COMPLEX STRUCTURE FORMATION IN ULTRATHIN PEO FILMS

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ABSTRACT. Our experimental studies focus on pattern formation of ultrathin crystallisable polyethyleneoxide (PEO) films on microheterogenous substrates. Films are formed during dip-coating from solutions on chemical heterogenized substrates. The resulting thin film polymer morphology of the crystallisable PEO reflects a complex scenario of various physical processes which include a) thin liquid film formation and dewetting on heterogenized surfaces, b) solidification of amorphous PEO, c) nucleation processes in ultrathin PEO films and d) the crystallization and growth morphologies of PEO in both lateral and thickness confining environment. We could elaborate experimental conditions which allowed us to a) prepare metastable non-crystallized microstructured PEO films which can be b) nucleated on demand to start PEO crystal growth into highly branched lamellae patterns which are typical for diffusive growth processes.

The diffusive growth in confined areas with limited materials (PEO) resources results in morphological changes of the branch structure.

Introduction

Dewetting in thin polymer films generally causes the formation of holes that are either nucleated by defect sites or that appear as the initial state of a spinodal type dewetting szenario [1,2]. Chemical heterogenization of surfaces into areas of different surface free energy (Fig.3) has been used to localize the dewetting process and therefore to prepare ordered thin film patterns [3]. Theoretical approaches have been elaborated to predict the dewetting patterns of polymer films in contact with microheterogeneous surfaces [4,5]. Morphological phase diagrams which relate the sizes and ratios of wettable and non-wettable striations with the film stability were calculated [4]. The topography of liquid thin films that result from dip-coating of a patterned surface have recently been investigated by Davis [6].

In thin films of amorphous polymers the dewetting process is the major process to determine thin film morphology. Investigations on thin film structure formation in crystallizable polymer systems are rare but an increasing number of research activities focuses on the crystallization of polyethyleneoxide (PEO) thin films.

Generally ultrathin polymer films of PEO prepared at room temperature show a highly branched lamella morphology of unilamella thickness (Fig.1). The underlying diffusive growth process which results in branched lamella were theoretically described and experimentally verified by Sommer and Reiter [7,8,9]. The dendritic growth patterns have also been observed during demixing and crystallization of PEO in PEO/PMMA blends in the experiments of Wang et. al. [10,11].

The branching morphology may completely disappear with increasing film thickness or with decreasing undercooling during crystallization [12].

Our experimental studies focus on a strategy to investigate the complex scenario that can occur in ultrathin crystallizable polymer films [13] and that should answer the following questions:
Is there any interaction (competition, synergism) between dewetting and crystallization process in polymer films prepared by dip-coating?

Is there an influence between dewetting patterns, crystallization behaviour and the crystallization morphologies?

Is it possible to control the morphological features in ultrathin films?

Fig. 1: Dendritic PEO lamella (thickness ~ 8 nm) observed in ultrathin PEO films (left low voltage SEM, right AFM)

**Surface patterning and crystallization behaviour**

Surface patterning creates a set of pre-defined surface areas in which the surface properties are determined by the appropriate molecular units (Fig. 2).

By thermal evaporation 50 nm thick gold layers were prepared either on silicon wafers or on glass slides. The gold surface was modified by self-assembly of thiol based molecular structures which resulted in either hydrophilic (molecular unit A, Fig. 2) or hydrophobic (molecular unit B, Fig. 2) surface properties.

Surface patterning is either achieved through micro-contact printing [14] of an ethanolic solution of Thiol B (Fig. 2) followed by the chemisorption of bare gold areas with compound A (Fig. 2) or by homogenous chemisorption of the gold surface with A and electron beam lithography of the self-assembled monolayer [15]. During electron beam irradiation the carboxylic groups of the molecule most probable degrade and an aliphatic entity similar to structure B results in the areas exposed to electrons.

Surfaces with different layout of hydrophilic and hydrophobic motifs (Fig. 3a, b) were dip-coated from a chloroformous solution of PEO (0.15 - 0.25 w %) with molecular weights (1500 < Mw < 10000).

The structural design for surface heterogenization in Fig. 3a was chosen so that the hydrophobic hexagonal pattern should become dewetted form the hydrophilic PEO polymer segments and the film formation and crystallization especially the growth of dendritic structures should follow the surface areas specified by the continuous hydrophilic surface pattern.

The surface pattern illustrated in Fig. 3b creates hydrophilic and therefore wettable surface domains of circular shape which are separated from the surrounding...
continuous hydrophilic surface area by a non-wettable circular ring (hydrophobic barrier) of typically 2 µm size.

Fig. 2 Molecular structure of thiols used for hydrophilic (A) and hydrophobic (B) areas.

Fig. 3 a, b Scheme of hydrophobic (white, B) surface and hydrophilic (red, A) surface patterns.

Fig. 4: Ultrathin Polyethylenoxide films obtained by dip-coating of surface modified substrates (see. Fig. 3 a, b). (a, b Low voltage SEM images)

As expected a continuous crystallized polyethyleneoxide film is grown around the non-wettable hexagons (Fig. 4a).

If we create micrometer sized isolated areas (Fig. 3b) we observe that these isles do not show any crystallization features while the continuous film crystallizes (Fig. 4b).

We assume that the non-crystalline state inside the isles is due to a lack of nucleation sites and that the initial state of the ultrathin PEO layer after dip-coating generally is a metastable amorphous state.
In order to prove this hypothesis further experiments on the heterogenous nucleation of the ultrathin PEO layers were done.

**Nucleation in ultrathin PEO films**

Fig. 5a demonstrates a more complex surface structure which again clearly reveals the crystalline branched morphologies present in the continuous film area outside the motif and the “non-crystalline” part inside the micrometer sized isolated film segments.

We could demonstrate that the initially amorphous PEO film within the complex structure is metastable and that dendritic crystallization can be nucleated by extern stresses (for example by AFM tip contact) (Fig. 5b)

![Fig. 5: a) Metastable amorphous PEO film segment which can be heterogeneous nucleated by AFM tip contact. b)orizontal nucleation on request allows to control morphological features in dependence of different physical parameters as for example temperature.

The combination of an optical reflection microscopic equipped with a AFM device allowed us to observe the ultrathin film in dark field mode and to place the AFM tip on the sample within a precision of ~ 5 µm. We could show by change in light microscope dark field contrast due to additional scattering of the dendritic patterned surface that the AFM tip initiates the dendritic crystallization.

In a set of different experiments we observe that heterogeneous nucleation in ultrathin PEO films may occur from

- Indentation by AFM tip
- Surface scratches
- Surface steps
- Rim structures arising from the dewetting process

The preparation of metastable amorphous ultrathin PEO films and the **nucleation on request** allows to control morphological features in dependence of different physical parameters as for example temperature.

**Thin film crystallization under lateral confinement and varying crystallization temperature**

In accordance with non-equilibrium growth processes highly branched lamella structures are formed for high undercooling conditions. Tip radius and correlation
length of dendrites as characteristic morphological features (8) grow with increasing crystallization initial temperature (Fig. 6 a-d). Additionally morphological peculiarities are observed in confined geometries. Due to the limited material reservoir in isolated areas the diffusion gradient is changed during the isothermal growth process resulting in an increasing tip radius and lamella thickening (Fig. 6c).

Fig. 6: Control of morphological features in confined ultrathin PEO-films crystallized at a) 20 C, b) 31 C, c) 33 C, d) 38 C

The molecular model of dendritic lamella growth in ultrathin films

The molecular model that is discussed for the dendritic crystallization in ultrathin polymer films (8) and that is able to explain the peculiar features of diffusion controlled crystal growth in confined systems is sketched in Fig. 7.

After dip-coating an initially 3-4 nm thick amorphous polymer layer forms on the substrate. After nucleation a lamella nuclei of ~ 8 nm is formed and due to volume conservation of the material a depletion zone results between the amorphous and the lamella boundary. For the further lamella growth process and the lamella morphology two different molecular process are important:

- The diffusion of macromolecules across the depletion zone
- Rearrangement of polymer chain segments at the lamella interphase
Compared to the general theories describing morphological features in DLA growth processes the peculiar features for this process are related to the segmental rearrangements of the polymer chain segments which causes a) less curved structure and b) thicker lamella structures under conditions where the segmental mobility of polymer chain segments at the crystal interface is increased which is the case at higher crystallization temperature.

At a given temperature the molecular rearrangement at the interphase is disturbed by chains diffusing along the depletion zone. The growth process in a confined area causes an increase in the depletion zone with progressing crystallization. As the depletion zone increases the number of molecules/time that diffuses across the zone and that interfere with the segmental reorganization at the lamella interface decreases. Therefore the rearrangement process dominates which results in thicker and less curved lamella.

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REFERENCES