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11.1 Introduction

The fabrication of large area polymer structures with feature sizes ranging from few microns down to the molecular level is key to various technologically important areas, examples of which include molecular electronics [1], flexible display screens [2], optical sensors [3], structural color [4], reusable super adhesives [5], super hydrophobic [6] and self cleaning surfaces [7], and scaffolds for tissue engineering [8]. The length scale of interest here, often referred to as the 'meso' scale, ranges from a few nanometers to hundreds of nanometers and interfaces the molecular and the macroscopic worlds. Thus, it becomes possible to observe simultaneous signatures of molecular interactions as well as macroscopic effects at these length scales, often giving rise to exciting new phenomena like quantum size effects (OSEs) [9], single electron tunneling (SET) [10], Coulomb blockade, and so on [11]. None of these effects can be realized either in purely macroscopic or molecular regimes. However, the success of the desired applications, harvesting the extraordinary scientific phenomena occurring at these length scales, depends strongly on the availability of suitable, easy to implement patterning techniques that can create defect-free structures over large areas. Present-day technologies offer three distinct approaches for mesoscale patterning. Two of the more popular ones are 'top-down' methods, that include various types of lithography and the serial writing methods [12-17] and 'bottom-up' self-assembly (SA) techniques, where individual components assemble in a desired fashion to form structures [18-20]. However, neither bottom-up nor top-down patterning techniques by themselves are capable of achieving structural control at the molecular and mesoscopic level combined with macroscopic addressability. Detailed discussion on either top-down lithography methods or bottom-up self-assembly methods are beyond the scope of this chapter, and an interested reader may refer to several excellent reviews and text books which are already available [12, 21-23].

A third approach which is gaining significant attention as a viable patterning technique, particularly in the context of liquid and soft solid thin films, is based on the

fact that small-scale or highly confined systems are usually unstable or can be made unstable by application of a suitable external field. Evolution of instability in the form of spatially periodic modes progressively alters the shape to a more intricate pattern which minimizes energy. The pattern morphology and length scale are governed by a competition among the destabilizing forces (e.g., van der Waals and electrostatic fields) and stabilizing forces (e.g., surface tension, elastic strain). The existence of such instabilities have been known for more than a century now [24, 25]. Thus, an understanding and control of instabilities can be employed to fabricate mesoscale patterns starting from a simple, but unstable shape such as a flat thin film. The approach, which we will refer to as self-organized patterning, is based on instabilitymediated disintegration of thin films. Instabilities which are often considered undesirable because they tend to destroy the coating itself, are harnessed for the creation of meso- and nanoscale surface structures [40-281]. Due to several key factors (discussed later) the methods are particularly well-suited for polymeric films and surfaces [47-56]. Though there are several forms of instabilities, this chapter will focus primarily on morphological evolution and pattern formation caused by the spontaneous or externally stimulated growth of capillary waves, which are omnipresent on the surface of a thin visco-elastic film [26-28]. These surface capillary waves, resulting from molecular level thermal fluctuations have extremely low amplitudes (a few nm) [27] and are hardly of any significance in the macroscopic world. However, at the meso- and nanoscopic length scale, where intermolecular interactions are strong compared to the gravitational field, these fluctuations become important and significantly influence the stability of a thin film. These initial fluctuations can grow because of various forces such as the conjoining pressure resulting from the van der Waals forces [29, 30, 73-75], electrostatic forces [31], steric forces (molecular level entanglement, significant in polymers) [28, 110], and forces arising from the spatial confinement of fluctuation spectrum (like Casimir force) [32]. The growing fluctuations may lead to a progressive roughening of the surface of an initially flat film [33-170]. Eventually, either the growth stops to form a spatially periodic structure before the film ruptures, or the film break-up occurs leading to hole growth and coalesce to form larger scale patterns [33–39, 65]. These instabilities are mostly manifested in liquid or soft (elastic modulus < 1 MPa) solid films, as the flow and deformation caused by the intermolecular interactions are rather weak. Dewetting is observed in ultrathin metal, polymer and solid films occurs only when they are molten, or, (above their glass transition) or have a small elastic modulus [40, 41]. The surface of a ruptured liquid film subsequently undergoes morphological evolution (like dewetting) that leads to the reduction of the free energy of the system [37, 38]. Understanding the science of instabilities is also of key importance in a variety of settings, including various industrial applications, such as enhancement of the stability of foams and emulsions, oil recovery, flotation, service life enhancement of coatings, vapor condensation on a tube wall, and detergent action in the cleaning of oil films [42]. Instabilities also play a critical role in host of biological and physiological phenomena particularly the small-scale deformations of membranes [43], such as the onset of microvilli in normal and neoplastic cells, the deformation and rhythmic movement (flickering) of red blood cells, adhesion,

fusion, and attachment of cells and micro-organisms and phagocytosis, occurrence of tear film break up and dry eye syndrome [44].

While the science of dewetting of liquids on solid surfaces has been investigated for a long time [45], the spontaneous instability and film rupture continue to receive significant attention [47–171]. Energetically, the spontaneous break-up is only possible where the rupture and subsequent morphological rearrangement of the film results in the lowering of the system free energy as compared with an intact film [33–38]. A ruptured film may further evolve with morphological reorganization until thermodynamic equilibrium is attained [33–38, 56, 65, 84–88]. Interestingly, the morphology of the instability-induced structures in most cases bears the signature of the force that is responsible for the instability [56, 65]. Apart from spontaneous instabilities, the growth of the surface fluctuations can also be engendered by applying an external field (e.g., an electric field [230–264], or a thermal gradient) [265–270], or they can nucleate around heterogeneies or defects present in the film or on the substrate [117–139].

Irrespective of the precise mechanism leading to film instability, instability structures with lateral resolutions down to ~ 100 nm can evolve in an unstable film [47-171]. Thus, based on thin film instabilies, it may in principle be possible to achieve structures having sub-micron lateral resolutions. It is this particular aspect which has led to a paradigm shift in the nature of research in the area of polymer thin film instability. Research, starting in the early 1990s, in the area focused more on the fundamental issues relating to the origin and the spatio-temporal growth of the instability due to various forces that are often antagonistic [65, 98, 123]. The basic intention was to enhance stability of thin films against dewetting based on the complete understanding of the physics leading to the destabilization process. In contrast, recent attention is significantly on exploring the possibility of using dewetting and other instability induced methods as viable surface patterning techniques for the fabrication of meso-and nanoscale structures, particularly in soft materials like polymers [172-281]. In this chapter, we will present a brief overview of some of the recent developments in the field of patterning, based on instabilities in thin polymer films [172-281].

Incidentally, most instability-mediated techniques result in structures with a welldefined mean length scale, lacking long-range order and desired detailed shapes [47–171]. Such isotropic and random structures have limited practical application, as most applications require regularly ordered and high-fidelity structures. Most soft lithography techniques can easily create such defect-free ordered structures over large areas [13]. Thus, strategies are necessary to impose long-range order on the final structures in order to develop instability-mediated morphologies as a viable surface patterning technique. This is often achieved by suitable templating strategies, such as the use of a patterned substrate or confining mask [174–229]. Templating, in conjugation with careful control of initial conditions such as the film thickness, surface and interfacial tensions and so on, offers a great deal of flexibility, allowing the tuning of the morphology, feature size, and pitch of the structures, thereby leading to the realization of novel concepts, such as *patterns on demand, reconfigurable structures*, and *patterning beyond the master*.

11.2

Origin of Surface Instability

The different mechanisms that may lead to instabilities in thin polymer films can be broadly subdivided into two major categories: instability resulting from the inherent dynamics of the system and instability triggered by an external field.

The first type of instability can be engendered by (i) spontaneous instability or spinodal dewetting, which can be caused by the amplification of surface fluctuations due to the action of intersurface forces, such as van der Waals, electrostatic and others [56–106]. It has very recently been shown that spontaneous dewetting can also be triggered due to release of residual stresses accumulated during film preparation, because of polymer chain entanglement and adsorption on the substrate, where many aspects of instability evolution as well the dewetted pattern morphology are similar to that observed in spinodal dewetting [106–116]; (ii) nucleated dewetting, which may be further subdivided into a heterogeneous nucleation [117–139]. On a chemically heterogeneous surface, the gradient in wettability contrast is responsible for engendering an instability, leading to dewetting rather than the nonwettability of the substrate itself, as in the case of spinodal dewetting [129].

An external field-mediated instability can be engendered due to the application of a field like a thermal gradient or electrical field [236–281]. Some other causes, like density variations within the film, have also been proposed which may operate in special circumstances such as nanoparticle- or nanodefect-filled films [144, 282– 284].

Interestingly, while spontaneous instabilities are possible only in thermodynamically unstable ultrathin films (<100 nm), nucleation can lead to the disintegration of thicker metastable films. Further, with the application of an external field it is even possible to destabilize a reasonably thick film (~500 nm) where the stabilizing influence of gravity is significant [123, 129, 137, 138]. Of all these mechanisms, only stress-induced instabilities caused by the deformation of polymer coils in the film are specific to high molecular weight polymers [107–116] and the rest are rather generic and independent of the precise nature of the liquid. As polymers are long chain molecules, the entanglement- and adsorption-mediated residual stresses generated, by non-equilibrium conformations of the individual molecules during spin-coating and solvent drying can influence the stability of the system significantly [107–116], an aspect that has been realized only very recently [108–116].

Irrespective of the precise origin of an instability, the amplification of the capillary waves leads to the deformation of the free surface (film–air interface) and results in localized flow of liquid from the thinner parts to the thicker parts of the film [38, 56–168]. This phenomenon eventually results in the rupture of the film with the formation of dry patches or holes, when the growing amplitude of the capillary wave spectrum equals the film thickness [65]. As the film ruptures, the two distinct interfaces (film–air and film–substrate) merge and a three phase contact line (film–air–substrate) is formed. Depending on the thermodynamics of the system,

a ruptured hole may grow further with time, resulting in a subsequent morphological rearrangement of the film on the substrate [37, 38]. The role of surface tension during film instabilities needs a special mention. While it opposes the growth of the capillary waves, thereby playing a stabilizing role before a film has ruptured, it aids the growth of a hole after the rupture of the film [90].

11.3 Polymer Thin Film Dewetting

11.3.1

Spontaneous Instability or Spinodal Dewetting: Theoretical Aspects

In this section we review the theoretical framework that describes spontaneous instabilities or spinodal dewetting [33-39, 57, 64-67, 76-91]. A spontaneous instability is only possible in a thermodynamically unstable thin film. Thus, it is important to clearly define an unstable film and contrast it with other types of films, namely stable and metastable films [38, 65, 138]. The classification of films in terms of their stability is best understood in terms of excess free energy (ΔG), disjoining/conjoining pressure (Π), or effective interface potential (Φ) [65]. All three quantities manifest the excess energy in a thin film, as compared to the bulk, stemming from interactions between the two interfaces [38, 57, 64, 65, 138]. ΔG is a measure for the excess free energy per unit area required to bring two infinitely separated interfaces to a finite distance h. In the case of a thin film, the two interacting interfaces are the film-substrate and the film-air interfaces and h corresponds to the film thickness [65]. The disjoining pressure (Π) is the negative derivative of the excess free energy (per unit area) with respect to the film thickness ($\Pi = -\partial (\Delta G)/\partial h$) and is a measure of the excess pressure in a thin film arising from the interaction of the two interfaces [46, 65]. In a different notation, Φ refers to the effective intermolecular potential and is a measure of the excess intermolecular free energy per unit volume in the film $(\Phi = \partial(\Delta G)/\partial h)$. It is obvious that for a thin film Φ is identical to the negative of the disjoining pressure, $-\Pi$ or conjoining pressure. In order to eliminate possible confusion we want to emphasize that some groups use the symbol Φ to represent socalled effective interface potential which is identical to the excess free energy (ΔG), in the notations used in this text [138].

The condition of instability vis-a-vis stability of a thin film in terms Φ or Π (or ΔG) as a function of *h* emerges from linear stability analysis (LSA) [33–38, 65]. In order to facilitate the discussion of LSA, a brief summary of the key theoretical results on thin film instability is presented here.

The general framework of the hydrodynamics of a free liquid surface have emerged after more than four decades of work by various researchers including Cahn [33], Vrij [34, 35], Ruckenstein and Jain [37], Williams and Davis [39], Derjaguin [36], Sharma [38, 64–67], and many others. The governing equation describing the two-dimensional (2D) dynamics and the shape of a thin film of Newtonian liquid on a flat substrate, neglecting the effect of evaporation/condensation and gravity is

given as Equation 11.1:

$$3\mu \frac{\partial h}{\partial t} + \frac{\partial}{\partial x} \left[\gamma h^3 \frac{\partial^3 h}{\partial x^3} \right] + \frac{\partial}{\partial x} \left[-h^3 \frac{\partial \Phi}{\partial h} \frac{\partial h}{\partial x} \right] = 0, \qquad (11.1)$$

where h(x,t) is the local film thickness, x is the co-ordinate parallel to the substrate surface, t is time, μ is the viscosity, and γ is the surface tension of the liquid. The simplification of the x component of the Navier–Stokes equation in the limit of long wavelengths (or small slopes) combined with the continuity equation provides the individual components of velocity (*u*, *w*) along the *x* and *z* axes as functions of *h*, Φ and x [37, 38, 65, 67]. The small-slope approximation $(\partial h/\partial x \ll 0)$ originates from the assumption that the wavelengths of the surface fluctuations (λ) are much larger ($\lambda \gg$ h_0 compared with the mean film thickness (h_0), and is reasonably successful in capturing the essential physics of the system, unless the film thickness is of molecular dimensions [37, 38]. The velocity components are substituted in the 'kinematic boundary condition' $\partial h/\partial t + u_s \partial h/\partial x = w_s$, which is akin to the local mass balance at any point on the free liquid surface, and correlates the two components of velocity at the interface. The solution of Equation 11.1 gives the mean film thickness h as a function of the spatial coordinate (x) and time (t). When $h_t = 0$, the steady state film thickness is of the form h(x), implying a spatial variation of film thickness even at a steady state. The consequent situation can be regarded as a dynamic steady state and can now be correlated to the preceding discussion on how surface tension opposes this spatial variation of film thickness engendered by molecular level fluctuations in favor of a flat surface, giving rise to surface capillary waves [38, 90].

Each of the constituent terms of Equation 11.1 represents a distinct force field. From left to right the terms represent the contributions of viscous forces, surface tension forces due to the curvature at the free interface (Laplace pressure), and the excess intermolecular forces (disjoining pressure) respectively [37, 38, 65, 67]. The viscous force in no way influences the stability as it merely controls the dynamics of the system. For tangentially immobile films, the prefactor of the viscous term **3** is replaced by **12** [38, 65]. The Laplace pressure arising from surface tension has a stabilizing influence, as already discussed. Thus, the only term that may induce an instability in the system is the one representing the excess intermolecular interactions [37, 38, 65].

The major practical use of Equation 11.1 lies in testing whether a film of uniform initial thickness h_0 remains stable or eventually become unstable with time. The solution of linearized equations of motion incorporating the effect of intermolecular forces, can be simplified by the lubrication approximation (non-inertial laminar flow in thin films) and admit space periodic solutions for the film thickness $h(x, t) = h_0 + \varepsilon \sin(kx) \exp(\omega t)$ with:

$$\omega = C[-\gamma_L k^4 - (\partial \Phi / \partial h) k^2] \tag{11.2}$$

Equation 11.2 represents the linear dispersion relation for the initial growth coefficient (ω) of an axis-symmetric perturbation on the free liquid surface with a small ($\varepsilon \ll h_0$) initial amplitude having wavenumber of instability *k* [65]. The parameter

 $C = (h_0^3/3\mu)$ depends on the film thickness and inversely on the film viscosity, but not on k. The necessary condition for the instability is a positive value of ω , which implies that the initial amplitude of the perturbation will grow with time. It can be seen from the expression of ω in the dispersion relation that both the term *C* and the first term with in the parenthesis (γk^4) are always positive and thus, growth of an instability ($\omega > 0$) is only possible for a negative spinodal parameter $(\partial \Phi / \partial h < 0)$ [65]. In addition, for higher values of k, the k^4 term dominates over the term containing k^2 so that ω is negative even when $\partial \Phi / \partial h < 0$ for sufficiently high wavenumbers, signifying stability of the film. Thus, $\partial \Phi / \partial h < 0$ is the necessary condition for film instability. The sufficiency condition lies in values of k being in the range (0, $k_{\rm C}$), where $k_{\rm C}$ is a critical wavenumber corresponding to $\omega = 0$ which is obtained by setting the dispersion equation to zero and solving for k. This observation implies that higher wavenumbers $(>k_c)$ or low frequency oscillations fail to destabilize even intrinsically unstable films. It is also obvious that if $\partial \Phi / \partial h > 0$, the film is unconditionally (thermodynamically) stable. In such a film the conjoining pressure arising from the repulsive interaction between the two interfaces augments the Laplace pressure, imparting stability to the film [38, 65, 67]. Also, by setting $\partial \omega / \partial k = 0$, it is possible obtain an expression for the dominant wavenumber of the instability ($k_{\rm m}$) and the fastest growth coefficient ($\omega_{\rm m}$). $k_{\rm m}$ is related to the length scale or periodicity of the fastest growing mode of instability as $\lambda_{\rm m} = (2\pi / k_{\rm m})$ [38, 65, 67]. The dominant length scale of instability ($\lambda_{\rm m}$) is an important parameter as it can be measured in dewetting experiments and can therefore be directly compared with theoretically predicted values. Physically, a negative value of $\partial \Phi / \partial h$ implies an attractive interaction between the film–air and film-substrate interfaces. This attraction, in the absence of any significant repulsive (stabilizing) forces, favors the growth of the deformations at the film-air interface which eventually results in rupture and subsequent dewetting of the film on the substrate, leading to the formation of a random collection of droplets [38, 57, 65]. During the growth of the deformation the flow of liquid is from the thinner zones of the film to the thicker parts, which is an example of negative diffusion.

It can be seen from the preceding discussion that the condition of instability of a thin film is purely thermodynamic and is independent of the film rheology. It critically depends on the sign of variation of Φ with the film thickness *h*. Thus, it becomes important to understand the forces that constitute the excess free energy (Φ) [65, 98]. For an unstable or a metastable film Φ is made up of antagonistic (attractive and repulsive) interactions with different distance variations (short and long range) [67, 98]. While surface instabilities require a negative disjoining pressure, contact line retraction upon hole formation is possible only with dominant shortrange repulsion in the proximity of the substrate. In the absence of significant electrical double layer effects, which are unlikely to play a role for apolar polymer films in air, the key constituents of the excess intermolecular free energy (Φ) are the long-range apolar Lifshitz-van der Waals (LW) interaction and the much shorter ranged polar 'acid-base' (AB) interactions [31], which are often quantified as hydrophobic repulsion, hydration pressure, and so on [67]. The AB interactions can only occur between molecules that display conjugate polarities as measured by their electron (proton) donor and acceptor capabilities and thus, such interactions are also

ruled out in most polymers such as PS, which are weakly electron-donor monopolar material and therefore cannot form hydrogen bonds.

Further, in situations where there is no physical origin of any short range repulsion (implying that $\Phi \rightarrow -\infty$ as $h \rightarrow 0$) a 'contact' repulsion of the form β/h^9 is included to remove the (nonphysical) singularity of Φ as $h \rightarrow 0$ [64, 65, 67]. Based on these conditions, a popular representation of the potential for a unstructured polymer thin film is given as Equation 11.3 [65]:

$$\Phi = (A_{\rm S}/6\pi h^3) - \left(\frac{S_P}{l_P}\right) \exp(-h/l_P) - (\beta/h^9), \tag{11.3}$$

where, $A_{\rm S}$ denotes the effective Hamaker constant arising from the van der Waals interaction between the two interfaces of the film on a semi-infinite thick substrate. A positive or a negative value of $A_{\rm S}$ denotes a long-range attraction (the possibility of instability driven by van der Waals force) or repulsion (stabilizing role of van der Waals force), respectively. $S_{\rm P}$ in Equation 11.3 denotes the strength of a medium-range attraction ($S_{\rm P} < 0$) or repulsion ($S_{\rm P} > 0$) with $l_{\rm P}$ being the corresponding correlation (decay) length [65].

This term, though not significant for most polymer films, accounts for the AB-type interactions in polar liquids (for example, for water it accounts for the 'hydrophobic repulsion' with $S_P > 0$, $l_P \sim 0.2-1$ nm). The entropic confinement effects in polymer films due to adsorption/grafting at the film–substrate interface is also taken into account by this term and for this case $l_P \sim R_g$ (radius of gyration of the polymer).

For spinodally unstable films, LSA of Equation 11.1 gives the short-time initial length scale of instability, λ , the number density of features, *N*, and the time scale for the appearance of the amplified wave (τ) as:

$$\lambda = \left[-8\pi^2\gamma/(\partial\Phi/\partial h)\right]^{1/2} \tag{11.4a}$$

$$N = \lambda^{-2} = \frac{-(\partial \Phi/\partial h)}{8\pi^2 \gamma}$$
(11.4b)

$$\tau = 12\gamma\mu[h^3(\partial\Phi/\partial h)^2]^{-1}\ln(h/\epsilon)$$
(11.4c)

Equations 11.4 predict $\lambda \sim h^2$ and $\tau \sim h^5$, as well as $N \sim h^{-4}$ for instabilities driven by nonretard van der Waals interaction, and are widely used for the interpretation of thin film stability and determination of interaction potentials from measurements of λ , obtained from experimental results [65, 91].

Predictions based on LSA, although extremely useful and widely used in the analysis of instability results, is limited to the prediction the wavelength of the fastest growing mode of instability and the initial shape of two-dimensional axis-symmetric holes formed in the film [76–85], and cannot fully capture the morphological evolution during different stages of dewetting, and correlate the evolved patterns to the surface properties and intermolecular interactions, as surface evolution is inherently nonlinear. More detailed studies are based on full three-dimensional (3D) nonlinear simulations that provide a formalism for correlating the film morphology

with the interfacial interactions and the film thickness, which makes it possible to directly compare theoretical predictions with experimental observations and therefore among other things, allow addressing the inverse problem of identifying the forces responsible for the instability based on the observed morphology [64].

11.3.2

Dewetting: Experiments

Polymer systems are preferred for dewetting experiments for several reasons: (i) the ability to switch between a liquid and a solid state by varying the system temperature above or below the glass transition temperature (T_o) . This implies that while the dynamic and morphological reorganization of the film takes place in the liquid state, the structures can be made permanent by simply quenching below T_{g} ; (ii) the low vapor pressure of polymers ensure that the geometry of the final structures do not change with time because of evaporation; (iii) the viscosity of the polymers can be tailored easily by adjusting the molecular weight, thereby controlling the dynamics of the system, enabling time-resolved experiments [47-56]. The films, which are solid at room temperature, are either heated beyond T_{g} or exposed to solvent vapor to decrease their $T_{\rm g}$ below the room temperature. It may be noted that instability-induced pattern formation is neither material specific (unlike techniques such as photolithography, which can directly pattern only optically-active photo resists) [12] nor limited to homopolymers. A variety of materials such as solid films [41], liquid crystals [40], functional polymers and polyelectrolytes [170, 171], conjugated polymers [172], blends, and block co-polymers [173], have been successfully patterned by this approach.

Very thin films (< 50 nm) of simple homopolymers such as polystyrene (PS), poly (methyl methacrylate) (PMMA), poly(acrylamide) and so on, coated on cleaned silicon wafers, quartz, cleaved mica or glass substrates by spin- or dip-coating from diluted solutions of the respective polymers dissolved in suitable solvents, are preferred model systems for studies on thin film instabilities [59-63, 65, 68-73, 93-98, 100-128, 137-139, 141-158]. Evaporation of the solvent during and after the coating leads to the deposition of thin layers of the polymer. The film thicknesses can be as low as few nm (~4 nm) and in most experiments involving dewetting, films thinner than \sim 100 nm are used. Films thicker than \sim 100 nm typically dewet only due to nucleation. On the other hand, it becomes progressively challenging and difficult to obtain smooth films of uniform thickness in films thinner than ${\sim}10$ nm, as the inhomogeneities and defects present on the substrate adversely affect the quality of the films [57, 91]. For many polymers the glass transition temperatures $T_{\rm g}$ are around 100 °C or more and therefore, the films are solid-like at room temperature. Consequently, in order to engender dewetting, the samples are either heated beyond $T_{\rm g}$ or exposed to a solvent vapor. While heating beyond $T_{\rm g}$ liquefies the polymer (with several orders of magnitude reduction in the viscosity), exposure to solvent vapor also leads to the same effect, by reduction of the effective T_{g} below room temperature [172]. This happens by the penetration of solvent molecules into the polymer matrix, which results in a swelling of the film and reduction of the intermolecular cohesive interaction.

Experimentally, dewetting of an unstable polymer thin film on a defect-free smooth surface was first demonstrated by Reiter in 1992 [59, 60], where thermal dewetting of sub-100 nm-thick polystyrene films on non-wettable silicon wafer substrates was shown. The first signature of true spinodal dewetting in a polymer film was captured by Xie *et al.* [62]. and subsequently by several other groups [63, 138]. The scaling relations observed from the experiments agreed well with the theoretical predictions based on LSA [59, 60, 65]. The length scale of the dewetted features were seen to scale with the interfacial tension as $\lambda \sim \gamma^{0.5}$ [59, 60, 65]. However, it is important to point out that the scaling relations depend strongly on the precise decay behavior of intersurface forces, slippage at the interface [159–168], thermocapillarity, surfactant Margoni flow and heterogeneities of the substrate.

Dewetting experiments by Reiter [59–61] and subsequently by many others [62–66, 68–75, 92–128, 137–164] revealed the morphological evolution, self-organization, and pattern formation in thin polymer films. In most experiments the onset of instability is with the form of an undulation of the film surface (Figure 11.1a) [62] or the appearance of fairly equally sized but random collection of holes (Figure 11.1b) [59, 60]. The mean



Figure 11.1 Examples of typical morphologies observed in different stages of dewetting of thin polymer films: (a) Undulations in the early stages of dewetting in a 4.5 nm-thick PS film annealed at 115 °C for 4 mins (Reproduced with permission from [62]. Copyright © (1998) American Physical Society); (b) formation and growth of holes in a 30 nm-thick PS film; (c) polygonal patterns observed in a 10 nm-thick PS film on a silanized silicon wafer; (d) final morphology of a dewetted film in the form of aligned polymer droplets where cellular patterns form, in a 25 nm-thick PS film. Such structures are due to the breakage of the polymer ribbons due to Rayleigh instability (b to d: Reproduced

with permission from [60]. Copyright © (1993) American Chemical Society); (e) signatures of rim instability and detachment of droplets from the retracting three-phase contact line (inset) in a 35 nm-thick PS film on a silicon wafer substrate (Reproduced with permission from [155]. Copyright © (2004) American Institute of Physics); (f) final morphology of a dewetted film comprising a random collection of polymer droplets where rim instability is present, as observed after complete dewetting of a 24 nm-thick PS film on a crosslinked PDMS substrate. (Reproduced [207]. Copyright © (2008) The Royal Society of Chemistry.)

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Figure 11.2 The shape of the rim during early stages of dewetting of thin visco elastic polymer films on nonadsorbing substrates. (a) The sequence of three fundamentally different shapes of the rim found experimentally; (b) a typical optical micrograph $(50 \times 50 \,\mu\text{m}^2)$ taken at the edge of the sample obtained after partial

dewetting. The dewetted distance (*l*) and the width of the rim (w) are indicated. The colors can be directly related to the thicknesses, e.g, the brighter the blue, the thicker the film; (c) a typical rim profile as determined by AFM. (Reproduced with permission from [111]. Copyright © (2005) Macmillan Publishers Ltd.)

distance between the holes corresponds to the fastest growing mode of instability λ_m . Further morphological evolution of the film is associated with the spatial growth of the holes. The growth of holes in most dewetting experiments without polymer slippage on the substrate is associated with the formation of sharp rims or capillary ridges surrounding the holes (Figure 11.2) [111]. The rims result from a mismatch in the rates at which polymer retracts as the hole opens and subsequent redistribution of material to other thicker and intact parts of the film [59, 60, 65, 110, 111, 143, 147]. Further propagation of dewetting proceeds with the growth of the holes and retraction of the three phase contact line, until the rims of the adjacent growing holes touch each other, forming an interconnected ribbon structure of polymer, which is often referred to as the polygonal or cellular pattern (Figure 11.1c) [59]. The polymer ribbons subsequently breaks down due to a Rayleigh instability [25, 26], forming a polygonal array of isolated polymer droplets, as shown in Figure 11.1d [59, 60]. In some experiments, particularly on low-wettability substrates, the rims of the growing holes themselves become unstable, exhibiting a fingering instability (Figure 11.1e) [110, 143, 145, 153, 158, 168]. Droplets detach from the unstable rims of growing holes and the polygon formation is suppressed (Figure 11.1f), leading to the formation of a completely random collection of droplets [110, 143, 145, 153, 158, 168].

For a visco-elastic thin film with interfacial slippage, the shape of the rims progressively changes as dewetting proceeds and, based on the detailed geometry of the rim, three distinct regimes of dewetting have been identified [111, 146, 147]. At the onset of the instability, the energy resulting from capillary forces is primarily dissipated by means of viscous losses around the vicinity of the hole edges, which ensures that no rims form (Figure 11.2a) [111]. When the radius of the growing hole becomes larger than the decay length $\Delta = (h_0 b)^{0.5}$, where *b* is the slippage length $(\sim \eta / \zeta; \zeta$ is the coefficient of friction and η is the viscosity), the influence of friction at the substrate–film interface becomes significant and consequently, the velocity of the dewetting front reduces [111]. This eventually results in the appearance of a highly

asymmetric rim (Figure 11.2b). While the steep side of the rim reaches up to a height H next to the three-phase contact line, an exponentially decaying profile of the rim with a decay length $\sim\Delta$ forms on the film side. At later stages of dewetting, because of the influence of surface tension, the sharp edges eventually become rounded, with further reduction in the dewetting velocity, resulting in a scaling of $v \sim t^{-1/3}$ at this stage [111].

A classic example of how the stability of a thin film is strongly influenced by the nature of interaction between the two interfaces (film–air and film–substrate) can be seen in the work by Reiter *et al.*, where they were able to 'switch on' the instability in a stable thin film by inverting the role of dispersion forces from stabilizing to destabilizing by replacing the bounding media [66]. A thin liquid PDMS film on a silicon wafer in air is thermodynamically stable, as in a system comprising silicon–PDMS thin film–air the effective Hamaker constant is negative, signifying a long-range repulsion ensuring the stability of the film. However, when the same film was submerged under water the sign of the effective Hamaker constant became positive, which implies an attraction between the interfaces, resulting in immediate



Figure 11.3 Changes in the length and time scales of break-up of a 60 nm-thick PDMS film under bounding liquids which have a varying level of compatibility with PDMS. The interfacial tensions change from $38.4 \pm 3\%$ mN m⁻¹ in pure water (series A) to $8.1 \pm 8\%$ mN m⁻¹ in series B (PP) and then finally to $0.3 \pm 33\%$ mN m⁻¹ in series C (L77). The increasing levels of gray denote thicker portions. In each series three (1, 2, and 3) representative snapshots mark the different stages of evolution of instability. The actual times for series A, B, and C are (25, 65, and 200 s), (15, 45, and 100 s) and (5, 10, and 15 s), respectively. The area shown in

frames of series A and B is $100 \times 100 \,\mu m^2$. For clarity the results for series C are shown in an area which is 16 times smaller $(25 \times 25 \,\mu m^2)$. A rather smooth surface of the film evolves into a collection of circular depressions (frames A1, B1, and C1). These shallow depressions develop into circular holes (frames A2, B2, and C2) which grow laterally, coalesce with other growing holes and form long cylindrical ridges (frames A3, B3, and C3) that break up into small drops later. (Reproduced from [66]. Copyright © (2000) American Physical Society.) rupture and dewetting of the film (Figure 11.3). The magnitude of the destabilizing attractive force could further be tailored by using dilute aqueous solutions of different surfactants resulting in changing the interfacial tension between the PDMS film and the bounding liquid [66].

11.3.3

Heterogeneous Dewetting

In reality most surfaces used for dewetting experiments are chemically heterogeneous on a submicron or nanometer length scale and therefore nucleated instabilities are present in most real settings [57, 91, 117-139]. It has been shown that the presence of chemical heterogeneities even at length scales significantly smaller than the spinodal length lead to a gradient of chemical potential along the solid-liquid interface [119, 129, 131, 133]. This in turn results in flow of liquid from lower wettability zones to higher wettability zones, resulting in the rupture of the film [119, 129, 131, 133]. Heterogeneous nucleation can lead to a rupture even in a spinodally stable film. For metastable films, once the local thickness at a depression is reduced to a point where the remnant film becomes spinodally unstable, both mechanisms of instability become active concurrently [121-123, 129, 133]. However, the time scale of heterogeneous dewetting is typically much faster than the spinodal time scale, especially near the critical thickness, and therefore signatures of nucleated dewetting become more pronounced [129]. The hallmarks of heterogeneous nucleation induced dewetting, particularly close to a heterogeneous patch are: (i) much faster evolution of the instability leading to film rupture; (ii) the absence of surface waves preceding the rupture of the film; and (iii) a local ordering of pattern around a heterogeneity. Interestingly, for nucleation over a chemically heterogeneous zone, it is not at all necessary that the heterogeneous zone has to be less wettable compared to its surroundings [129]. More-wettable patches are equally efficient in causing film rupture, as they lead to an inward flow of liquid from the patch periphery towards the center, thus causing a thinning of the film around the patch and lead to the formation of a annular holes. Thus, depending on the patch size (with respect to spinodal length scale), and film thickness extent of wettability contrast, and also on whether the heterogeneous patch is more or less wettable in contrast to the rest of the substrate, a variety of patterns can form, as can be seen in the different frames of Figure 11.4 [129]. In some experiments, satellite holes are seen to form around nucleated holes [121, 122]. It has been captured in experiments, and has been shown based on simulations, that satellite holes originate in the depression in the film adjacent to liquid rim, and in particular in the vicinity of regions where the rim is thicker. Over these regions, the Laplace pressure inside the depression acts as preferred nucleation center for the formation of the satellite holes [120-123].

The discussion up to this point may give the impression that polymer thin films dewetting experiments are rather simple, as they involve a few easy steps like film preparation, heating/solvent vapor exposure and finally, characterization of the evolved structures with an optical or atomic force microscope. However, extracting the exact information about the dewetting mechanism from a particular experiment



Figure 11.4 Morphological evolutions in a 30 nm-thick film on a heterogeneous substrate (a) with a less-wettable patch of diameter 31 μ m. The figures from left to right correspond to nondimensional times 278, 3487, 7620, 13 598, and 24 710, respectively; (b) with a less-wettable patch of diameter 496 μ m. The figures from left to right correspond to nondimensional

times 1485, 2247, 8208, 17 269, and 20 838, respectively; (c) with a more-wettable patch of diameter 352 μ m. The figures from left to right correspond to nondimensional times 63, 3164, 7608, 12 271, and 23 444, respectively. (Reproduced with permission from [130]. Copyright © (2001) American Institute of Physics.)

is a complicated exercise, primarily due to multiplicity of dewetting mechanisms like (spinodal, nucleation, release of residual stresses etc.) [57, 91, 111, 124, 133]. For thicker films, dewetting by heterogeneous nucleation of holes pre-empts the onset of the instability even for spinodally unstable films. Thus, even in films of the same polymer with same molecular weight, under identical film preparation and other experimental conditions but with slight variations in the initial film thickness, completely different evolution sequences and final morphologies may result, depending on which precise mode is dominant during the initial phases of the instability [91, 96, 137–139]. For example, Tsui et al. have shown that on oxide-coated silicon wafers, while dewetting of PS films having thickness (h) > 13 nm is dominated by heterogenous nucleation, films thinner than 13 nm dewetted by spinodal mechanism [139]. Seemann et al. have observed three distinct rupture mechanisms in the dewetting of low-molecular-weight PS thin films on silicon substrates: (i) spinodal dewetting in 3.9 nm-thick PS film on a silicon wafer; (ii) thermal nucleation in a 4.1 nm-thick film; and (iii) heterogenous nucleation in 6.6 nm-thick films [96, 138]. Even in unstable films that have initially ruptured by nucleation, rows of satellite holes are often seen forming around the rims of a nucleated hole once it (the hole) has grown to a certain size [121–123]. This type of hole-forming cascade, corresponding to a complex film rupture process, which is neither simply spinodal nor nucleated, has been captured in 3D numerical simulations [123, 131]. The coexistence of different modes in dewetting experiments has prompted researchers to define two distinct regimes of the spinodal instability itself: deep inside the spinodal territory (DIST) for the thinner

films (< \sim 5 nm-thickness) and defect-sensitive spinodal regime (DSSR) for slightly thicker films [57, 91].

11.3.4

Influence of Residual Stresses on Film Rupture and Dewetting

An unresolved issue in the area of polymer thin film dewetting that existed for a significant period of time, probably ever since research in the area started in the early 1990s, is the dewetting of thermodynamically stable films, and that too, resembling several features of spinodal dewetting! For example, there are reports on the dewetting of PS thin films on non-hydrophobized silicon wafer substrates. Bolline et al. have reported the dewetting of thermodynamically stable PS films on silicon substrates in which the behavior resembles spinodal dewetting though the process does not strictly follow the model for spinodal dewetting [142]. Another anomalous observation which has been reported is the spinodal-like dewetting of thicker films [59, 60, 65]. Ideally, in thicker films the influence of dispersion forces should be rather low and they are very unlikely to cause film instability. It may however be noted that most such conclusions on 'spinodal-like' dewetting are drawn from matching the length scale exponents to the scaling relations show in Equations 11.4a–11.4c. This approach of concluding about dewetting mechanism simply by observing the morphological evolution sequence or by checking how close the length scale exponents match the theoretically predicted values is itself questionable, as it has already been discussed how various destabilization modes arising from the interplay of different interactions are simultaneously present in typical dewetting experiments [91]. However, it has almost become customary to fit λ or N obtained experimentally with h on a double logarithmic plot, and if the exponents are close to 2 or -4, respectively, it is generally argued that dewetting is spinodal in nature [59, 60, 65, 91]. Thus, in cases where spinodal dewetting of thermodynamically stable films are reported, the essential logic for arriving at the conclusion is based on observed values of length scale exponents were close to 2 and -4 for λ and N with respect to h respectively [142, 143].

Several mechanisms, such as local density variation with film thickness [144], deformation of polymer molecules during film preparation [112], or even the influence of surface cleaning [169] have been proposed which are all aimed at explaining some of these anomalies, with limited success, as none of them could be convincingly proved in experiments. It was realized recently that the conditions of film preparation have a crucial role on the stability of the system. The rapid solvent evaporation during spin coating in all probability leads to a nonequilibrium conformation of the polymer molecules within the film, frozen-in during the vitrification of the material, resulting in accumulation of residual stresses within the films [108–116]. As the film is heated or exposed to solvent vapor for liquefaction of the polymer, these stresses are rapidly released, thereby providing additional driving force for dewetting that augments with the conjoining pressure [111]. Even at room temperature, these stresses are slowly released, and thus the level of residual stress in the film depends on the aging time of each sample (time between coating of the film

and performance of the dewetting experiment) [111]. During aging, the chainlike molecules tend to adopt conformations closer to their equilibrium configuration, thereby reducing the extent of accumulated stresses. Further the probability of rupture strongly depends on the level of accumulated stresses [109, 111]. It seems that the magnitude of the force field arising from the release of the residual stresses is much stronger compared to the forces due to intermolecular interaction in thin films, and therefore irrespective of the thermodynamics of the system the release of the stresses dominate the dewetting scenario in some films [111]. This recent hypothesis in many ways explains the anomalous dewetting behavior of low energy spinodally stable films on high energy substrates [111]. However, the theoretical understanding of residual stress-induced dewetting is far from complete. It is also worth noting that there are several other issues involving the viscoelascticity of the polymers [100-106], extent of slippage at the interface [159-168], late stage coarsening [148-150], fingering instabilities around hole rims and so on [110, 143, 145, 151, 153, 158, 168], all of which significantly influence the dewetting process in thin polymer films and are therefore active topics. The details of these aspects of dewetting are beyond the scope of this chapter and the interested reader can refer to several good papers that are already available on some of these themes.

11.3.5

Pattern Formation in Polymer Thin Film Dewetting

While initial research on polymer thin film instabilities was focused more towards the basic issues such as the mechanisms of dewetting, correlating the length scale of the features with initial film properties and so on [59-86, 89-98, 117-126], recent emphasis is significantly on using instability-engendered morphological evolution as a viable and flexible meso patterning technique [87, 127–129]. This approach is based on the fact that, irrespective of the precise mechanism, in most dewetting experiments the final morphology comprises of a random collection of isolated but nearly equal sized droplets [59-168]. As mentioned already and shown in Figure 11.5, the periodicity and size of the droplets depend on initial film conditions such as the film thickness and surface and interfacial tensions of film and substrate [59, 65]. This provides a 'handle' to control the feature sizes by simply varying initial conditions without changing the generic morphology of the patterns. Further, a variety of distinct morphologies like holes, ribbons, droplets, or a combination of all of them can be formed by quenching or stopping the evolution sequence of the dewetting film at an intermediate stage [65, 87]. Additionally, in many nonlinear and complex systems, the equilibrium state is often not unique, as several metastable states of local energy minima exist, which enables a variety of different morphologies to be achieved, simply based on a judicious selection of the initial conditions and extent of dewetting. However, the lack of a long-range order of the structures formed, by dewetting or for that matter by most spontaneous selforganization processes, limits their use in practical application. In order to overcome this limitation, and to present dewetting as a truly effective patterning



Figure 11.5 Double logarithmic plot of average diameter of droplets (D_d) and the average number of droplets per $10^4 \mu m^2 (N_d)$ as a function of film thickness (*h*). The symbols

 $(\blacksquare, \bigtriangledown)$ and (\Box, \bigcirc) refer to N_d and D_d respectively, for two different types of wafers, A and B. (Reproduced with permission from [59]. Copyright © (1992) American Physical Society.)

method, comparable to various soft lithography techniques, offering even more flexibility, it is important that a certain degree of long-range order is imposed on the resulting morphological structures [173–282].

11.4 Dewetting on Patterned Substrates

Dewetted structures have been successfully aligned by using either a chemically [176–190], physically [191–202], or physico-chemically patterned substrates, or even by simpler approaches such as rubbing [173–175]. The possibility of aligning the isotropic and randomly oriented dewetted structures was first demonstrated by Higgins and Jones by simply rubbing the substrate with a lens tissue before coating the film, resulting in the formation-aligned ridges on the substrate in the direction of rubbing [173]. The resulting directionality of the substrate influenced the dewetting pathway of the PMMA film and led to the formation of strongly anisotropic structures comprising a series of continuous lines running across the sample surface following the ridges [173]. Zhang et al. demonstrated a similar concept by brushing the surface of a coated PS films with a hard brush. This resulted in a subtle topographic alignment on the film surface, which influenced the dewetting pathway in a significant manner [174]. A variety of aligned structures such as nanogrooves, lines, and droplets formed during the intermediate and final stages of dewetting. More complex patterns were created when the film was coated on a photolithographically patterned substrate comprising a grating structure and then rubbed in a direction perpendicular or parallel to the stripes [174]. Dewetting of such films resulted in multi length scale structures, as shown in Figure 11.6, where the finer structures along the stripes are due to rubbing. These types of structure are useful in areas where strongly anisotropic patterns are necessary, for example involving liquid crystals for 234 11 Surface Instability and Pattern Formation in Thin Polymer Films
 (a) (b)
 (b)
 (c)
 (c)</l

Figure 11.6 Structures formed by dewetting of a 6 nm-thick, rubbed PS film on a photolithographically patterned substrate, with the rubbing direction (a) orthogonal and

(b) parallel to the direction of the patterns (chromium stripes). (Reproduced with permission from [174]. Copyright © (2005) Elsevier.)

various novel optical applications [176–178]. Müller-Buschbaum *et al.* have successfully created shallow (~5 nm high) nanochannels by dewetting of PDMS solution, by wiping a glass substrate with a lint-free paper pre-soaked with diluted PDMS solution, in a particular direction at very low (~few kPa) contact pressures [175]. The competition between oriented deposition of the solution and spontaneous dewetting resulted in the formation of the aligned structures with a periodicity of ~166 nm [175].

11.4.1

Dewetting on Chemically Patterned Substrates

While rubbing-based techniques are useful in demonstrating conceptually that isotropic dewetted structures can indeed be aligned [173–175], it is not possible to achieve patterns with a high degree of accuracy in terms of periodicity, fidelity, precise control of morphology, and long-range order by merely extending any of these methods. A systematic approach in this regard is to use physically (topo-graphically) or chemically patterned substrates for dewetting a polymer thin film [176–202]. Such substrates are generally created by any of the existing lithography techniques, and thus pattern-directed ordering of dewetted structures is regarded as a hybrid approach, combining both top-down lithography and self-organization techniques.

The ordering of dewetted structures on a chemically patterned substrate, comprising microcontact printed patches of hydrophilic 11-mercaptoundecanoic acid (MUA) on a gold-coated glass substrate was first demonstrated by Meyer and Braun [179, 180]. The dewetting of a PS thin film on such a substrate was seen to initiate only over the MUA patches, which acted as preferred nucleation sites [179]. The dewetted structures aligned in commensuration with the chemical patterns on the substrate [179, 180]. It was subsequently shown by Sehgal *et al.* that even on a chemically patterned substrate, the extent of ordering of the dewetted structures depends strongly on the commensuration between the initial film thickness (h_{0}) and the periodicity of the patterned substrate (λ_s). They reported the dewetting of PS thin films on chemically patterned substrates comprising arrays of progressively

11.4 Dewetting on Patterned Substrates 235

narrower stripes (1–15 µm) of alternating –CH₃ (lower surface energy) and –COOH (higher surface energy) end-terminated self-assembled monolayers (SAMs) [181]. Using a library of patterns with varying feature sizes on the same sample allowed rapid comparative screening of the influence of the symmetry-breaking chemical field on dewetting behavior, while eliminating the possibilities of experimental errors involving different samples which invariably leads to slightly different initial conditions [181]. A variety of ordered, partially ordered and even disordered structures form on topographically smooth chemically patterned substrate, depending on the film thickness and the periodicity of the patterns. For ultrathin, spinodally unstable films (~12 nm-thick) on the patterned areas, the intermediate stages exhibited strong anisotropy imposed by the underlying chemical patterns and superposition of spinodal-like structures. For a given film thickness, the final morphology of the dewetted structures was strongly influenced by λ_s , as shown in Figure 11.7 [181]. For the wider stripes ($\lambda_s = 12-15 \,\mu m$), two columns of droplets are seen to form per band. For narrower stripes ($\lambda_s = 9 \,\mu m$), the lateral confinement causes the coalescence of the two droplets and an array of aligned single droplets is seen. Further confinement of the substrate pattern to $\lambda_S = 6 \,\mu m$ resulted in distorted oval shaped droplets. Subsequent reduction of λ_S leads to a loss of order and resulted in relatively distorted morphology. For the narrower patterns



Figure 11.7 The influence of pattern dimension on the final morphology (aligned, partially aligned and random droplet arrays) of structures resulting from dewetting of a 12 nmthick PS film. Optical micrographs and insets show transition from the doublet state (15–12 μ m stripe width), to coalescence (9 μ m), confinement (6 and 3 μ m), and a

heterogeneous morphology (1 μ m) with bridging over multiple bands. Dashed lines (insets) indicate registry with the underlying chemical pattern period. AFM images (9 and 6 μ m) highlight control of droplet size and spatial position. (Reproduced with permission from [181]. Copyright © (2002) American Chemical Society.)

 $(\lambda_{\rm S} \sim 3 \,\mu{\rm m})$ the droplets and smaller and have distorted ellipsoidal shapes with the major axis oriented along the direction of the stripes. A late stage bridging transition leads to the coalescence of highly anisotropic (high surface energy) droplets across unfavorable -- CH₃ bands to more rounded, lower energy structures spanning the very narrow stripes ($\lambda_{\rm S} \sim 3 \,\mu{\rm m}$) [181]. Zhang *et al.* were successful in creating ordered 2D structures by using square-patterned substrates consisting of alternating high energy SiO_x recessed squares in a low energy ocadecyltrichlorosilane (OTS) grid [182, 183]. In addition to wettability contrast the substrate also exhibited a distinct topography contrast arising from the presence of the OTS layer. Dewetting of a polymer film on such a substrate is triggered by the combined influences of topographic and wettability contrasts. The film ruptured at the edges of the squares, breaking-up into two isolated fragments on the silica and OTS patches [183]. Subsequent dewetting of the films over each fragment continued separately at a different pace, as shown in Figure 11.8. Dewetting of the detached film fragments on the silica squares lead to the formation of single isolated droplets in the center of each area. In contrast, dewetting of the remnant part of the film on the OTS grid surrounding the squares resulted in the formation of oval-shaped PS lines between two adjacent squares and larger spherical droplets at the corners of every square patch caused by the retraction of the contact line (Figure 11.8f) [183]. Several other groups have reported results on the ordering of dewetted structures by chemically patterned substrates for the creation of structures with a variety of



Figure 11.8 Morphological evolution sequence of a 47 nm-thin PS film on OTS squares patterned substrate. The substrate had alternating OTS and SiO_x squares. The film was annealed at 170 °C for (a) 0 min; (b) 0.5 min; (c) 1 min; (d) 8 min; (e) 12 min and (f) 20 mins respectively. The scale bar is 30 mm. (Reproduced with permission from [183]. Copyright © (2003) Elsevier.)



Figure 11.9 (Top) Schematic of the gradient test pattern illustrating pattern and gradient orientation in the experiments. (Middle) PS dewetting library compiled from 1900 contiguous optical micrographs over the entire specimen. Regions I, II and III, noted on the figure, are discussed in the text. (a–d) Strips of OM data extracted from the library

showing the transition from pattern-directed to isotropic dewetting. Insets $(250 \,\mu\text{m} \times 250 \,\mu\text{m})$ show magnified optical micrographs of representative dewetting morphologies. (Reproduced with permission from [190]. Copyright © (2007) The Royal Society of Chemistry.)

morphologies and geometries in many materials [184], including fluorescent and conducting polymers [185–189].

Julthongpiput *et al.* have recently shown how the magnitude of the wettability contrast (difference in surface energy, $\Delta\gamma$) in the substrate pattern affects the morphology and alignment of the dewetted polymer droplets [190]. For this purpose, a combinatorial test surface was used, with gradient micropatterns consisting of a series of 20 µm wide *n*-octyldimethylchlorosilane (ODS) lines with continuously changing surface energy (γ) with respect to a constant surface energy background. The lateral separation between the ODS stripes was constant at 4 µm. Figure 11.9 summarizes the variation of the dewetted pattern morphology on the gradient

micropatterned surface as a function of $\Delta\gamma$ and shows the existence of three distinct regimes. Regime 1, corresponding to high $\Delta\gamma$ (~43 mJ m⁻²), single aligned arrays of droplets distributed along the center of both the matrix and SAM portions of the patterns were observed. Regime II exhibits a crossover where the droplets gradually lose the extent of ordering in the direction of the stripes with decrease in the wettability contrast ($\Delta\gamma$), maintaining a subtle signature of directionality. In Regime III, the droplet arrangement was completely isotropic for $\Delta\gamma$ (~4 mJ m⁻²) and the substrate patterns completely failed to impose any directionality on the dewetting process [190].

11.4.2

Dewetting on Physically Patterned Substrates

Dewetting on a physically or physico-chemically patterned substrate is in many ways more exciting and complex in comparison to dewetting on a substrate with chemical patterns only. The presence of the topographic contrast, in addition to influencing the dewetting pathway, also significantly affects the initial film preparation conditions, as direct spin coating on a topographically patterned substrate leads to nonuniformities in the initial film thickness over different areas [191]. In fact Bao et al. [192] and very recently, Ferrell and Hansford [193] have used dewetting during spin coating of a polymer solution on a topographically patterned substrate for fabricating micro- and nanoscale polymer structures. Bao et al. directly spun coated PMMA and polycarbonate (PC) solutions on topographically patterned silica substrates coated with a higher surface-energy silane on the raised portions and a lower-surface energy silane over the recessed zones. The coated polymer preferentially wetted the higher-surface energy zones, leading to the formation of well-aligned structures [192]. The final pattern morphology was strongly influenced by the geometry (height, lateral feature dimensions, and spacing) and polymer solution concentration [193].

Dewetting of a homopolymer film on a topographically patterned substrate was first reported by Rockfort et al., where striped substrates comprising periodically varying zones exhibiting polar (silicon oxide) and nonpolar (gold) interactions (stripe periodicity ~170 nm) were used to investigate dewetting of a 5 nm-thick PS film. It was seen that the PS film dewetted on the oxide stripes and segregated to the goldcoated domains, leading to the formation of strongly isotropic structures resembling the substrate pattern geometry [194]. Rehse et al. systematically investigated the stability of thin PS films of various molecular weights on regularly grooved silicon surfaces comprising triangular grooves or stripes with a mean stripe width of \sim 250 nm and a mean peak-to-valley height of \sim 5 nm without any surface energy contrast [195]. The films, which were directly spin coated on the patterned substrates showed a slight variation in thickness, in phase with the substrate geometry. The thickness of the coated films was slightly less over the raised parts of the stripes compared with the areas over the valleys. Rupture in such a films initiated over the thinner zones above the stripes, resulting in the break-up of the initially continuous film, forming isolated and long strips of polymer filling the grooves [195]. Thus, the

profile of the dewetted film replicated the inverse morphology of the substrate. However, the instability was manifested only for films below a critical thickness as thicker films were found to be stable even after several days of annealing [195, 196]. The critical thickness was shown to be a linear function of the radius of gyration of the polymer molecules, and the effective dependence was experimentally found as t_{Peak} ~0.55 R_g for PS, where t_{Peak} is the thickness of the thinnest part of the film [195]. Synchrotron X-ray reflection, in addition to atomic force microscopy (AFM) was used by some groups to understand how confinement affects liquid structure formation and spreading dynamics of a polymer thin film coated on a topographically patterned substrate. It was argued that in presence of an undulating substrate, the decay length of the surface modulation was much longer than that observed in case of simple liquids on a flat surface [196]. Several others have reported the strong influence of the substrate topography on the final dewetted morphology, in the form of aligned dewetted droplets [197-203]. For example, Yoon et al. have reported the influence of pattern geometry on the final morphology of the dewetted polymer films using both mesa and indent patterned substrates, where it was observed that dewetting initiated preferentially at the edges of individual pre-patterned mesas and subsequent morphological evolution lead to spherical cap domains located in the center of the mesas [199]. The domains were found to be much smaller than the individual mesas as a consequence of the significant pattern reduction. Arrays of 70 nm PS nanosphere caps were obtained from arrays of 200 nm square pre-patterned mesas. This method was also extended to other polymers such as poly(4-vinyl pyridine) (P4VP) containing Rhodamine 6G (Rh6G) dye on a pre-patterned PS substrate. The fluorescent polymer structures were found to be extremely stable [200]. Dewetting on topographically patterned substrates has been used by several groups to pattern functional photoluminescent materials as well as to fabricate organic polymeric thin-film transistors [204, 205].

The morphological evolution and pattern formation of polymer thin films with uniform thickness on topographically patterned substrates with different geometries has been investigated by Mukherjee et al. [206, 207]. In order to avoid thickness variations during direct spin coating, films of uniform thickness were initially spin coated on smooth surfaces and subsequently transferred onto topographically patterned substrates. It was shown that by adjusting the transfer conditions like, the rate and angle of lift-off, it is possible to control the initial morphology of the film with respect to the underlying substrate. For a faster pull rate with a horizontally held substrate, the overall morphology of the transferred films was nearly flat, with the films coming in contact only with the raised protrusions of the substrate pattern. This configuration has been termed as 'focal adhesion' or 'free hanging films' (Figure 11.10a) [206]. In contrast, a slow pull-off and vertical orientation of the capturing substrate results in the so-called 'conformal adhesion', where the film adheres closely to the contours of the substrate pattern (Figure 11.10c). With examples of dewetting on both striped as well as substrates comprising an array of square pillars, it was shown experimentally that the positioning of the dewetted droplets is strongly influenced by the nature of initial film adhesion. As shown in Figure 11.10, in the dewetting of a

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Figure 11.10 (a) A floated PS film conformally adhering to a topographically patterned substrate, comprising an array of square pillars (inset a 1). Inset a2 shows the line profile of the substrate and the film. (b) A perfectly filled and ordered dewetted structure resulting from the dewetting of a 24 nm-thick film on the substrate shown in inset a 1. (c) A 24 nm-thick floated PS film focally adhering to the same substrate as shown in a 1. Inset shows the film (dashed line) in contact with the raised protrusions of the substrate only and freely hanging over other intervening areas. (d) The dewetted droplets are positioned on top of each pillar roof. A portion with a slight defect was deliberately used by the

authors to distinguish between the dewetted droplets and the underlying pattern below, which can be seen at the place where the dewetted droplets are not placed on the pillar tops. (e–g) Variety of final dewetted morphologies as a function of initial film thickness for conformally adhering films: (e) Imperfect ordering with some missing droplets for an 11 nm film, (f) perfectly ordered but underfilled structure formation for a 17 nmthick film, and (g) distorted, overfilled structure with occasional oversized or interconnected droplets for a 31 nm-thick PS film. (Reproduced from [207]. Copyright © (2008) The Royal Society of Chemistry.)

24 nm-thick PS film on a patterned substrate, the final dewetted morphology comprises an array of droplets, the positioning of which depends entirely on the initial conformation of the films (Figure 11.10a and c) with respect to the substrate. Figure 11.10b shows that the dewetted droplets accumulate at the intersections of the channels around the pillars for conformally adhering films [205]. In contrast, the droplets are seen forming on top of the pillars for films with same initial thickness but adhering focally on to the patterned substrate (Figure 11.10d) [207]. Even for conformally adhering films it was shown that perfectly filled and perfectly

ordered structures form only for a narrow range of film thickness for a specific geometry of a 2D patterned substrate (Figure 11.10d). For thicker (31 nm, Figure 11.10g) or much thinner (~11 nm, Figure 11.10e) films, either some of the droplets remain connected or some locations remain vacant, respectively, with both the states exhibiting deviation from the perfectly filled and ordered configuration obtained by dewelting of a 24 nm-thick film on a substrate with identical patterns (Figure 11.10b). Figure 11.10f shows another distinct morphology resulting from the dewetting of a 18 nm-thick film on the same substrate, which is best termed as a perfectly ordered but underfilled structure, as the droplet sizes are smaller than the largest possible size that can be accommodated at each channel intersection. Thus, there exists a critical thickness range for which perfect ordering is possible on a topographically patterned substrate with 2D structures. For substrates with 1D stripes, the droplet periodicity as well as their size changes with varying film thickness [207]. While the size of the droplets was seen to be strongly influenced by the width of the stripes, the droplet periodicity (λ_D) gradually decreased as the stripes became narrower. With gradual increase in film thickness, partially disordered structures in the form of droplets connected across stripes started to appear. The critical film thickness around which disordered structures started to appear was found to be a function of the stripe periodicity (λ_s) and channel width [207].

Even on substrates with identical geometry, such as those used for the experiments in Figure 11.10, a distinctly different dewetting pathway is observed for films thicker than \sim 40 nm (Figure 11.11). For these films, the onset of instability is through the formation of larger holes, which are completely uncorrelated to the substrate pattern (Figure 11.11a). The morphology in this stage is in many ways similar to that observed during dewetting of films on flat surfaces. However, as shown in Figure 11.11b, the periphery and the rims around the holes were aligned to some extent with the substrate patterns, resulting in the formation of noncircular, rectangular holes. The AFM scan of the dewetted portion inside a hole reveals tiny polymer droplets at each channel intersection on the patterned substrate (Figure 11.11c), left behind by the retracting contact line of a growing hole. The final morphology in Figure 11.11e shows the existence of polymer patterns at two distinct length scales, the larger polymer droplets resting on the patterned substrate due to bulk motion of the contact line of the growing holes and the finer perfectly filled and ordered structures (inset Figure 11.11e2) correlated with the substrate patterns, caused by the detachment of polymer drops from the retracting contact line [207].

11.4.3

Pattern Directed Dewetting: Theory and Simulation

It is evident from the preceding discussion that, like any other highly nonlinear process, pattern-directed dewetting is also influenced strongly by the initial conditions. Based on experimental observations, we have already seen that a slight change in initial conditions leads to a drastic change in the pattern morphology (Figure 11.10) or dewetting pathway (Figure 11.11) [207]. Such transitions are often extremely difficult to track experimentally, as will become clear from the following example.



Figure 11.11 Dewetting pathway of a ~69 nmthick PS film on a patterned surface. The initial stage of instability is manifested in the form of nucleation and growth of random, large holes not correlated to the substrate patterns. (a) A large area optical micrograph showing the formation of random holes (scale bar 150 µm), (b) high magnification optical micrograph showing the exposed substrate patterns within a hole (scale bar 15 µm), and (c) an AFM image of a hole, revealing the presence of small polymer droplets at each interstitial position on the substrate within a hole. For images (a)–(c), exposure time is 4 minutes. (d) Formation of polymer ribbons after solvent vapor exposure for 11 minutes (scale bar $15 \,\mu$ m).

(e) Large area optical micrograph showing large polymer droplets, after solvent vapor exposure for 35 minutes (scale bar 100 μ m). The inset e1 is a higher magnification optical micrograph, showing that the large polymer droplets are resting on a cross patterned substrate (scale bar 15 mm) and the AFM scan in inset e2 shows the presence of polymer droplets at the interstitial positions on the substrate patterns, forming a perfectly ordered and filled pattern. (Reproduced from [207]. Copyright © (2008) The Royal Society of Chemistry.) Figure 11.10b and d–g and (11.11) shows the final dewetted structures of PS films having identical molecular weight but with thicknesses varying between 11 and 69 nm, respectively, on identical substrates. It is evident that not only the final morphology but also the dewetting pathway can be drastically different. As all experiments, however well-performed they may be, are associated with some degree of error, it is virtually impossible to determine the precise critical thickness at which the transformation in the dewetting pathway takes place! It is in situations like this where simulations are greatly useful, and thus form an important aspect of research on thin film instability on patterned substrates. Heterogeneous dewetting on patterned substrates, where the spatial variation of heterogeneity is well defined, is theoretically represented by Equation 11.5, which is obtained by slightly modifying Equation 11.1 with the incorporation of a parameter *a*, representing the roughness of the substrate (z = a f(x, y)). The local thickness of a film η is defined as $\eta = h(x, y, t) - a f(x, y)$ and the term *h* in Equation 11.1 is replaced by η [91, 208–217].

$$3\mu \frac{\partial \eta}{\partial t} + \frac{\partial}{\partial x} \left[\gamma_f (h-a)^3 \frac{\partial^3 \eta}{\partial x^3} \right] + \frac{\partial}{\partial x} \left[-(h-a)^3 \frac{\partial \varphi}{\partial \eta} \frac{\partial \eta}{\partial x} \right] = 0$$
(11.5)

On a chemically heterogeneous substrate, the interaction potential differs at different locations ($\Phi = \Phi(x,y)$) and the wettability gradient engenders the movement of fluid from less-wettable areas to the more-wettable ones, causing deformations of the free surface [206]. For topographically as well as chemically patterned substrates it has already been shown that there is a critical initial thickness range of the dewetting film (which to a large extent depends on the geometry and dimension of the substrate patterns) for which perfect ordering can be achieved. In addition, there can be initial thickness-dependent transitions between disordered to ordered states as well as morphological transitions between various ordered states. Although successfully captured experimentally with some degree of success by the groups of Karim [181] and Sharma [207] for some specific cases, such transitions are extremely difficult to capture experimentally. Kargupta and Sharma with their 3D nonlinear simulations have contributed significantly in this research topic. They have successfully predicted the morphology as well as dewetting pathways for films of various thicknesses on various types of chemically, topographically and physico-chemically patterned substrates, providing an understanding of the conditions under which the substrate patterns are faithfully reproduced into the film ('perfect templating'). In perfect templating, the final film morphology perfectly replicates the substrate surface energy map or the topographic pattern [206-214]. For example, the conditions for the evolution sequence of pattern replication on a substrate comprising alternating less and more-wettable stripes are as follows: (i) the periodicity of substrate pattern (λ_s) must be greater than the characteristic length scale of instability (λ_D) , corresponding to the film thickness, but must be less than an upper cut-off scale $(\sim 2\lambda_D)$; (ii) dewetting is initiated near the stripe boundary; (iii) the contact line eventually rests close to the stripe boundary; and (iv) the liquid cylinders that form on the more-wettable stripes remain stable [208, 209]. The relative combinations of film thickness (h_0), stripe width (l_p), and stripe periodicities (λ_s) are therefore crucial in

determining the morphology of the final pattern. Using simulations, a variety of parametric studies are easily possible, predicting most of the final morphologies with near perfection. Many of the predictions of simulations have subsequently been validated by experiments. For example, the influence of variation of stripe width on the dewetting pathway and morphology with constant substrate pattern periodicity $(\lambda_{\rm S})$ is shown in Figure 11.12 [208]. For small $l_{\rm P}$ (~0.4 $\lambda_{\rm S}$, Figure 11.12a), rupture is initiated in the center of the less-wettable stripes by the formation of depressions that coalesce to form rectangular dewetted domains which are wider than the stripe width. In contrast, for a larger stripe width ($l_{\rm P} \sim 0.8 \lambda_{\rm S}$), dewetting is initiated by formation of holes at the boundaries of the stripes (image 2 of Figure 11.12b) [208]. Coalescence of the two sets of holes leads to the dewetted regions comprising residual droplets (image 4 of Figure 11.12b). Upon further increase of the stripe width, the final pattern morphology changes to two rows of holes on each stripe separated by an elevated liquid cylinder (image 2 of Figure 11.12c). Interestingly, for this case at an intermediate stage of evolution, the number of cylindrical liquid ridges becomes twice the number of the more-wettable stripes on the substrate (image 3 of Figure 11.12c). The ordering is entirely lost with further increase in stripe width due to the formation and repeated coalescence of several rows of holes across stripes, eventually resulting in an array of isotropically arranged droplets

(a) 		
(b)		
(c)	-	

Figure 11.12Morphological evolution in a5 nm-thick film on a striped surface

 $(l_p = 3 \ \mu m = 2\lambda)$. W = 0.6, 1.2, 2.1, and 2.7 μm , respectively, for (a)–(d). The first image in this figure, as well as in the subsequent figures, represents the substrate surface energy pattern; black and white represent the more-wettable

part and the less-wettable part, respectively. For other images describing the film morphology, a continuous linear gray scale between the minimum and the maximum thickness in each picture has been used. (Reproduced from [208]. Copyright © (2001) American Physical Society.) (Figure 11.12d) [208]. The results suggest that the final morphology on a patterned substrate during dewetting of a thin polymer film can be greatly modulated by the competition between the different time scales (spinodal *vs.* heterogeneous dewetting) and length scales (spinodal, stripe width and periodicity, and film thickness) of the system.

Several other interesting case studies such as the dewetting on 2D patterned substrates with varying periodicity, patch dimension, topographic contrast, and dewetting on substrates with more complex patterns have been reported in great detail by the Sharma group. The morphology phase diagrams based on simulations, which correlates the nature of the final patterns to the initial conditions (film thickness, pattern dimensions, periodicity, etc.) for a specific pattern geometry are of significant importance. For example, the diagrams presented in Figure 11.13a and b summarize the major morphological transitions of the dewetted structures on a substrate comprising chemical patterns of more-wettable squares on a less-wettable substrate, and less-wettable squares on completely-wettable substrates, respectively, with respect to two normalized parameters: the dimensionless periodicity (l_P/λ_S) and the dimensionless width of the squares (W/λ_s). The dark shaded region in both the figures represents the parameter range for ideal templating. An interesting observation in Figure 11.13a includes the absence of heterogeneous rupture of the films (true dewetting) on substrates where $l_{\rm P} < 0.7 \lambda_{\rm S}$, with only partial thickness deformations following the geometry of the substrate pattern. Also, for less-wettable area fractions greater than 0.5 or for square widths below a transition length (boundary 2, Figure 11.13a), liquid bridging across the less-wettable regions occurs for $l_{\rm P}$ less than $1.5\lambda_{\rm S}$. An increase in $l_{\rm P}$ beyond boundary 3 eliminates the bridge formation at smaller W and produces trapped liquid domains on the less-wettable part, resulting in the



Figure 11.13 Morphological phase diagram for the isotropic substrate pattern consisting of (a) more-wettable blocks on a less-wettable substrate, lines 1, 2, 3, and 4 denote the boundaries between different regimes at the initial stage of dewetting. The dark-shaded region corresponds to the conditions for ideal templating; (b) less-wettable blocks on completely-wettable substrate. The lines 1, 2,

and 3 denote the boundaries between different regimes at the initial stage of dewetting. The shaded region corresponds to the conditions for ideal templating. The 3D microstructures corresponding to the five symbols are also shown in respective insets. (Reproduced with permission from [210]. Copyright © (2003) American Chemical Society.)

block mountain-rift valley' pattern. In contrast, on a completely-wettable substrate consisting of non-wettable squares, an increase in periodicity ensures ideal templating as long as the square width remains below a transition width (W_t , boundary 2, Figure 11.13b) [210]. For a pattern periodicity larger than λ , increasing the square width produces arrays of a 'castle moat' pattern (in parameter regime shown in a lighter shade), in which a liquid drop is trapped within a square-shaped region on each non-wettable area, while the liquid surface remains flat on the remaining completely-wettable areas. Many of the predicted morphologies on 1D and 2D patterned substrates by the Sharma group have been subsequently verified experimentally by other researchers. The availability of robust simulated phase diagrams is extremely useful in substantially reducing experimental efforts as they can be used to select the appropriate initial conditions (i.e., film thickness, pattern size and geometry etc.) to experimentally produce the desired final structures [210].

Pattern formation in films of block copolymers and blends are not covered in this chapter. A variety of interesting phenomena and mesoscale structures form in films of both types of materials on chemically and topographically patterned substrates, caused by the competition between the additional length scales of these systems. Several interesting papers in this field are available, some of which are cited here [194, 218-229]. For ultrathin polymer blend films, the morphological evolution reveals a coupling between the phase separation process and the surface deformation modes. The excitation of the surface modes occurs when the length scales of phase separation and the deformation modes are commensurate [219]. On the other hand, films of diblock copolymers can self-assemble into ordered periodic structures on the molecular scale [222]. However, in most cases perfect periodic domain ordering is achieved only over micron-sized regions separated by grain boundaries [223]. On a patterned substrate, it is possible to induce epitaxial self-assembly of the block copolymer domains, resulting in defect-free oriented patterns extending over large areas [224]. These structures are determined by the size and quality of the surface pattern rather than by the inherent limitations of the molecular level self-assembly process [224].

11.5

Instability due to Externally Imposed Fields

The discussion thus far has revealed how a thin polymer film becomes unstable and morphologically evolves as a result of the amplification of surface fluctuations engendered by a variety of causes, such as attractive van der Waals interactions [29, 30, 59–91], release of residual stresses [106–111], defects, and heterogeneities. In this section, we will discuss how a thin film can be destabilized by imposing an external field across the film. Examples of such external fields are electric fields [230–264], thermal gradients [265–270], or even a magnetic field [271]. Unlike spontaneous instabilities which occur only in very thin films (much below \sim 100 nm), external field-mediated instabilities are possible all the way up to macroscopic length scales, because of the strength and long-range nature of electrostatic interactions, as

compared to dispersion forces. They can therefore be used to destabilize thicker films by overcoming the stabilizing influence of the Laplace pressure (and possibly gravity for macroscopic liquid layers) and allow the control of structures on length scales which are difficult to manipulate in any other way. The influence of an electrical field on the surface of a viscous film was first investigated by Swan [230] as early as 1897 and was later proposed as an alternative to xerography [231–236]. However, the concept of using electro-hydrodynamic instabilities to pattern polymer thin films was demonstrated for the first time in 2000 by Schäffer *et al.* [237]; the technique has subsequently been christened as electro hydrodynamic (EHD) lithography. EHD surface instabilities are also important to a variety of other settings, for example in transformer oils, where instabilities lower the critical voltage and result in dielectric break-down [238, 239]. The existence of ripplons, a type of surface wave in liquid helium [240] and frosting in thermoplastics that lead to surface roughening, are also attributed to EHD instabilities [230].

A typical experimental set-up for electric field-induced pattern formation comprises sandwiching a liquid polymer film between two electrodes. The film is coated onto one of the electrodes, maintaining an air gap with the second electrode, as shown in Figure 11.14 [241–264]. A voltage is applied between the two electrodes, resulting in an electric field across the sandwiched film (Figure 11.14a). Upon application of the field, the capillary fluctuations at the liquid-air interface amplify in the direction of the field. This initially leads to an instability that is undulatory in nature (Figure 11.14b). With time the undulations amplify until the wave maxima touch the upper plate, thereby leading to the formation of polymer structures spanning the two electrodes [237, 241-248, 252-263]. The destabilization is engendered by the lowering of the total electrostatic energy in the capacitor for a liquid conformation that spans the two electrodes, compared with a layered structure of an intact film, which involves the build-up of energetically unfavorable displacement charges at the dielectric interface [237]. The final pattern morphology depends on several factors such as the field strength, the initial film thickness, the air-gap width, the surface tension, the structure of the film surface and so on [237, 241–243]. For example, as shown in Figure 11.14c, a random collection of columns spanning the two electrodes appears after annealing a 93 nm-thick PS film at 170 °C with an applied field strength of 50 V for 18 hours [237, 241]. Under similar conditions, a 193 nm-thick film shows much denser packing of the columns. This in turn results in a much enhanced electrostatic repulsion between the columns leading to formation of pillars with perfect hexagonal order (Figure 11.14d) [237, 241]. The ordering occurs because of the repulsion of equally charged peaks and valleys of the undulations. In most experiments, the two electrodes are never perfectly parallel which results in small lateral variation in the electric field. Consequently a variety of morphologies (undulations, columns) is generally observed on the same sample, as shown in Figure 11.14e [241]. In contrast to the hexagonally ordered structures shown in Figure 11.13d, a nucleated instability leads to a second-order effect as shown in Figure 11.14f [237, 241]. A locally higher value of film thickness at the point of nucleation leads to a higher strength of the local electric field, causing depletion of the nearest neighbor undulations. Amplification of the undulations occur again at the sites occupied by the next set of



Figure 11.14 (a) Schematic representation of the capacitor device used to study capillary surface instabilities under an externally applied electric field. (b-f) Optical micrographs of polystyrene films exposed to an electric field; (b, c) film thickness 93 nm annealed for 18 h at 170 $^{\circ}$ C with an applied voltage U \sim 50 V. The gap spacing was larger in (c) than (b) (scale bar 10 µm); (d) thickness of PS film 193 nm, other conditions are same as (b), resulting into a denser packing of the polymer columns (scale bar $5 \mu m$); (e) The figure shows a typical experimental scenario where the two plates are not perfectly parallel leading to a variation in pattern morphology. With decreasing plate

spacing from left to right (color change from green to purple), the number density and extant of ordering of the columns is seen to increase. (Image width 145 μ m); (f) a second-order effect is observed in a nucleated instability, in the form of a ring of 12 columns lies on a circle with a radius of 2λ . (scale bar 5 µm). The colors arise from the interference of light, and correspond to the local thickness of the polymer structures (for example, in f, yellow corresponds to a film thickness of \sim 200 nm, green \sim 450 nm). (a–d, f: Reproduced with permission from [237]. Copyright © (2000) Macmillan Publishers Ltd; e: Reproduced with permission from [243]. Copyright © (2001) Erik Schäffer.)

neighboring columns, resulting in a second-order ordering in the form of a rosette on a circle with a radius $r \sim 2\lambda_E$ and a circumference of $2\pi r < 12\lambda_E$, where λ_E is the characteristic wavelength of EHD instability. Beyond the circle of next-nearest neighbors, the instability decays with increasing distance [237]. In all the cases where EHD patterns are formed, the field strength is fairly high, on the order of $\sim 10^7$ Vm⁻¹. It has been reported by the Steiner group that no patterns form in the absence of an electric field, although pattern formation in the absence of electric fields had been claimed by the Chou group [272–277], which has been termed as lithographically assisted self-assembly (LISA).

In EHD instabilities, the fill factor, *f* (the ratio of the film thickness to the electrode spacing) is a parameter that significantly influences the pattern morphology, particularly during the later stages of pattern formation [237, 241, 251]. The initial phase of the film instability is qualitatively similar irrespective of the value of f. For low values of f (i.e., thin films compared to the electrode spacing) the wave maxima disconnect, giving rise to hexagonally-ordered columns with intercolumn distances that are commensurate with the wavelength of the initial instability. For higher values of f (~0.5), the film stays partially interconnected when the wave maxima make contact with the top electrode. In this case, the late-stage evolution of the patterns is governed by a ripening process that leads to coalescence of some of the columns. This effect 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 leading to an inversion of the initial column structure. In a recent work, Heier *et al.* have looked at the response of a thin liquid polymer to a spatially modulated, heterogeneous electric field [248]. Salac *et al.* have studied the effect of an in-plane electric field on a polymer thin film and observed the disintegration of the film into polymer islands. The resulting structure morphologically resembles a dewetted film on a flat substrate and exhibits a narrow size distribution and spatial ordering [253].

While the topographical evolution of a polymer film occurs spontaneously with the application of the field, further control of the lateral structure can be achieved by laterally varying the electrode spacing d or effective field strength by using a topographically patterned top electrode. As the gap between the electrode and the film is smaller below every raised feature of the top electrode, the onset time for the formation of the instability structures is much shorter than for the recessed areas of the patterned top electrode [237]. The emerging instability in the film is therefore oriented towards the electrode protrusions and the final structure is a positive replica of the patterned electrode, as opposed to a negative replica achieved by conventional imprinting techniques (Figure 11.15a) [237]. The EHD patterning technique has also been extended to various other materials beyond simple homopolymers. For example, Dickey and coworkers have used EHD instability to pattern thin films of various photocurable materials, such as epoxy, vinyl ether, acrylate, thiolene, and so on demonstrating the material-independent nature of this technique [258]. Low molecular weight, low viscosity polymers, the EHD structures form at room temperature and are subsequently frozen by in situ photocuring. Lower viscosities also result in faster pattern formation dynamics (~seconds) [258]. Voicu et al. have patterned films of a metal oxide (titania) precursor stabilized in alcohol by EHD, which subsequently underwent a sol-gel condensation reaction to solidify, yielding meso-patterned titania films after high temperature annealing [247]. This is a rare combination where a 'soft' pattering technique has been successfully combined with sol-gel chemistry to form 'hard' metal oxide structures. Figure 11.15b shows a variety of patterns formed in titania precursor solution films using a patterned electrode [247]. However, since the films are in the liquid state during the pattern formation, the viscosity, surface tension, dielectric constant and overall volume change continuously during EHD instability because of solvent evaporation. This in turn influences the final pattern morphology. In addition, as the samples are pyrolyzed at high temperatures for the formation of structured anatase, the height of the formed structures shrank by a significant percentage (\sim 85% in this case). The shrinkage is found not to significantly affect the lateral dimensions of the patterns. Using similar chemistries this method can be extended to pattern ferroelectric, piezoelectric, and ferromagnetic materials with high accuracy [247].



Figure 11.15 (a) Electrohydrodynamic lithography structures resulting from the use of a patterned top electrode (experimental arrangement shown in inset to a). The AFM image (a1; tapping mode at 360 kHz) shows 140-nmwide stripes (full-width at halfmaximum) which replicate the silicon master electrode (200-nm stripes separated by 200-nmwide and 170-nm-deep grooves). The crosssection (a2) reveals a step height of 125 nm; (b) Replication of patterns on a TiO₂ precursor solution film with patterned stamp: (b1), (b2) Conical pattern arranged in a square lattice. In addition to the replicated cones, a pattern in the center of the squares is observed. This pattern

stems from the electric field-aided dewetting of square shaped patches of precursor film that remained once the cones have formed. Both the conical shape of the replicated pattern and the central shapes are a consequence of the solidification of the precursor material before the liquid can attain its equilibrium shape; (b3) Three dimensional representation of b2; (b4) Replication of a simple square pattern, showing cones with a base width of 2.5 μ m and a height of 37.6 nm. (a: Reproduced with permission from [237]. Copyright © (2000) Macmillan Publishers Ltd; b: Reproduced from [247]. Copyright © (2007) The Royal Society of Chemistry.)

11.5.1

Electric Field-Induced Patterning: Theory

Theoretically, the origin of the film instability is best understood by considering the balance of forces acting at the polymer film–air interface. As discussed before, the film surface tension γ minimizes the area of the polymer–air interface and stabilizes the film. The electric field on the other hand polarizes the polymer resulting in an effective surface charge density. This result in an electrostatic pressure at the liquid–air interface. An expression for $p_{\rm EL}$ is obtained by minimization of the energy, $F_{\rm EL}$, stored in the capacitor with a constant applied voltage, *U*, as [29]:

$$F_{\rm EL} = \frac{1}{2}CU^2$$
(11.6)

The total capacitance, *C*, is given in terms of a series of two capacitances, the film and the air gap, with dielectric constants ε_P and ε_{air} (~1) respectively. For two capacitors in series $(1/C = 1/C_P + 1/C_{Air})$, 1/C is given as

$$1/C = [\varepsilon_P d - (\varepsilon_P - 1)l] / \varepsilon_0 \varepsilon_P A \tag{11.7}$$

where l is the thickness of the polymer layer, d is the distance between the two electrodes, and A is the capacitor area. The dielectric displacement, D, is constant across the layers and can be used to calculate the electric field in the polymer film as:

$$D = \varepsilon_0 \varepsilon_P E_P = \varepsilon_0 \varepsilon_{\text{Air}} E_{\text{Air}} \tag{11.8}$$

where, ε_0 is the dielectric vacuum permittivity and E_{Air} is the electric field in air. Considering that the applied voltage is a summation of the voltage differences across the two layers [$U = E_P l + E_{Air} (d - l)$], and substituting the expressions of E_P and E_{Air} we get,

$$E_P = U/(\varepsilon_P d - (\varepsilon_P - 1)l) \tag{11.9}$$

The electrostatic pressure (p_{EL}) that destabilizes the film is opposed by the stabilizing Laplace pressure originating from surface tension. The total electrostatic pressure in the film is given by:

$$p_{\rm EL} = -\varepsilon_0 \varepsilon_P (\varepsilon_P - 1) E_P^2 \tag{11.10}$$

The dispersion relation for a system dominated by electrostatic forces is given by [29, 243]:

$$1/\tau = -(l_0^3/3\eta)(\gamma q^4 + \partial_l p_{\rm EL}q^2)$$
(11.11)

This is in contrast to the inviscid, gravity stabilized case with $\tau^{-1} \sim q$ [279]; the $\tau^{-1} \sim q^2$ variation is a signature of a typical dissipative system [280]. The necessary condition for the amplification of the fluctuations is $\tau > 0$. Since $\partial_l p_{EL} < 0$, all modes with $q = q_C = (-\partial_l p_{EL}/\gamma)^{1/2}$ are unstable and are spontaneously amplified. The wavelength of the fastest growing mode (λ), which eventually dominate the instability, is given as:

$$\lambda = 2\pi \sqrt{\frac{\gamma [\varepsilon_p d - (\varepsilon_p - 1)\ell]^3}{\varepsilon_0 \varepsilon_p (\varepsilon_p - 1)^2 U^2}}$$

$$= 2\pi \sqrt{\frac{\gamma U}{\varepsilon_0 \varepsilon_p (\varepsilon_p - 1)^2}} E_p^{-\frac{3}{2}}$$
(11.12)

However, the experimental results differ by a factor of 2 from the theoretical prediction, an effect which is not entirely understood.

Based on the above theoretical considerations, the dynamics of pattern formation in EHD instability has been modeled using LSA [236, 237, 241, 249, 250], and 3D nonlinear simulations [251, 252]. Linear stability analysis accounts for the forces acting on the film interface to determine the fastest mode of growth. The stability

analysis of an interface between a dielectric and a conducting fluid by Herminghaus show that the electric fields can also arise naturally from the contact potentials of such an interface, giving rise to instabilities [236]. Pease and Russel have shown that for leaky dielectric liquids, finite conductivity leads to patterns of smaller wavelength and larger instability growth rates [249, 250]. Based on full 3D nonlinear simulations Verma *et al.* have simulated the electrostatic field-induced instability, morphology, and patterning of thin liquid films confined between two electrodes for both spatially homogenous and heterogenous fields [252]. In addition to the spinodal flow resulting from the lateral variation of the electric field arising from local film thickness changes, a laterally heterogenous field also causes the flow of liquid from the regions of low to high field strength, allowing precise control over the replicated pattern morphology [252]. For a patterned substrate, the simulations suggest that the electrode pattern is replicated into the film only when the pattern periodicity, $L_{\rm P}$, exceeds the instability length scale calculated for the minimum inter-electrode separation distance. Thus, the formation of secondary structures (deviating from the template) can be suppressed by employing a patterned electrode with a high aspect ratio topography, giving rise to stronger field gradients. Simulation results by Verma et al. suggest that the number density of the electric field-induced structures can be controlled by tuning the mean film thickness, the fill ratio, periodicity and aspect ratio of the topography of the top electrode, and the applied voltage [252]. These observations have been substantiated experimentally by several groups [246].

11.5.2

Electric Field-Induced Patterning of Polymer Bilayers

When the electric field is applied across a polymer bilayer sandwiched between two electrodes (with or without an air gap, Figure 11.16a), it destabilizes both the air-polymer and the polymer-polymer interfaces [254-260], thereby resulting in the formation of more complex instability structures [257-260]. An electric field applied normal to an interface between two dielectric materials with different polarizabilities leads to an interfacial electrostatic pressure, which arises from the uncompensated displacement charges [260]. It is seen that there is a substantial amplification of the thermal fluctuations at an interface between two liquid films, owing to the reduced interfacial tension [254-256]. This leads to a significant reduction in feature size and periodicity, in addition to a much faster growth of instability compared to EHD instability in a single film [254, 255]. The field strength has a very strong influence on the evolution sequence in a polymer bilayer, as there are different hydrodynamic regimes based on low and high field strengths [255]. In a bilayer comprising a PS film coated on a PMMA thin film, heterogeneous nucleation can lead to the formation of holes in the films before the onset of electrostatically driven instability when the field strength is low. In this case, the dewetting kinetics is only marginally influenced by the applied electric field [254, 255]. Application of a stronger field leads to the build-up of electrostatically amplified surface waves which pre-empts heterogeneous nucleation and results in the formation of columns that span from the bottom layer right up to the top electrode [254-256]. The two regimes



Figure 11.16 (a) Schematic representation of the capacitor device used to study capillary surface instabilities in a polymer bilayer comprising a PS top layer and a PMMA bottom layer with an externally applied electric field; (b, c) AFM images of a single column before and after removing the PS phase by washing the sample in cyclohexane, respectively. The PMMA phase in (b) forms a mantle around the PS column with a height of 170 nm and a width of

 \sim 200 nm; (d, e) EHD structures formed by using a stripe patterned electrode. Figure (d) shows the replicated stripes and (e) the secondary PMMA structures after washing the sample in Cyclohexane, removing PS preferentially. Feature height \sim 160 nm, width \sim 100 nm. (Reproduced with permission from [257]. Copyright © (2002) Macmillan Publishers Ltd.)

are drastically different in terms of hydrodynamic time scales [256]. While a slowpaced motion of the contact line during dewetting leads to only a small deformation of the lower liquid layer, a faster collective motion driven by the EHD instability in a stronger field leads to high shear stresses and therefore a more significant deformation of the PMMA contact line [256].

Electrohydrodynamic instabilities in a polymer bilayer have also been used to engineer hierarchical patterns exhibiting two independent and distinct characteristic length scales [257]. This was shown by Morariu *et al.* for a PS–PMMA bilayer. In their system, the time constant for destabilization of the air surface was smaller compared to the polymer–polymer interface [257]. This led to the destabilization of the top PS film on the PMMA underlayer [257]. The resulting lateral redistribution of PS induced a secondary instability in the PMMA underlayer, thereby creating a hierarchy of length scales of the formed structures. The distinct rim around the columns in Figure 11.16b is morphologically different from the columns formed in single layer films under similar conditions [237, 257]. The rims are the signature of a composite core–annular structure consisting of a cylindrical PS core surrounded by a PMMA shell, which is revealed when PS is selectively removed (Figure 11.16c) [257]. The composite patterns/hollow structures thus created can further be aligned using a

patterned electrode, as shown in Figures 11.16d and 11.16e. While the overall EHD morphology induced by a stripe patterned stamp was indeed the positive replica of the electrode master (Figure 11.16d), each of these replicated stripes consisted of a PS core surrounded by a thin PMMA wall (Figure 11.16e) [257]. The height and width of the structures and their aspect ratio can be controlled by adjusting the electrode spacing, the lateral density of topographic features on the patterned electrode, and the initial film thickness of the layers [257].

It has also been shown that EHD instabilities in conjugation with dewetting at the polymer-polymer interface result in a variety of complex 3D structures [258-260]. The dielectric constant of the polymers in the two layers as well as their relative ordering are important parameters that strongly influence the morphology of the resulting pattern. In a PS-PMMA bilayer, PMMA has a higher dielectric constant compared to PS [257, 259]. The formation of cage type structures (Figure 11.17) was observed in a bilayer of PS on top of PMMA in a combination of dewetting and EHD. The top PS film initially dewetted on the PMMA surface before the electric field was switched on [259]. The PMMA meniscus showed a fingering instability around each PS column which originated from the transformation of the dewetted PS droplets into columns. This fingering instability is caused by the flow of PMMA along the outside PS columns driven by the electric field, eventually forming narrow strands surrounding each PS column. The PMMA, upon reaching the top electrode, which was chromium-coated, preferentially wetted the chromium surface displacing the PS layer thereby, detaching the PS columns from the top electrode and confining PS within a 'top-covered' PMMA cage. This can be clearly seen in Figure 11.17b where the PS has been selectively removed, revealing the cage-like PMMA structure. In contrast when the top electrode was coated with a fluoropolymer, the PMMA did not spread on the top electrode, the PS columns remained connected to the top electrode, with an open cage structures (Figure 11.17c) for an identical bilayer. In contrast, when PMMA was on top of PS, film the resulting morphology resembled closed-cell structures, confirming the importance of the layer sequence [259, 260]. While the size and spacing of the resulting structures are controlled by the electrostatic forces, it was



Figure 11.17 (a) SEM image of a single EHD column. The dark recesses along the height of the pillar are due to PMMA that has been degraded because of e-beam exposure in the SEM; (b) a single 'cage', after the sample was washed in cyclohexane to preferentially remove

PS; (c) structures obtained with hydrophobic chromium layer coated on the top electrode after washing with cyclohexane. The structures are hollow and do not have ceiling. (Reproduced with permission from [258]. Copyright © (2006) American Chemical Society.)

the dewetting kinetics that dictated the order in which the two interfaces became unstable [259]. Further, a closed-cell structure formation is favored when a low molecular weight PS bottom layer is used [259].

11.5.3 Thermal Gradient-Induced Patterning

A polymer film can also be destabilized by an external thermal gradient [265–270], in a fashion similar to the application of an electric field [230–264]. This approach has been successfully used by several groups for patterning thin polymer films and to make meso- and nanoscale structures. The experimental set-up is similar to that of the electric field-mediated patterning, as the film is sandwiched between the substrate and a top plate, with an air gap separating them. Typically the two plates are maintained at two different temperatures [265-269]. The uniform temperature gradient across the air-polymer interface directs the interfacial instability in the direction of the temperature gradient, and consequently a variety of patterns, including columns and stripes, form, which span between the two plates. As shown in Figure 11.18, two distinct morphologies, columnar (Figure 11.18a) and stripes (Figure 11.18b) appear in experiments. The precise morphology depends on initial conditions such as the film thickness, the gap distance between the two plates, the magnitude of the thermal gradient, as well as the temperatures of the two plates. When the separation distance between the two plates (*d*) is large compared to the film thickness (*h*) the columnar morphology is predominant. Lower values of d/h lead to the formation of striped patterns [266]. Both the morphologies exhibit a single dominant length scale (λ) which depends inversely on the initial heat flux between the plates [266]. The formation of various other morphologies such as spirals patterns, or co-existence of several different



Figure 11.18 Optical micrographs of structures that have formed in polystyrene films sandwiched between two plates at different temperature. (a) Columnar patterns formed for film thickness ~309 nm, gap between plates ~755 nm and $\Delta T = 28$ °C; and (b) stripe patterns formed for film thickness ~130 nm,

gap between plates ~250 nm and $\Delta T = 19 \,^{\circ}$ C. The colors stem from the constructive interference of the white microscope illumination and are an indication of the local film thickness. (Reproduced with permission from [266]. Copyright © (2003) American Chemical Society.)

morphologies on the same sample, have also been reported [275, 276]. Some experiments showed that the morphology of the patterns is also influenced by the proximity of the edges [276].

It is important to note that the nature of the instability and pattern formation in a thin film subjected to an externally imposed field is fundamentally different from a spontaneous process such as dewetting, where the morphological transformation is the transition from an unstable or metastable thermodynamic state to a stable state, corresponding to a lower free energy configuration [65]. In presence of a temperature gradient the system is intrinsically out of equilibrium and the definition of an equivalent of the Gibbs' free energy is not usually possible [281]. In contrast to the energy minimization for spontaneous instabilities, the morphological evolution maximizes the heat flux. Schäffer *et al.* found that the acoustically propagating phonons are reflected at the polymer–air interface, thereby exerting a destabilizing radiation pressure that eventually leads to an instability in the direction of the





(c) $w = 4.5 \,\mu\text{m}$: drop-shaped columns only; and (d) $w = 2 \,\mu\text{m}$: plugs spanning the confining walls. The size of optical microscopy images are $70 \times 70 \,\mu\text{m}^2$. The height of the polymer columns and plugs and is determined by the distance of the line grooves to the substrate (580–630 nm). (Reproduced from [281]. Copyright © (2005) The Royal Society of Chemistry.) imposed field or gradient [265]. Nedelcu *et al.* have reported a pattern formation process by imposing a 1D confinement in the form of a 1D stripe patterned top plate under the influence of a temperature gradient. The presence of the patterns on the plate guides capillary instability along the stripe direction [281]. The final morphology of the patterns depend on the extent of confinement, which quantitatively is the ratio of the groove width of the confining stamp to the diameter of unconfined columns, that are formed in a laterally homogeneous temperature gradient with a flat top plate. Using a stripe-patterned stamp, two competing pattern formation mechanisms are coexistent: (i) amplification of capillary instabilities, leading to columns that span across the two plates; and (ii) thermocapillary driven flow that leads to the rise of the polymer meniscus along the confining walls. The final pattern morphology is a combination of both types of transport. Increasing the extent of lateral confinement leads to a transition from circular columns to wall-adsorbed columns with a drop-shaped cross section [281].

11.6 Conclusion

In this review we have summarized recent developments on unconventional surface patterning in thin, soft polymeric films, which are based on the morphological evolution arising from film instabilities. In this approach, pattern formation is engendered by a spontaneous or external field-mediated amplification of the capillary waves which are omnipresent on the free surface of a liquid film. This approach is thus distinctly different from the top-down replication based on standard soft lithography techniques. In this chapter we have primarily covered the instabilitymediated pattern formation in homopolymer thin films in the liquid state (polymers heated beyond glass transition temperature or exposed to solvent vapor). We show that several distinct force fields such as the surface forces (in the form of surface and interfacial tensions of the substrate and polymer), intermolecular van der Waals forces, molecular level stresses, external force fields (electric field or a thermal gradient), and residual stresses in the film play a significant role in determining the evolution pathway, time and length scales, as well as the morphology of the final structures. Subsequent discussion on thin film instability has been classified into two parts. The first part covers the theoretical and experimental aspects of spontaneous dewetting in ultrathin films, and the second part deals with instability mediated by the application of an external field.

From the standpoint of patterning, both approaches are advantageous in terms of the flexible morphological control of the structures that can be created. For example, the feature size can be controlled by simply varying initial conditions, such as the film thickness, the magnitude of the applied external field, the gap between electrode and film, the fill ratio, and so on. This is in contrast to the necessity for a fresh stamp, master or a mask in any existing top-down technique whenever a change in feature size is required. In addition, it is also possible to control the morphology of the structure to a large extent by controlling the time evolution. For example, dewetting of

a thin polymer film on a flat surface eventually leads to a random array of nearly equalsized droplets. However if the dewetting experiment is allowed to proceed only up to an intermediate level, it is possible to obtain arrays of holes or ribbon like patterns, which appear as intermediate structures in the evolution sequence. This chapter cites many recent experimental and theoretical examples of how instability-mediated patterning enables flexibility and control over the resulting pattern morphology. Several key scientific issues are discussed, such as the role of surface tension during the various stages of dewetting, the formation and growth of rims, which are not only important in dictating the pattern morphology but are also of scientific interest, with many issues yet to be fully resolved.

Many instability-induced structures lack long-range order, and therefore find limited practical application. We have discussed several templating strategies which have been applied to overcome this limitation by using a chemically or topographically patterned substrate. The mere use of a template does not necessarily translate to perfect ordering, as the key issue is the commensuration between various length scales, mainly the intrinsic length scale of instability as well as the geometry and periodicity of the structures. With the help of several examples it is shown how a slight variation in the initial conditions can lead to a variety of evolution pathways and final pattern morphologies. This emphasizes the need for simulations that are able to accurately predict the final morphology.

The last topic of the chapter covers the external field-mediated instabilities and pattern formation. We have shown several examples of the suitability of EHD to become a novel and versatile patterning method. For example, it is a rare technique where it is possible to obtain structures with a reasonable degree of long-range order (hexagonally packed columns, for example) even when a flat, featureless top electrode is used. By using a polymer bilayer, several unique types of structure such as enclosed patterns, buried patterns and hierarchical structures have been successfully created by EHD, which are almost impossible to fabricate by existing lithography techniques.

The topics presented here are a subset of self-organization and pattern formation processes, which are also seen in various other settings such as evaporation, condensation, elastic instabilities in various materials including elastomers, block copolymers, blends, and liquid crystals. An interested reader is advised to consult some excellent review papers on each of the themes, some of which are cited in the reference section.

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