University of Groningen

Surface forces and narorheological properties of adsorbed polymer monolayers.

Belder, Gerald Frederik

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1995

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
Belder, G. F. (1995). *Surface forces and narorheological properties of adsorbed polymer monolayers.* s.n.

This thesis is concerned with the behaviour of adsorbed polymer layers at the solid-liquid interface. The instrument that plays a central role is the so-called Surface Forces Apparatus (SFA), that allows for direct measurement of the interaction between two surfaces as a function of their separation. By applying adsorbed polymer layers to one or both of the surfaces, the interactions between a polymer layer and a bare surface or between two polymer layers can be measured in a liquid medium. These interaction play an important role in many technological processes, such as the stabilization of colloidal dispersions, adhesion between two surfaces and lubrication of two surfaces in sliding contact. The contents of this thesis will now be summarized for each chapter.

Chapter 1 gives a general introduction about polymers at interfaces. The first SFA experiments on polymers were carried out with adsorbed homopolymers. In this case adsorption is caused by the affinity of individual segments for the surface. If a sufficient number of segments is simultaneously in contact with the surface, the total adsorption energy is sufficient for irreversible adsorption of the chain. Adsorption of block copolymers with one adsorbing and one non-adsorbing block is another possibility. The non-adsorbing block is connected indirectly to the surface in this case. A non-adsorbing polymer can also be anchored onto the surface by means of a special end-group. The interactions between polymer layers can be divided into:

- Osmotic interactions between segments of the chain. These interactions are repulsive in a good solvent and attractive in a bad solvent.
- Interactions due to entropic elasticity. These interactions are repulsive when the chain is compressed and attractive if the chain is extended.

The force-distance curve is determined by the balance of both contributions. The remainder of this chapter describes some shear experiments on polymer layers between two surfaces. The most general conclusion to be drawn from these dynamic experiments is that the relaxation processes are orders of magnitude slower than in the bulk.

Chapter 2 describes the SFA and its operation in full detail. Some modifications for performing shear experiments are also described.

Chapter 3 describes the design of a new SFA based on the experience gained during the period of this thesis work. The most important changes are:

- A simple modular design, less susceptible to disturbances like mechanical backlash and thermal drift.

- An integrated shear mechanism. No modifications to the apparatus are required to perform shear experiments.
- The use of a special force sensor that allows for real-time measurement of both normal and lateral forces during the experiment.
- Automation of the measurements. This improves the reliability and reproducibility of the experiments.

Chapter 4 is concerned with adsorbed layers of PS/P2VP block copolymers in a toluene environment. The P2VP block adsorbs and 'anchors' the PS block, which does not adsorb itself. The interaction between this kind of layers are repulsive in a good solvent for PS (like toluene). The layer thickness follows directly from the force-distance curve. In this chapter the dependence of the layer thickness on the size of the P2VP block is studied, at constant size of the PS block. It turns out that the variation of the layer thickness with varying P2VP block size is much less than expected from some existing simple models. These models wrongly suppose that the P2VP blocks lie on the surface as collapsed, adjacent discs.

Chapter 5 describes the first SFA measurements on so-called depletion forces between surfaces - carrying anchored polymer layers - in a solution containing free chains. Depletion forces arise from depletion zones. A depletion zone is a zone adjacent to the surface where the chain concentration is lower than in the bulk. Such a zone appears when a surface is placed in a solution of a non-adsorbing polymer. Because the surface is impenetrable, the number of chain conformations at the surface is restricted. Thus it is unfavourable for a non-adsorbing chain to be located at the surface. When two surface approach, their depletion zones will start to overlap. This creates an attractive force originating from the osmotic pressure of the bulk. In a colloidal dispersion this may lead to flocculation. In this chapter it is shown that the attractive force is even stronger when anchored chains are present on the surfaces.

Chapter 6 describes the interactions between anchored PS layers and bare surfaces. Two different systems are studied:

The first system is PS with an end-functional thiol (-SH) group. By means of this thiol group the PS can be anchored onto certain metal surfaces like silver and gold. By fitting the SFA with one silver and one mica surface, the interactions between a PS-SH layer on silver and bare mica surface can be measured in a good solvent (toluene). The layer thickness follows immediately from the measurements.

Using an Atomic Force Microscope (AFM), the structure of a dried PS-SH layer can be made visible. The average distance between the anchor points can then be determined and

points are far enough apart to avoid overlap between neighbouring chains. The observed stretching of 40-50% with respect to their dimension in the free state is therefore ascribed to the presence of the surface.

The second system is a PS/P2VP block copolymer with a very small P2VP anchor block, adsorbed onto mica from toluene. This can effectively be regarded as end-grafted PS. By comparing the force-distance curve for one layer against a bare mica surface with the curve for two such PS layers against each other, it can be determined whether The PS layers interpenetrate during compression of the surfaces. It turns out that this does not occur, or at most very slightly. It can be concluded that both layers shrink independently during compression of the surfaces.

Chapter 7 presents the first results obtained on the shear behaviour of an adsorbed polymer monolayer against a bare surface. The system used is PS/P2VP. Two models are introduced in this chapter. First a mechanical model to derive the effective shear moduli. Second a semi-quantitative molecular model relating the shear moduli to the elasticity of the chains and a hydrodynamic layer, that is assumed to be present adjacent to the bare surface in this model. The chain ends located in this hydrodynamic layer are trapped on the time scale of the experiment. This causes an elastic response, because the chains are forced to stretch during the shear. The viscous response is attributed to the flow of solvent through the hydrodynamic layer. At increasing compression both the elastic and the viscous response increase. The elastic response increases faster though. This means that the overall elasticity of the polymer layer increases. This effect can be attributed to the increasing number of chain ends getting trapped in the hydrodynamic layer.