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Electric-Field-Induced Pattern Morphologies in Thin Liquid Films**

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Liquid-polymer films sandwiched between two electrodes develop a surface instability caused by the electric field, giving rise to polymer structures that span the two plates. This study investigates the development of the resulting polymer morphologies as a function of time. The initial phase of the structure formation process is a sinusoidal surface undulation, irrespective of the sample parameters. The later stages of pattern formation depend on the relative amount of polymer in the capacitor gap (filling ratio). For high enough filling ratios, the final morphology of the pattern is determined by the partial coalescence of the initial pattern. The introduction of lateral-field heterogeneities influences the initial pattern formation, with columns nucleated at locations of highest electric field (isolated points or edges). The subsequently formed secondary columns have higher degree of lateral symmetry compared to the pattern formed in a homogeneous field. The nucleation of individual columns or plugs also dominates the pattern formation in the presence of an electrode consisting of an array of lines. The results of this study therefore allow us to draw the conclusion that the accurate replication of structured electrodes typically proceeds by the initial nucleation of individual columns, followed by a coalescence process that yields the polymer replica.

1. Introduction

Soft lithography, while still in its developing phase, is set to become an important technology for low-cost pattern replication for a number of applications.^[1] Some soft-lithographic methods (e.g., microcontact printing and micromolding) make use of a rubber stamp to transfer a pattern onto a surface. Alternative methods, such as hot-embossing, employ a rigid patterned template, which is pressed into a liquid layer. Recently, several soft-lithographic methods were devised that minimize the contact between the template and a liquid resist layer.^[2–6] In these techniques a capillary film instability is directed towards the protrusions of a template facing a liquidpolymer film. The polymer is drawn towards these protrusions, thereby creating a positive replica of the template. As opposed to embossing methods, this lithographic mode minimizes the contact area of the template and the resist, significantly facilitating the template release. While a number of film destabilization mechanisms were recently reported,^[7-14] the amplification of surface waves by an electric field is the most popular implementation. Electrohydrodynamic (EHD) lithography involves the use of a polymer-air bilayer in a capacitor device.

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The practical implementation of any lithographic method requires a high amount of robustness of the techniques. It is therefore necessary to determine the detailed mechanisms by which film instabilities replicate a master pattern. Such a study was recently performed using computer simulations.^[15] Verma et al. predicted that the pattern-replication mechanisms depend on a number of parameters, such as the mismatch between the template periodicity and the intrinsic instability wavelength, the ratio of the film thickness and the air gap, and the magnitude of the lateral field variation. The work presented here is an experimental study that complements the results from these simulations.

In a simplified description, the pattern selection of electrohydrodynamic instabilities are given in terms of a linear stability analysis.^[16-20] The dominant wavelength

$$\lambda = 2\pi \sqrt{\frac{2\gamma}{\frac{-\partial p}{\partial h}}} \tag{1}$$

is given by a "force balance" between the destabilizing pressure gradient with respect to the local film thickness, h, and the surface tension, γ . For an applied voltage, U, the destabilizing pressure, p, scales with the square of the electric field in the polymer layer $E_{\rm p}$

$$p = -\varepsilon_0 \varepsilon_p (\varepsilon_p - 1) E_p^2 \tag{2}$$

where

$$E_p = \frac{U}{\varepsilon_{\rm p}d - (\varepsilon_{\rm p} - 1)h} \tag{3}$$

with the capacitor plate spacing, d, the dielectric permittivity of vacuum, ε_0 , and the dielectric constant of the polymer, ε_p . This

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results in the electric-field dependence of the most unstable mode of

$$\lambda \sim E^{-3/2} \tag{4}$$

The onset of the instability is quantified by the characteristic time constant

$$\tau \sim E^{-6} \tag{5}$$

The pattern selection given in Equation 1 is valid only in the long-wavelength limit, that is, during the early stage of the film instability. As the instability amplitude becomes comparable to the capacitor plate spacing, d, other mechanisms become important.

The late stage of the pattern-formation process is qualitatively determined by the electric field. Since dielectric interfaces are electrostatically unfavorable, the initial undulations develop towards a liquid morphology spanning the two electrodes, separated by nearly vertical side-walls. For high enough fields, the electrostatic driving force overpowers other interfacial pressures, such as the van der Waals disjoining pressure or the Laplace pressure, which are expected to play a role in the near surface regions (~ 1 nm) only. For this reason, the choice of polymer and surface materials are of little importance.

This study addresses the qualitative evolution of the initial undulation pattern towards steady state over long time periods. An important morphological parameter that is not included in the simple stability analysis argument is the fractional "filling" of the capacitor gap (i.e., the ratio of the polymer-film thickness to the width of the air gap). For a laterally varying electric field, the mismatch of λ compared to the relative lateral variation of the field strength is important. It is the purpose of this study to experimentally explore part of this parameter space.

2. Results and Discussion

2.1. Homogeneous Electric Field

In a first experiment, polymer–air double layers were sandwiched between two planar electrodes. Instead of a constant electrode spacing, a wedge geometry was chosen, in which the plate spacing varied by a few micrometers over a lateral distance of a few centimeters (Fig. 2a). The advantage of such a combinatorial sample design is that the temporal evolution of the instability can be visualized in a quasi-static fashion on a single sample. Since the characteristic time constant for the instability to set in scales with the electrode spacing to the sixth power, even small variations of the plate spacing (i.e., small variations of the electric field) give rise to a substantial spread in the time constant for the onset of the film instability. Therefore, for a given annealing time, different stages of the instability can be observed on a single sample.

The onset of the instability is described by the result of the linear stability analysis from Equation 1. Irrespective of the other sample parameters, this results in a low-amplitude sinusoidal undulation with a wavelength, λ . As the instability evolves, other mechanisms come into play. An important parameter is the filling ratio $f = h_0/d$ of the gap, quantifying the relative fraction by which the gap is filled with polymer. Three different cases of *f* are distinguished.

The final morphology of the film for a filling ratio ($f \sim 0.25$) is shown in Figure 1a. It is characterized by monodisperse column diameters and a local hexagonal symmetry. The two-dimensional symmetry corresponding to the in-plane closest



Figure 1. Pattern formed in an electric field at a low filling ratio. a) A 78 nm thick polystyrene (PS) film spin-cast on to a silicon wafer in a homogeneous electric field (U=80 V). The patterns have formed after heating the sample for 20 h at 170 °C. The filling ratio is \approx 0.25. The columns are laterally disconnected and have a narrow diameter distribution. b) A simulation result by Verma et al. [15] for f=0.25.

packing arises from the repulsion of wave maxima and minima, respectively, which is caused by the differing polarization charges at these locations. The final columnar array is long-lived metastable. The individual columns are not interconnected (a thin connecting layer in the final morphology is electrostatically unfavorable) and the inter-column distance is too large for interfacial fluctuations to bridge the columns. Coarsening is therefore suppressed. Figure 1b shows, in comparison, the simulation result by Verma et al.^[15] for f = 0.25.

Long-range hexagonal symmetry, as reported earlier,^[3] was not observed. Such a high degree of symmetry possibly requires the detailed interplay of a sufficiently high lateral packing (implying a high value of f) and the suppression of coarsening (requiring a low enough value of f). We therefore expect highly ordered arrays of columns only in a very narrow f range.

Figure 2 shows the case of an increased filling ratio, for a polymer film with a thickness $h_0 \approx 125$ nm and a plate spacing $d \approx 255$ nm, corresponding to a filling ratio of $f = 0.49 \pm 0.1$. In Figure 2b, the film initially develops a wave pattern, which is visible in the homogeneous areas of the frames corresponding to the wave evolution time of 682 min (t=0 corresponds to the earliest time a surface wave can be optically discerned). The wave pattern is amplified and, with time, columns are formed. Due to the increase in *d* from top-left to bottom-right, the instability has a propagation direction indicated by the arrow. In comparison, Figure 2c shows the simulation results of Verma et al.^[15] for f=0.5.

While the initial pattern-formation process is very similar to the low f case, the late-stage distribution of the columns differs, showing a more irregular distribution of the columns. Careful





Figure 2. Electrohydrodynamic pattern formation in a homogeneous electric field. a) Schematic representation of the capacitor set-up. A brominated PS (PBrS) film was deposited onto an indium tin oxide (ITO) covered glass slide. A polished silicon wafer was used to confine a polymer–air gap. The plate spacing varied by $\sim 1 \,\mu$ m over a lateral distance of $\sim 1 \,\text{cm}$, giving rise to a slight lateral variation of the electric field. b) Optical microscope images showing the development of an instability in a $\approx 125 \,\text{nm}$ thick PBrS film at 164 °C. The filling ratio was 0.49 ± 0.1 . The arrow shows the direction of the field variation. After an annealing time of 682 min, the onset of a capillary instability was observed. The times in (b) are relative to this time. The film undulation leads initially to isolated columns, which partially fuse during the later stage of the instability (270 min). The experimental results are similar to the simulation results by Verma et al. [15] shown in (c) for f = 0.5.

examination of the sample after t = 270 min shows that some of the columns have coalesced to form larger, sometimes elongated structures. This is reproduced by the simulation results by Verma et al.^[15] shown in Figure 2c. The similarity of the simulation results and experiments is seen more clearly in a different sample, shown in Figure 3. It shows a 58 nm thick polystyrene (PS) layer that was annealed for 41 h at 170 °C and an applied voltage of 80 V. While the filling ratio of $f=0.38\pm0.1$ was somewhat lower compared to Figure 2, coalescence patterns that are reminiscent of those predicted by the simulations in Figure 2c are clearly discernible.

The difference between the two different filling ratios $(f \sim 0.25 \text{ and } f \approx 0.5)$ lies in the connectivity of the columns in the advanced stages of structure formation. For $f \le 0.25$ the

areas surrounding the wave maxima are quickly depleted, laterally disconnecting the regions of increased film thickness. This suppresses a coarsening of the columns as the instability progresses. For larger filling ratios the wave maxima stay interconnected even when they have reached the confining surface (particularly well visible in Fig. 2c). This allows a coarsening of the pattern to proceed, until the columns are fully disconnected from each other at a later stage.

The amount of column coalescence during pattern formation increases with increasing filling ratio. This is shown in Figure 4. Instead of the temporal variation of a single sample area, different areas corresponding to a variation of d values are shown for a sample with $h_0 = 85$ nm for an annealing time of 30 min at 170 °C and an applied voltage of 50 V. The variation of d from ≈ 110 nm to ≈ 90 nm in Figure 4b (R1–R5) has two consequences. Firstly, since the time constant of the instability varies as E^{-6} (Eq. 5), the images R1-R5 correspond to different stages of the instability. Despite the large change in τ , the scaling of λ with a much lower power of the electric field strength in Equation 4 resulted in only a small spatial variation of the initial instability pattern. Secondly, a variation of d at constant h_0 leads to a variation of f. In Figure 4 f varied from ~ 0.75 (R1) to 1 (R5, left). While a time series of a single sample area with a fixed value of f is preferable, the experiment shown in Figure 4b is easier to perform and analyze, while showing a very similar behavior to a time series.

The initial instability (R1 and R2) is reminiscent of the cases of lower values of f, consisting of a film undulation with a well-defined wavelength followed by the formation of isolated structures that make contact with the upper electrode. The large amount of polymer in the gap leads to a growth of the columns and to an increasing coalescence. For large enough values of f (f > 0.75) this leads to an inversion of the topographic structure, from isolated columns to isolated holes

in a polymer matrix. This evolution from R1 to R5 in Figure 4b is mirrored by the simulation results of Verma et al.^[15] for f=0.75 in Figure 4c.

2.2. Nucleated Instability-Single Point

EHD pattern formation can be spatially controlled by introducing a lateral heterogeneity into the electric field. The most simple case is a single elevated point protruding from the top electrode, or any other point-like perturbation inside the capacitor gap. For a polymer–air bilayer with $f \approx 0.5$, Figure 5a shows the progress of an EHD instability initiated at a single point, most likely a spike of the indium tin oxide (ITO) layer.

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Figure 3. Coalescence of columns during EHD pattern formation. The atomic force microscopy (AFM) image shows a 58 nm thick PS film that was annealed for 41 h at 170 °C at an applied voltage of 80 V (f=0.38).



Figure 4. Electrohydrodynamic pattern formation at a high filling ratio (f > 0.75). a) Schematic representation of the capacitor set-up, indicating the different image regions of the sample shown in (b), a 85 nm thick PMMA film annealed at 170 °C at an applied voltage of 50 V. As opposed to Figure 2, the sample was imaged at a single annealing time of 30 min, at locations of decreasing plate spacing d, which is equivalent to increasing annealing times at fixed d. Despite the large variation in the temporal development of the polymer morphology, λ changed only by $\approx 10\%$ from R1 to R5. The instability in (b) proceeds by an initial undulation followed by the formation of separated columns. With increasing time (i.e., decreasing values of d), the columns grow and coalesce. This eventually leads to an inverted topographic morphology. The locations R1-R5 correspond to increasing filling ratios: R1: $f \sim 0.75$, R2: $f \sim 0.8$, R3: $f = 0.83 \pm 01$, R4: $f = 0.87 \pm 0.1$, R5: $f \approx 0.92$ (right), $f \approx 1$ (left). This is analogous to the simulation results by Verma et al. [15] for f = 0.75 in (c). The columns of images in (b) and (c) are two- and three-dimensional representations of the same image areas.



Figure 5. Nucleated pattern formation in an electric field. a) The image sequence shows a ≈ 125 nm thick PBrS film confined with $f \approx 0.5$ at an applied voltage of 10 V. After an annealing time of 478 min at 164 °C a single column appeared (t=0) surrounded by a depletion region and a rim. 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 visible.

The nucleated column is surrounded by a radial wave propagating outward from the nucleation point—a depletion ring followed by a rim are visible Figure 5a (0 min). The rim develops a lateral undulation, leading to the formation of columns along the rim (7–70 min). Once the first shell of columns is complete, this process is continued radially outward: rims surrounding the columns lead to the nucleation of further columns. For sufficiently long times, this nucleated column formation process competes with the pattern formation caused by the homogeneous field.

A second example of an instability nucleated by a single point is shown in Figure 6, proceeding in a similar fashion. In this sample, $f \approx 0.6$. In comparison to Figure 5a, nucleation is much weaker. When the first nucleated column appears (t=0), the surface undulation of the film caused by the electric field is already clearly visible. As a consequence, the formation of a cluster of nucleated columns is more quickly overtaken by the spontaneous pattern formation caused by the homogeneous electric field.

The main difference between the two cases concerns the structure periodicity near the nucleation point. While the pattern periodicity in Figure 6 is always close to the value that is predicted in the absence of nucleation (i.e., for a homogeneous electric field), this is not observed in the results of Figure 5. The mean distance of the nucleation point to columns in the first row is larger by approximately one third compared to the characteristic inter-column distance elsewhere on the sample.

As a consequence these columns have a larger diameter compared to the others. This, in turn leads to a further increase in column diameter by Ostwald ripening at the expense of the initially nucleated column, which decreases in diameter with increasing time. For long annealing times (t > 200 min), the central column is fully depleted and only the initial nucleus (most likely an ITO spike) remains in the center of the nucleated patch of columns, as verified by atomic force microscopy (AFM) (result not shown). The cause of the nucleation observed in Figure 6 is not revealed, since it remains obscured by the polymer column.

Figure 6b shows the simulation results by Verma et al.^[15] for f=0.25. While similar, two differences emerge. In analogy to the homogeneous case, the more ordered arrangement and more monodisperse diameters of the columns is most likely due to the lower *f*-value of the simulation. Secondly, the experimental results show a symmetry breaking of the rim and a sequential appearance of the secondary columns, whereas the columns on the first rim appear simultaneously in Figure 6b.

Since both nucleation types are regularly observed, often on the same sample, the difference is unlikely to be system dependent. The simulation results in Figure 6b are similar to the case shown in Figure 6a. Since a nucleation patch with an extended diameter (comparable to the wavelength) was used in the simulation, we speculate that the size (and possibly the nature) of the nucleation point may play a role. An extend nucleation patch leads to columns with a similar diameter to the secondary columns, while small nucleation sites lead to smaller column sizes that are subject to higher internal capillary pressures and are therefore depleted by the surrounding secondary columns.

2.3. Nucleated Instability-Straight Edge

The observations for an instability that was nucleated by a single point (with dimensions smaller than λ) are also reproduced for an extended heterogeneity in the electric field. This is shown in Figure 7a. The images show the sample near the edge of the confining electrode (a planar silicon wafer). The presence of the edge causes a sharp lateral gradient in the electric field, giving rise to the nucleation of the EHD instability along the edge. The image series of Figure 7a shows sample locations of slightly increasing electrode spacing, corresponding to the temporal development of the instability. The result of an experiment in which the instability was observed at one location as a function of time was very similar (see Supporting Information). The first frame of Figure 7a shows an increase in the local film thickness at the location of the edge and a secondary maximum. The right part of the frame shows the film undulation caused by the homogeneous field. An instability along the primary rim gives rise to the nucleation of columns.



Figure 6. Nucleated pattern formation in an electric field. a) The image sequence shows a ≈ 125 nm thick PBrS film with $f \approx 0.6$ at an applied voltage of 10 V. After an annealing time of 460 min at 164 °C a single column appeared (t=0) surrounded by a depletion region and a rim. With increasing time, further columns are nucleated radially outward from the initial columns. All images also show undulations of the surrounding film (caused by the homogeneous electric field). The images in (b) show simulation results for f=0.25 by Verma et al. [15].





Figure 7. Electrohydrodynamic pattern formation initiated by a straight edge. a) A 78 nm thick PS film was spin-cast onto a silicon wafer. The sample was partially covered with a planar electrode ($f \approx 0.25$) and annealed for 20 h at 170 °C and U = 80 V. The sequence of images correspond to different locations on the sample with slightly increasing *d* values. The left part of the images show the pattern formation caused by the straight edge of the top electrode. The edge-induced nucleation of columns competes with the EHD instability caused by the homogeneous field (right part of the images). b) Simulation results of Verma et al. [15]. The edge corresponds to a change in plate spacing from 193 nm in the left half of the images to 150 nm (right half). The film thickness was 50 nm, corresponding to f = 0.33.

The pattern formation proceeds "row by row" to the right. Once a row of columns has formed, it is accompanied by a region of material depletion followed by an elevated rim. This elevated rim gives rise to the nucleation of further columns. For long enough times, this propagating nucleation process competes with the EHD instability caused by the homogeneous electric field.

A further consequence of pattern formation by nucleation is the degree of order. A higher degree of order is observed for the 3–4 rows of columns that were nucleated by the edge. This extends, however, no further than four rows of columns away from the edge, limited by the competing EHD instability. The row of columns immediately adjacent to the edge has a slightly higher density (i.e., the columns have on average a larger diameter). This arises presumably from the fact that more material (stemming from the stable film on the left) is available to these columns.

An interesting further phenomenon often observed for edgenucleated EHD instabilities is shown in Figure 8. The lower left part of Figure 8a shows a 58 nm thick PS film sandwiched between two electrodes ($d=1.2 \mu m$, U=80 V) that was annealed for 41 h at 170 °C (the upper right part was not part of the sandwich). Rather than nucleated columns with an intercolumn distance of $\approx \lambda$, an alternating sequence of columns and wave maxima were observed. The difference between Figures 7 and 8 lies in the filling ratio. For $f \approx 0.05$ in Figure 8 there is not enough material for each column to fully form. A column that is nucleated first depletes the surrounding film on the expense of the neighboring columns. The next-nearest neighbors, on the other hand, benefit from the reduced column growth, which leads to the alternating pattern in Figure 8.

In addition, due to the large value of the plate spacing, the field inhomogeneity caused by the edge affects the polymer distribution over large lateral distances, drawing material towards the edge location.

2.4. Nucleated Instability-Array of Lines

The preferred generation of EHD film instabilities at locations of highest electric field lies at the base of the EHD lithographic process. A common strategy is the use of topographically patterned top electrodes.^[2-6] To explore the kinetics of pattern replication, the EHD instability induced by a topographic line grating as the top electrode was explored. Differing from the samples, in which the electric field is predominantly homogeneous, the lateral-field variation determines the initial shape of the instability. The filling ratio (defined as the ratio of the film thickness to



Figure 8. Nucleation of alternating columns induced by a straight edge, a) optical microscope image, b) AFM image. A 58 nm thick PS film was partially covered by a planar electrode (bottom-left). The sample was annealed for 41 h at 170 °C at an applied voltage of 80 V. The plate spacing was 1.2 μ m, corresponding to a $f \approx 0.05$. The color change in (a) in a $\sim 20 \ \mu$ m area adjacent to the edge is due to the overall accumulation of polymer drawn towards the edge by the strong field gradient.

the minimum of the plate spacing) plays a role in the late stage of the pattern-formation process. Since both parameters are a function of the minimum of the electrode distance d, these two quantities are coupled, giving rise to a large parameter space.

Figure 9a shows the instability of a film with $f \approx 0.25$ (*d* is the distance between substrate and the downward protruding lines) at an applied voltage of 30 V. After annealing for 108 min undulations appear under the downward protruding lines, with an intrinsic wavelength that is comparable to the periodicity of the electrode grating. With time the columns

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Figure 9. Nucleation of columns induced by an electrode with an array of lines. a) A ~ 125 nm thick PBrS film was spin-cast onto a ITO-covered glass slide and covered by an electrode that had linear grooves. The filling ratio was $f \approx 0.25$. After annealing for 108 min at ≈ 22 °C and U=30 V, undulations at locations of smallest electrode distance appear (t=0). The intrinsic wavelength of these undulations is comparable to the periodicity of the grating. With increasing time, columns appear in the stripe-patterned regions of the electrode and the diameter of the columns grow, as material is drawn in from the areas between the stripes. b) Simulation results of Verma et al. [15] for f=0.5. Since parameters of the simulation differ from those of the experiment (a mismatch of λ and the grating periodicity by a factor of 2), columns are nucleated only on every second line.

make contact with the electrode, resulting in linear arrays of columns. Figure 9b shows, in comparison, the simulations of Verma et al.^[15] for a system with f=0.5. The simulations are qualitatively similar to the experimental results. Due to the nature of the contrast of the optical images, we cannot discern the first stage shown in the simulation results, the possible sinusoidal deformation of the film in synchronization with the electrode grating. The subsequent instability of the ridges and the column formation is very similar. Since the wavelength of the intrinsic instability, λ , is larger by a factor of two compared to the periodicity of the grating in Figure 9b, only every second line of the grating is replicated.

A further example of a film instability is shown in Figure 10. In this sample there was a large mismatch between the intrinsic length scale λ and the grating periodicity (by a factor of ~6.5). Careful examination of the images shows that the film develops long-wavelength undulations, which seem to be essentially unmodified by the line grating-the film destabilizes in the averaged electric field. This is particularly visible in the upper part of the image frames, where a circular undulation develops during a period of 58 min. Once the wave maxima make contact with the electrode grating, the polymer spreads along the first line of contact to form an elongated plug (circles in the 58 min and 105 min frames). The propagation of these plugs from the lower left corner stems from a slight increase in plate distance towards the upper right corner of the images. The mismatch of λ and the grating periodicity has a consequence for the plug density. Measuring perpendicular to the lines, approximately only every third line is occupied by a linear plug, in qualitative agreement with the simulations by Verma et al.^[15] (Fig. 9).

3. Conclusions

We have presented a series of experimental results that show the EHD pattern formation in polymer films sandwiched between two electrodes for a number of different electrode conformations. While the initial phase of the film instability is qualitatively the same for all samples, the ratio of the film thickness to the electrode spacing (fill factor, f) determines the late-stage pattern morphology in homogeneous electric fields. For low values of f the wave maxima disconnect, giving rise to hexagonally ordered columns with inter-column distances that mirror the wavelength of the initial instability. For higher values of f ($f \sim 0.5$), the film stays partially interconnected when the wave maxima make contact with the top electrode. The late-stage evolution of the pattern is therefore governed by a ripening process that leads to coalescence of some of the columns. This process is even more pronounced for very high values of f, where the extensive coalescence of the initial wave pattern leads to a continuous polymer film with included voids, an inversion of the initial column structure.

The lateral structure of the EHD pattern can be controlled by introducing a inhomogeneity into the electric field. The most simple case, a point defect, leads to the nucleation of a single column followed by the radial outward propagation of the nucleation process. This sequential nucleation process gives rise to a higher degree of lateral symmetry compared to the columns that were formed in a homogeneous field. Interestingly, two different mechanisms were observed at the nucleation site itself. In some of our experiments, the initially nucleated column disappeared as the secondary columns were formed. In others, this was not the case and the final nucleation pattern was distinguishable from the column morphology on other parts of the sample only by its higher degree of lateral symmetry.

The situation is similar for the nucleation pattern caused by a linear edge in the upper electrode. The field heterogeneity results in the nucleation of columns along the edge, followed by the formation of secondary columns. The near-edge pattern has





Figure 10. EHD film instability induced by an array of lines. A ~ 125 nm thick PBrS film was spin-cast onto a ITO-covered glass slide and covered by an electrode that had linear grooves. The filling ratio was $f \approx 0.25$. After annealing for 32 min (t=0) at ≈ 208 °C and U=20 V, a first film undulation is visible in the upper part of the frame. The wavelength of this undulations is much larger than the periodicity of the grating (by a factor of ~ 6.5). When the undulations make contact with the electrode grating, elongated plugs are formed (marked with circles in 58 min and 105 min frames). The instability proceeds from the lower left corner due to a slight gradient in the electrode spacing.

a higher degree of lateral symmetry compared to the columns formed by the homogeneous electric field.

For electrodes consisting of a linear array of lines, columns form along the downward protruding parts of the top plate. The shape of the nucleated pattern depends on the ratio of the initial film undulation wavelength (caused by the laterally averaged electric field) and the periodicity of the line grating. This is in contrast to some of the simulation results by Verma et al.,^[15] in which the direct replication of a grating pattern (by the formation and amplification of entire rims) was seen.

The important issue addressed by studies of EHD instabilities in laterally heterogeneous electric fields concerns the control of the pattern morphology. Our results shed some light on the mechanism by which the pattern of the top electrode is accurately replicated into the film. All our experiments indicate that EHD pattern starts as a surface undulation that is triggered by the laterally averaged electric field. As this undulation is amplified, wave maxima are guided in the directions of the highest field gradient, forming columns or elongated plugs as they touch the top electrode. The pattern evolves further by drawing in material from the remaining film, or by coalescence with already formed structures.

While we have not observed the complete replication of a patterned electrode structure in the experiments reported here, these results allow us to draw conclusions about the kinetics of complete pattern replication. Since the pattern replication for all parameters of this study proceed via the nucleation of columns (or elongated plugs), it seems likely that complete pattern replication involves the formation of columns on the parts of the electrode that have the smallest distance to the film. These columns draw in more material and coalesce, thereby replicating the electrode pattern. The important parameter for pattern replication is therefore the filling ratio. Accurate pattern replication requires enough material for the coalescence to proceed sufficiently far.

In summary, we have conducted a number of EHD experiments to study the pattern formation as a function of time. For the parameters of our experiments, we find that all pattern formation occurs initially by the generation of individual columns. In the presence of sufficient material, the final pattern morphology is determined by the partial coalescence of the initial columnar morphology.

4. Experimental

Three experimental systems were used: 1) brominated polystyrene (PBrS, 40 % bromination) on indium tin oxide (ITO)-covered glass substrates; 2) polystyrene (PS) on silicon wafers; and 3) poly(methyl methacrylate) (PMMA) on titanium dioxide-covered silicon wafers. The characteristics of the polymers are given in Table 1. Films with thicknesses of 58–125 nm were spin-cast from toluene solutions (2 % polymer by weight).

The substrates had dimensions of $2 \text{ cm} \times 2 \text{ cm}$. 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 soap solution (70 °C) and rinsed with Millipore water. To remove the soap and other surface contaminations, the substrates were further



Table 1. Characteristics of the polymers used.

Polymer	Molecular weight	Polydispersity	Surface tension	Dielectric constant
PBrS	154 kg mol ⁻¹	1.02	≈30.0 mN m ⁻¹	5.5
PS	94.9 kg mol ⁻¹	1.06	29.7 mN m ⁻¹	2.5
PMMA	9.6 kg mol ⁻¹	1.03	30 mN m^{-1}	3.6

cleaned in an ultrasonic bath in acetone and isopropyl alcohol and then spun dry. The substrates were then heated for 10 min at 120 °C in a convection oven, followed by 20 min of UV–ozone treatment. Silicon wafers were first cleaned in a 3:1 (by volume) solution of sulfuric acid (98 %) and H₂O₂ (30 %) (Piranha solution) followed by an etch in a HF solution (1:80 by volume in water). Titanium dioxide substrates were prepared by the deposition process described in [21]. All substrates, as well as the electrodes covering the films were subjected to snow-jet cleaning [22] 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 as topographically structured surfaces were used. While the use of spacers allows the control of d [23], the two surfaces were brought directly into contact in the experiments reported here. In this case, a finite air gap arises from deviations in the planarity of the two surfaces and by a low concentration of defects (dust particles) that are trapped between the two plates.

A voltage of 10–80 V was applied between the two plates and the temperature of the device was raised to 165–225 °C (above the glass-transition temperature 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). At the end of the experiment, the sample was cooled down to room temperature and the electric field and the top wafer were removed. The lateral distribution of the polymer film was analyzed by optical microscopy and tapping-mode atomic force microscopy (AFM, Digital Instruments D3100). The AFM measurements also yielded the plate spacing d.

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