the spreading of molecularly thin films and the adsorption induced scission of carbon-carbon bonds, there is still much work to be done.

Chapter 9.1 Sensing the Pressure Gradient in Films of Linear Polymers

The brush-like macromolecules have been found to be useful as molecular pressure sensors. The next step would be to employ them into the melt of a linear polymer to observe the pressure gradient. This is important as most applications do not involve branched macromolecules, but their linear counterparts.

Preliminary results have shown that the brushes are able to sense the pressure gradient that exists within the flowing film of a linear polymer. They have been seen changing conformation throughout the precursor film (Figure 42). While we have done extensive work on calibrating the molecular pressure sensor in dense films, some of the calibrations used do not apply to single molecules (i.e. number density of molecules per area). It was also found that there may be flow fractionation of smaller brush molecules during flow or at the interface between the precursor film and the macroscopic drop. Further studies are needed to check investigate these concerns.
Figure 42. Brush-like macromolecules imbedded in the precursor film of a spreading linear polymer. As you travel from the film edge to the foot of the drop, one can see the changes in conformation of the brush molecules.

Chapter 9.2 Scission during the Spreading Process

During our previous work with brush molecules, we discovered the remarkable phenomenon that molecular brushes with long side chains undergo scission of the backbone covalent bonds as a result of adsorption onto a substrate. Preliminary results indicate that this phenomenon is very sensitive to the interaction with the substrate. As such, one can use the scission reaction as a very accurate probe for measuring flow properties of polymer monolayers along with interfacial interactions in thin films (Figure 43).
Figure 43. Brush-like macromolecules undergoing the scission process while flowing across the surface. As you travel from the film edge to the foot of the drop, one can see that the molecules are getting shorter.

Chapter 9.3 Effect of Surface Energy on the Rate of Scission of the Backbone

Our understanding of this phenomenon is in its infancy. At this stage, the primary goal of the experimental studies is to understand what controls the rate constant of the scission process and the stress distribution within adsorbed macromolecules. Note that the force value is proportional to the molecule’s width $d$ and also depends on the surface energy of the substrate. Therefore, in order to generate large forces and challenge the carbon-carbon bonds in the backbone we first need to measure the rate constant of the scission process as a function of the molecular architecture and the interaction with substrate. Preliminary experiments have been undertaken to verify the effects of the interaction with the substrate. In our experiments, we give a preference towards liquid substrates that allow gradual variation of the surface energy by mixing two different
liquids (propanol and water) and also facilitate rapid equilibration of the monolayer structure (Figure 44). Both factors ensure reproducibility of the kinetics studies.

**Figure 44.** The effect of variations in the surface energy on the rate of the scission. As can be seen in the inset AFM images they molecules are drastically different in appearance after the same time of exposure on different surface energy substrates.
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