Pattern formation in ultrathin polymer films prepared on microstructured surfaces

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Abstract. Film formation of ultrathin polymers on microheterogeneous surfaces is strongly influenced by molecular surface patterns which cause local wettability differences for liquid phases in contact with the surface. Surface coverage with polymers transferred by dip-coating from polymer solutions is controlled by surface heterogeneities prepared by softlithography or by electron beam lithography of self-assembled monolayers. Using crystallisable polymers for ultrathin film formation (polyethyleneoxide (PEO) we could carefully investigate the competition in pattern formation resulting from the dewetting process and patterns which result from lamella crystallization of PEO in ultrathin films. For the first time we could observe that ultrathin polymer films of crystallisable polymers which are prepared in absence of any substrate surface defects form a metastable state in which they can exist over days and weeks without crystallization. Heterogenous nucleation in these metastable films can be done by external stresses such as contact with an AFM tip. The nucleation on demand allowed us to study the diffusion controlled pattern formation that is observed during lamella crystallization and the growth process resulting in different morphological features could be studied at elevated temperatures and in lateral confined areas which were realized by the film preparation on the microheterogenized surfaces.

1. Micropatterned surfaces based on self-assembled monolayers
Self assembled monolayers (SAM) of organic thiols that chemisorb to gold substrates are an ideal tool for tuning surface properties such as wetting or adsorption or introducing chemical surface functionality in order to immobilize biomacromolecules. Several methods especially microcontact printing [1] and electron beam lithography [2] (Fig.1) are used to create microheterogeneous surfaces in which different chemical groups are arranged in predefined surface areas. For visualization of micro-contact printed SAM’s (thickness ca.3 nm) low energy scanning electron microscopy ($E_0 < 1$ keV ) is used. Concerning surface wettability methylterminated SAM’s favour hydrophobic surface properties while carboxy terminated SAM’s create hydrophilicity and in addition they offer hydrogen bonding sites for appropriate chemical entities such as aminogroups.

Surface areas of different wettability can control wettability patterns of liquid phases as well as dewetting patterns of ultrathin polymer layers [3] that are formed during a dip-coating process [4].

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2. Thin film patterns of PEO

2.1. PEO film preparation
Polyethylenoxide (PEO) is a hydrophilic, crystallizable [5] and water soluble polymer which is often used as a biomaterial that rejects non specific protein adsorption on surfaces. Although the mechanism of protein rejection or antifouling is not understood there is some evidence that morphological and structural features of the PEO layers strongly influence the adsorption behaviour [6]. This motivated us to explore the complicated morphological behaviour especially of ultrathin PEO coatings which were prepared by dip-coating of hydrophilic surfaces from PEO solutions.

2.2. PEO film crystallization
In ultrathin films (thickness < 3nm ) PEO can crystallize in highly branched structures as schemed in Fig.2 A. The dendritic structures result from a diffusion limited aggregation process (DLA) in which highly branched polymer lamella grow [7]. The surface heterogenization described in section 1 allowed us to follow the influence of different surface properties on the thin film structure formation.

Figure 1. I: General scheme of a self assembled monolayer (SAM) attached to a gold surface by Sulfur - Gold interaction
II: General scheme of a microheterogeneous surface with hydrophobic and hydrophilic surface groups
III: Preparation of micropatterned surfaces by A) micro-contact printing and B) E-beam lithography of SAM
IV: Imaging of ultrathin layers by Low Voltage Scanning Electron Microscopy (LVSEM)
The preparation of hydrophobic parts which separate a hydrophilic surface domain from its surrounding causes dewetting of the PEO film during dip-coating [8]. The PEO film formed within this isolated domain appears to be non crystalline as to recognize from the missing dendritic features. From imaging ellipsometry we determined the layer thickness of this non-crystalline PEO to be 4 nm. We could demonstrate by contact with an AFM tip that the material undergoes the dendritic crystallization immediately after the tip contact. From these observations it is obvious that the PEO films are initially amorphous after the dip-coating process and that the metastable film can be nucleated to start dendritic growth after applying some external stress. We identified surface steps, scratches and rims that result from dewetting processes as additional nucleation sites. These experiments demonstrate for the first time that avoiding heterogeneous nucleation events ultrathin PEO layers can form metastable states which can be transformed into crystalline state upon demand.

2.3. E-beam lithography of PEO films
For experiments focussing on the protein adsorption of PEO films with different morphologies the ultrathin film need to be immobilized on the surface in order not to be dissolved after film exposure to water. We could demonstrate that e-beam lithography is a reasonable way to achieve this goal. Structural features that are initially present in the film can be preserved during the e-beam lithographic process as demonstrated in Fig.3.

2.4. The crystallization process
The molecular ordering process which describes the transformations from an molecular thin PEO layer into a PEO lamella crystal has been described in detail by [7],[8] and is schemed in Fig.4. Basically the transformation of the polymer chains from the amorphous state into the lamella is accompanied with an increase in film thickness and consequently with the formation of a lateral depletion zone ahead of the crystallization front. Molecules attaching to the lamella interface have to pass this zone by diffusion. Furthermore relaxation processes of polymer chains at the interface have to be taken into account for the simulation of the details of branching structures.
Figure 3. PEO films with different structural features immobilized at the surface by e-beam lithography. A) Rapid crystallized monolamella dendritic features B) Multilamella stacks. Non-irradiated areas are dissolved in water. C) AFM image of rapid crystallized dendritic sample thermally treated above melting temperature. Initial structures are stabilized by ebeam lithography surrounded by dewetted areas above $T_m$.

Figure 4. Diffusion controlled crystallization process of ultrathin amorphous PEO layers

Conclusions
Self-assembled hydrophilic monolayers were locally hydrophobized by ebeam lithography in order to create microheterogeneous surfaces as a base for the generation of micropatterned ultrathin PEO films by controlled dewetting. Morphologies of monolayers and ultrathin polymer films were analyzed by low voltage SEM. PEO films could be attached to the surface by ebeam lithography and therefore becoming insoluble upon water treatment. Comparison of fixed (by electron irradiation) and non fixed PEO areas allows the investigation of structural rearrangements (lamella thickening etc.) due to thermal treatment or other environmental influences (humidity).

References
[1] Xia Y and Whitesides G 1998 Angewandte Chemie International Edition 37 550–575
[2] Carr D, Lercel M, Whelan C, Craighead H, Seshadri K and DL A 1997 Journal of Vacuum Science and Technology A 15 1446–1460
[3] Braun H G and Meyer E 1999 Thin Solid Films 345(2) 222–228
[4] Darhuber A A, Troian S M, Davis J M, Miller S M and Wagner S 2000 Journal of Applied Physics 88(9) 5119–5126
[5] TakahashY and Tadokoro H 1973 Macromolecules 6(5) 672–675
[6] Harder P, Grunze M, Dahint R, Whitesides G M and Laibinis P E 1998 Journal of Physical Chemistry B 102(2) 426–436
[7] Sommer J U and Reiter G 2000 Journal of Chemical Physics 112(9) 4384–4393
[8] Meyer E and Braun H G 2005 Journal of Physics-Condensed Matter 17(9) S623–S635