

Dendritic crystallization in ultrathin microstructured poly(ethylene oxide) (PEO) films

Ultradünne Polymerfilme finden sich in zahlreichen High-Tech-Anwendungen funktionaler Polymere. Hierzu zählen photo- oder elektronenstrahlempfindliche Resiste, die zur Strukturierung in der Mikrotechnologie eingesetzt werden ebenso wie Polymerschichten zur Biokompatibilisierung verschiedenster Materialoberflächen. In vielen Anwendungsbereichen werden strukturell homogene defektfreie Schichten angestrebt. Um dieses zu erreichen ist ein grundlegendes Verständnis der strukturbildenden Prozesse bei der Filmbildung erforderlich. Die Be- und Entnetzungsprozesse auf homogenen Substratoberflächen standen hierbei bislang im Vordergrund des wissenschaftlichen Interesses. Mit den Möglichkeiten einer zielgerichteten Veränderung lokaler oberflächenchemischer Eigenschaften, wie sie durch neuere Methoden der Softlithographie [1] bzw. der Elektronenstrahlolithographie selbstordnender Monoschichten [2] zur Verfügung stehen, rückt die Untersuchung und Nutzung der Strukturbildung auf heterogenen Oberflächen zunehmend in den Vordergrund. Darüber hinaus werden mit Anwendung kristallisationsfähiger Polymerstrukturen, wie sie z.B. in Poly(ethylenoxid)ketten oder Kettensegmenten in PEO-Blockcopolymeren vorliegen und bei der Biokompatibilisierung von Bedeutung sind, auch Kristallisationsprozesse in ultradünnen Schichten interessant.

Es konnte gezeigt werden, dass die chemische Strukturierung von Oberflächen die Filmbildungsprozesse von Polymeren auf diesen steuern kann [3,4]. Bei PEO wird die Kristallisation in ultradünnen [5-8] strukturierten [9-11] Filmen oder in Blendsystemen [12,13] in komplexer Weise beeinflusst.

Filmbildung und Kristallisation sind zwei zeitlich voneinander getrennte Prozesse. Erfolgt die Filmbildung auf strukturierten Oberflächen unter Ausbildung isolierter Domänen im Mikrometerbereich kann heterogene Nukleation vermieden werden, sodass ultradünne PEO-Filme über mehrere Wochen im amorphen Zustand existieren. Die Nukleierung, die durch Oberflächenheterogenitäten (Kanten, Entnetzungswülste etc.) oder mechanische Spannungen initiiert werden kann, führt zu einem lamellaren Wachstum im Polymerfilm, das bei ultradünnen Filmen aufgrund der diffusionskontrollierten Wachstumskontrolle hoch verzweigte dendritische Strukturen der Kristall-Lamellen aufweist. Der diffusionskontrollierte Wachstumsprozess ist durch geometrisch einschränkende Diffusionsbedingungen in lateral strukturierten Filmen deutlich beeinflussbar.

Introduction

A number of applications of functional polymers require their preparation as ultrathin films on various substrates. Examples from emerging technologies are biocompatible surface coatings or polymer resist films for lithographic structuring technologies. The understanding of basic physical and physicochemical structure formation processes in ultrathin films is a prerequisite for their successful use in high-tech applications. The most investigated interfacial process that is known to influence the structural features of ultrathin films is dewetting. Dewetting is generally accompanied by rupturing processes in ultrathin films which consequently cause

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lateral defects generally seen as an unfavourable process during film formation. Nevertheless dewetting can become an important step in surface controlled structure formation of ultrathin films if the process can be controlled locally as for example in contact with heterogeneous surfaces [3,4]. The lateral control over surface interactions can be achieved by surface patterning techniques as micro-contact printing [1] appropriate molecular units or by electron beam lithography of self-assembled monolayers [2].

Besides dewetting crystallization in ultrathin films (thickness < 10 nm) determines the morphological features of these films [5-7]. Compared to dewetting processes crystallization behaviour in ultrathin films has attracted much less attention during the past mainly due to the fact that most polymers chosen for ultrathin film applications are amorphous. In case of crystallizable polymers such as poly(ethylene oxide) (PEO) or PEO blockcopolymers, which both play an important role in biocompatibilization, film formation and features of the ultrathin films are also affected by crystallization behaviour.

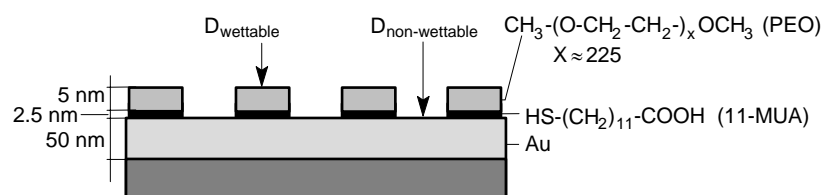
The experimental results [8-13] which are obtained from ultrathin PEO films formed on micro-heterogeneous surfaces (dip-coating) demonstrate that

- surface heterogenization directs the dewetting behaviour,
- thin film formation of polymers and crystallization can be well separated in time and
- ultrathin films on micrometer sized isolated areas are amorphous and can be meta-stable with respect to crystallization over a period of weeks.
- nucleation of these meta-stable films can be initiated by external stresses or surface defects.
- the lamellae crystallization can results in highly branched morphological structures which are originating from a diffusion controlled growth process.
- the diffusion processes and, consequently, the resulting morphologies can be strongly influenced by the under-cooling and lateral confinements of the ultrathin film.

Surface design

As substrates for film formation of PEO ($M_w = 10000; 6000; 2000 \text{ g}\cdot\text{mol}^{-1}$) gold layers were used which were heterogenized by appropriate thiols using either micro-contact printing or electron-beam lithography of self-assembled monolayers. The carboxylic endgroups of carboxy-terminated thiols e.g. ω -mercapto undecanoic acid (11-MUA) (Fig. 1) which are self-assembled at the gold substrate provide a hydrophilic surface. Electron-beam irradiation of 11-MUA disintegrates the carboxylic groups and changes the irradiated domains into hydrophobic areas. Ultrathin film formation of PEO is generated by dip-coating of micro-patterned substrates bearing hydrophilic and hydrophobic units into chloroform solutions of PEO. During the film formation the hydrophilic PEO is completely removed from hydrophobic surface areas resulting in a patterned film. The overall surface structure is schemed in Fig. 1

Fig. 1:
Heterogeneous surface design used for PEO film formation. Lateral size and shape of both wettable (11-MUA) saturated and non-wettable (e-beam irradiated) domains can be chosen arbitrarily. X = degree of polymerization



Dewetting of polymers on micro-patterned surfaces [3,4]

A typical PEO pattern (Fig. 2, left) obtained by wetting on a hydrophilic patterned 11-MUA motif (bright areas in Fig. 2, left) demonstrates that the polymer distribution on the pre-patterned surface can be significantly guided. While the film formation in contact with hydrophilic structure elements larger than $\approx 4 \mu\text{m}$ shows the same structural elements for the film as predefined by the heterogeneous surface the smaller sized striations clearly show a disintegration of the polymer film into small droplet shaped structures. This result confirms theoretical predictions about the dewetting of solutions on striated hydrophilic/hydrophobic surfaces [14]. Within the small sized hydrophilic striations the liquid polymer solution transferred to the substrate by the dip-coating process becomes instable due to the Rayleigh instability and decomposes into lines of isolated droplets instead of forming a homogenous polymer layer.

As a consequence for possible application of surface directed film formation sub-micrometer patterning of films by heterogenized surfaces can be excluded.

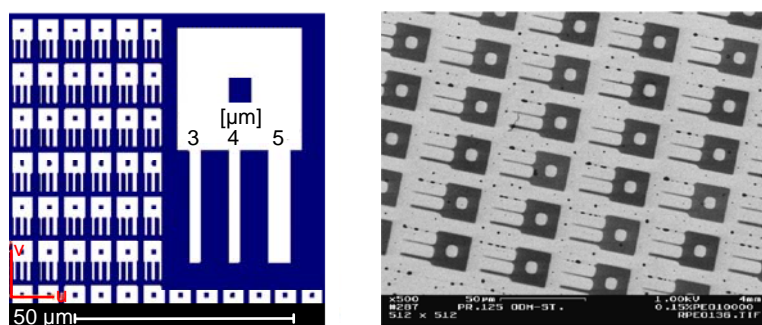


Fig. 2: Predefined motif of hydrophilic (bright) and hydrophobic (dark) surface areas (left) and resulting PEO distribution after dip-coating from chloroform solution of PEO (right). Small sized ($3 \mu\text{m}$) lines are broken due to droplet formation through Rayleigh instability of liquid phase (SEM)

PEO film morphology as prepared and its change due to nucleation

By control over the dewetting process during dip-coating PEO film segments can be laterally isolated from others by hydrophobic barriers. As demonstrated in Fig. 3 (left) the isolated ultrathin film segments appear homogenous while the continuous PEO film, which extends over large (mm) surface areas, shows the growth of dendritic lamella structures of PEO ultrathin films which result from a diffusion controlled crystallization process of PEO.

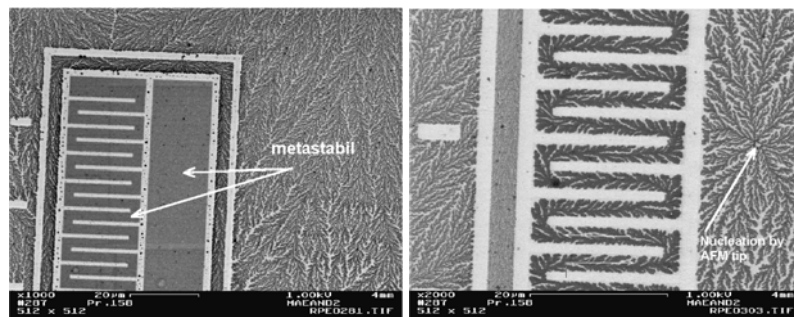


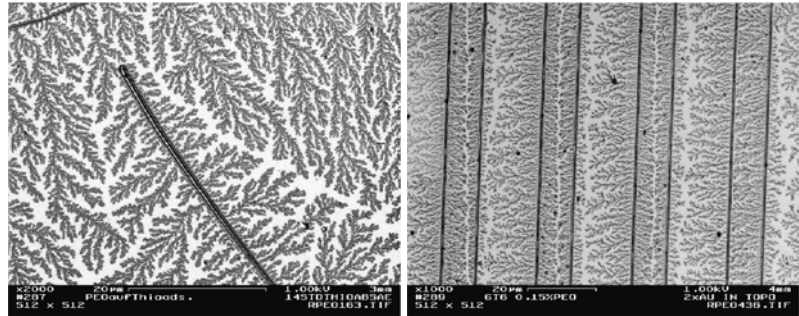
Fig. 3: PEO film segment separated by hydrophobic barriers from the crystallized sample in its initial state (left) and after nucleation with an AFM tip (right) (SEM).

The crystallization of the amorphous PEO layer can be triggered for example by contact with an AFM tip as indicated in Fig. 3 (right). The experiment is done on a reflective light microscope equipped with an AFM measurement device which can replace an ordinary objective lens in the microscope. This setup allows the μm sized preposition of the AFM tip inside the structure film which can

be visualized in the dark field mode of the light microscope. Darkfield imaging permits to visualize the growth fronts of the dendritic structures and to determine growth velocities of the dendrites.

Nucleation of the crystallization can be initiated by surface defects like scratches (Fig. 4, left) or well defined steps within the surface topography (Fig. 4, right).

Fig. 4:
Dendritic growth structures initiated from a surface scratch (left) and from step (≈ 40 nm) in the gold substrate (right). Substrates are chemically homogeneous but topographically structured (SEM)

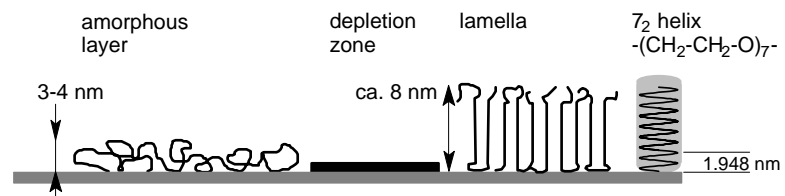


In presence of nucleation sites the branched lamellae structures grow from the nucleation site into the amorphous film. Branches that grow from different nucleation sites never contact each other due to a depletion zone that occurs in front of the branches. The experimental control over the nucleation process enabled us to nucleate the crystallization within laterally structured film segments and to follow the dendritic growth process within confining 2d structures.

The diffusion controlled growth process in ultrathin films

The appearance of highly branched structures due to diffusion controlled aggregation processes both in 3d and 2d systems is described for such different processes as the growth of bacteria colonies on agarose gels [15], the electrolytic deposition of metals on electrodes or other growth processes far from thermodynamic equilibrium. Recently it has as been experimentally observed for the crystallization of PEO blockcopolymer substrates on homogeneous surfaces [5-7], and a theoretical model for the polymer crystallization in ultrathin polymer films has been proposed which is well applicable to understand the specific features that appear for the growth in confined structures. The underlying molecular model that predict the characteristic features of the branched structures quantitatively is schemed in Fig. 5.

Fig. 5:
Molecular model for the structural changes during crystallization from ultrathin PEO films



A key point is the increase in film thickness which occurs during crystallization from the amorphous layer of 3 nm to 4 nm in our case into the lamellae of 8 nm up to 14 nm. With constant volume the increase in layer thickness necessarily causes a depletion zone between the non-crystalline and crystalline area. This depletion zone has to be overcome by surface chain diffusion. Morphological features as depletion zones, tip radius of crystalline branches, correlation length and lamellae thickness can be influenced by crystallization temperature (under-cooling) or by

crystallization in confined areas. Fig. 6 shows the developing growth features at different under-cooling conditions. The change of branched structures during the isothermal growth process (increasing tip radius etc.) as pronounced to see in Fig. 6c arises from the increasing depletion zones and, consequently, the decreasing of the diffusion coefficient due to the limited material reservoir in confined areas.

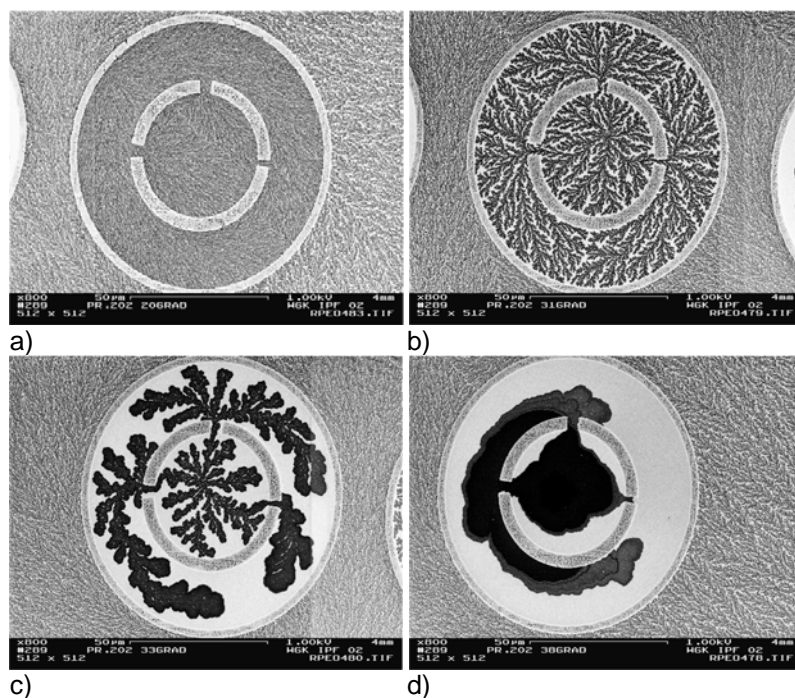


Fig. 6: Dendritic growth features observed at decreasing under-cooling. Nucleation is always from the center of the inner structure. Fig. 6c shows the increase in tip radius of branches during the growth within the confinement (SEM)

Reorganization processes of thin PEO films after water microdroplet impact by a microspotting device

The miniaturization of analytic devices as done in biochips requires the handling of small liquid volumes (e.g. aqueous solutions). Micro-droplet generation in piezo-driven droplet generators similar to ink-jet plotters has become a major principle for the transfer of low viscosity liquid phases onto surfaces. The combination of micro-droplet generators with appropriate positioning devices allows the deposition of liquids at predefined positions on a surface as demonstrated in Fig. 7 (left). The behaviour of the liquid phase on the surface is of great interest. To obtain information about the real impact zone of micro-droplets (water) hitting a surface and reorientation processes of water soluble polymer layers thin PEO layers which were already crystallized were chosen as substrates for micro-drop deposition experiments.

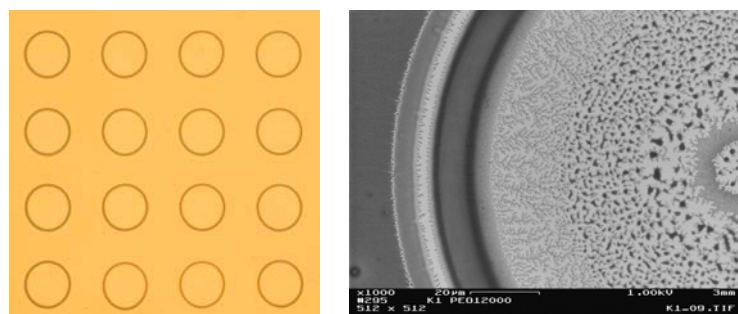


Fig. 7: Regular pattern of holes in PEO film prepared by micro-droplet spotting (left, light micrograph) and morphological features of the PEO film after water drop impact (right, SEM).

The morphology of such a PEO layer hit by a single water microdroplet is shown in Fig. 7 (right). A detailed inspection of the morphological elements within the impact zone reflects three dominant features:

- the center zone (which is dominated by dewetting structures of a thin polymer layer which obviously remains at the surface after dissolution of most of the PEO layer in the propagating aqueous phase),
- the recrystallized ultrathin PEO layer (featuring the typical dense branched morphology of lamella PEO crystals),
- the thick rim of the PEO layer (that has accumulated at the circumference of the drying water/PEO system and from which the recrystallization process starts).

These ongoing experiments will allow a much deeper insight into structure formation processes during material deposition by microdroplet technology.

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