



# Patterning dewetting in thin polymer films by spatially directed photocrosslinking

Gregory T. Carroll<sup>a,\*</sup>, Nicholas J. Turro<sup>a,b</sup>, Jeffrey T. Koberstein<sup>b</sup>

<sup>a</sup> Department of Chemistry, Columbia University, 3000 Broadway, MC 3157, NY 10027, United States

<sup>b</sup> Department of Chemical Engineering, Columbia University, 500 West 120th Street, NY 10027, United States

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## ABSTRACT

In this report we examine the dewetting of spin-cast poly (styrene) films in a confined geometry. We designed a platform for laterally confining PS by photo-patterning crosslinks in spin-coated thin films. Heating the patterned film above the glass transition temperature of PS results in localized dewetting patterns in regions that were not crosslinked, while the crosslinked pattern serves as a rigid barrier that confines the retraction of the uncrosslinked polymer in micron-sized domains. The barriers also provide a favorable surface that the liquid PS wets onto, forming a rim at the boundary of crosslinked and uncrosslinked polymer. The resulting patterns are shown to be dependent on the irradiation and annealing time, the dimensions of the uncrosslinked region and the thickness of the film.

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## 1. Introduction

Self-organization processes offer exciting opportunities in generating micro- and nano-scale architectures and materials. The resulting interfacial structures generated by such processes can imbue a material with unique physical properties. For example, the undulating pattern of the inner membrane of the mitochondria results in a very large surface area, increasing the amount of possible locations for the presentation of ATP synthesizing proteins [1]. The surfaces of many organisms contain micro- and nano-structured motifs that provide important functions such as the self-cleaning abilities of the lotus leaf [2,3] and wings of the cicada [4], water-harvesting by the Namib desert beetle [5] and the hydrophobic “water-walking” legs of the water strider [6,7]. A common goal in materials science is the utilization of self-organizing processes to create three-dimensional structures and patterns on surfaces to facilitate the fabrication of devices. Pertinent applications include anti-fog and anti-reflection coatings [8], water-harvesting surfaces [9], decontaminating surfaces [10], surface roughness-enhanced adsorption [11], surface-enhanced spectroscopic signals [12], micro- and nano-containers [13–16] and the study of fluid flow in confined spaces [17,18].

Many reports have described methods that allow for polymer films and other materials to organize into characteristic structures [19–23]. Surface tension can lead to interesting morphological structures in polymer films. An important surface-tension driven

process is the dewetting of thin polymer films where a macromolecular layer retracts from a surface that does not favor spreading [24–26]. A classic example is the dewetting of poly styrene (PS) on silicon wafers. Smooth thin (typically less than 100 nm) PS films can be prepared on Si substrates by spin-coating, however upon heating the films above  $T_g$ , the polymer dewets, forming droplets with finite contact angles. Dewetting proceeds by the formation of isolated holes, followed by their growth through the retraction of the hole perimeter into the liquid film. A rim of liquid is created ahead of the retracting front, which eventually contacts other rims forming ribbons. The ribbons eventually break into drops splayed in a cellular structure. Additionally, a bicontinuous pattern has been observed for very thin films [27]. The origin of the holes at the earliest stages of the dewetting process has been attributed to two mechanisms: spinodal decomposition and nucleation onto defect sites [28]. In the spinodal mechanism, thermal undulations (with wavelength  $\lambda$ ) increase the interfacial area, which raises the free energy (in proportion to the surface tension,  $\gamma$ ). The undulations also change the local film thickness  $h$ , and hence locally change the free energy per unit area of the van der Waals interactions in the film:

$$F(h) = -A/12\pi h^2, \quad (1)$$

where  $A$  is the Hamaker constant of the polystyrene/SiO<sub>2</sub> system. When the spinodal parameter  $d^2F/dh^2 < 0$  (i.e.  $A > 0$ ), the van der Waals interactions cause the film to rupture for wavenumbers ( $2\pi\lambda$ ) smaller than a critical value as given by:

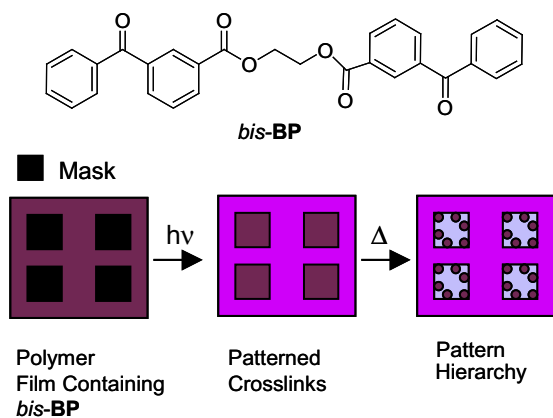
$$k_c^2 = -1/\lambda d^2F/dh^2. \quad (2)$$

\* Corresponding author.

E-mail address: gtc Carroll@gmail.com (G.T. Carroll).

The second mechanism of hole formation derives from heterogeneities (particles, air bubbles, etc.) in the film, which nucleate holes as the polymer dewets around the defect.

In some cases it is possible to control the spatial layout of surface structures that form as a result of dewetting or other instabilities by confining surface organization to a defined geometry [29–37]. In this report we examine pattern formation when PS dewets in a confined geometry defined by spatially directed photocrosslinking. Dewetting of the thin film is confined to masked regions of a photolithographically patterned film (i.e., negative patterning). The masked regions remain uncrosslinked, allowing the polymer to flow when annealed at elevated temperature. We have previously shown that a bifunctional benzophenone derivative, *bis-BP*, can photo-crosslink PS films and that the resulting films resist dewetting when heated above the glass transition temperature,  $T_g$ , or exposed to solvent vapor [38]. The photochemical nature of the method renders the technique amenable to patterning by irradiation through a photomask as depicted in Fig. 1. A spin-cast thin polymer film on a substrate that favors dewetting is patterned with regions of stable branched/crosslinked polymer and unstable linear polymer. Morphological changes occur under



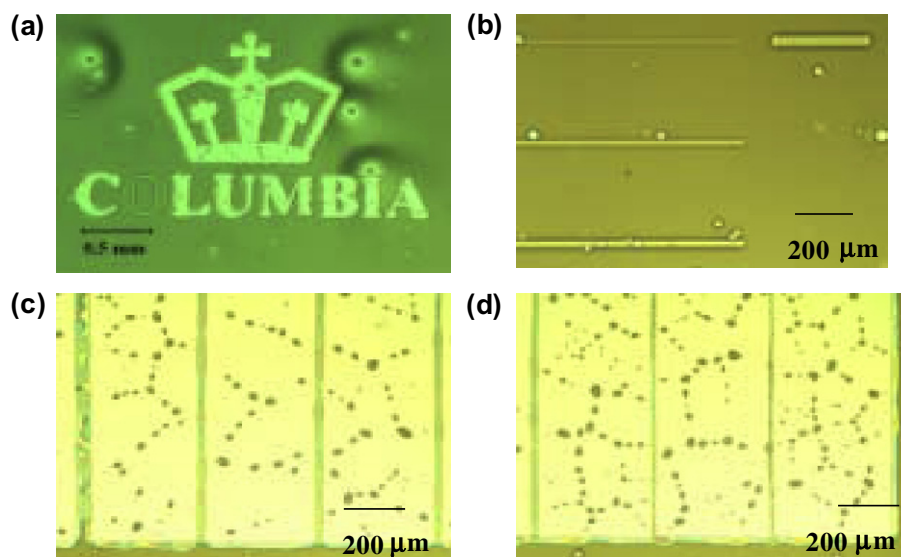
**Fig. 1.** Photochemically patterning crosslinks into a thin polymer film on a substrate that favors dewetting results in a hierarchy of patterns after heating above  $T_g$ .

thermal annealing to form dewetting patterns that reflect the initial mask pattern used to induce spatially directed crosslinking.

## 2. Results and discussion

In our initial studies we spin-coated PS films containing *bis-BP* of approximately 30 nm onto Si wafers containing a thin layer of  $\text{SiO}_2$  that were exposed to a solution of  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  at 95 °C for 1 h. The surfaces were irradiated with a 350 nm lamp through a photomask in contact with the film. As expected, the film dewets in the masked areas after heating at 170 °C in a vacuum oven as shown in Fig. 2. An unirradiated film of this thickness ruptures into droplets forming a polygonal pattern (see Supporting information, S1) as is expected for PS films of this thickness [24]. However, the crosslinked PS film provides a stable and energetically favorable surface for the PS to flow onto, forming a robust “rim” of polymer straddling the interface of crosslinked and uncrosslinked polymer. The height of the rim is dependent on the area of the masked region and reached a maximum value of approximately 100  $\mu\text{m}$  and a width of a few microns for films prepared in this way (see Supporting information, S2). A variety of patterns were photo-generated. Optical microscopy images show that the annealed polymer can recognize and is stabilized at both straight and curved crosslink boundaries as shown in Fig. 2. Fig. 2b–d shows that when the crosslinked polymer is confined to an area that is sufficiently large, a polygonal pattern of droplets forms within the defined area. Droplet formation can be prevented by decreasing the width of the channels. As the size of the pattern decreases, the droplets of dewetted polymer can no longer form a polygonal pattern. When the area is sufficiently small the uncrosslinked polymer completely drains onto the crosslinked film. As the channels decrease in width less material becomes available to collect at the interface and the heights of the resulting “rims” decrease (see Supporting information, S2).

The morphological features form as a result of patterning robust networks in the film that resist the capillary interactions responsible for dewetting and provide a favorable interface for nearby PS chains to flow onto. The surface tension-directed motion of the polymer onto the crosslinked film rather than next to the pattern is evident in Fig. 2c and d where mobile polymer localizes onto crosslinked strips of PS with a width of only a few microns. Note



**Fig. 2.** A variety of patterns can be generated by a combination of photochemically patterned crosslinking followed by dewetting of the uncrosslinked polymer.

that in 2c the uncrosslinked widths are wider than in 2d and hence the width of the ribbon of dewetted polymer that localizes onto the pattern is wider. If the polymer merely assembled next to the crosslinked area a valley would emerge with the crosslinked polymer as the trough and the dewetted polymer as the peaks. Instead, a thin rim of polymer covers the crosslinked base and maintains similar dimensions. The smallest rims formed in this way have widths as small as approximately 4  $\mu\text{m}$ . Rims wider than the extreme ends of the overall pattern can be generated through the coalescence of dewetted polymer flowing onto the crosslink base from both sides. This is most evident by comparing the first polymer rim in Fig. 2c with the rim at the bottom of the dewetted area where the overall pattern terminates. Once the size of the mask becomes 48  $\mu\text{m}$ , the crosslinked PS is no longer completely covered as shown in S3 of the Supporting information (3rd space between channels starting from the left).

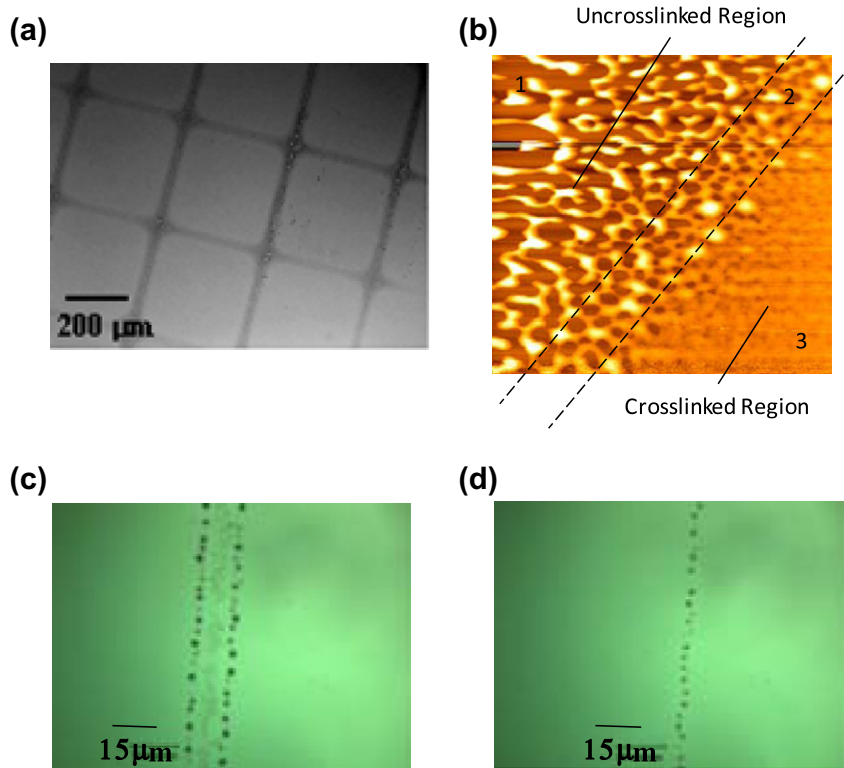
The physical properties of polymer layers have been shown to be affected by film thickness [39–41], including the dewetting mechanism. Films of less than 10 nm in thickness can rupture by spinodal dewetting whereas films greater than 10 nm are said to dewet by nucleation onto defect sites [27]. We examined the effect of film thickness on the confined dewetting behavior. Fig. 3 displays OM images of 7 nm films patterned and annealed as described above. One of the obvious observations from patterning films of this thickness is that rims of polymer do not form at the interface. In many cases the dewetting morphologies resemble a spinodal-like pattern reminiscent of spinodal decomposition in immiscible mixtures. Although we often observed this morphology in our thinner films as have others [27], in some cases our films formed droplets rather than an undulating bicontinuous pattern, indicating competition with a nucleation mechanism.

In order to visualize the edge of the pattern we obtained AFM images of the surface. Fig. 3b shows an AFM image of the edge of

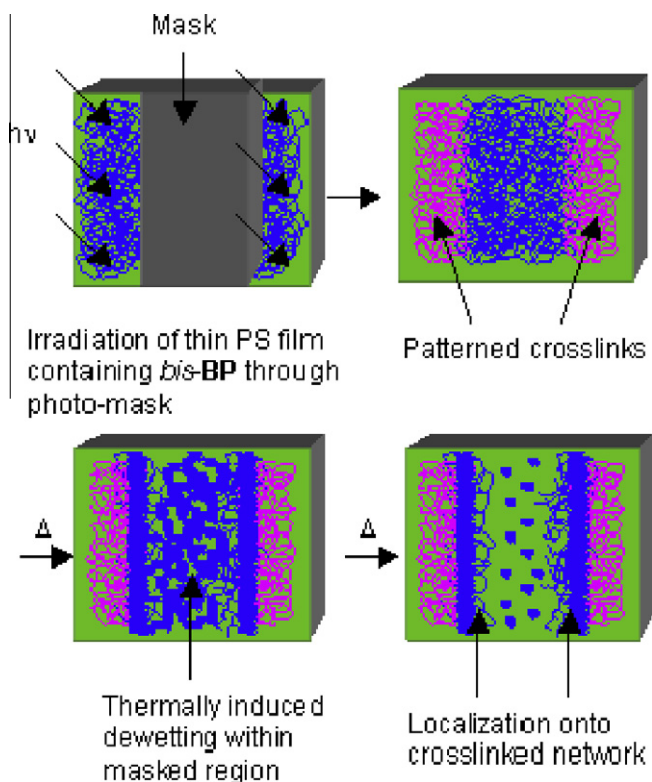
a channel within a patterned 7 nm film. Three distinct structural regions are evident from this image: (1) the uncrosslinked region, (2) the interphase region between the crosslinked and uncrosslinked film and (3) the smoother crosslinked area. The uncrosslinked region shows an undulating pattern associated with spinodal dewetting. As the interphase between the crosslinked and uncrosslinked region is approached, the morphology changes to randomly distributed holes. As the interphase region approaches the crosslinked area, the holes shrink and the surface roughness ultimately appears more constant. The final area of interest is the crosslinked film. This part of the film resists dewetting and has smaller surface features (approximately 5 nm) compared to the interphase and uncrosslinked phase, which show heights exceeding 50 nm.

We investigated the effect of the channel width on the resulting patterns for the 7 nm film. Fig. 3c and d shows a PS film that was patterned as described above. Typically one finds an inner undulating pattern surrounded by droplets. As the uncrosslinked polymer is confined to a smaller width the resulting pattern is reduced to droplets.

In addition to changes brought about by film thickness, the resulting patterns can also be controlled by changing the dosage of photons and annealing time (see Supporting information, S4 and S5). Changing the irradiation time allows for complex patterns to be generated. Additionally, control over the crosslink/branching density in this way demonstrates the effect of the width of a crosslinked strip of polymer on its stability. Wider networks are more stable than thinner networks within a given film as shown in S4 where the thinnest strip breaks down upon annealing whereas the wider strips remain stable. The dependence of the morphology of the annealed films on the irradiation time is consistent with spatially-controlled photochemical crosslinking as the basis for the observed patterns. Control over the annealing time also affords the possibility to control the resulting patterns. Reducing the heating



**Fig. 3.** Photochemically patterned dewetting in 7 nm PS films. The AFM image (b) is  $20 \times 20 \mu\text{m}$ . The division between the uncrosslinked (1), interphase (2) and crosslinked (3) areas in (b) are approximated by the dashed lines (see text). The area to the far left of the line shows a clear dewetting morphology whereas the area to the far right shows the crosslinked region which has a smoother morphology.



**Fig. 4.** The resulting film morphologies result from capillary interactions that favor dewetting of the  $\text{SiO}_2$  surface and wetting of the PS network.

time generates localized holes within the film, the first stage of dewetting, as opposed to droplets which form at the final stage when the film is subjected to longer annealing times. For thinner channels of uncrosslinked polymer the area for dewetting is confined to a small enough width such that single lines of holes are formed, allowing for a greater degree of order over the resulting macroscopic morphology.

The morphologies observed in the present system are a result of dewetting induced pattern formation as well as capillary flow of the mobile uncrosslinked polymer onto the immobile crosslinked network. The process is qualitatively considered in Fig. 4. Below  $T_g$  the film is frozen in a metastable state. Irradiation of this film through a photomask results in a pattern of crosslinked polymer. When the sample is heated well above  $T_g$  the uncrosslinked polymer chains can flow on the substrate. Additionally, dewetting processes contribute to patterns of droplets forming within the channels. However, as the size of the channels decreases the dewetting pattern disappears while the polymer continues to collect in rims localized at the edge of the crosslinked film due to the incompatibility of the polymer with the surface. The length scale dependence of the formation of droplets within the channels reflects other systems in which templating of soft materials by dewetting in confined environments has been demonstrated. Both experimental and theoretical work has emphasized that (for  $d^2F/dh^2 < 0$ ), the spinodal droplet cellular patterns only develop when the critical wavelength for the instability is smaller than the dimensions which confine the dewetted area. In a system composed of PS confined by PDMS walls, dewetting to form ordered polymer droplets was shown to take place only when the wavelength of the capillary wave is smaller than the characteristic length of the physical confinement [35]. Similarly, simulations on heterogeneous substrates consisting of less wettable and more wettable stripes showed that heterogeneous rupture does not occur when

the width is below a characteristic wavelength of the film instability [42].

The critical conditions for the formation of the droplet cellular structure are also affected by the capillary flow onto the crosslinked sections, which reduces the thickness of the mobile layer. The thinning of the film decreases the critical wavelength for spinodal dewetting and makes droplet formation more likely as reflected in the differences between the thicker and thinner films shown in Figs. 2 and 3. A similar effect of film thickness has been observed in other systems. In the simulations mentioned above thicker films on patterned surfaces were shown to match the confining pattern while for thinner films droplets were observed. Similarly, in a deuterated poly (styrene)/poly (butadiene) blend that undergoes phase-separation on patterned self-assembled monolayer (SAM) surfaces, it was shown that while self-organized patterns resembling the SAM pattern can be obtained, as the film thickness decreases the patterns break up into droplets [43].

### 3. Conclusions

We have shown that a bifunctional benzophenone derivative, *bis-BP*, can be used to pattern crosslinks into polymer thin films. The crosslink reaction most-likely occurs by photo-induced hydrogen abstraction followed by radical recombination. When heated above  $T_g$  dewetting of “mobile” polymer occurs only in the regions that were masked, while the unmasked regions serve as rigid barriers that confine the retraction of the uncrosslinked polymer. The barriers serve a secondary role as well. Unlike the case of the  $\text{Si}/\text{SiO}_2$  surface, the liquid PS wets over the crosslinked surface and hence as the film dewets material is drawn onto the surface of the crosslinked regions that surround the uncrosslinked areas. When the uncrosslinked region is sufficiently small, dewetting droplets do not form in the dewetted area. The resulting surface patterns that occur within the uncrosslinked areas can be controlled by varying the irradiation and heating times as well as the film thickness. The present system may provide some insight into the wetting behavior and assembly of soft materials and liquids in confined environments and how such materials can sense and transport to a given interfacial environment. We expect that other polymeric systems that can reorganize after given an appropriate stimulus should be amenable to hierarchical pattern formation by this approach.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jcis.2010.07.070](https://doi.org/10.1016/j.jcis.2010.07.070).



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