The spring constant, \( k_{\text{spring}} \), can be determined using the tip. This can be done by measuring the deflection of a silicon-oxide tip. The theoretical value is 0.04 times the spring constant.

Summary

This thesis contains the results of a Scanning Force Microscopy (SFM) study on several polymer surfaces. In chapter 1, a review on Scanning Probe Microscopy in general, a short historical overview of the 'scanning probe'-techniques is presented. Scanning Probe techniques are those techniques which make use of a sharp probe tip which is scanned across the surface of interest. Due to a specific interaction between tip and surface the surface topography and/or properties can be determined. This specific interaction is an electric current (the tunneling current) in the case of a Scanning Tunneling Microscope (STM). When a voltage is applied between tip and sample, a current can flow at a distance of about 1 nm. This is the quantum mechanical tunneling current. The magnitude of this current is extremely sensitive with the distance between tip and sample. This explains the very high resolution of the STM in the normal (z) direction. With STM, only (semi)conducting samples can be investigated. In case of a Scanning Force Microscope (SFM) the specific interaction is a force. The sharp tip is integrated with a soft spring (cantilever) whose deflection can be measured. Because of the fact that the tip is in repulsive contact with the sample, also in SFM a high resolution can be attained. A clear advantage of SFM is that conducting as well as nonconducting surfaces can be studied. In Scanning Probe Techniques, the scanning motion is performed using piezoelectric elements which translate the sample (or the tip) in three dimensions. With STM and SFM, in some cases atomic or molecular resolution is feasible. Binnig and Rohrer, the inventors of the STM technique (1981), were awarded the Nobel price for physics already in 1986. This illustrates the fact that the Scanning Probe Techniques STM and SFM have become important analytical tools in science, becoming more and more integrated with standard laboratory equipment. The invention of STM has initiated the development of several other scanning probe techniques based on STM technology. These spin-off techniques will also be briefly explained in the first chapter.

In chapter 2 the SFM technique will be explained further. The various forces that can exist between two surfaces will be mentioned, such as Van der Waals forces (attractive and repulsive), electrostatic and magnetic forces. Subsequently, the most important element in any force microscope, the tip, will be explained. The dimensions of the tip are crucial for the resolution that can be attained. For detection of the cantilever deflection, several schemes are possible, the most common one being the laser beam deflection technique. A laser is focused onto the back side of the cantilever and its reflection is directed onto a position sensitive detector consisting of two segments. When the cantilever deflection changes due to an interaction force between tip and surface, the intensities of the two segments change. The intensity difference between the two segments is a measure for the force between tip and sample. Different scanning modes are available for the data acquisition. An electronic feedback circuit can be used which maintains the cantilever deflection during the scanning motion at a preset value. This scanning mode is referred to as the "constant force" mode. The height of the sample is continuously...
adjusted in the z-direction in order for the cantilever deflection to stay at its constant value. The topographic information is therefore contained inside the z-piezo driving signal. Another way of data acquisition is to disable the feedback system and measure directly the deflection of the cantilever. The height of the sample is now constant (constant height mode). Apart from the two previous modes there is one more scanning mode which deserves some special attention. This mode is called the 'edge enhanced imaging' mode and gives a much more detailed overview of sample morphology, especially when samples with large variations in height are investigated. This scanning mode is illustrated in the case of poly(ethylene) single crystals. Finally, the experimental set-up will be presented in this chapter.

Chapter 3 contains the SFM results on several classes of samples:

- **Thin films of highly oriented poly(tetrafluoroethylene)**
  This study shows that SFM is very well suitable for the determination of thin film morphology from nanometer till micrometer scales. Even molecular resolution has been achieved. The degree of film orientation is depending on the film thickness. Thinner films show a higher degree of orientation.

- **Polymer single crystals of poly(ethylene) and poly(paraxylylene)**
  A long-standing problem in the field of polymer crystallization is the chain folding problem. Polymer single crystals consist of thin (10 nm) lamellae, several micrometers in size. The length of a polymer chains equals many times the lamellar thickness and from X-ray studies it is well known that the chains are aligned perpendicular to the lamellae. Therefore they have to adopt a folded conformation. The two existing models are the adjacent reentry model and the switchboard model. In the adjacent reentry model, the chains fold back in the adjacent position, so the surface in this case is very regular. In the switchboard model the chains folds are more chaotic and a less regular surface results. The morphology of the polymer single crystals can be easily visualized with SFM: single and multilamellar crystals, growth spirals (single and double) have been observed. It was not possible to obtain information corresponding to the chain folds. Probably the folds of the polymers at the surface are a little bit mobile which prevents a stable image to be acquired. In an indirect way it was possible to obtain information of the folding surface of the crystals. This was done using a decoration technique. The PE crystals are showered with short polyethylene fragments which crystallize on the folding surface of the polymer crystals giving rise to the formation of small PE rods. The orientation of these rods indicates if a preferable direction of the chain folds exists. The orientation of the rods was such that they were oriented perpendicular to the growth faces of the polymer crystal. This elucidates the four quadrants of the PE single crystal because in every quadrant the orientation of the rods is different. This is an indirect evidence that the fold surface of the PE single crystals is well ordered. The decorated PPX single crystals do not exhibit any orientation of the PE rods. From this fact the conclusion that the fold surface of PPX single crystals is not ordered, can not be justified because incompatibility effects may play a role.

- **Crystals of the cyclic compound [T(SiMe₃)₄]₂**
  Polymers with alternating blocks of silicon and thiophene are becoming more and more important because of their possible application in non-linear optics and LED's. A byproduct of such a synthesis was the cyclic compound [T(SiMe₃)₄]₂ of which very nice single crystals could be grown. These have been investigated with SFM. The molecular period-
SUMMARY

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a- and c-direction as measured with X-ray diffraction.

• Circular DNA on a mica substrate

SMF is also very well suitable for the investigation of biological samples such as DNA

molecules. The DNA polymer consists of two complementary strands who carry the four

bases adenine (A), guanine (G), thymine (T) and cytosine (C). In this study individual

DNA molecules were visualized on a mica substrate. The DNA molecules are circular

and can be easily distinguished from features arising from the substrate. The contour

length of the DNA molecules as determined from the SFM topography measurements is

in agreement with the value determined from TEM reference samples. The DNA appears

in the topography image as a 30–40 nm wide strand, which is several times its natural

value width of 2 nm. This can be explained by convolution effects. The tip has an end

radius of about 20 to 40 nm. When the tip passes over the DNA molecule, the DNA

molecule effectively scans the tip because the DNA molecule is much sharper than the tip.

It is clear that sharper tips have to be used to diminish these shape convolution effects.

It is to be expected that SFM will be able to recognize the different bases inside the DNA

molecule in the future.

The main part of this thesis is described in chapter 4. The subject of investigation are thin

lamellar films of the symmetric diblock copolymer PS/P2VP. Because of the phenomenon of mi-
crophase separation block copolymers are of great technological interest, e.g. in polymer blends,

for colloidal stabilization and in high-impact polymer systems. Also block copolymers can be

used for modification of surface properties. When a thin film of block copolymer is deposited

onto a flat substrate, the difference in surface energies of the two blocks leads (upon annealing)
to an orientation of the lamellae parallel to the substrate and hence to an accompanying quanti-
tization of the film thickness in the ordered state. The local film thickness satisfies the equation

\[ d_n = nH \text{ or } d_n = (n + 1/2)H, \]

depending on whether like or unlike blocks are present at the air-polymer and substrate-polymer interface. \( H \) is the lamellar periodicity of the system which depends on the molecular weight of the block copolymer. Samples were prepared by spin-coating onto silicon substrates from a solution in toluene, yielding flat films with a thickness \( d \) of 1000 to 2000 Å. The thickness \( d \) of the film immediately after spin coating will in general not be identical to any of the equilibrium values \( d_n \), that is to say \( d_n \leq d \leq d_{n+1} \) for some integer value of \( n \). In the ordered state, the surface will therefore consist of areas with thickness \( d_n \) and areas of thickness \( d_{n+1} \). These are islands or holes with equal depths or heights \( H \) which are formed by nucleation on the free surface during the annealing process. With increasing

annealing time, these domains (islands or holes) will grow in such a way that the total length of the domain boundaries decreases. The pattern of domains on the surface can be characterized by the mean radius of the domains \( R \) or by \( \lambda \), the mean interdomain distance. With SFM it is possible to investigate the growth pattern of the domains. For this purpose a 'hot-stage' for the SFM was designed to allow for in-situ annealing of the samples, so that exactly the same sample area could be relocated after annealing. In the growth phase three different processes could be identified: growth of individual domains, coalescence of domains and dissolution of domains. All three processes are evidently visible from subsequent SFM topography images. The analysis of the measurements showed that in general, the mean radius followed the growth law \( R \propto t^\alpha \), where \( \alpha \) is the critical growth exponent and \( t \) the annealing time. Theoretically, \( \alpha \) should be 1/3 according to the classical Lifshitz–Slyozov result. But the system in that case
was treated as an ordinary two-phase system. In the theoretical analysis in this chapter the influence of the molecular structure on the growth behaviour of the surface pattern has been investigated in detail. Also the dependence of $\alpha$ on the surface coverage of the domains ($\Phi$) has been studied. It turned out for all samples, the critical growth exponent $\alpha$ was less than 1/3. Possible explanations of this discrepancy between theory and experiment have been presented. For example, not all of the domains necessarily belong to the same lamellar layer, which causes a disturbance of the growth process and a decrease in the value of $\alpha$. During the formation stage of the domains, also ordinary defects can be formed, who seem to play a crucial role in the domain growth process. Also the existence of ordinary defects in the lamellar structure leads to a decreased growth exponent.

The last chapter deals with the characterization of (sub)monolayers of polystyrene and the determination of the elastic properties of such layers with SFM. Macromolecular systems are very complex. In order to understand the properties of these systems, a different point of view will be taken by approaching the problem from the molecular level. Assessing specific material properties at the molecular level is becoming increasingly important because of the continuous miniaturization in technology. One of these specific microscopic properties is the entropic spring constant of a single polymer chain. In order to be able to measure this quantity, a situation had to be created in which isolated polymer chains exist. This has been achieved by making use of Self Assembling Monolayers (SAM). The system is based on a mixed monolayer of dodecanethiol and thiol-terminated polystyrene. When a mixture of these compounds is adsorbed from toluene onto a gold surface, a mixed monolayer results, in which isolated polymer chains, covalently attached to the substrate, are present. The polystyrene molecules do not overlap and are randomly distributed on the surface. This is evident from the SFM topography measurements which have been performed after the adsorption process. In the SFM topographs small protrusions are observed on the otherwise flat gold terraces which represent isolated polymer chains in a collapsed state. If more polystyrene is added to the adsorbing solution an increase is found in the number of molecules observed on the surface.

With SFM, lateral variations in surface elasticity have been measured. In this case the sample was vibrated in the $z$-direction with a frequency of about 10 kHz and an amplitude of about 1 Å. The response of the cantilever, in contact with the sample surface, was measured as a function of the lateral position of the tip. In case of a hard surface, the cantilever amplitude will be equal to the sample amplitude. In case of a soft surface, the cantilever amplitude will be less than 1 Å because of indentation of the sample surface. Applying this method to the mixed monolayers resulted in the observation that the polystyrene molecules were softer than the surrounding monolayer of dodecanethiol. The theoretical and experimental values for the spring constant of a single chain measured under compression are in reasonable agreement. The use of mixed self-assembling monolayers has proven to be suitable for studying isolated polymer chains with scanning probe techniques.