



# Edge-defined metric buckling of temperature-responsive hydrogel ribbons and rings



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## ABSTRACT

We report the temperature-responsive buckling of ribbon-like hydrogel thin films based on photo-crosslinkable copolymers of poly(*N*-isopropyl acrylamide) (PNIPAM) with pendent benzophenone units. Due to the finite resolution of the photo-lithographic patterning method—here dominated by the convergence of light from the illumination source—nominally homogeneous layers are always surrounded by a more highly swelling border with a lateral size scale similar to the film thickness. As one of the in-plane dimensions of the gel sheet is reduced to only several times its thickness, this edge effect serves as a sufficiently large imperfection to drive buckling of the otherwise metrically flat ribbon. Due to the symmetric geometry, the resulting geometry has essentially constant curvature of the mid-line of the ribbon, with a radius of curvature defined by its thickness and width. In this manner, we prepare thermally responsive overcurved rings that buckle into more highly coiled configurations as they swell, due to the mismatch in metric curvature relative to the geometric shape of the object. We consider the conditions for unfrustrated coiling of both circular and polygonal rings in terms of the number of self-crossings made upon wrapping the surface of a sphere, and demonstrate the fabrication of ‘self-cinching unknots’, i.e. coiled ribbons that can fasten themselves onto other objects upon deswelling, due to topological constraints.

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## 1. Introduction

Recent years have seen great interest, and rapid advances, in the development of stimuli-responsive polymer networks for the fabrication of actuating and shape-reconfigurable materials [1–7]. A key strategy that has emerged from this work is the programming of thin sheets with in-plane non-uniformities in shrinkage, growth, or shape distortion, a principle that is also frequently found in natural morphogenetic processes [8–14]. Such patterns of deformation define a set of equilibrium distances between neighboring points (called the ‘target metric’ of the sheet) that are incompatible with the initially planar geometry of the film, thereby driving buckling into 3D shapes possessing distributions of Gaussian curvature that are defined by the pattern of distortion [15]. While considerable progress has been made in understanding and predicting the deformation of these ‘non-Euclidean plates’ [16–25],

and in fabricating buckled structures by patterning the swelling/shrinking of hydrogels [26–31], and the director orientation in liquid crystalline polymers [32–37], many open questions remain.

One area that remains incompletely understood is the importance of the sheet boundaries. Even for an idealized process that would yield a perfectly controlled metric, the presence of free boundaries can distort the shape of a finite thickness sheet, due to incompatibility of the curvature defined by the metric with the preferred (zero) mean curvature of the plate [21,38]. Further, in any real process to fabricate non-Euclidean plates, the boundary is a natural location where non-idealities may occur that give rise to imperfections in the metric. However, the sensitivity of the metric to such edge defects remains largely unexplored.

One case in which boundaries are likely to play a particularly important role is that of ribbons, where the width of the sheet is greatly reduced compared to its length. Marder and Papanicolaou found that ribbons patterned with linear variations in growth across their widths will adopt helical configurations [16], while Efrati et al. showed that hyperbolic metrics—exhibiting more extensive growth at both edges than in the center—would yield either helicoid- or catenoid-like shapes, depending on the form of

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the metric [39]. Chen et al. and Efrati et al. studied hyperbolic metrics on closed (annular) ribbons, and found that when the target Gaussian curvature and ring dimensions were commensurate, the system would adopt a ‘resonant’ state consisting of an integer number of wrinkle periods around the ring [38–40]. The complementary problem of ‘overcurved’ rings, i.e., with preferred mean curvature that does not match the geometric dimensions of the ring was studied by Mouthuy et al.; in this case, increasing overcurvature was shown to cause buckling first into a saddle-like shape, and then into multiply looped structures [41].

In the current report, we consider the importance of edge-induced ‘metric imperfections’ in driving the buckling of hydrogel strips and rings. Specifically, we employ a photo-crosslinkable hydrogel material that our groups have recently used to pattern discontinuous [27,28], or effectively continuous [26], variations in the swelling of thin gel sheets through a dual-mask photo-lithographic approach. Here, we show that as the width of the patterned gel objects is reduced to only several times their thickness, the lightly crosslinked regions at the sample edges that result from lithographic patterning give rise to a metric curvature even in nominally homogeneous gels. This provides a very simple, single-mask lithographic route to prepare temperature-responsive coiled strips, overcurved rings, and structures that tighten themselves around other object due to changes in temperature, which we dub ‘self-cinching unknots’.

## 2. Experimental section

### 2.1. Materials

A photo-crosslinkable, fluorescent, and temperature-responsive polymer was synthesized by free-radical polymerization at 80 °C in 1,4-dioxane for 15 h, following three freeze–pump–thaw cycles and a nitrogen purge, with re-crystallized azobisisobutyronitrile (AIBN, Aldrich) as an initiator, as reported previously [26]. The monomer, solvent and initiator concentrations were used as follows: *N*-isopropylacrylamide (NIPAm; 3 g, Tokyo Chemical Industry Co., Ltd), acrylamidobenzophenone (AAmBP; 533 mg), acrylic acid (AAc; 114.5 μL), rhodamine-B-labeled methacrylate (RhBMA; 47.6 mg), and AIBN (5 mg), in 30 mL of 1,4-dioxane, resulting in a copolymer with 87.2 mol% NIPAm, 7 mol% AAmBP, 5.5 mol% AAc, and 0.3 mol% RhBMA, as confirmed by <sup>1</sup>H NMR (Bruker DPX300). This PNIPAM copolymer was purified by precipitation into stirring diethyl ether, washed by filtration, and dried in a vacuum oven overnight.

### 2.2. Methods

We employ a single-mask lithographic patterning of photo-crosslinkable copolymer films. To prepare copolymer films, 3 wt% poly(sodium acrylate) (Sigma–Aldrich,  $M_w = 30$  kg/mol) was spin-coated onto a pre-cleaned  $1 \times 1$  cm<sup>2</sup> silicon substrate, yielding a ~100-nm thick film. The residual solvent was evaporated on a 150 °C hot plate for 2 h, then the film was soaked in 1.35 M CaCl<sub>2</sub> solution for 20 s to form a Ca<sup>2+</sup>-crosslinked sacrificial layer [42]. A 100 μL drop of copolymer solution in chloroform (1 wt %) was spread on the sacrificial layer, and the solvent was slowly evaporated for 5 h at 50 °C in a closed glass bottle (0.13 oz capacity glass jar, Freund Container) to yield 7–14 μm thick films, as measured using a stylus profilometer (Dektak, Veeco).

We designed mask patterns in AutoCAD (AutoDesk), and the designed patterns were printed on transparent photomasks (Front Range PhotoMask). The PNIPAM copolymer films were crosslinked by using an epi-fluorescence microscope (Zeiss Axiovert 200) and a homemade mask aligner. The film was exposed to 30 J cm<sup>-2</sup> of UV

light (excitation filter: 365 nm) through the photomask, using a 10× objective of an epi-fluorescence microscope, with the sample plane much closer to the objective than the focal plane, to improve the uniformity of illumination. This dose was found to be sufficient to fully convert the benzophenone crosslinkers within the exposed region of the film. The film was submerged in a mixture of water and ethanol (1:2 by volume) to dissolve uncrosslinked portions, then immersed in an aqueous medium (containing 1 mM NaCl, and 1 mM phosphate buffer, pH 7.2) to dissolve the sacrificial layer and induce swelling of the patterned gel films.

To demonstrate self-cinching behavior, a cylindrical glass capillary (1 mm outer and 0.6 mm inner diameters, World Precision Instruments) was tapered to a sharp tip (~10 μm diameter) using a Narishige PC-10 micropipette puller and MF-900 microforge.

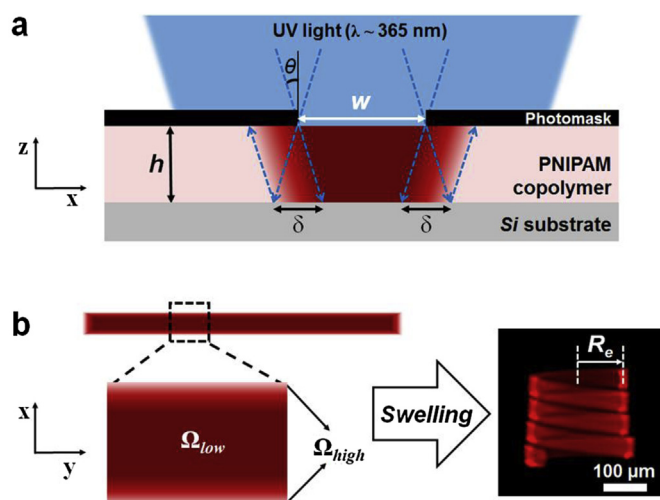
### 2.3. Characterization

Fluorescence and bright-field optical micrographs and movies were obtained using a Zeiss Axiovert 200 inverted optical microscope with either a 2.5× or a 100× oil-immersion objective, and a QImaging camera (Retiga-2000R). A swelled hydrogel reference disk was characterized using laser scanning confocal fluorescence microscopy (LSCM) (Zeiss LSM 510 META, 10× objective), wherein a HeNe laser (wavelength: 543 nm) was used to excite rhodamine-B (detection filter: 560 nm), and the 3D reconstruction performed using ImageJ software. The radius of curvature  $R_e$  of swelled strips, measured as the distance from the coil axis to the midplane of the gel, was determined from fluorescence images. The thermal response of rings was measured over the range of 22–55 °C using a microscope heat stage (Tempcontrol 37-2 digital, PeCon GmbH).

## 3. Results and discussion

### 3.1. Edge-induced metric curvature of hydrogel strips

Our approach to prepare photo-patterned gel films, as illustrated in Fig. 1, involves illumination of a photo-crosslinkable poly(*N*-isopropyl acrylamide) (PNIPAM) copolymer film of



**Fig. 1.** (a) A schematic illustration of the photo-lithographic patterning of a PNIPAM copolymer film supported on a silicon substrate, exposed using defocused UV light from an optical microscope. The convergence of the UV light leads to a gradient edge region of width  $\delta$  with a lesser degree of crosslinking than the bulk. (b) These lightly crosslinked edges give rise to a larger degree of swelling ( $\Omega$ ) compared to the center region, which upon swelling drives the sufficiently narrow strips to coil with a constant radius of curvature  $R_e$ .

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