Swelling-Induced Delamination Causes Folding of Surface-Tethered Polymer Gels

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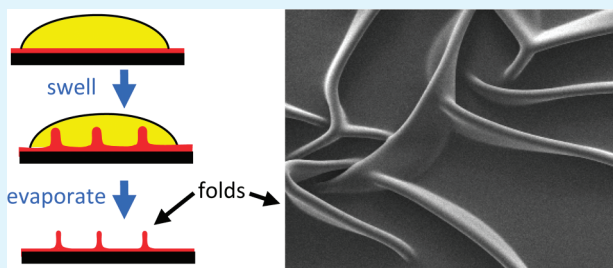
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Ⓢ *Supporting Information*

ABSTRACT: When a polymer film that is weakly attached to a rigid substrate is exposed to solvent, swelling-induced compressive stress nucleates buckle delamination of the film from the substrate. Surprisingly, the buckles do not have a sinusoidal profile, instead, the film near the delamination buckles slides toward the buckles causing growth of sharp folds of high aspect ratio. These folds do not result from a wrinkle-to-fold transition; instead, the film goes directly from a flat state to a folded state. The folds persist even after the solvent evaporates. We propose that patterned delamination and folding may be exploited to realize high-aspect ratio topological features on surfaces through control of a set of boundary constraints arising from the interrelation of film-surface adhesion, film thickness and degree of swellabilty.

KEYWORDS: *folds, delamination, creases, buckles, wrinkles, swelling*

Buckling plays a significant role in pattern formation in a diverse range of phenomena such as the shapes of fruits,[1] the edge-curling of leaves,[2] the folds (sulci) on brain tissue,[3] and fingerprint formation.[4] More recently, buckling phenomena have been exploited to characterize the properties of thin films,[5,6] develop flexible electronics,[7] develop antifouling surfaces,[8] or pattern surfaces.[9]

The swelling of polymers with solvent can lead to one class of such buckling phenomena in which an osmotic stress applied to a homogeneous body leads to nonhomogeneous deformation.[10−12] One of the simplest geometries in which this can happen is the swelling of a cross-linked polymer film that is attached to a rigid substrate. If the extent of swelling is sufficiently large, the film swells nonhomogeneously and the free surface develops cusp-like creases and rounded wrinkles.[12−15] Recent research[13,16] has clarified the mechanism of crease formation: lateral film swelling (i.e., swelling perpendicular to the film normal) is constrained by the rigid substrate, and hence the free surface of the film is under compressive stress. It is this compression that induces the creasing instability at the free surface. In this paper, we show that a new buckling phenomenon can also occur in the same situation: if the film is not strongly bound to the rigid substrate, a second kind of buckling instability can lead to large scale folding of the film. This Letter describes the basic phenomenon, clarifies the conditions under which folding does or does not occur, and proposes a schematic model for the process.

Experiments were conducted using PDMS (Sylgard 184) films swollen with toluene. Sylgard is a two-part silicone rubber formulation in which the base resin and the cross-linker are usually mixed in a 10:1 ratio. For most of our experiments however, the ratio of the base resin to cross-linker was 10:0.4 which resulted in a lower cross-link density. The shear modulus of these films was 18 kPa (in contrast to 54 kPa for 10:1 ratio), and the films swelled 380% by weight with toluene.[17] Films were prepared by spincoating the PDMS mixture onto acrylic sheets, letting them cross-link overnight, and then completing the cross-linking reaction for one hour at 75 °C. Film thickness was measured with a profilometer at three locations on the spincoated films. Thickness variation was less than 15%. Sections of the films, roughly 25 × 25 mm in size were peeled off the acrylic sheets and carefully placed (without entrapping air bubbles) on glass slides. The slides had been previously rinsed with deionized water and dried. The desired solvent was then directly deposited on the films. The region of the film wetted by the solvent was not allowed to reach the edge of the film so as to ensure that the solvent would not be imbibed between the PDMS film and the glass slide; instead swelling occurred only from the top surface of the film.
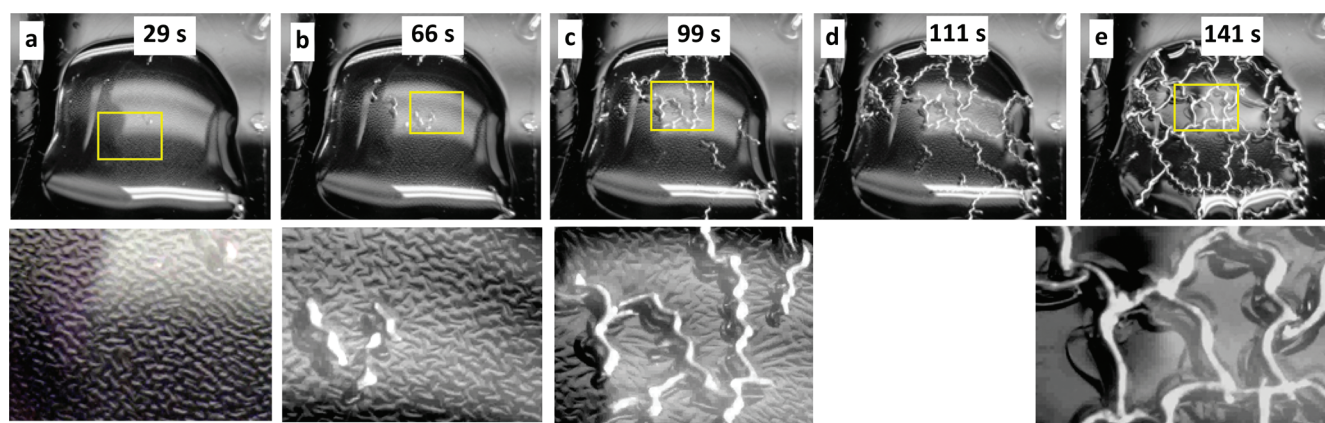
Figure 1. Images of the swelling process described in the text. The ~25 mm wide PDMS film occupies nearly the entire width of the frame, whereas the large irregular region in the center of the frame is the toluene drop. Other details are much clearer in the Supporting Information. The yellow rectangles in **a**, **b**, **c**, and **e** have been magnified in the lower row. The width of the top frames is ~30 mm. These images are extracted from the Supporting Information Movie 1.

We will now describe in detail one specific example of swelling a 102 μm thick film with toluene. Roughly 0.6 mL of toluene was placed on the middle portion of the film to cover an area of roughly 15 × 15 mm. This volume of toluene is many times larger than that needed for equilibrium swelling of the wetted portion of the film. The Supporting Information Movie 1 shows the entire swelling process, and frames extracted from the movie are shown in Figure 1. The sequence of events is as follows: immediately upon placing a drop of toluene on the film (Figure 1a), a creased surface is evident over the entire region exposed to toluene. These creases are similar in appearance to those observed previously,[12−14] and as mentioned above, they occur because the confinement of the film along its bottom surface induces a lateral compressive stress in the film. Figure 1b shows that after about a half minute, the length-scale of the creases increases consistent with Tanaka's observations,[12] but a new phenomenon also appears: the surface develops features that are visually similar to cracks. The movie and Figure 1c−e show that over the next two minutes these crack-like features propagate, as well as new ones develop, until they cover the entire wetted area. In fact these features are not cracks, but localized buckles and their formation and evolution is the chief subject of this Letter. We will now describe the most remarkable aspect of the swelling process: namely, after a buckle is formed, it rapidly grows vertically until it eventually reaches 1−2 mm in height. This vertical growth is not clearly evident in the movie or in Figure 1 since the imaging direction was along the film normal. However, Supporting Information Movie 2 shows another example taken from a shallower viewing angle which shows the vertical growth clearly. The width of the buckles in Figure 1, estimated from the images, is between 200 and 300 μm and does not change significantly as the buckle grows. Accordingly, as the height grows, a "wall" of high aspect ratio (roughly 5) emerges. Thus the final shape of these buckled structures is altogether different from the roughly sinusoidal shape of buckles well-known in the thin film literature.[18] For this reason, and consistent with the literature,[19,20] we dub these sharply curved features as "folds". The mm-scale height of the folds is over ten times the original film thickness. Considering that the equilibrium swelling is only 380 wt %, such a large increase in height cannot be explained by strictly local swelling, suggesting that material near a fold must contribute to the fold height. Supporting Information Figure S2

discussed below will confirm that the near fold material slides toward the fold and causes vertical growth of the fold. Over the 2−3 min following fold formation, the movie shows that the toluene evaporates and deswelling occurs. Videos taken at an angle (such as Movie 2) show that deswelling causes the height of the film to reduce due to deswelling. However the film does not revert back to its flat state, instead the folded structure becomes permanent. Remarkably, this final permanent structure can be exposed to high vacuum (e.g., in a scanning electron microscope) without destroying the folds. This strongly suggests that there are no air voids trapped under the folds; instead, each fold appears to be self-adhering along its entire underside.

Figure 1c−e show that buckles propagate in a sinusoidally meandering fashion. The velocity with which buckles propagate is highly nonuniform; a buckle may grow slowly for some time, then advance in a sudden burst, and then slow down again. Some of the rapid advances are almost "instantaneous", that is, faster than the 10 Hz video frame rate. This is illustrated in the Supporting Information Figure S1. The high speed at which the buckles can propagate implies that solvent redistribution because of concentration or stress gradients is not likely to be the mechanism driving buckle propagation. Small-molecule diffusivity in PDMS is typically less than 10^{-9} m^2/s,[21] sometimes much lower.[22] Hence, the time for diffusing the solvent through the 100 μm film thickness is at least 10 s, that is, solvent uptake is a relatively slow process. Accordingly, such fast propagation of buckles suggests that some mechanism other than gross volume change is involved in buckle formation. Finally from both the Supporting Information movies and from Figure 1e, it is apparent that in the regions adjacent to each fold, the original creases vanish completely. This does not happen immediately after the buckle forms, but instead occurs concurrently with the growth of the fold. This indicates that the compressive stress that had caused the creases early during swelling is relieved by the vertical growth of the fold.

It is crucial to reiterate that in the case discussed above and all the cases discussed in this paper, a sharply defined fold does not result from an initially wide and smooth buckle collapsing into a fold during evaporation. Instead a sharply defined fold is present from the earliest stages of buckle growth. This is most clear from Supporting Information Movie 2 which was taken

Table 1. Summary of Folding Behavior[a]

case	resin to cross-linker ratio	substrate during spincoating	substrate during solvent exposure	solvent	folding?	remarks
1	10:0.4	acrylic	glass	toluene	yes	corresponds to Figure 1
2	10:0.4	acrylic	glass	**_n_-tetradecane**	no	peeled and transferred to glass
3	**10:1**	acrylic	glass	toluene	no	peeled and transferred to glass
4	10:0.4	acrylic	**acrylic**	toluene	yes	**no peeling and transfer**
5	10:0.4	**glass**	glass	toluene	no	**no peeling and transfer**
6	10:0.4	acrylic	**acrylic**	**methylethyl ketone**	yes	**no peeling and transfer**
7	10:0.4	acrylic	glass	**methylethyl ketone**	yes	peeled and transferred to glass

[a]Case 1 corresponds to Figure 1 and the corresponding movie. Each of the other rows correspond to variations (indicated by the bold and underlined items) as compared to Case 1.

from a shallow viewing angle. To the best of our knowledge, such swelling-induced growth of a sharp fold has not been reported previously. Folds, defined as contours of localized high curvature, have been observed upon compression of stiff elastic films supported by compliant substrates (e.g., a softer elastic solid or a liquid layer).[19,20] In such cases, initial compression causes the entire film to show a uniformly wrinkled state at a specific wavelength. Upon further compression, some regions develop a progressively higher curvature, whereas the remaining regions flatten, thus forming folds. Upon further compression, each fold contacts itself. An exact analytical solution for such folds has been obtained recently.[23] The present situation is distinct from these previous observations in that [1] the soft PDMS layer does not have a stiff surface skin, and [2] there is no wrinkle-to-fold transition; instead folds appear directly from a more-or-less flat film. (The film is not exactly flat prior to folding; it is creased. However, below we will show that creases are not the precursor to folds; in fact folds can appear even without pre-existing creases.) In summary, the fold formation seen here is qualitatively different from previous observations of folding.

The general observations of fold formation remain valid as long as a sufficiently large area of the film is wetted by the toluene. Experiments with a much smaller wetted area show strong edge effects where the folds are localized around the circumference of the drop. For example, with a toluene drop volume of only 5 μL, folds developed along the periphery of the drop, and upon evaporation, resulted in a corral (Supporting Information Figure S2). Sometimes such corrals are complete circles, that is, a single continuous fold forms the periphery of the corral. More often, the corrals are "C"-shaped or broken as in Supporting Information Figure S2. The relatively small size of such corrals allows a complete two-dimensional map of the height profile using a profilometer and reveals a significant region around the fold that has an elevation that is lower than the undisturbed film far away. This strongly suggests that the near-fold region contributes to the fold: it is this region of the film that, during swelling, contributed material to the fold. Upon evaporation this region is left thinner than the original film, that is, in a permanently stretched state.

All the above observations of fold formation require that there be at least a 2−3 mm wide region at the periphery of the film that is not wetted by the toluene, and hence remains flat and unswollen. In contrast, if the toluene touches the edge, swelling induces out-of-plane curling of the edge, and the toluene is able to flow between the film and the glass slide causing large-scale distortion of the film.

Several variations of the experiment of Figure 1 have been examined, and Table 1 summarizes the results of when buckling and folding is or is not observed. All these films had thicknesses ranging from 80 to 100 μm. Case 1 corresponds to Figure 1. In each of the other cases the bold and underlined text indicates the differences as compared to Case 1. These experiments identify two criteria that are necessary for folding to occur, and these will be discussed next.

Cases 2 and 3 show that when the same experiment was conducted under conditions when the swelling was much less (225% by weight for n-tetradecane swelling a 1:0.4 ratio film, and 190% for toluene swelling a 10:1 ratio film), folding did not occur. These two cases suggest the first criterion for folding, namely, folding requires that the films must swell to a sufficiently large degree so as to create a sufficiently large compressive stress near the upper surface of the film; the film then tends to locally buckle in order to relieve this compressive stress. This buckled region, now less constrained on its lower surface, can swell further.

Cases 4−6 eliminated the potential impact of transfer of the film from one substrate to another. Case 4 shows that the peeling and transferring step is not critical; when the film was exposed to toluene while it was still on the acrylic substrate, folding was still observed. SEM images of the closeup view of folds from Case 4 is shown in Supporting Information Figure S3. Case 5 shows that when the film was directly spuncoated onto glass and exposed to toluene, folding was eliminated, although creasing still occurred. Incidentally, the obvious variation of spincoating onto glass and transferring onto another substrate could not be conducted because films spuncoated onto glass were strongly attached and could not be peeled off without tearing. Cases 6 and 7 shows that toluene is not unique: even solvents such as methylethyl ketone with far less swelling capability (<200%) can induce folding given the correct substrate adhesion. Interestingly, in cases 6 and 7 creases were not visible. Lack of creases is consistent with Trujillo's observation that a minimum of ~230% swelling was necessary for crease formation. Thus folding can occur even without surface creases implying that these are independent phenomena. Together, these cases indicate that folding is not solely determined by the swellability; the interaction of the film with the substrate plays a crucial role. Specifically, spincoating directly onto glass gives a film that is strongly attached to the substrate, whereas transferring peeled films onto glass or spincoating directly onto acrylic results in much weaker attachment.[24] Such weak attachment to the substrate appears to be critical to induce folding. These experiments suggest that the root cause of the initiation of buckling is delamination: we hypothesize that in cases of weak attachment, the compressive stress due to swelling can nucleate buckle delamination of the film from the substrate. Once the buckle is nucleated, the
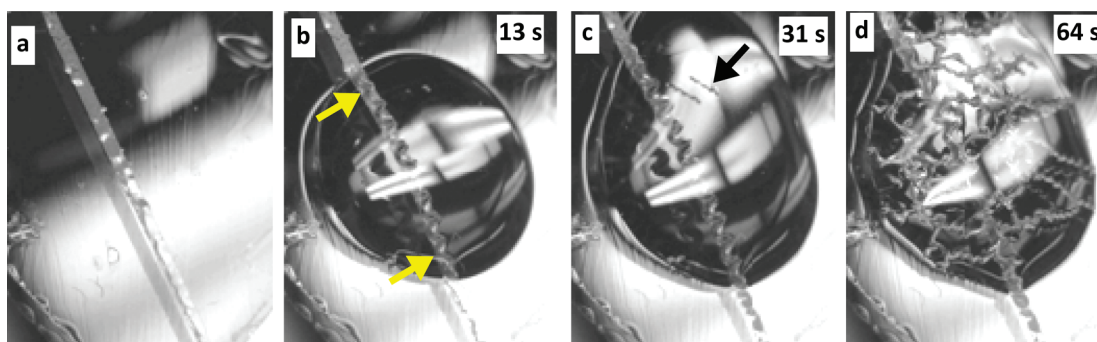
Figure 2. a. PDMS film (prior to toluene exposure) with a line defect (see text) clearly visible. **b.** Toluene drop causes a fold over the defect. The two yellow arrows (colored online) approximately mark the two ends of this fold. **c.** The original fold is still visible, but a new fold (indicated by the black arrow) starts far from the defect. **d.** Entire region shows folds.

delaminated region swells further and furthermore the surrounding film slides toward the buckle allowing it to grow into a tall fold. The hypothesis that delamination is the initiation step of buckling is also consistent with two of the observations of Figure 1. First, we noted above that late during the swelling process, the almost instantaneous propagation (i.e., faster than the 0.1 s between successive video frames) of some buckles cannot be explained by gross volume changes alone since significant solvent uptake cannot occur over 0.1 s time scales. In contrast, local delamination can propagate rapidly, and hence can explain the rapid propagation of buckles. Second, the sinusoidal meandering of the propagating buckles strongly resembles the telephone cord buckling instability that occurs when a stiff film locally delaminates from a substrate because of a compressive stress.[18] Accordingly, we propose the second criterion to observe folding: the adhesion of the film to the substrate must be sufficiently weak to permit buckle delamination.

To further verify the role of delamination, a patterned folding experiment was conducted: a low-adhesion line defect of roughly 1.5 mm width was created by spraying fluoropolymer particles on the glass substrate while the rest of the substrate was masked off. The mask was removed, the PDMS film was placed on the substrate, and the swelling experiment was repeated. Figure 2 shows that a sinusoidally meandering fold forms only a few seconds after toluene exposure as the swelling film undergoes buckle delaminaton off the line defect. Tall "walls" of hydrogel attached to a rigid substrate swell into a similar meandering pattern suggesting that once delamination occurs, a fold behaves qualitatively similar to a tall wall that is fixed at its base but free to swell along its top.[15,25,26] In Figure 2, the remainder of the film displays folding as well, but at a later stage during swelling. The similarity between the early "programmed" fold and the later "uncontrolled" folds suggests that delamination is the mechanism for both. Incidentally, if a much larger patch of fluoropolymer is created, folding is not observed; instead, the film laying over the low-adhesion patch forms a single delaminated blister. These observations strongly indicate that folding requires local buckle delamination, but not global delamination over the entire wetted region.

On the basis of these results, we propose the schematic of Figure 3 for uncontrolled folding, i.e. folding that is not mediated by deliberately programmed defects. The three key features of this schematic are [1] Swelling-induced compressive stress in the film induces buckle delamination at random defect sites. The delaminated region can then swell further. [2] The compressive stress in the surrounding region forces the gel film
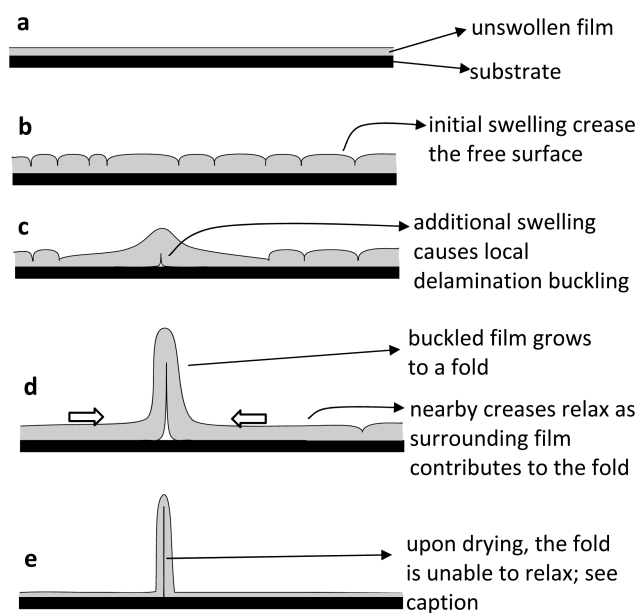

Figure 3. Schematic of the cross section of the gel film during swelling and folding. **a.** Initial film before solvent is added. **b.** Addition of solvent swells the film and the lateral compressive stress induces surface creases, **c.** local delamination buckling initiates a fold, **d.** compressive stress forces the gel to slide laterally and contributes to fold growth while also relaxing the neighboring creases, **e.** upon drying, the fold persists due to self-adhesion along the underside, and the stiction at the film−substrate interface. The schematic illustrates a void under the delaminated region, but this may not be true in practice. Local damage to the gel, that is, a local large deformation or facture, may be involved in delamination. The final evaporated structure definitely does not have a void since it can be exposed to the high vacuum of an SEM (Supporting Information Figure S3) without any noticeable change in structure.

to slide laterally toward the fold; this allows the surrounding film to contribute to the growth of the fold, relieves the compressive stress further away from the fold, and hence relaxes the neighboring creases. [3] As the solvent evaporates, the fold is unable to relax due to self-adhesion of the film along the underside of the fold as well as stiction resistance to sliding the near-fold region back to its original location. Accordingly, the fold becomes permanent. This physical picture suggests that uncontrolled folding requires the adhesion to be sufficiently weak to permit local delamination, but not so weak that the entire film delaminates as a blister. In the case of programmed folding of a low-adhesion defect, Figure 3 would still remain a

valid picture, except that the location and width of the fold would be determined by the location and size of the defect. In this case, if the film is strongly attached to the substrate in the region surrounding the defect, lateral sliding of the film may not occur, and the compressive stress in the neighborhood of the fold will not be relieved.

There have been two reports in the literature that describe similar swelling-induced fold formation. Singamaneni et al.[27,28] examined poly-2-vinylpyridine (P2VP) gel films ranging from 20 to 90 nm thick that were spuncoated onto silica surfaces and exposed to acidic conditions. Film swelling led to large amplitude folds which were observed by AFM imaging. These authors did not report on the dynamics of the fold-formation process, thus it is not clear whether the sequence of events was identical to that shown in Figure 1 and discussed above. Nevertheless the AFM images of the final structure[27,28] bear a striking resemblance to the folds seen here, especially to Supporting Information Figure S3, suggesting that similar phenomena may be at work. While Singamaneni et al.[27,28] have not fully elucidated the mechanism of fold formation, they suggest that the folds originate from creases and preserve the original geometric characteristics of the creases. In contrast, our results show that creases do not transform into folds, and indeed Case 6 in Table 1 shows that folds can arise even without creases. Singamaneni et al. also do not mention delamination as the initiation step of fold formation; indeed they state that folding requires the films to be strongly attached to the substrate, also in contradiction with our results.

In summary, our experiments show that solvent swelling of a polymer film weakly attached to a rigid substrate can lead to the formation of high aspect ratio folds. Fold formation is initiated by highly localized buckle delamination of the gel film from the substrate. Buckle delamination is well-known in nonswelling systems. For example, buckle delamination can occur when a thin film attached to a substrate experiences a compressive stress due to differential thermal expansion of the film with respect to the substrate.[18,29] Similarly, stiff strips bound to elastomeric substrates or to liquid surfaces also buckle when compressed.[30−32] From this perspective, buckle delamination due to swelling-induced compression, while not reported previously, is not altogether surprising. In contrast, the growth of permanent, irreversible folds is a new phenomenon not identified previously in swelling or nonswelling systems. We have observed swelling-induced delamination and folding in films ranging from 250 to 6 μm thickness. If Singamaneni's observations[27,28] on 90−20 nm thick films are also attributable to the same mechanism, it would indicate that the delamination/folding phenomenon scales 4 orders of magnitude. Accordingly, it may prove useful for fabricating high-aspect ratio surface features across a wide range of length-scales.

The overall process described here is complex and governed by four subprocesses: swelling, buckle delamination, vertical fold growth, and evaporation. This paper has only described the main features of the entire phenomenon and provided a qualitative model of the process. Several questions remain, most importantly what determines the spacing between folds, what determines the velocity of buckle propagation, and how film thickness affects the fold structure.[33] Yet, our physical picture of the folding process suggests that a simple way of controlling the location and structure of the folds is to pattern the substrate with regions of low adhesion that are bounded by regions of high adhesion. Delamination folding will occur in the regions of low adhesion, whereas the films will remain attached in the high adhesion regions. Unlike uncontrolled folding, the width of the folds will be set by the geometry of the low-adhesion region. Such low-adhesion patterns may be realized readily with elastomeric stamps. This strategy of programmed buckle delamination has been used in the context of flexible electronics, although in that case the delaminated region underwent simple Euler buckling into wide sinusoidal buckles rather than the sharp high-aspect ratio folds in the present paper.[34]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Two movie files and three additional figures are available as Supporting Information. This information is available free of charge via the Internet at http://pubs.acs.org/.

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■ ACKNOWLEDGMENTS

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■ NOTE ADDED IN PROOF

After this Letter was accepted, we became aware of another article[35] that observes irreversible fold formation in hydrogels and identifies film-sliding as the mechanism that permits fold growth.