Chapter 6

Pattern Formation in Thin Polymer Films Induced by Electric Fields
6.1 Introduction

The stability and pattern formation in thin films are of considerable scientific and technological interest. From a fundamental point of view, quantifying thin film instabilities is a means of detecting and measuring interfacial forces that are otherwise difficult to investigate. The dewetting of a liquid thin film from a solid or liquid substrate is a well-known example of the effect of interfacial forces on the stability of a thin film. Film stability is of great importance to technological applications such as the manufacture of coatings, membranes and optical devices, and for photolithography.

In addition to spontaneous film instabilities driven by intermolecular forces, pattern formation induced by external fields have also been observed. Introducing interfacial pressures stemming from an electric field or a temperature gradient yields a morphology with a distinct characteristic periodicity that arise from a similar process.

The application of an external force provides a control over the instabilities, because the magnitude of the force can be varied. This chapter discusses capillary instabilities in a polymer film that are induced by an externally applied electric field. The findings are compared to a theoretical study by Verma et al.\textsuperscript{16} In addition to an experimental report on the evolution of the instability with time, insights on pattern formation and pattern replication in an electric field are provided. These results were obtained in a collaboration with N.E. Voicu.

The characteristic wavelength of an instability that develops at a polymer/air or polymer/liquid surface, subjected to an electric field, is known to depend on the force balance at that interface\textsuperscript{5–8,11,13,14}. Verma et al.\textsuperscript{16} recently published 3D simulations on the morphology obtained for polymer/substrate systems, which are similar to those described in this chapter and to the references mentioned above. In many related studies of thin film instabilities, the primary means to theoretically model structure formation induced by electric fields and other interfacial forces has been the linear stability analysis. The linear stability analysis has proven useful to describe the mean length scale and the time scale of an instability during the early stages of film destabilization. To address the problem of nonlinear pattern selection and its control by an applied electric field, Verma performed nonlinear 3D simulations.

A major difference with our experimental system lies in their adoption of a Si–PS–air–Si system. In addition to the van der Waals interfacial potential that describes this system, they also included the extremely short ranged Born repulsion. The Born repulsion provides a short-range cut-off of the (otherwise diverging) van der Waals potential and avoids a contact-line singularity. It ensures that the liquid does not penetrate the top surface upon pinning. In contrast, our experiments consist of a Si–SiO–PS–air system, as described in Chapter 3, which includes the interactions between the polymer and a native silicon oxide layer. Verma adopted a system without the destabilizing influence of the native oxide layer of the silicon wafer. As mentioned in the previous chapter, the electrostatic forces greatly overpower the van der Waals forces. In our electrohydrodynamic model, we therefore neglect the minor influence
of the van der Waals potential. The simulation results and our experimental data are therefore in good agreement.

6.2 Experimental

Two experimental systems were used: 1) brominated polystyrene (PBrS, 154 kg/mol, \( P_d = 1.02 \), 40% bromination grade) on indium tin oxide (ITO) covered glass substrates and 2) polystyrene (PS, 94.9 kg/mol, \( P_d = 1.06 \)) on silicon wafers. Films with thicknesses of 58 - 125 nm were spin-cast from a toluene solutions (2-3% polymer by weight). The ITO covered glass had a 105 nm thick ITO layer with a resistivity of 80 \( \Omega/\text{cm}^2 \). To remove ITO spikes, the substrates were scrubbed for several minutes in a hot SDS soap solution (70 \(^\circ\)C) and rinsed with Millipore water. To remove the soap and other surface contaminations, the substrates were further cleaned in an ultrasonic bath in acetone and isopropanol and then spun dry. The substrates were then heated for 10 minutes at 120 \(^\circ\)C in a convection oven, followed by 20 minutes of UV-ozone treatment. The silicon substrates and the electrodes covering the films were subjected to ”snow-jet” cleaning immediately before film deposition and device assembly. After film deposition, a silicon wafer was placed on top of the sample, with its polished side facing the polymer film, leaving an air gap (\( d - h_0 \)). Top wafers with planar as well topographically structured surfaces were used. To release the top surface without damage to the polymer film, the surface was rendered apolar by surface grafting of an octadecyltrichlorosilane self-assembled monolayer. Both capacitor plates were electrically contacted using silver paint (Electrodag 1415M). A voltage of 10 – 80 V was applied between the two plates and the temperature of the device was raised to \( T = 165 – 225 \, ^\circ\text{C} \) (above the glass transition of the polymer film) for periods of time ranging from several minutes to several hours. When using PBrS on glass, the film was monitored throughout the heating phase, using an inverted optical microscope (Olympus GX51). The heating was provided by a copper block on the top electrode. At the end of the experiment, the sample was cooled down to room temperature and the electric field was removed. After disassembling the sample, the lateral distribution of the polymer film was analyzed by optical microscopy (Olympus BX60 or GX51) and ”Tapping Mode” atomic force microscopy (AFM, Digital Instruments D3100).

Verma used a polymer/substrate system that is stabilized by the influence of van der Waals interactions (Hamaker constant \( A < 0 \)). The polymer films on the silicon substrates had a dielectric constant equal to that of PS (\( \varepsilon = 2.5 \)) and an initial thickness between 25 and 75 nm. A voltage of 70 Volts was applied with an electrodes spacing of 80–100 nm. Both flat and topographically structured top surfaces were used in the simulations.
6.3 Spontaneous pattern formation

In the previous chapter, an electrohydrodynamic model was introduced that describes the evolution of sinusoidal perturbations in a thin polymer film in the long wavelength limit \((h \ll \lambda)\). In a homogeneous electric field, the force balance at the polymer/air interface leads to amplification of surface waves. Fig.[6.1] shows the evolution of a spontaneously forming structure formation in a \(\approx 125\) nm thick PBrS film. The assembly was heated by a copper block on the top silicon wafer to 190°C. The temperature near the polymer film was independently measured to be 164°C (\(> T_g\)). The geometry in Fig.[6.1] deviated from the ideal parallel arrangement. During device assembly, a non-parallel (wedge) geometry was obtained by a dirt or silicon dust particle at one of the corners or sides of the top wafer. For our observations, a non-parallel geometry...
is not unfavorable. With a linearly varying plate spacing in lateral direction, the electric field varies linearly as well. The associated time constant $\tau$ scales with the plate spacing $d$ as $\tau \propto d^6$. In a wedge geometry, the spontaneous instability therefore propagates towards decreasing confinement, as visualized in Fig.[6.1].

The wedge geometry corresponds to an increase in plate spacing in direction of the arrow in Fig.[6.1]a), related to the lateral coordinate, of $\sim 1 \mu m/cm$. Fig.[6.1]a) shows the onset of a capillary instability after an annealing time of 667 min. The surface waves are visible as color variations. The interference colors arise from the interference of light from a three-layer system: glass-polymer-air. The glass is 1 mm thick and the interference colors are for this reason not similar to those described in Chapter 3 (section Optical Microscopy). In Fig.[6.1]b-f), the surface waves were amplified and were pinned to the top surface (silicon wafer). Once a polymer structure spanned the distance between the substrate and confining wafer, it appeared as a dark colored circular or oval shaped pillar. The height of these polymer structures are $\approx 250$ nm and have a diameter of 2-2.5 $\mu m$.

To compare our results to the 3D simulations performed by Verma, the film thickness $h$ and plate spacing $d$ are expressed as a ratio $h/d$, the filling ratio. The experimental and simulation data are categorized in terms of the filling ratio and compared. For a flat plate geometry, the experimental and simulation conditions are listed in Table[6.1].

<table>
<thead>
<tr>
<th>Source</th>
<th>Polymer</th>
<th>$h$ (nm)</th>
<th>$d$ (nm)</th>
<th>$h/d$</th>
<th>$U$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sim</td>
<td>PS</td>
<td>25</td>
<td>100</td>
<td>0.25</td>
<td>70</td>
</tr>
<tr>
<td>Sim</td>
<td>PS</td>
<td>50</td>
<td>100</td>
<td>0.50</td>
<td>70</td>
</tr>
<tr>
<td>Sim</td>
<td>PS</td>
<td>75</td>
<td>100</td>
<td>0.75</td>
<td>70</td>
</tr>
<tr>
<td>Exp</td>
<td>PBrS</td>
<td>90</td>
<td>1100</td>
<td>0.08</td>
<td>30</td>
</tr>
<tr>
<td>Exp</td>
<td>PBrS</td>
<td>100</td>
<td>390</td>
<td>0.25</td>
<td>40</td>
</tr>
<tr>
<td>Exp</td>
<td>PBrS</td>
<td>125</td>
<td>255</td>
<td>0.51</td>
<td>10</td>
</tr>
<tr>
<td>Exp</td>
<td>PMMA</td>
<td>85</td>
<td>113</td>
<td>0.75</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 6.1: Parameter space explored in both simulation (Sim$^{16}$) and experimental (Exp) studies for a liquid polymer film of thickness $h$ sandwiched in between silicon wafers with spacing $d$ with a voltage $U$ applied. The air gap between the polymer layer and the top electrode is $d - h$ and the filling ratio is given by $h/d$.

In Fig.[6.1], a spontaneously developing instability led to the formation of individual columns. The filling ratio $f = h/d = 0.49 \pm 0.1$. Several columns in Fig.[6.1]f) are in close proximity to other columns. Comparing this morphology to the simulated counterpart of this system, Fig.[6.2], an very similar morphology is seen. The time scales leading to Fig.[6.1] and Fig.[6.2] are quite different due to a large difference in the viscosities, varying several orders of magnitude. One difference is the cause of the distribution in the columnar diameter that is clearly visible in Fig.[6.1]. This
Pattern Formation Induced by Electric Fields

distribution is caused by 1) time dependent pinning of the columns to the top surface, and quite possibly by 2) lateral coarsening (or coalescence). Columns that are pinned to the top surface in an earlier stage accumulate more polymer material than those that are pinned in a later stage of structure formation. Fig.[6.2] shows another often observed cause of a variation in columnar size and spacing, namely lateral coarsening. In Fig.[6.2]c), adjacent columns touch, coarsen and in a later stage (not shown here) become a single column with an increased diameter. In the image sequence Fig.[6.1]d-f), coalescence of neighboring polymer structures is not as clearly visible as in Fig.[6.2]c). At other locations in the sample, coalescence was observed for polymer structures of similar height and spacing (not shown here). It can therefore not be ruled out that after a longer period of time lateral coarsening may occur for the structures in Fig.[6.1]f).

Figure 6.2: 50 nm thick film between two electrodes separated by 100 nm (f = h/d = 0.50). Black represents the minimum thickness; white represents the maximum thickness. Adapted with permission from R. Verma, A. Sharma, K. Kargupta, and J. Bhaumik, Langmuir 2005, 21, 3710–3721. Copyright 2005, American Chemical Society.

At lower filling ratio’s, coalescence is observed less frequently or is excluded entirely. During the growth of the surface waves, polymer material is transported from thinner to thicker film regions. Upon pinning to the top surface, the area surrounding the polymer cylinders is drained empty, leaving an equilibrium layer of a few nm thick. For a low enough filling ratio, the polymer cylinders are detached from the surrounding film during an earlier stage of the instability. For two reasons lateral coarsening is suppressed. 1) Upon pinning, the surface wave maximum is in direct contact with the top silicon wafer. At this point, the film bridges the distance between the wafers and has two liquid/solid interfaces. Lateral motion proceeds much more slowly for two liquid/solid interfaces as compared to a single liquid/solid interface 2) Once a surface wave maximum is pinned, it drains the surrounding film and creates a depletion zone. Lateral coarsening requires an interconnecting film between two or
more surface waves that coarsen. In effect, a pinned polymer structure surrounded by a depletion zone is rendered immobile and coalescence cannot take place.

In the absence of an intermediate film, that serves a liquid bridge between a polymer column and the surrounding film, coalescence is unable to occur. This was observed for a filling ratio of 0.25. Fig.[6.3] shows the evolution in a 100 nm PBrS film. The images were taken after disassembling the device following 20 h of annealing at 165°C with an applied voltage of 40 V. The electrode spacing was 390 nm and varied by 1.5 µm/cm (wedge geometry). As mentioned before, the time constant is a function of the plate spacing. A lateral variation of the plate spacing also implies that the time constant is a function of the lateral coordinate. This allows the observation of several stages of an instability on a single sample. Qualitatively, such observations are similar to in situ time-resolved detection of film destabilization and are therefore included in the discussion of the temporal evolution of EHD instabilities in an electric field. An intentional wedge geometry is obtained by introducing non-conductive spacers to the setup. This principle, that allows control over the capacitor geometry and the plate spacing, is further elaborated in Chapter 10.

![Figure 6.3](image)

Figure 6.3: Pattern formed in an electric field at a low filling ratio. A 100 nm thick PBrS film spin-cast on to a silicon wafer ($U = 40$ V). The patterns formed after heating the sample for 20 h at 165°C. The filling ratio is $\approx 0.25$. The columns are laterally disconnected and have a narrow diameter distribution.

The plate spacing for Fig.[6.3f] was 390 nm, with an initial film thickness of 100 nm. This corresponds to a filling ratio $f \sim 0.25$. While in f), the undulations were pinned to the top surface, in c), the undulations had not reached the top surface yet. This
indicates that the plate spacing for c) was higher than for f). The locations where the images are approximately 750 μm apart. The plate spacing varied by ∼110 nm over this distance. From a) to c), the peak to valley distance increased to 250–350 nm with $d \approx 450$ nm. The columns in d) are 500 nm high and are spaced apart by $4.5 \pm 0.4 \mu m$; f) shows an optical micrograph of a region where nearly all polymer material had been redistributed into 390 nm high polymer cylinders with a lateral spacing of $4 \pm 0.4 \mu m$.

A constant filling ratio, combined with a variation in the plate spacing, gives rise to a wide range of field strengths, which has consequences for the pattern formation mechanism. With decreasing field strength and polarization of the polymer, the repulsion between electric field induced structures is weaker. Combined with an increased film thickness and a slower dynamics (larger $\tau$), a lateral redistribution of material becomes increasingly influential. Fig.[6.4] shows surface waves with a lateral periodicity of ∼25 μm in a ∼90 nm PBrS film annealed at 223 °C. It should be noted that this temperature was measured inside a copper block that was heated by thermo-couples. The temperature of the polymer layer was ∼20–30 °C lower. In a wedge geometry with a large lateral variation in plate spacing (6.5 μm/cm), the polymer structures are exposed to an electric field gradient. The direction of increasing electric field strength is depicted in a) as a vertical arrow.

As described in the previous chapter, the electrostatic pressure at the interface drives a flow of material towards increasing pressures. Although this description was given for a polymer film in a homogeneous electric field, it is also valid for surface waves in a wedge geometry. In a), the surface waves have a uniform distribution. Arrow (1) points out two wave maxima in close proximity that coalesce and form a column b). In a-f), indicated by arrow (2), two wave maxima, which were initially spaced apart by $\lambda$, merged to form a single column in e). The wave maximum moved downwards, in direction of increasing electric field strength. Once close to the second wave maximum, a liquid bridge was formed in between the two maxima d). The column arises from the coalescence of the two wave maxima by a material transfer from both wave maxima into the liquid bridge. This indicates that the formation of a single structure with lower surface area that spans the gap between both electrodes is energetically favorable compared to the existence of two separate surface waves.

The arrows (3) and (4) in c) and f) point out wave maxima in close proximity to liquid cylinders that had already been pinned to the top surface. Although the two neighboring wave maxima coalesce (3), they contained insufficient material to form a column that reaches the top surface. The merged wave maximum in f) is close to a fully formed polymer column, but was not incorporated into the structure. Arrow (4) points out a wave maximum that is incorporated into polymer column that recognizably had increased its diameter. The likely difference between situations (3) and (4) is the existence of a depletion zone. Without a liquid bridge or a wetting film in between the two liquid structures, coalescence cannot take place. The behavior shown in Fig.[6.4] at large plate spacing resulting in a low filling ratio has a profound influence.
Chapter 6

Figure 6.4: Coalescence in a 90 nm PBrS film annealed 30 Volts during 11 hours. Both electrodes were aligned in a wedge geometry of 6.5 µm/cm. Column formation took place at a plate spacing of 1.1 µm for a filling ratio $f \sim 0.08$. The arrows (1) and (2) point out two of the 5 cases of coalescence in an area of 90 x 90 µ². b-f) were taken at times relative to a). a) was taken 487 min after initiation of the experiment.

on the wavelength data obtained by *ex post facto* AFM measurements. Fig.[6.4] a) and f) show a remarkably different wavelength distribution that leads to a scatter in the data, though extensive coalescence (as shown below) has not taken place.

Under experimental conditions where the film is relatively thick compared to the plate spacing (Fig.[6.5]), coalescence dominates the morphology. The structure formation in Fig.[6.5]b) proceeds by the formation of individual columns. Due to the large amount of polymer material in the capacitor gap, the substrate is not exposed between the pinned structures. This allows all neighboring columns to fuse as their diameter exceeds half the intrinsic wavelength. The intermediate state of randomly oriented liquid plugs formed by coalescing columns gradually reshapes to a polymer matrix containing air pockets.

The sample (Fig.[6.5]b) was imaged at a single annealing time of 30 min, at locations of decreasing plate spacing $d$, which is equivalent to increasing annealing times
Pattern Formation Induced by Electric Fields

Figure 6.5: Morphology at a filling ratio of 0.75, observed in simulations a) using a 75 nm polymer film in a between two electrodes spaced apart by 100 nm with 70 V applied\textsuperscript{16}. Adapted with permission from R. Verma, A. Sharma, K. Kargupta, and J. Bhaumik, Langmuir 2005, 21, 3710–3721. Copyright 2005, American Chemical Society. b) 85 nm thick PMMA film on a silicon wafer, annealed at 170\textdegree C at an applied voltage of 50 V. $R_1$: $f \sim 0.75$, $R_2$: $f \sim 0.8$, $R_3$: $f = 0.83 \pm 0.1$, $R_4$: $f = 0.87 \pm 0.1$, $R_5$: $f \sim 0.92$.

at fixed $d$, as shown in the simulations by Verma et al. in Fig.[6.5]a). Both morphologies, obtained from the experimental results in Fig.[6.5]b) and the simulation study in Fig.[6.5]a) show a final morphology of an inverted topographic morphology.

6.4 Nucleated Instability

Fig.[6.6] formed around a central column and is shown for several stages of development. Structure formation proceeded after the central column was nucleated. Various sources lead to the nucleation of instabilities (dewetting or induced by an electric field) in liquid polymer films on solid substrates. Solvent evaporation during spin-coating of a polymer thin film builds up stresses that relax when the film is liquefied. It was also suggested that air pockets in polymer films lead to heterogeneous nucleation of instabilities\textsuperscript{4}. Organic residues, glass ITO spikes, silicon dust, or other dirt particles that have adhered to the substrate surface can trigger the formation of a thin film instability.

The instability in Fig.[6.6] was most likely nucleated by a spike in the glass/ITO substrate. In addition to the similarity with Fig.[6.1], a different evolution characteristic can also be distinguished. As opposed to the amplification of capillary waves throughout the film at similar plate spacings (spontaneous film destabilization, Fig.[6.1]), in Fig.[6.6] column formation proceeds radially outwards from a central pil-
Figure 6.6: Nucleated pattern formation in an electric field. a) The image sequence shows a 125 nm thick PBrS film confined with $f \sim 0.5$ at an applied voltage of 10 V. After an annealing time of 478 min at $T = 164^\circ C$ a single column appeared ($t = 0$) surrounded by a depletion zone (solid arrow) and a rim (dashed arrow). With increasing time, further columns are nucleated radially outward from the initial column. For $t > 130$ min, the undulations of the surrounding film (caused by the homogeneous electric field) are clearly visible.

lar (spike). The (local) plate spacing in Fig.[6.1] varies only by a few nm (roughness of Si). In Fig.[6.6], the ITO spike disturbed the homogeneous electric field sufficiently to nucleate the formation of the first column (a).

The thickness of the region surrounding the nucleation center decreased as it was drained of polymer material. This depletion zone is visible in Fig.[6.6]a) by its color that darkens from a-c), indicating further depletion (solid arrow). The material from the depletion zone is drawn towards the column and the unperturbed film on the other side of the depletion zone (dashed arrow). The material flow towards the film increases its thickness, which is visible as the dark rim in a). The increase in film thickness is accompanied by an increase in electrostatic pressure. In b), 99 min after a) three columns had developed on the rim while the surrounding film remains intact.
Pattern Formation Induced by Electric Fields

The time scale of nucleated structure formation is clearly smaller compared to the spontaneous EHD instability.

The rim adjacent to the depletion zone has an increased film thickness and therefore experiences a larger electrostatic pressure. This triggers an earlier onset of the EHD instability of the rim compared to the unperturbed film. In Fig.[6.6], a), the rim has a width that is comparable to the diameter of the nucleus ($\sim 1.5 \mu m$). In b), three liquid cylinders have formed; in c), six polymer columns have formed in the ring. The lateral distance between the hexagonally ordered columns is equal to the intrinsic wavelength of the instability ($3.3 \pm 0.3 \mu m$). Each polymer structure is itself surrounded by a depletion zone and, as a consequence, by a secondary rim. At the intersection of two secondary rims of neighboring columns, the next generation of columns is spawned. This enhances the hexagonal order with a lateral distance $\lambda$ that is preferred by the system. The instability propagates radially outwards by nucleating columns on the intersections of each consecutive secondary rim e)–f). The hexagonal ordering from a nucleated instability in Fig.[6.6] was enhanced for $\approx 3$ generations, after which a defect in the ordering disturbed the theorized pattern geometry.

6.5 Rim Profile of a Nucleated Instability

Although Fig.[6.6]b) and e) show the nucleation of new columns in the rim, the shape of both rim and column were not captured by our optical microscopy set-up. To elucidate the details of this particular step in the evolution of column formation an AFM image of a comparable situation is presented in Fig.[6.7]. A 130 nm PMMA film was annealed at 30 V during 22 h in an oven preheated to 170°C. Fig.[6.7]a) shows satellite columns in various stages of development surrounding three mature columns. The stages of growth that precede the AFM image are the nucleation of the three large columns and the liquid ridges around them (not shown here). The numbered profiles in b) corresponds to numbered cross-sections in a). The profiles (1) to (3) in b) represent the early stage, late state and intermediate stage of development, respectively. The cross-section profile (2) is a mirrored image of the left side of cross-section (3). Profile (1) was taken from the cross-section (1) in a) and shows the profile of the ring around the central column.

The sequence 1-3 in Fig.[6.7]a) shows the emergence of a column in the rim of the central column that developed at a nucleus (compare with Fig.[6.3]a), c), f)). Comparing the arrow indicated by (1) with (2) and (3), the polymer material flows towards the emerging column from a direction perpendicular to cross-section (3). This is in agreement with Fig.[6.7]b), where the columnar diameter increases at the expense of the material in the elevated ridge. The cone shape of the intermediate stage is quite peculiar and is the result of the amplification and pinning of the wave maximum in (1) and (2) before absorbing surrounding polymer material. Once pinned to the top surface, the cone shaped structure makes a transition to the cylindrical shape (3).
Figure 6.7: Nucleated film instability in a 130 nm PMMA film that was annealed at 170°C during 22 hours with 30 V applied. In a), an AFM image of the film morphology is shown. The propagation of the film instability (from 3 central columns outwards) was frozen-in, thereby capturing the growth sequence of columns on the elevated rims. The cross-sections through an emerging (1, 2) and a mature column (3) are presented in b).

and absorbs polymer material from all directions. In between stages (2) and (3), the column appeared to pop up, as seen in the lower right corner of Fig.[6.7]b) (blurred rim segments). Interestingly, an additional maximum in the profile is visible in AFM cross-section (3) (arrow in Fig.[6.7]b). If this secondary maximum is not fully drained during the expansion of the emerging column, it leaves a patch of residual material on the substrate. It can be imagined that this residual material results in the formation of columns at a later stage with a far smaller diameter (secondary column formation) leading to a scatter of the wavelength data (in addition to coalescence). Patches of residual polymer material are frequently observed during film destabilization (for both dewetting and induced by an electric field, see Fig.[6.3]f) and are caused by contact line pinning of the three phase contact line by chemical heterogeneities or dirt particles on the substrate.

The rim profile shows great similarities to the rim profiles observed for dewetting induced instabilities in thin polystyrene films\textsuperscript{3,15}. Fig.[6.8] shows a nucleated film instability in a $\approx$125 nm thick PBrS film confined by a silicon surface at $d = 250 \pm 5$ nm ($f = 0.5$). The AFM image and cross-section (b) show a rim profile that corresponds to a dampened oscillation. Where the rim meets the unperturbed film, the height profile displays a minimum in the film thickness. In c), 3 height profiles of dewetting fronts are given. These were reported by Herminghaus et al.$^3$ in a study of a dewetting instability in thin (40 nm) polystyrene films. They varied the molecular weight of the polystyrene (2, 100 and 600 kg/mol) and imaged the dewetting fronts by atomic force microscopy. They observed a gradual decrease of the rim profile in between the rim maximum and the unperturbed film (see 4,5) for molecular weights above the
Figure 6.8: Nucleated film instability in a 125 nm PBrS film (154 kg/mol) annealed at 164°C during 16 h at 10 V. a) AFM image of a nucleated film instability. The height profile b) corresponds to the cross-section in a) through two columns and the adjacent rim. The distances in vertical direction 1)–3) are 45, 85, and 35 nm, respectively. c) Height profiles of dewetting fronts in 40 nm films of (4) 101 kg/mol and (5) 600 kg/mol. The height profile of a dewetting rim in a 4.9 nm film for 2 kg/mol polymer is shown in (6)\(^3\).

entanglement limit \((M_e \approx 19 \text{ kg/mol})\). Below the entanglement limit, for a 2 kg/mol polystyrene, the height profile showed a sharp maximum at the dewetting front (6) with a local minimum in between the elevated rim and the unperturbed film. The difference in the dewetting fronts suggests a dampening effect on the height profile stemming from the stabilizing influence of the viscoelasticity on surface fluctuations\(^1\). To explain the difference in the rim profile in b), that formed in an electric field, and the rim profile observed for a dewetting instability (5) for a similar molecular weight, the coupling of the applied electric field to the height profile should be considered. This causes an additional flow of material towards the region of maximal rim height. The surrounding area is drained, driven by the strong electrostatic pressure gradients in the film, and for a height profile, like (5), most of the material originates from the area between the rim maximum and the unperturbed film. Gradually decreasing height profiles are therefore not expected to exist in the presence of an electric field. The resulting rim profile of a high molecular weight polymer in a destabilizing electric field is similar to that of a low molecular weight dewetting front ((6) in Fig.[6.8]c)).

### 6.6 Cascading Rim Profiles

The minimum in the height profile (6) is the onset of a depletion zone. The difference in film thickness of the depletion zone (thinner) and the unperturbed film (thicker) leads to the formation of a secondary maximum by an electrostatic pressure gradient towards increasing film thickness. In the case where coupling of the electric field to the secondary rim maximum occurs before pinning of the first rim maximum to the silicon surface, a cascading rim profile is obtained.
Chapter 6

Fig.[6.9]a) and b) show the optical microscopy images of two examples where the film shows a cascading height profile (direction of the arrow). In c), a cascading dewetting front is shown from the study by Herminghaus et al., which was observed in ultrathin (3.9 nm) polystyrene films\textsuperscript{3}. The molecular weight of the polystyrene, 2 kg/mol, was well below the entanglement limit. For a film thickness smaller than the film of Fig.[6.8]c), for profile (6) $h = 40$ nm, the depletion zone in the profile reached the substrate. The rim was disconnected from the undisturbed film that retracted from the substrate and formed a second rim maximum. Fig.[6.9] demonstrates that the repetition of minima and maxima is also observed for nucleated instabilities in polymer films above the critical entanglement limit in an applied electric field. Before the spontaneous instability sets in, a nucleated instability is able to propagate radially outwards from the nucleus. The cascading circular rims of a nucleated film have the appearance of Fig.[6.8]c) until 1) the spontaneous instability sets in, or 2) any of the cascading rims are pinned to the confining silicon surface, or 3) the rims destabilize and break-up into columns with a spacing that corresponds to the wavelength of the electric field induced instability (visible in Fig.[6.8]a)).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6_9.png}
\caption{a) and b) show two cases of cascading profiles of a $\sim 100$ nm PS films with a molecular weight $M_w$ of 100 kg/mol that was annealed for 3 hours at 200°C. c) Cascading dewetting profile of a dewetted 4.9 nm thick film with a molecular weight $M_w$ of 2 kg/mol\textsuperscript{3}. The colors of the two optical micrographs a) and b) are influenced by birefringence (double reflection) in the glass slide and therefore do not correspond to the interference colors shown in Chapter 3.}
\end{figure}

6.7 Ordering of a Nucleated Instability

The hexagonal order is not always obtained if the EHD instability is nucleated, as is evident when comparing Figures [6.9], [6.8] and Fig.[6.6]. The sequence of events that leads to the formation of a heptagon, shown in Fig.[6.8]a), is similar to that of Fig.[6.6], but differs in the time at which the instability was nucleated. A relation between the nucleus and the ring size is likely, as the nucleation of a column results in
the formation of the circular elevated rim surrounding the nucleus. During formation of the elevated rim and expansion of the central column, the depletion zone is drained and exposes the substrate surface (except for an equilibrium film thickness). Once the substrate is exposed, the polymer retracts from the surface and accumulates in the rim. The distance between the nucleus and the rim maximum increase with time. Eventually, the elevated height of the rim couples to the electric field and triggers the formation of columns along the rim. A larger nucleus is expected to trigger the nucleated instability in an earlier stage than a smaller nucleus, thereby increase the expansion time of the rim. The minimum radius $R$ for a hexagonal ordering is $\lambda$, which is the wavelength of the intrinsic instability. A longer expansion time due to an earlier onset of nucleation increases the radius to $\Delta R$. To define the onset of nucleation, the distance between the nucleus and the confining surface was taken, which is defined as $\Delta d$ (see Fig.[6.10]b). In Fig.[6.10]c), the relative ring radius $\Delta R$ is plotted against the relative size of the air gap above the nucleus $\Delta d/d$. The graph, presented in Fig.[6.10]c), shows that an earlier nucleation of the central column due to a higher nucleus triggers an earlier formation of the rim and leads to a higher radius $R$. The occurrence of heptagons, octagons, up to the dodecagon obtained by E. Schäffer$^{14}$ can thus be explained by a time difference between nucleation and the coupling of the elevated rim with the electric field.

Figure 6.10: Relation between the height of the nucleus and the ring size. In a), the dodecagon observed by E. Schäffer$^{14}$ is shown. Used with permission. b) The nucleation of the instability at the black particle leads to the formation of a rim with radius $R$. The plate spacing is indicated by $d$ and the air gap by $\Delta d$. In c), relative size of the radius $\Delta R/\lambda$ is plotted against the relative size of the air gap between the nucleus and the top wafer $\Delta d/d$.

The simulation by Verma, shown in Fig.[6.11] corresponds to the evolution observed for a nucleated instability forming a hexagonally ordered array of columns. They used the inverse of our geometry and situated a single circular patch at the top
surface. At the location of the nucleus, the electrode spacing is smaller, resulting in an increased electric field strength. Their data show the onset of a liquid flow towards the area of increased confinement. Their simulations also confirm the experimentally observed formation of a depletion zone and an elevated liquid ridge and predicts a distance from the nucleus to the ridge that corresponds to the characteristic length scale of the instability.

Figure 6.11: Evolution of an EHD instability in a plate capacitor underneath a plate containing a single protruding circular patch\(^{16}\). The electrode spacing under the patch is 80 nm, elsewhere \(d = 100\) nm. Adapted with permission from R. Verma, A. Sharma, K. Kargupta, and J. Bhaumik, Langmuir 2005, 21, 3710–3721. Copyright 2005, American Chemical Society.

The geometry adopted by Verma in Fig.[6.11] corresponds to the case of a heterogeneously nucleated thin film instability. Introducing an electrode with a surface topography is in fact commonly used for lithographic purposes using polymers. This topic is discussed in the next chapter.

The observation of an instability that was nucleated by a single point (with dimensions smaller than \(\lambda\)) is related to an extended heterogeneity in the electric field. This is shown in Fig.[6.12]. The presence of an edge causes a sharp lateral gradient in the electric field, that gives rise to the nucleation of the EHD instability along the edge.

Fig.[6.12] shows an instability that developed in a 125 nm thick PBrS film at 190 °C with 10 V applied over a period of 16 hours. The structures in a) were observed after 874 min and were monitored from this time on. The vertical solid lines correspond to \(d \sim 1\) \(\mu\)m and are etched into the confining silicon wafer. The structures observed in Fig.[6.12] developed at a plate spacing of 500 ± 15 nm (\(f \sim 0.25\)). The difference in plate spacing gives rise to an electric field gradient at all edges. In the area of interest here, at the arrow in a), the arrow points out the first line of columns that was nucleated by the straight edge.
Pattern Formation Induced by Electric Fields

**Figure 6.12:** Evolution of an instability triggered by a large electric field gradient at an edge. In a) and b), the schematic drawings point out the first and second generation by the solid and dashed arrow, respectively; c-e) shows the evolution of an instability in a 125 nm PBrS film in a capacitor with a top plate that consisted of several etched-in lines ($d' \approx d + 450$ nm). The plate spacing of the areas of interest (see arrows) is $d' = 500 \pm 15$ nm ($f \sim 0.25$). f-h) Simulation data of an instability of a 50 nm thick film in a capacitor. The top electrode had a step, causing the distance between the two electrodes to vary from 150 nm to 193 nm at the left and right halves of the images, respectively. Adapted with permission from R. Verma, A. Sharma, K. Kargupta, and J. Bhaumik, Langmuir 2005, 21, 3710–3721. Copyright 2005, American Chemical Society.

The lateral variation in electric field strength at the crossover step from $d'$ to $d$ induced a pressure gradient in the polymer film. A flow of polymer material towards increasing electrostatic pressure accumulated material in a ridge underneath the edge. Associated with the ridge is the formation of a depletions zone, followed by a secondary
ridge. An instability was triggered at the ridge. Similar to the instability that was initiated by a single nucleus, the instability propagated outwards row by row.

A depletion zone was formed around the columns in a) that drove the formation of a neighboring rim. The ordering obtained for the straight-edge nucleated instability is hexagonal and more perfect than observed for the spontaneous instability. For a long time, the nucleated instability competed with the spontaneous instability, that in c) appears in the left part of the image.

6.8 Conclusion

In this chapter, the formation of an electrohydrodynamic instability in polymer films was discussed. Using several examples, taken from a vast parameter space, the competition between the spontaneously developing instabilities and the nucleated instability is discussed. The morphologies for both instabilities of the experimentally found instabilities showed a great similarity to non-linear 3D simulations by Verma et al. Clearly, both studies complement one another.

The presence of a nucleus that locally varies the film thickness or plate spacing, such as a surface defect, a surface roughness, or a height variation in the top surface triggers an early onset of the instability. A single circular patch on the top electrode, for instance, yields the same morphology as a surface defect on the substrate. A highly ordered array of polymer columns is obtained for both a single point nucleated instability and a straight edge induced instability. The order observed in the nucleated morphology exceeds that of a spontaneously developing instability. The stepwise column formation, imposed by a nucleus of any kind, permits only little mobility for surface waves. In addition to the influence of nucleation on the degree of order obtained during structure formation, thinner films yield more highly ordered columns and a narrow distribution in column diameters and wavelengths as coalescence is less influential. As shown for a film in a geometry that corresponds to a low filling ratio, surface waves are unable to span the gap between the capacitor plates without merging with one or more other surface waves. The surface waves migrate across the sample in direction of increasing electric field and coalesce to complete structure formation.

The observation that a design top surface with a single circular patch or a straight edge initiated structure formation can be applied to replicate larger areas of complex structures. This type of pattern replication, that uses polymers or similar materials, is one of the techniques that is known as soft lithography, a topic that is discussed in Chapter 8. In the next chapter, a similar instability as described in this chapter, but induced by a temperature gradient, is introduced.
Bibliography

1. S.Y. Chou, and L. Zhuang,  
S. Y. Chou, L. Zhuang, and L. Guo,  

2. S. Harkema, E. Schäffer, M.D. Morariu, and U. Steiner,  

3. S. Herminghaus, R. Seemann, and K. Jacobs,  

4. K. Jacobs, K.R. Mecke, and S. Herminghaus  


6. Z. Lin, T. Kerle, T.P. Russell, E. Schäffer, and U. Steiner,  
   *Macromolecules*, **2002**, *35*, 3971

7. Z. Lin, T. Kerle, T.P. Russell, E. Schäffer, and U. Steiner,  
   *Macromolecules*, **2002**, *35*, 6255

   *Nat. Mater.*, **2003**, *2*, 48

9. G. Reiter,  

10. M.S.M. Saifullah, K.R.V. Subramanian, E. Tapley, D.-L. Kang, M. E. Welland, and M. Butler,  
    *Nano Letters*, **2003**, *3*, 1587

11. E. Schäffer,  
    *Dissertation*, **2001**, University of Konstanz

12. E. Schäffer, S. Harkema, M. Roerdink, R. Blossey, and U. Steiner,  

13. E. Schäffer, T. Thurn-Albrecht, T.P. Russell, and U. Steiner,  
    *Europhysics Letters*, **2001**, *53*, 518
14. E. Schäffer, T. Thurn-Albrecht, T.P. Russell, and U. Steiner, 
Nature, 2000, 403, 875

15. R. Seemann, S. Herminghaus, and K. Jacobs, 

16. R. Verma, A. Sharma, K. Kargupta, and J. Bhaumik, 
Langmuir, 2005, 21, 8, 3710