Nanoscale Block Copolymer Self-Assembly and Microscale Polymer Film Dewetting: Progress in Understanding the Role of Interfacial Energies in the Formation of Hierarchical Nanostructures

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1. Introduction

The self-assembly (SA) of block copolymers (BCPs) into ordered nanostructures on solid surfaces is a promising candidate for next-generation lithography which is reaching real-world applications, for instance, in the creation of fin-field effect transistors, surface enhanced Raman spectroscopy-active surfaces, magnetic storage media, or electrochemical sensors.[1–6] BCP lithography is based on the so-called microphase separation of block copolymers containing two (or more) blocks of incompatible polymer species: Depending on block length ratio, Flory–Huggins parameter, and polymerization degree, the BCPs separate into arrays of the different blocks, leading to versatile structures with nanoscale feature size and periodicity. Several excellent review papers were published during the last decades, including fundamental early work on block copolymer thermodynamics,[7] the specific behavior of BCPs in thin films,[8] efforts made within the last ten years to render BCP-SA applicable for surface nanopatterning[9] as well as most recent insights into synthesis and characterization of new BCPs suitable for lithography applications[10] or approaches to enable new BCP morphologies.[11] One crucial issue in advancing BCP lithography to its next technological level, i.e., rendering the technique applicable for versatile device integration, is the fundamental understanding of the self-assembly process enabling control of the pattern formation and its guiding into desired surface architectures. In particular, interactions between the polymer and solid surfaces determine the morphology of nanostructures: polymer wetting behavior,[12–14] nanopattern orientation,[15–18] nanopattern uniformity through a thin film,[19,20] and defect density[21,22] in BCP thin films are fundamentally investigated by research groups contributing with insights from chemistry, physics, and material science.

A crucial parameter in BCP lithography which needs perspectives form different research fields are the interactions of block copolymer thin film with a solid substrate.
These interactions are much more complex than recognizable on the first sight. There are two dominating mechanisms contributing to pattern formation: One is the (de-)wetting of (block co-)polymer films on surfaces. It plays a major role determining the film morphology and topography on the microscale. The other is the microphase separation of block copolymers into ordered nanoscale patterns guided by the internal interfacial energies. What makes the understanding difficult is the fact that these two ordering mechanisms are interdependent. For instance, enabling nanoscale minimum energy configurations can lead to a change of the microscale polymer distribution. Both individual effects are widely investigated in literature. However, literature concerning the combination and interplay of these effects is limited\cite{14,26–29} and—to a large extent—recent progress is made in exploiting the combination of BCP dewetting and SA for the creation of hierarchical nanostructures rather than disentangling the interdependent, fundamental effects leading to such BCP morphology formation.

Thus, this report will give an overview of the progress in understanding the interplay of block copolymer microscale film modulation by dewetting and nanoscale microphase separation during block copolymer self-assembly (Figure 1). The article will shed light on the role of interfacial energies in both redistribution mechanisms. Finally, examples will be shown in which the combination of dewetting and microphase separation is exploited to create hierarchical nanostructures from block copolymers.

In particular, the first part of this report will focus on microscale processes determining the topography of block copolymer films, i.e., hole/island formation and dewetting into droplets (shaping the film morphology in Figure 1). The second part gives a perspective on the nanoscale internal energy minimization (indicated by red polymer domains in blue polymer matrix in Figure 1) driven by a sum of several interfacial energies. Recent insights into the nanopattern orientation dependency on the polymer film thickness are presented. The influence of surface polarity on the nanopattern/substrate interface will be critically discussed. The third section of this progress report will present examples of the successful combination of microand nanoscale energy minimization of block copolymer films for the creation of hierarchical nanostructures. The last section gives an outlook into the exploitation of this combination approach applied on prepatterned surfaces in order to control position and morphology of the hierarchical nanostructures for advanced lithography and more versatile surface architectures suitable for device integration.

2. Microscale Modulation of BCP Film Topography

Block copolymer thin films exhibit much more complex interactions with solid surfaces than homopolymer films as, e.g., one of the two polymer species can preferentially wet the surface. This leads to block copolymer films being stable against dewetting even at very small film thicknesses\cite{30–32}. Experimentally, stable polystyrene-block-polymethylmethacrylate (PS-b-PMMA) films were observed by Lupi et al.\cite{29} at film thicknesses as small as 3 nm.

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Figure 1. Overview of the micro- and nanoscale events driven by interfacial energies taking place during block copolymer dewetting and microphase separation.
A measure for the stability of films is the spreading parameter $S$, which sets a relation between the surface tension of a substrate $\gamma_s$ and a liquid $\gamma_l$ and their interfacial energy $\gamma_{s-l}$:

$$S = \gamma_s - (\gamma_{s+} + \gamma_l)$$

If the spreading parameter $S$ is positive, films are stable as the interface exhibits a smaller free energy than the difference of the free surface tensions of the components. Vice versa, for $S < 0$ films are unstable and dewet forming droplets.

A stability estimation calculating the spreading parameter of the widely used PS-b-PMMA block copolymer indicates that the BCP will form a stable film on a SiO$_2$ substrate $s$. Weighted mean values of PS and PMMA matching their block length ratio in the BCP, i.e., 70% PS and 30% PMMA, were used to determine $\gamma_{s+}$ and $\gamma_l$, as the interfacial energies $\gamma_{s+}$ between PS-s and PMMA-s measure $\approx 5$ mN m$^{-1}$, while the surface tensions, i.e., the polymer interface with vacuum $\gamma_s$, of PS-v and PMMA-v are in the order of 30 mN m$^{-1}$ as was shown by Brassat et al.\cite{Brassat2014} using the OWRK method. As the surface free energy of SiO$_2$ is 48 mN m$^{-1}$, in this example the spreading parameter is positive and stable films form.

### 2.1. Hole/Island Formation

Upon annealing, which is usually applied to induce block copolymer microphase separation, the polymer films become “structured liquids.” Block copolymer thin films—in contrast to homopolymer thin films—redistribute in a way that films of locally quantized film thicknesses are formed. The driving force is the redistribution of polymer chains such that internal minimum energy configurations are achieved. The stable thicknesses correlate with the intrinsic structure periodicity, i.e., the equilibrium polymer domain spacing in microphase-separated block copolymers, typically referred to as $L_0$.\cite{Fleischer1999, Miller2014}

![Figure 2](image)

**Figure 2.** a–d) Hole/island formation in PS-b-PTMSS films by thermal annealing at 180 °C for different times. BCP is deposited onto a nearly neutral surface of silica functionalized with a PtBS-r-PMMA-r-PVBzAz brush. The free surface is toward air. Top row shows AFM height images, the bottom row presents corresponding line plots. Initial thicknesses on (a,b) was $1.35 \times L_0$ and $1.65 \times L_0$ in (c,d). Reproduced with permission.\cite{Maher2016} Copyright 2016, American Chemical Society.

During annealing of a block copolymer film with an initial film thickness not matching this periodicity $L_0$ the polymer redistributes on the surface forming locally different film thicknesses matching integer $n$ multiples or $(0.5+n)$ multiples of $L_0$. This process can lead to the generation of holes and is referred to as hole/island formation.\cite{Maher2016, Brassat2014, Brassat2015} The term hole might be misleading because it implies that the bare substrate gets exposed. This however is not necessarily the case as will exemplarily be shown in the following.

**Figure 2** shows an example of the hole/island formation of polystyrene-block-4-trimethylsilylstyrene (PS-b-PTMSS) films with initial film thicknesses incommensurate with the periodicity $L_0$, i.e., $1.35 \times L_0$ (Figure 2a,b) and $1.65 \times L_0$ (Figure 2c,d), respectively. In these investigations by Maher et al.,\cite{Maher2016} the progression of the hole/island formation during thermal annealing of the BCP films was analyzed at different times. In Figure 2a, mesas with a thickness of $1.5 \times L_0$ are formed containing holes of $1 \times L_0$ after 10 min of annealing. Further annealing in Figure 2b leads to the coarsening of the size distribution of $1 \times L_0$ holes and the formation of additional troughs with a thickness of $0.5 \times L_0$. In case of an initially thicker film in Figure 2c, islands with a thickness of $2 \times L_0$ form on a film of $1.5 \times L_0$ after a short time. Again, further annealing leads to a progression of redistribution and islands grow to a larger mean diameter and plateaus with a thickness of $2.5 \times L_0$ (Figure 2d).

The driving force for the hole/island formation stems from the elastic energy of the polymer chains necessary to compensate the mismatch between $L_0$ and the actual film thickness. If the film thickness is incommensurate with $L_0$, chains need to stretch or compress. This, however, increases the total free energy of the system as further stated next ($F_{\text{elast}}$ in Equation (4)). The hole/island formation reduces this thermodynamically unfavorable stretching and compression of polymer chains, leading to a microscale modulation of the BCP polymer film topography.
2.2. Dewetting of Very Thin BCP Films

The redistribution of polymer during annealing of very thin block copolymer films (with film thicknesses below a critical thickness)\[29,45,46\] can initiate complete film dewetting. In general, thin polymer films on solid surfaces can destabilize due to long-rang forces, polar interactions, and molecular forces.\[47\] The dewetting is dependent on these polymer–substrate interactions along with film thickness, molecular weight, viscosity, and surface tension.\[35,48–52\]

Dewetting of very thin films typically occurs by two mechanisms: spinodal dewetting or nucleation and growth. Spinodal dewetting is caused by fluctuations of the film thickness forming capillary waves which can spontaneously amplify.\[47\] This mechanism typically takes place in polymer films of small thicknesses. In thicker films, holes can form at defective sites and then nucleate, i.e., dewetting follows a nucleation and growth mechanism.\[47\] A review summarizing mechanisms of the formation of mesoscale morphologies in polymer films can be found in ref. \[52\].

It was observed that BCP film dewetting follows a nucleation and growth mechanism if the BCP microphase separation is induced by solvent annealing while spinodal dewetting occurs in thin BCP films during thermal annealing. Dewetting mechanisms of several block copolymers were investigated in literature using both solvent and thermal annealing, e.g., for polystyrene-block-polyisoprene (PS-b-PI),\[53,54\] polystyrene-block-polyethyleneoxide (PS-b-PEO)\[32,55\] and polyisoprene-block-polyethyleneoxide (PI-b-PEO).\[56\] Specific studies on the nucleation and growth mechanisms during solvent annealing of PS-b-PEO on silica were performed by Choi et al.\[32\] the kinetics of the spinodal-like dewetting of PS-b-PI during thermal annealing was investigated by Cheng and Perahia.\[33\]

An additional dewetting mechanism observed in block copolymer thin films on solid substrates is the so-called *autophobic dewetting*. As the different polymer species of a BCP can asymmetrically interact with the substrate a brush-like wetting layer of a preferentially wetting polymer species can form, creating a new interface with the rest of the polymer film. This autophobic dewetting was, for instance, investigated by Choi et al.\[32\] and Lee et al.\[37\] and specifically found by Epps et al.\[57\] as the predominant mechanism for dewetting of PI-b-PS-b-PEO triblock terpolymers.

Depending on the initial film thickness dewetting of block copolymer films can result in either holes in polymer films or bicontinuous structures or droplets.\[29,32,53\] An example for such dewetted BCP films is shown in Figure 3 where Choi et al.\[32\] investigated the dewetting of PS-b-PEO block copolymer films of different thicknesses on silica during solvent annealing. Figure 3a shows an atomic force microscopy (AFM) height

![Figure 3](image_url)

*Figure 3.* AFM height images of PS-b-PEO after solvent annealing in benzene for 12 h. a–e) Initial film thicknesses were 30, 25, 19, 16, and 13 nm. Reproduced with permission.\[32\] Copyright 2012, American Chemical Society.
image of a stable microphase-separated PS-b-PEO film with an initial film thickness of 30 nm. Figure 3b,c shows films with initial thicknesses of 25 and 19 nm, respectively, which both dewetted into films with holes. It is to note that fewer holes with larger size form in Figure 3c for a smaller film thickness. Further decreasing of the film thickness leads to film dewetting into droplets, as visible in Figure 3d,e, where the initial film thicknesses were 16 and 13 nm, respectively. These experiments clearly show that dewetting during BCP SA shapes the film topography.

3. Energy Minimization during BCP Microphase Separation at the Nanoscale

The microphase separation of block copolymers into ordered nanoscopic polymer domains in bulk material is exclusively determined by the mixing energy $F_{\text{mix}}$ of the polymer species $A$ and $B$ in the block copolymer. This internal nanoscale energy minimization in block copolymers can be described by a minimization of the Gibbs free mixing energy $\Delta G_{\text{mix}}$, which is mainly dependent on the Flory–Huggins parameter $\chi_{AB}$ of the BCP species and their polymerization degrees$^{[58-61]}$

$$
\Delta G_{\text{mix}} = RT(n_A \ln(\phi_A) + n_B \ln(\phi_B) + n_A \phi_B \chi_{AB})
$$

with $n_{A,B}$ the number of moles of polymers $A$ and $B$, respectively, and $\phi_{A,B}$ their volume fractions. The Flory–Huggins parameter can be split up into an entropic component $\chi_s$ and an enthalpic component $\chi_H$.$^{[62,63]}

$$
\chi_{A,B} = \chi_s + \chi_H / T
$$

For block copolymer lithography purposes, BCPs consisting of polymer species with high, positive Flory–Huggins parameters are chosen. In this case, mixing of same polymer species $A$-$A$ or $B$-$B$ is energetically favorable while the mixing of $A$-$B$ is endothermic. Thus, the Gibbs free energy decreases.

It is to note that the interface forming upon microphase separation between the polymer species $A$ and $B$ is not sharp, but has an interfacial width which is not neglectable. It was estimated by Black et al.$^{[64]}$ that the interfacial width in a PS-b-PMMA BCP with feature sizes of 20 nm, for instance, is between 3 and 5 nm, i.e., about 25% of the polymer domain sizes. Modi et al.$^{[65]}$ found that this interfacial width is also dependent on the microphase separation conditions.

If BCP SA takes place in a thin film on a solid surface, the total surface free energy $F$ of microphase-separated block copolymer thin films (Equation (4)), the polymer domains can arrange themselves with different orientations with respect to the substrate, i.e., polymer domains can arrange parallel or perpendicular to the substrate (Figure 4a). In these different geometries, distinct interfacial areas are minimized or maximized enabling a conformation with minimum total free energy.

Due to the different geometries the absolute interfacial areas change with varying polymer film thickness, thus, the individual contributions of the different interfacial energies to the total free energy change with film thickness, too. Thus, the minimum energy orientation is film thickness dependent (Figure 4b,c)$^{[14,19,67,68,77-80]}$. Figure 4c,d gives examples of the changing polymer domain orientation with increasing polymer film thickness. The scanning electron microscopy (SEM) image in Figure 4c shows a film thickness gradient of a cylinder-forming PS-b-PMMA block copolymer on a nonfunctionalized silica surface after thermal annealing in vacuum.$^{[14]}$ The film thickness increases from left to right. Along this gradient, the orientation of PMMA cylinders in a PS matrix changes from parallel (stripe patterns from top view) through a mixed region to perpendicular cylinders (dots from top view). In the lower left corner, the film thickness is very small not exhibiting any patterns. This corresponds to a transition from the “no order” regime in the sketch in Figure 4b to the perpendicular regime on the very right. Figure 4d presents a tapping mode scanning force microscopy (TM-SFM) image of a microphase-separated polystyrene-block-polybutadiene-b-polystyrene (SBS) triblock copolymer film after solvent annealing.$^{[86]}$ The film exhibits a thickness gradient with increasing thickness from left to right.
Different pattern domains are marked by white lines. A corresponding sketch of the pattern evolution with increasing film thickness is presented in Figure 4c. The phases corresponding to the SEM image in Figure 4d are from C_{\|1} to C_{\|2}.

Again, energetically favorable configurations correlate with the film thickness in units of $L_0$. This effect was, for instance, investigated by Perego and co-workers\cite{81} on random copolymer (RCP) functionalized silica and by Brassat et al.\cite{14} on preferentially wetted silica as well as on platinum and gold surfaces. Thus, during hole/island formation or dewetting of BCP films, which both lead to local changes of the polymer thickness, different polymer orientations can form locally minimizing the total surface free energy $F$ by optimization of the interfacial areas.

3.2. Optimising Surface Wetting Preferences

Since block copolymer self-assembly was found suitable for lithography purposes large effort was invested to control the orientation of polymer domains with respect to the substrate because only perpendicular orientations of polymer cylinders, gyroids, or lamellae allow for their use as shadow masks during lithography processing.\cite{25,64,82,89} It was shown before that the orientation can be controlled by adjustment of the film thickness, minimizing the total free surface energy by optimization of interfacial areas due to polymer geometry. Alternatively, the system can be guided into a minimum energy configuration by modification of distinct interfacial energies, e.g., the surface free energy of the polymer interfaces with the substrate. As the interfacial area of the distinct polymer species is very different for parallel and perpendicular domain orientation, control of the interfacial energy between polymer species and substrate enables orientation control.

The correlation between interfacial energies and polymer domain orientation is usually categorized into neutral and preferential wetting of the substrate with the polymer species. These wetting states are defined by comparison of the surface energy difference of the distinct polymer species A or B, respectively, and the substrate. These energy differences $\Delta \gamma_{A,B-S}$ are typically quantified by

$$\Delta \gamma_{A,B-S} = |\gamma_{A,B} - \gamma_s|$$

(e) Reproduced with permission.\cite{68} Copyright 2002, American Physical Society.
with $\gamma_{A,B}$ and $\gamma_s$ being the surface tensions of polymer A or B, respectively, and the surface free energy of the substrate s.\cite{64} A smaller value of $\Delta \gamma_{A,B}$ then refers to favorable enthalpic interactions with the substrate.\cite{42,90,91} Comparing the energy differences between each polymer species and the substrate, one can differentiate between the wetting categories:

- **Preferential** wetting, which occurs if the formation of an interface between one polymer species and the substrate is energetically preferable compared to an interface between the other species and the substrate

$$\Delta \gamma_{A,B} < \Delta \gamma_{B,B}$$

(7)

In this example, the formation of a wetting layer of A and to a parallel orientation of A domains (Figure 4a (right)) is preferred.

- **Neutral** wetting conditions if the energy differences between the polymer species and the substrate are similar

$$\Delta \gamma_{A,B} \approx \Delta \gamma_{B,B}$$

(8)

and polymer domains orient perpendicular to the surface (Figure 4a (left)).

The BCP thin film has a second interface, the one with the vacuum, which might have slightly different wetting preferences to the polymer species due to different polymer surface tensions. Thus, in addition to the distinction between neutral and preferential wetting as discussed before, one additionally differentiates between symmetric and asymmetric wetting preference at both interfaces of the polymer to vacuum and the interface to the substrate surface. If wetting preferences at both interfaces are similar, symmetric wetting conditions are apparent, if wetting preferences are different, asymmetric wetting occurs (Figure 5g). Neutral, nonpreferential substrates usually wet symmetrically, in case of preferential substrate wetting, however, both states, symmetric and asymmetric wetting, can occur.\cite{92} A detailed experimental and theoretical analysis of the domain orientation under (a-)symmetric wetting conditions was performed by Willson and co-workers.\cite{93} Very recently, extensive theoretical studies were also performed to understand and predict BCP chain arrangement and thus the polymer domain shape at surfaces with different surface free energies by Man and co-workers.\cite{94}

In order to engineer surface wetting preferences, i.e., interfacial energies, different experimental approaches were established to render substrate surfaces “neutral” or nonpreferential in order to guide the system into perpendicular polymer domain orientation for lithographical purposes. Among these techniques are surface exposure to X-ray radiation and UV-ozone (UVO) treatment,\cite{12,20–100} surface functionalization with chlorosilanes,\cite{12,13,17,101,102} or the deposition of other functional layers.\cite{35,103} The most widespread technique is the deposition of a RCP brush containing the same polymer species as apparent in the block copolymer.\cite{24,65,72,78,99,104–109}

Although the comparison of the total surface free energies of polymers and substrate gives a solid rule of thumb to distinguish between either neutral or preferential wetting conditions, examples were shown where this estimate did not hold and predictions differed from experimental results. It was investigated by Epps and Shelton,\cite{43} Han et al.,\cite{15} and Brassat et al.\cite{19} that it is necessary to analyze the individual contributions of polar and dispersive energy components to the total surface free energy to fully understand and predict the block copolymer self-assembly behavior.

For a detailed analysis of interactions leading to the wetting behavior of liquids on a solid surface, it was originally shown by Fowkes\cite{110} that the surface tension $\gamma_A$ of a material can be written as the sum of the polar surface tension component $\gamma_{p,p}$, i.e., the energy contribution due to static dipole–dipole interactions, and the dispersive surface tension component $\gamma_{d,d}$ arising from dispersive London and van der Waals forces

$$\gamma_A = \gamma_p + \gamma_d$$

(9)

Owens and Wendt\cite{111} developed this (using Young’s equation (Equation (11))) further into the following expression

$$\gamma_{A,s} = \gamma_p + \gamma_d - 2 \left( \gamma_p \gamma_d \right)^{1/2}$$

(10)

where the interfacial energy between two media, here, for instance, polymer A and substrate s, $\gamma_{A,s}$, can be calculated from the total surface tension of these materials and their polar and dispersive energy components. By this approach long-range and attractive interactions between polar and dispersive moieties can be decoupled from short-range and repulsive interactions when describing the total surface free energy at interfaces.\cite{12,13,17,43}

Surface energies and their polar and dispersive components can be determined experimentally by contact angle measurements using different test liquids with known polarities, for instance, using the Owens–Wendt (OW) method\cite{111} or the Owens–Wendt–Rabel–Kälble (OWRK) method.\cite{111–113}

Epps and Shelton\cite{43} and Brassat et al.\cite{19} determined the polar and dispersive components of surface free energies of several material surface using these methods (Table 1) and investigated the influence of the surface polarity on the BCP SA. Brassat et al.\cite{19} investigated the morphology of polymer domains of PS-h-PMMMA block copolymers on SiO$_2$, TiO$_2$, RCP, Au, and Pt surfaces. While the total surface free energies of these materials are in a comparably narrow regime (36–48 mN m$^{-1}$), their polarities differ strongly from 0.1% on gold to 46% on bare silica (Table 1 (a)). Measurements of contact angles and resulting calculated interfacial energies of these different material surfaces are compiled in Table 1 (a). Interfacial energies and their polar and dispersive parts were determined by the OWRK method (Equation (10)).

Figure 5a–f shows SEM images of the PS films after selective PMMA removal on bare and RCP-functionalized SiO$_2$ (a, b), bare and RCP-functionalized TiO$_2$ (d, e), as well as on bare gold (c) and platinum (f). It is striking that exclusively on the much more polar bare silica in Figure 5b, preferential wetting leads to a PMMA domain orientation being parallel to the surface while on all other predominantly dispersive surfaces PMMA is perpendicularly oriented, thus wetting conditions seem neutral.

Han et al.\cite{15} investigated the microphase separation of PS-h-PMMMA block copolymers on different PS-h-PMMMA
random copolymer brushes. The brush polarity was varied by introduction of hydroxy and epoxy groups. Again, even though the total surface free energy of the RCP brushes was similar, perpendicular polymer domain orientations were observed on brushes of low polarity and parallel orientation on polar surfaces.

Epps and Shelton [43] investigated the interactions of PMMA-b-PnBA block copolymers on different silane surfaces exhibiting a broad range of total surface free energies (30–77 mN m⁻¹) as well as polarities (7–45%) as summarized in Table 1 (b). These values were calculated by the OW method. UVO treatments of the different silanes were applied to increase their polarities even further. Their studies focussed on distinguishing between symmetric and asymmetric wetting, as depicted in Figure 5g. It was found that similar to the experimental results provided by Han et al. [15] and Brassat et al. [19] not only the total free energies of the interfaces with both BCP polymer species need to be taken into account to explain the BCP–surface interactions, but that the polarity strongly influences the wetting behavior. Here, it was shown that irrespective of different total surface free energies the higher the polarity the stronger the asymmetric wetting with the more polar polymer species, as summarized in Figure 5h. The PMMA-b-PnBA BCP forms a PMMA wetting layer on bare silica as well as on UVO-treated chlorosilanes.

Figure 5. a–f) SEM images of microphase-separated PS-b-PMMA (after PMMA removal) on SiO₂ surface functionalized with RCP, SiO₂ without RCP, electron beam evaporated gold, TiO₂ with RCP, TiO₂ without RCP, and electron beam evaporated platinum. (a–f) Reproduced with permission. [19] Copyright 2018, The Royal Society of Chemistry. g) Schematics of asymmetric wetting (left) and symmetric wetting (right) on a preferentially wetted substrate. h) Summary of surface wetting behavior of PMMA-b-PnBA BCP on surfaces with different polar and dispersive surface free energy contributions. (g,h) Reproduced with permission. [43] Copyright 2015, American Chemical Society.
Due to both, micro- and nanoscale energy optimization, such volume ratio and contrasting them to 3D bulk and 2D films. As 1D systems in literature emphasizing their large surface/non-negligible volume these droplets are often referred to dewetting of very thin BCP films. Even though containing a It was shown before that BCP droplets can form during 4.1. Nanostructures in Block Copolymer Droplets on Surfaces effects can be exploited for the formation of hierarchical nanostructures. As discussed before, in 2D thin films interfacial energies influence the polymer domain orientation, wetting preferences result in symmetric or asymmetric wetting conditions on the nanoscale and on the microscale incommensurate film thicknesses are balanced by hole/island formation. The interplay and interdependency of these micro- and nanoscale effects can be exploited for the formation of hierarchical nanostructures.

4.1. Nanostructures in Block Copolymer Droplets on Surfaces

It was shown before that BCP droplets can form during dewetting of very thin BCP films. Even though containing a non-negligible volume these droplets are often referred to as 1D systems in literature emphasizing their large surface/volume ratio and contrasting them to 3D bulk and 2D films. Due to both, micro- and nanoscale energy optimization, such droplets of structured liquids can exhibit unique properties. For instance, droplets do not necessarily have rotational symmetry following Young’s equation. Examples of noncircular block copolymer droplets are shown in Figure 3e. Moreover, terraced hyperbolic structures after dewetting of PS-b-PMMMA microdroplets[114] or hierarchical serpentine microstructures in PS-b-PMMMA block copolymer droplets due to fingering instabilities[115] were observed.

An example of hierarchical block copolymer nanostructures was presented by Lupi et al.[29] Figure 6a–d shows PS-b-PMMMA droplets formed due to dewetting of a 3 nm thin BCP film after thermal annealing on silica surfaces functionalized with PS-PE-PMMMA random copolymer brushes of either 2 or 7 nm thickness. Dewetting of the BCP films in this material system results in the formation of droplets which exhibit approximately circular shape. Thus, in order to further evaluate the droplet morphologies Young’s equation[33,34,116] can be applied

\[ Y_1 \cos \theta = Y_\text{ad} \]

The contact angles \( \theta \) of the BCP droplets on the two RCP surfaces are with \( \theta_{\text{H}_2\text{O}} = 11.7^\circ \) and \( \theta_{\text{H}_2\text{O}} = 7.4^\circ \) different as also visible in the AFM images in Figure 6b,d. Thus, as apparent from Equation (11), interfacial energies between the BCP and the substrate surfaces must be different.

The authors[29] explain this by assuming an interpenetration depth of the block copolymer chains into the random copolymer brush. They find that the height of the thinner RCP brush of 2 nm is smaller than this interpenetration depth (≈3 nm), thus not preventing the BCP from partially interacting with the underlying SiO2 surface, which exhibits preferential wetting conditions as was discussed before (Figure 5b). Nevertheless, polymer domain orientation is perpendicular to the substrate in both cases, indicating that sufficiently neutral wetting conditions are present.

| Table 1. Contact angles of different test liquids on several surfaces and calculated total surface free energies and polar and dispersive contributions. (a) Contact angles on different materials surfaces. SFE determined by OW method. RCP refers to a PS-co-PMMMA random copolymer. Adapted with permission.[19] Copyright 2018, The Royal Society of Chemistry. (b) Contact angles on different silane monolayers on silica. The silica surface was processed in an UVO cleaner. SFE determined by OW method. Adapted with permission. [43] Copyright 2015, American Chemical Society. |
|---|
| (a) | SiO2 + RCP | SiO2 | TiO2 + RCP | TiO2 | Au | Pt |
| CA [°] | |
| H2O | 80 | 54 | 78 | 75 | 92 | 68 |
| CH3I2 | 42 | 58 | 49 | 47 | 34 | 44 |
| EtGly | 57 | 42 | 58 | 53 | 59 | 47 |
| SFE [mN m⁻¹] | 39 | 48 | 36 | 39 | 46 | 40 |
| Dispersive | 91% | 54% | 86% | 93% | 99.9% | 88% |
| Polar | 9% | 46% | 14% | 7% | 0.1% | 12% |
| (b) | Bare silica | Aceto silane | Benzyl silane | Methacryl silane | N-butyl silane |
| CA [°] | |
| H2O | 6.4 ± 0.3 | 69.5 ± 2.0 | 81.6 ± 0.6 | 80.7 ± 0.7 | 91.6 ± 1.2 |
| CH3I2 | 33.5 ± 1.0 | 49.0 ± 0.2 | 43.1 ± 0.4 | 49.9 ± 0.4 | 60.2 ± 0.8 |
| SFE [mN m⁻¹] | 77.4 ± 0.5 | 44.0 ± 0.8 | 41.3 ± 0.3 | 38.7 ± 0.3 | 30.6 ± 0.6 |
| Dispersive [mN m⁻¹] | 42.7 ± 0.4 | 34.8 ± 0.1 | 38.0 ± 0.2 | 34.3 ± 0.2 | 28.4 ± 0.5 |
| Polar [mN m⁻¹] | 34.7 ± 0.3 | 9.1 ± 0.8 | 3.3 ± 0.2 | 4.4 ± 0.3 | 2.2 ± 0.3 |
Another interesting observation underlining the major influence of the interfacial interactions in 1D droplets is that no evidence of a thickness-dependency is found in this system. This becomes apparent from the SEM images in Figure 6e,f. Even though film thicknesses in the droplets are different (≈15–20 and 35–40 nm which corresponds to 1/2L₀ and L₀ of the BCP, respectively) polymer domains are oriented perpendicular to the substrate in both cases. The thinner droplets exhibit polycrystalline polymer domain arrangement, while the polymer arrangement is more uniform at the higher thickness, but no change of polymer domain orientation with respect to the substrate takes place.

Hur et al. [28] also investigated the microphase separation of PS-b-PMMA in small droplets on silica surfaces. They used RCP brushes with different PS content, enabling either preferential or neutral wetting. Employing experimental and theoretical methods they found different dependencies of the BCP SA on these different surfaces. Similar to results in ref. [29] the polymer domain orientation was found to be independent of the size and film thickness of the droplet on neutral surfaces. However, on preferentially wetted surfaces a pronounced dependency on the droplet size is found. Either perpendicular domain orientations or "bottle cap"-like patterns form as shown in the SEM image in Figure 6g. The pattern morphology depends on the droplet size as well as the height, even though droplets are found to never exceed a maximum height of the order of 1/2L₀. Self-consistent field theory (SCFT) calculations using a coarse grained model were performed to understand the influence of droplet size and surface wetting preferences on the orientation of the polymer domains. Monte Carlo simulations were applied to explore the equilibrium polymer configuration considering intermolecular, intramolecular, and polymer–substrate interactions. Figure 6h confirms the independence of the polymer domain orientation of the droplet size (and volume) on a neutral substrate, as observed in refs. [28] and [29]. In contrast, Figure 6i presents simulation results of the size-dependent droplet morphology on a preferentially wetted substrate surface. As observed in Figure 6g the polymer domain orientation changes from perpendicular in small droplets to the bottle cap configuration in larger droplets.

These examples show that in 1D BCP droplets, comparable to 2D BCP thin films, the internal polymer domain orientation as well as the microscopic (droplet or film) shape are determined by the balance between surface and interfacial energies. However, the impact of individual interfacial energies differs in the 1D and 2D systems.

4.2. Combined Dewetting and Microphase Separation of Block Copolymers on Prepatterned Surfaces

In order to render such hierarchical block copolymer architectures more versatile and to enable integration into complex device designs, it is desirable to control the position of nano-patterned patches as well as their internal structures. Precise control of dewetting and self-assembly processes can be achieved using prepatterned surfaces.
The (de-)wetting behavior of (homo-)polymers on planar surfaces can be described by the spreading parameter and Young’s equation and these models even render the more complex dewetting of block copolymers sufficiently predictable, as stated before. The wetting of films on nonideal surfaces, however, is much more complex. In general, the wettability of chemically or topographically inhomogeneous surfaces can be described using the models of Cassie and Baxter[117] and Wenzel,[118] respectively. These models set the ideal Young contact angle (Equation (11)) of a liquid on a surface in relation to contact angles apparent on nonideal surfaces. However, these models do not hold if nanoscale systems are investigated.[119] To date, the wettability of chemically and topographically nanostructured surfaces is not fully understood thus remains unpredictable. In addition, the complex wetting behavior of block copolymers on surfaces makes this problem even more demanding.

Efforts were made to develop models on the wetting of polystyrene on patterned silica surfaces by Roy et al.[120] directed polymer dewetting was investigated by Ramanathan and Darling,[52] soft lithography approaches such as microcontact printing were applied to control the polymer deposition and dewetting,[121,122] chemical patterning was used to induce dewetting at specific sites,[123] and polymer microstripes were created by dewetting in trenches.[124,125] Even though the exact dewetting mechanisms of polymers on structured surfaces are not fully understood, all these approaches result in a tailored distribution of polymer material correlating with the prepattern geometry. Working with very thin films of (block co-)polymers on prepatterned surfaces, which dewet during annealing, allows to guide the formation of dewetted polymer patches at predefined positions.

BCP SA can be tuned applying directed self-assembly (DSA) processes. Extensive literature including comprehensive review articles on the directed self-assembly of block copolymers is available.[126–129] Many DSA approaches, for instance, aim at improving long-range order in BCP SA,[127,130] to enable pattern density multiplication[131,112] and to guide BCP domains into distinct patterns matching requirements of semiconductor technologies.[133] The guiding structures in DSA are mostly realized by chemical or topographical prepatternning of surfaces.[134] In most cases, these prepatterns change the interfacial energies between substrate and polymer locally, thus controlling polymer wetting preferences on the nanoscale.

Thus, using prepatterned surfaces the hierarchical nanostructures formed by microscale dewetting and nanoscale BCP SA presented before can be arranged to regular arrays. For instance, the formation of rows of hierarchically structured BCP droplets by directed polymer dewetting in trenches and on stripes was shown by Ramanathan et al.[52] and more recently by Lupi,[129] respectively. Figure 7 shows droplets of PS-b-PMMA on chemically functionalized stripe patterns created by laser lithography. These stripes exhibit a chemical contrast between a 2 nm PS-r-PMMA random copolymer brush and bare SiO2 with neutral and preferential wetting conditions, respectively. This prepattern allows for both control of the polymer domain orientation to be perpendicular to the surface on the RCP stripes as well as for positional control of the droplets. During dewetting, the polymer migrates toward RCP-covered areas, because this surface exhibits lower interfacial energies with the BCP. Thus, BCP patches align along the RCP stripes forming a row of droplets (Figure 7a). In addition to this alignment, Figure 7b–e demonstrates that the droplet size can be adjusted by changing the width of the trenches allowing for further pattern control. 

Farrell et al.[135] investigated the dewetting of PS-b-PMMA BCP on films of silsesquioxane (SSQ), which were prepatterned with micro- and nanoholes with different diameters and distances by reverse UV nanoimprint lithography. They found that thin BCP films dewet on these surfaces forming both polymer patches inside the nanoholes as well as on the SSQ mesas between the holes. As the silsesquioxane exhibits nonpreferential wetting conditions to the BCP a variety of nanopatterns was observed to form during BCP SA within the polymer droplets (Figure 7f–k). It was shown that depending on the prepattern dimension the size of polymer droplets changes. Along with this change of size the shape of the droplets changes from a square with rounded edges for large droplets (1–2.5 μm diameter) to circular shapes for smaller droplets (200–1000 nm) as depicted in Figure 7k. Even though Farrell et al. do state that the thickness of the droplets influences the polymer domain orientation within the droplets, they emphasize that the in-plane radius of curvature at the contact line of the polymer droplet with the SSQ leads to a reorientation of the polymer domains. They find that a high curvature induces parallel orientation as, for instance, visible at the corners of the rounded squares in Figure 7l. Decrease of the droplet diameter consequently was observed to lead to the formation of concentric rings within the droplet (Figure 7j).

Brassat et al.[136] investigated the dewetting of PS-b-PMMA block copolymers on nanohole-patterned thin films of different materials created by nanosphere lithography. The nanoholes were fabricated such that they extended through the whole top-surface thin film, revealing the SiO2-covered Si substrate at the bottom. Thus, the prepatterning was both topographical and chemical. It was found that dewetting of the polymer into nanoholes is strongly dependent on the wettability of the patterned thin film material. While polymer dewetting into nanoholes was observed on metal surfaces, e.g., from gold and platinum (Figure 8a,b, respectively), TiO2 surfaces (Figure 8c) remain wetted by a continuous polymer film even after BCP SA. Thus, material choice allows to control the dewetting and consequently the BCP film morphology resulting in either site-selective or surface-covering nanopattern formation.

If one, in addition, controls the amount of BCP deposited inside nanoholes, the polymer domain orientation of the BCP can be tailored, as was investigated in detail by Brassat et al.[136] In this approach, the film thickness dependence of the minimum energy configuration of the BCP SA is exploited. Thus, either concentric nanorings parallel to the substrate surface (Figure 8d) or perpendicular nanopores (Figure 8e) form within the prepatterns at small or large polymer thicknesses, respectively.

This observation was explained by calculations of the total surface free energies for parallel and perpendicular domain orientations within a cylindrical nanohole considering the different contributions of individual interfacial energies for the different geometries. As shown in Figure 8f comparison of the total surface free energies for both domain orientations in dependence of the polymer thickness allows for the ascertainment of film thickness windows within which either parallel or perpendicular polymer domain orientation is energetically favorable.
These examples of hierarchical block copolymer nanostructure formation on prepatterned surfaces demonstrate how the precise control and modification of interfacial energies can be exploited to engineer the microscale polymer topography as well as the nanoscale block copolymer self-assembly on complex surfaces.

5. Conclusion

The influence of interfacial energies on the microscale film modulation of block copolymers and the nanoscale microphase separation during block copolymer self-assembly is highlighted in this progress report.

Microscale processes determining the topography of (block co-)polymer films are discussed. The present understanding of interfacial energies and surface wettability is presented and specifics of block copolymer dewetting compared to homopolymer dewetting are distinguished. For instance, it is shown that hole/island formation occurs as BCP films are only stable at specific film thicknesses corresponding to the equilibrium polymer domain periodicity \( L_0 \) or an integer multiple evolving during nanoscale microphase separation. It is also pointed out that dewetting strongly depends on the initial film thickness which may result in the formation of holes in films or nonideal droplets. Superimposed to such macroscopic changes of film morphologies is the internal reorganization of BCP films by demixing.

Nanoscale microphase separation of block copolymers into polymer domains is shown to depend on different contributing (interfacial) energy terms. Different approaches are discussed leading to energetically favorable polymer domain orientations. A polymer film thickness dependent reorientation of polymer domains is shown to allow for the minimization of the total surface free energy in a BCP thin film. Examples are presented in which the pattern orientation changes from parallel to perpendicular with increasing polymer thickness. It is discussed that manipulation of the interfacial energies between BCP polymer species and substrate surfaces also allows for the polymer domain orientation control. Specifically, it is discussed that surface polarities play a crucial role here.

Finally, examples are given showing how the combination of microscale dewetting and nanoscale microphase separation can be exploited to create hierarchical nanostructures from BCPs. BCP droplets formed by dewetting of very thin films are presented and their internal nanopattern formation is discussed. Directed self-assembly approaches are presented rendering such hierarchical block copolymer architectures even more
versatile and enabling integration into complex device designs. This allows to guide the position of nanopatterned patches to regular arrays as well as to control their internal structure. Such control of position and morphology of the hierarchical nanostructures is particularly promising for the creation of advanced surface architectures.

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Conflict of Interest
The authors declare no conflict of interest.

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block copolymers, dewetting, hierarchical nanostructures, interfacial energies, self-assembly

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Figure 8. a–c) SEM images of nanohole-patterned thin films of Au, Pt, and TiO$_2$ serving as templates for the (directed) self-assembly of PS-b-PMMA BCPs. Reproduced with permission.[19] Copyright 2018, The Royal Society of Chemistry. d,e) Concentric nanorings and perpendicular nanopores formed the BCP SA at small and high polymer thicknesses inside the prepatterns, respectively. f) Calculation of the total surface free energy of BCP nanostructures with parallel and perpendicular polymer domain orientation in dependence of the polymer thickness. d–f) Reproduced with permission.[14] Copyright 2019, Wiley VCH.
