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14. ABSTRACT This project has been focused on developing new materials chemistry and fundamental understanding that enables fabrication of new classes of micro-patterned polymer constructs containing stimuli-responsive elements. This opens the door to materials that can, for example, undergo controlled shape morphing, exhibit motility in response to a driving stimulus, or adapt their material properties in response to environmental cues. The project was highly successful, leading to 13 peer-reviewed publications, including in high impact journals. Major achievements included: (i) improved fundamental understanding of UV crosslinking of copolymers containing benzophenone					
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## Report Title

Final Report: Active Microstructured Polymer Systems

### ABSTRACT

This project has been focused on developing new materials chemistry and fundamental understanding that enables fabrication of new classes of micro-patterned polymer constructs containing stimuli-responsive elements. This opens the door to materials that can, for example, undergo controlled shape morphing, exhibit motility in response to a driving stimulus, or adapt their material properties in response to environmental cues. The project was highly successful, leading to 13 peer-reviewed publications, including in high impact journals. Major achievements included: (i) improved fundamental understanding of UV-crosslinking of copolymers containing benzophenone units, enabling development of a diverse library of photo-patternable polymer and nanocomposite materials, (ii) methods to fabricate responsive hydrogel films with precisely targeted three-dimensional shapes based on in-plane patterns of swelling, (iii) a simple new approach to characterize mechanical properties of soft and flexible polymer films, and (iv) 'continuously reprogrammable' materials capable of rapidly shifting between a nearly arbitrary number of different programmed 3D shapes over time.

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**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
12/01/2016	14 Dayong Chen, Chia-Chih Chang, Beth Cooper, Angela Silvers, Todd Emrick, Ryan C. Hayward. Photopatternable Biodegradable Aliphatic Polyester with Pendent Benzophenone Groups, Biomacromolecules, ( ): 3329. doi:
12/01/2016	15 Jun-Hee Na, Nakul P. Bende, Jinhye Bae, Christian D. Santangelo, Ryan C. Hayward. Grayscale gel lithography for programmed buckling of non-Euclidean hydrogel plates, Soft Matter, ( ): 4985. doi:
12/01/2016	16 Seog-Jin Jeon, Adam W. Hauser, and Ryan C. Hayward. Shape Morphing Materials from Stimuli-Responsive Hydrogel Hybrids, Accounts of Chemical Research, ( ): . doi:
<b>TOTAL:</b>	<b>3</b>

**Number of Papers published in peer-reviewed journals:**

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**(b) Papers published in non-peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
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**TOTAL:**

## Number of Papers published in non peer-reviewed journals:

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### (c) Presentations

“Defining reconfigurable 3D structures through buckling of polymer plates, shells, and multilayers”, International Workshop on Pattern Formation in Soft Materials, Tianjin, China 6/2/15

“Optically programmed buckling of polymer nanocomposite gels”, American Chemical Society, PMSE Division, Symposium on Stimulus-Responsive Assemblies and Materials, 3/22/15.

“Patterning, manipulating, and characterizing polymer gel sheets and multilayers with programmed 3D configurations using optical microscopes”, New England Society of Microscopy Meeting, UMass Amherst, 10/2/14.

“Swelling-driven shaping of responsive polymer sheets and multilayers”, IUTAM Symposium on Soft Active Materials, Haifa, Israel, 5/14/14

“Measuring mechanical properties of thin hydrogel sheets by elasto-capillary origami”, APS March Meeting, Denver, CO, 3/5/14 (contributed: J. Bae presenting)

“Buckling instabilities of polymer multilayers”, APS March Meeting, Denver, CO, 3/4/14

“Patterned sheets and multilayers of photo-crosslinkable polymers”, American Institute of Chemical Engineers, San Francisco, CA, 11/5/13

“Photo-crosslinkable polymers for responsive gel sheets and multilayers”, American Chemical Society Fall Meeting, Indianapolis, IN, 9/12/13

“Polymer networks for the design of soft active materials”, American Chemical Society Fall Meeting, Indianapolis, IN 9/8/13 (Journal of Polymer Science Innovation Award Talk)

“Grayscale gel lithography: From multi-strips to responsive origami”, American Physical Society March Meeting, Baltimore, MD, 3/21/13 (Contributed, M. Byun presenter)

“Photo-crosslinkable materials for responsive origami”, Interdisciplinary Meeting on Adaptive Origami, Dayton, OH, 1/16/13

“Responsive Materials by Buckling of Soft Elastic Sheets”, Materials Research Society Fall Meeting, Boston, MA 11/29/12

“Patterned growth of photo-crosslinkable polymer sheets”, Workshop: Modern Perspectives on Thin Sheets: Geometry, Elasticity, and Statistical Physics; Lorentz Center, Leiden, Netherlands, 9/5/12

“Patterning growth with photo-crosslinkable copolymer films”, Warwick 2012, Warwick, UK, 7/12/12

“Photo-patterned growth of stimulus-responsive gel sheets”, American Chemical Society Spring Meeting, San Diego, CA, 3/25/12

“Reversible folding of micro-patterned hydrogel sheets”, Pacific Polymer Chemistry, Jeju Island, Korea, 11/11

“Swelling of constrained and patterned hydrogel sheets: New approaches to active surfaces and polymer micro-devices”, American Chemical Society Colloid and Surface Science Symposium, Montreal, CA, 6/21/11 (Unilever Award Plenary Lecture)

“Rolling, folding, and creasing of photo-patterned hydrogel sheets”, MRSEC Spring Workshop, University of Massachusetts Amherst, 5/12/11

Number of Presentations: 18.00

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**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

Received      Paper

**TOTAL:**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

Received      Paper

**TOTAL:**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

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**(d) Manuscripts**

Received      Paper

12/01/2016 9.00 D. Chen, J. Yoon, D. Chandra, A.J. Crosby, R.C. Hayward. Stimuli-responsive buckling mechanics of polymer films,  
Journal of Polymer Science Part B: Polymer Physics (08 2014)

**TOTAL:      1**

Number of Manuscripts:

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**Books**

Received      Book

**TOTAL:**

Received      Book Chapter

**TOTAL:**

**Patents Submitted**

A.W. Hauser, R.C. Hayward, Method of preparing polymer nanocomposites, Provisional Patent Application UMA 15-037  
~~(Filed with US PTO Jan. 13, 2015).~~

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**Patents Awarded**

**Awards**

2014 Dudley A. Saville Lectureship (Princeton University)  
2014 John H. Hillon Medal, American Physical Society  
2013 Journal of Polymer Science Innovation Award  
2011 American Chemical Society Division of Colloid and Surface Chemistry Unilever Award

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**Graduate Students**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Names of Post Doctorates**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Names of Faculty Supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Names of Under Graduate students supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Student Metrics**

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 5.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 5.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 3.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 4.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 1.00

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**Names of Personnel receiving masters degrees**

<u>NAME</u>
<b>Total Number:</b>

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**Names of personnel receiving PHDs**

<u>NAME</u>
<b>Total Number:</b>

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**Names of other research staff**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Sub Contractors (DD882)**

**Inventions (DD882)**

**Scientific Progress**

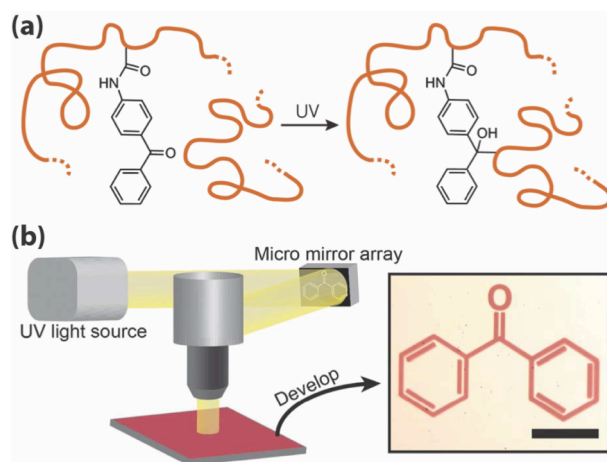
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**Technology Transfer**

The goal of this project has been to develop the materials chemistry and fundamental understanding needed to enable fabrication of new classes of micro-patterned polymer constructs containing stimuli-responsive elements that give rise to, for example, controlled shape morphing, motion, and adaptive material properties. As summarized below, the project was highly successful, leading to 13 peer-reviewed publications, including both primary research articles in high impact journals (*Science*, *Angewandte Chemie International Edition*, *ACS Applied Materials & Interfaces*) and two invited review papers (in *Journal of Polymer Science B* and *Accounts of Chemical Research*) describing work supported by this award alongside other important work in the field. We divide the progress made during this project into three major themes: (i) chemistry of photo-crosslinkable copolymer materials, (ii) geometry and mechanics of shape-morphing hydrogels, and (iii) continuously reprogrammable materials.

### *Chemistry of photo-crosslinkable copolymer materials*

The first aim of our work has focused on the development of libraries of copolymers containing pendent benzophenone (BP) photo-crosslinkers, which can be excited to a triplet diradical state under UV irradiation and, under appropriate conditions, yield covalent crosslinking via hydrogen abstraction and radical coupling (Figure 1a). Although this basic photochemistry has long been known, and even applied to generate photo-crosslinkable polymer films, our fundamental studies shed new light on the mechanism of crosslinking and the dependence on the chemistry of the BP-containing copolymer [1]. In particular, we established that the placement of highly abstractable hydrogen species (such as on tertiary or benzylic carbons, or those located alpha to ethers or amines) pendent to the copolymer chain, rather than on the polymer backbone, are essential for efficient crosslinking. Using this understanding, we have shown how a wide variety of materials can be effectively photo-patterned [1], including numerous examples of stimuli-responsive hydrogels, rigid (glassy) polymers, elastomers, and biodegradable polymers [2]. We further extended these studies to photografting of polymers to nanoparticles (NPs) bearing ligands with sites highly reactive to abstraction by triplet BP, yielding a simple approach to well-dispersed and photo-crosslinkable polymer nanocomposites (Figure 1b) [3]. Finally, we used BP-containing photo-crosslinkable hydrogel films, in concert with a newly developed method for measuring the elastic modulus of thin films through elasto-capillary bending, to correlate the degree of crosslinking with the modulus and swelling ratio of these materials [4]. This allowed us to verify the



**Figure 1.** (a) UV-crosslinking of copolymers containing pendent BP moieties. (b) Schematic (left) of photo-patterning of a BP-containing film and optical micrograph (right) of a patterned film of a polymer nanocomposite containing gold NPs (scale bar: 300  $\mu\text{m}$ ).



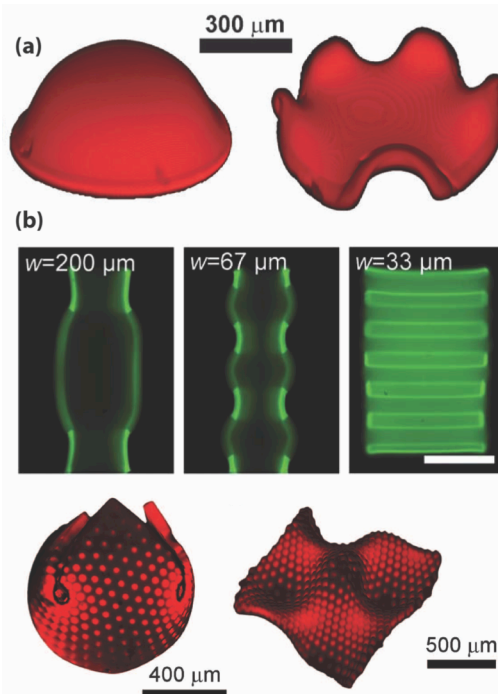
previously untested prediction that the volumetric swelling ratio depends on crosslink density to the  $-3/2$  power in polyelectrolyte gels at low salt concentrations, in strong contrast to the much weaker  $-3/5$  dependence for neutral gels, a key enabling feature in the use of these materials for shape-morphing hydrogels.

### *Geometry and mechanics of shape-morphing hydrogels*

Enabled by this powerful material system of photo-crosslinkable BP-containing copolymers, we were able to develop a new paradigm for fabrication of shape-morphing materials and shed fundamental insight on the underlying geometry and mechanics. As the conversion of BP units to crosslinks depends on the dose of light received, it is straightforward to pattern the degree of crosslinking, and therefore the volumetric swelling of the resulting hydrogel, simply by exposing a polymer film to different doses in different regions. Since crosslinking is carried out in a polymer film (often in the glassy state), lateral diffusion is essentially negligible, leading to a spatial resolution that is limited only by the lithographic patterning process employed. As described in more detail in our review articles [5,6], and references therein, such lateral variations in swelling drive buckling of the initially planar sheet into curved 3D shapes. Critically, this provides a route to shapes with *non-zero Gaussian curvature*, i.e. having curvature along multiple directions at each point on the surface (like a sphere or a saddle). This is in stark contrast to strategies based on through-thickness variations in swelling, which generally yield only shapes that are locally cylindrical. This principle is well known in differential geometry (i.e., Gauss’s *Theorema Egregium*) and cartography (i.e., the distortion inherent to flattening the globe), and has been appreciated as a key mechanism in biological morphogenesis, but prior to our work, no methods existed for introducing truly 2D patterns of swelling in stimuli-responsive polymer films.

In one approach, we use a maskless grayscale lithographic method, enabled by a digital micromirror array device connected to an inverted optical microscope (Figure 1b) to assign the UV dose received at each pixel to one of a large number of discretely spaced values (e.g., 256). Since the difference in swelling between each of the discrete levels is very small, and the spacing between pixels ( $1.4\ \mu\text{m}$ ) is similar to the optical resolution of the projection system, the resulting spatial distribution of swelling is smooth. This allows us to prepare precisely defined 3D shapes in a deterministic fashion based on the geometric correspondence between variations in swelling and Gaussian curvature, for example the spherical cap and 5-fold wrinkled surfaces shown in Figure 2a [7].

Although quite powerful for defining controlled 3D shapes, this grayscale approach is likely to be challenging to scale to smaller dimensions and parallel fabrication. Thus, we also sought to understand how hydrogel films with discrete features, which can easily be prepared by conventional high-contrast (“black and white”) photolithography, as well as any number of other



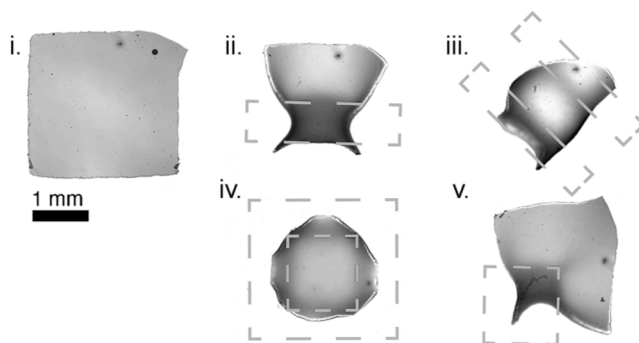
**Figure 2.** (a) Programmed shapes prepared by grayscale lithography. (b) Sheets with alternating stripe width  $w$  roll for large  $w$  but remain flat for small  $w$  (scale bar:  $400\ \mu\text{m}$ ). (c) Programmed shapes prepared by halftone lithography.

patterning/printing methods across a wide range of length-scales. Previous to our work, however, there was little understanding of how a sharp in-plane discontinuity in swelling would drive deformation of a thin film. Thus, we first studied the simple case of sheets patterned with alternating parallel stripes of high- and low-swelling regions [8, 9]. Interestingly, we discovered that the sheets seek to roll around the axis perpendicular to the interfaces, yielding a ‘bottleneck’ shape around each interface that connects two (zero Gaussian curvature) cylinders of different sizes via a transition zone that contains both positive and negative Gaussian curvature (Figure 2b). The sharp contrast in swelling favors a tight transition, but this also requires a small radius of curvature, which costs a large amount of bending energy. Thus, the system selects an intermediate value of curvature that depends on both the sheet thickness and the lateral dimensions of the stripes. Remarkably, for ribbons of hydrogel with sufficiently small in-plane dimensions and nominally homogeneous crosslinking, it is even possible to see this effect due to the swelling variations at each edge of the ribbon (defined by the lateral broadening introduced by the lithographic process) [10].

While this picture works well for sufficiently thin sheets (or sufficiently wide stripes), it breaks down as the sheet thickness approaches the stripe dimensions, and instead the sheet becomes an anisotropic composite that swells unequally along the two in-plane directions, but remains globally flat (Figure 2b). At some level this transition is not surprising, as we know that embedding stiff fibers that are very small compared to the sheet thickness should provide a composite response. What is remarkable, however, is that the transition occurs when the characteristic spacing between stripes is still fairly large, roughly 5 times the film thickness in our experiments. Thus, even with a relatively low-resolution lithographic process and/or a relatively thin film, it is possible to prepare micro-patterned composites. Importantly, similar arguments apply equally well for two-dimensional swelling patterns, and indeed we found that for circular dots on a hexagonal lattice, the transition to a composite response occurred at a slightly larger multiple of the film thickness ( $\approx 8$ ) [11]. Using this principle, we showed how a ‘halftone’ lithography approach, requiring only two high-contrast photo-masks, could be used to effectively simulate smooth patterns in swelling simply by introducing spatial variations the size of highly crosslinked dots in a lightly crosslinked matrix (and therefore the local composite swelling response). Similar to the grayscale method, we were able to prepare a variety of precisely-targeted and non-zero Gaussian curvature shapes, including the nearly complete sphere and corrugated surface shown in Figure 2c [11, 12].

### *Continuously reprogrammable materials*

A key limitation of the shape-morphing materials described above, and nearly all other approaches in the field prior to our work, is that they can only access a continuous trajectory of shapes between the initial flat state and one (or sometime several closely related) target shape pre-programmed into the material. This informed the third major goal of the project, which was to develop a route to continuously reprogrammable materials. To achieve this goal, we designed a system of nanocomposite photo-thermally responsive hydrogels based on poly(*N*-isopropyl acrylamide) copolymer networks containing embedded plasmonic gold NPs



**Figure 3.** An initially planar (i) sheet of photo-thermally addressable nanocomposite hydrogel is reversibly deformed into four qualitatively different shapes in sequence (ii – v) by shining spatially patterned light as denoted by the dotted boxes.

[13]. Local illumination of a thin sheet of composite gel with visible light leads to heating based on the surface plasmon absorption of the gold particles. Although the resulting temperature profile is broadened by thermal diffusion, this effect can easily be modeled and accounted for. Thus, by shining a time-varying pattern of light on the material, it is possible to continuously redefine the spatial temperature (and therefore swelling) profile, and thus the 3D shape adopted. The reliance on photo-thermal heating, rather than photochemical switching, provides rapid response kinetics for sufficiently thin sheets (limited by mass transfer of water into and out of the hydrogel) and a high degree of reversibility. In addition to allowing a single composite sheet to be shaped and reshaped into several qualitatively different shapes (Figure 3) designed according to the principles described above, repeated sweeping of a band of light across the sheet was found to drive controlled locomotion.

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