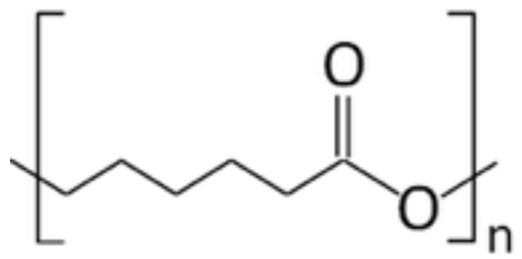
# Stimuli Responsive Polymer

Nov 18, 2014

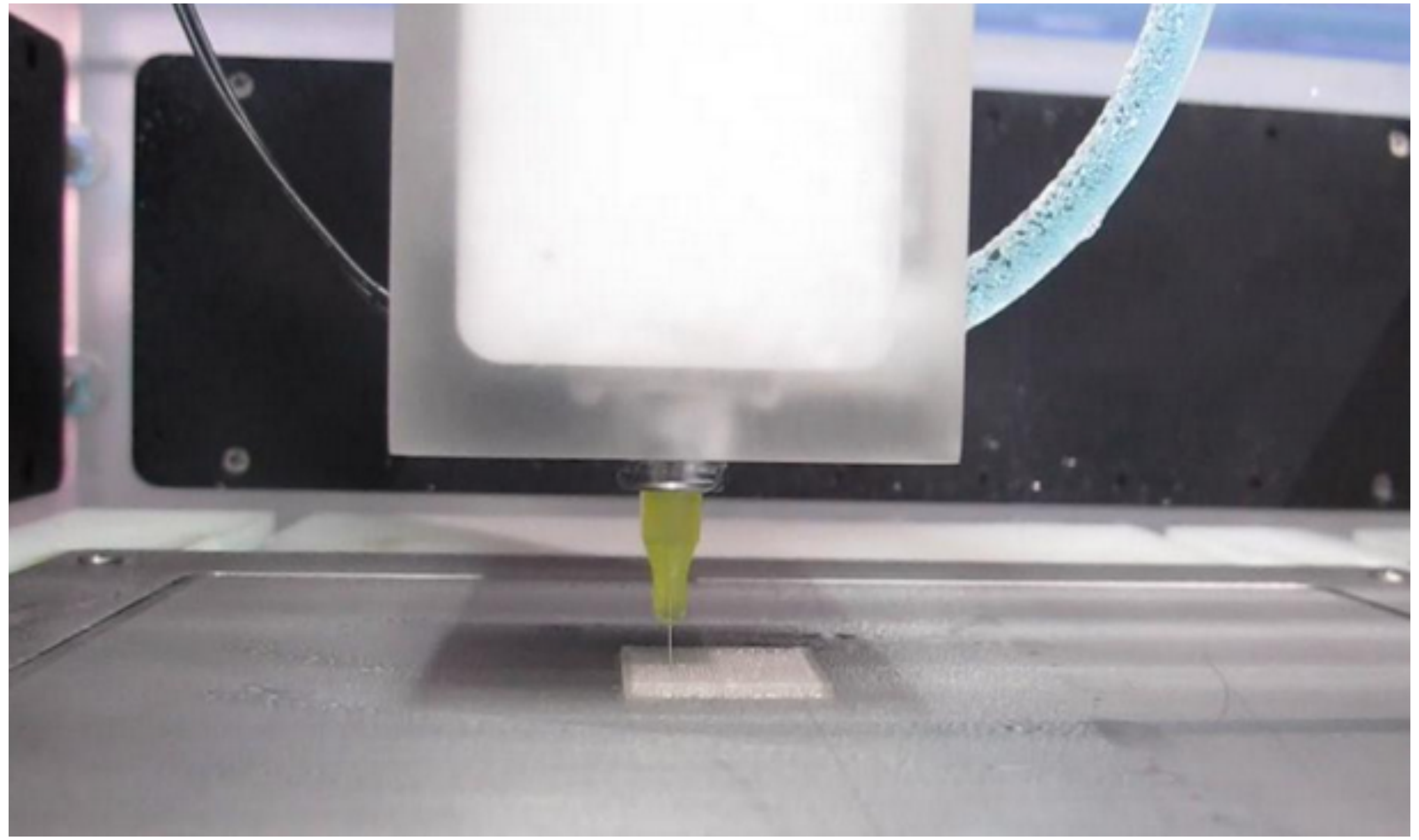
**PCL (polycapro-lactone)**

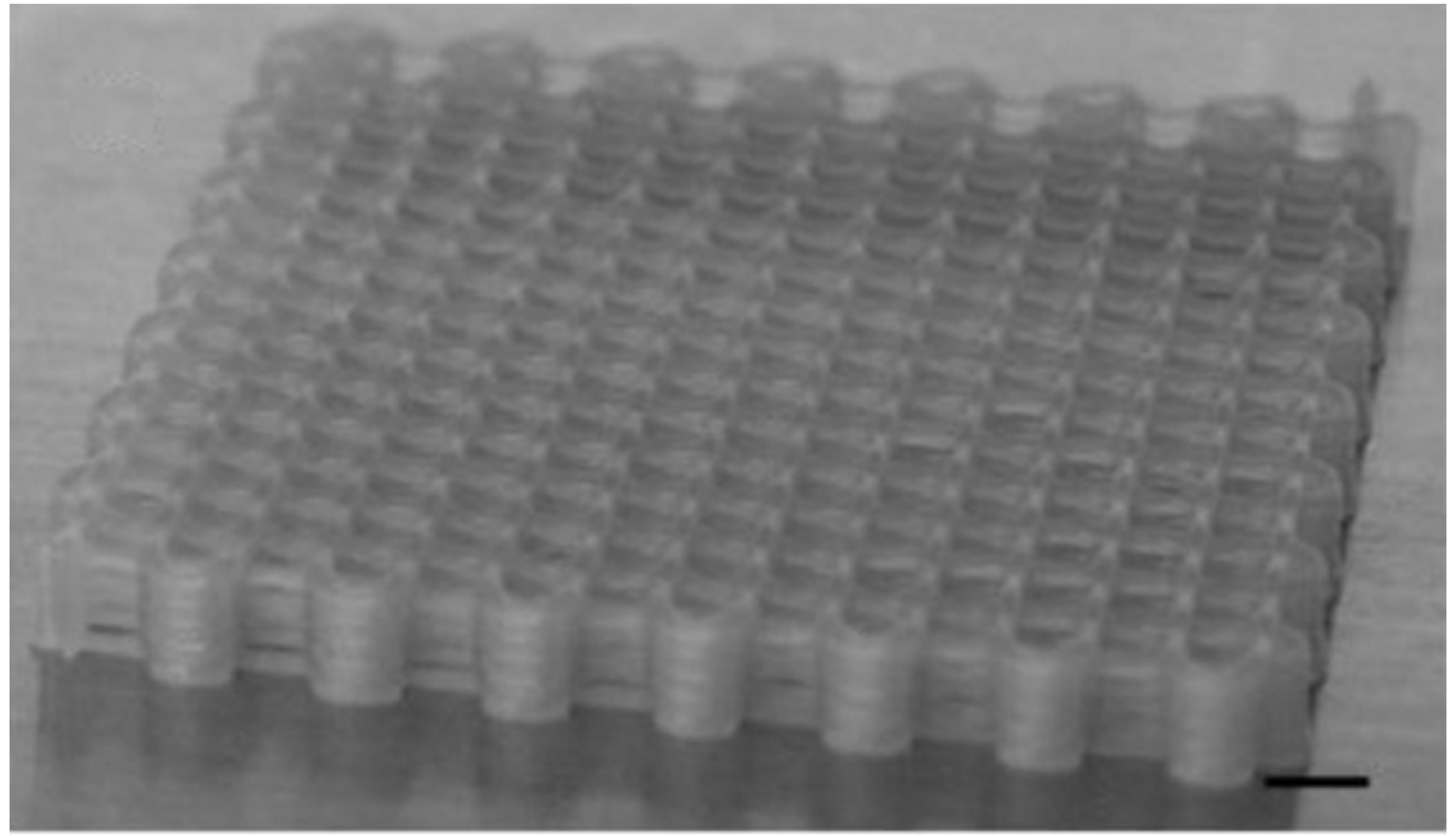
**Principles**

Polycaprolactone (PCL) is a biodegradable polyester with a low melting point of around 60°C



3D bio-printer





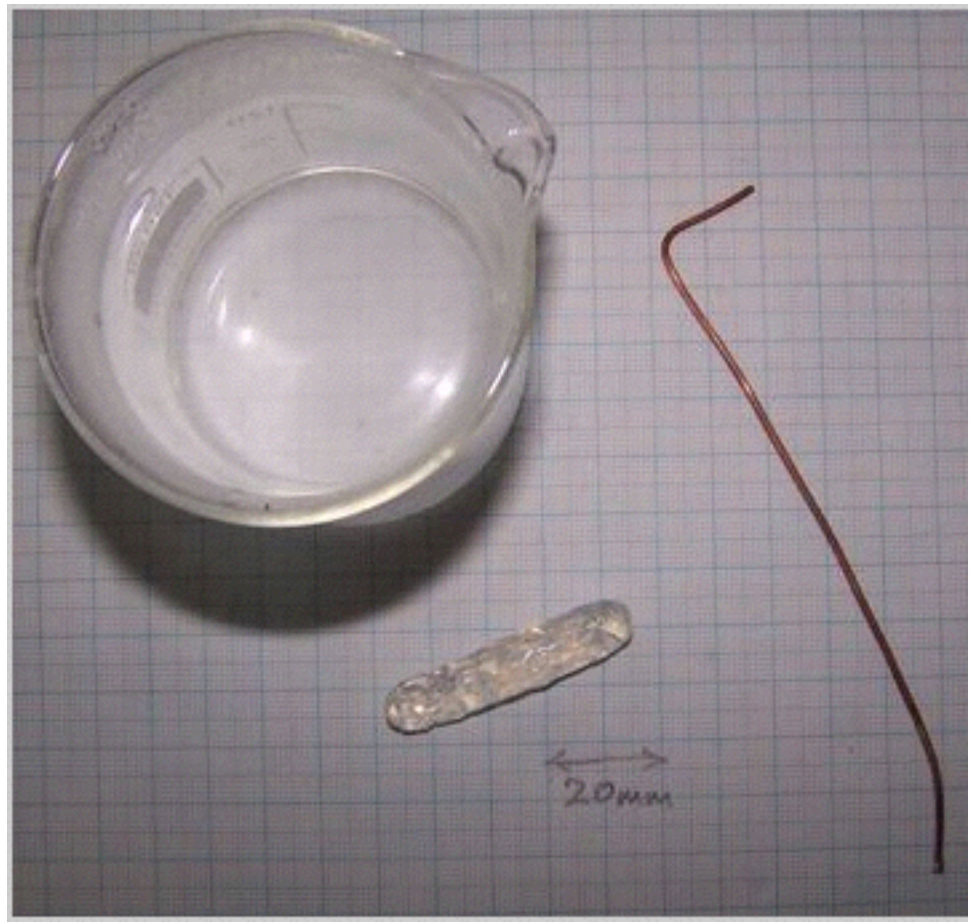
**Example 3D-printed scaffold (bar is 1mm)**

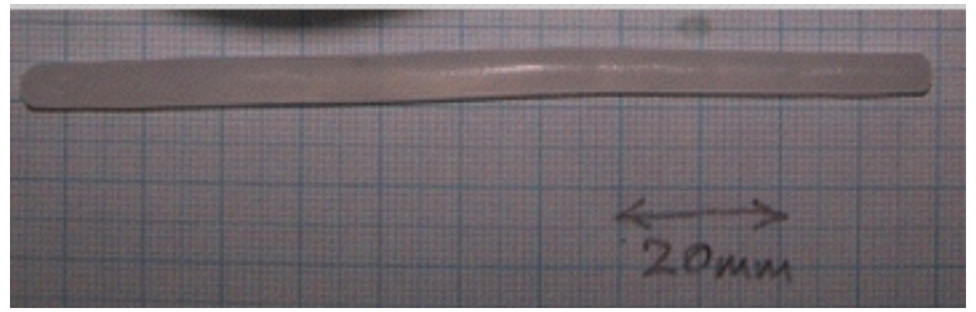
Image From: Seyednejad, Hajar, Debby Gawlitta, Wouter JA Dhert, Cornelus F. van Nostrum, Tina Vermonden, and Wim E. Hennink. "Preparation and Characterization of a 3D-printed Scaffold Based on a Functionalized Polyester for Bone Tissue Engineering Application." *Functionalized Polyesters* 7, no. 5 (2012): 87.

http://www.youblob.com/content/regenovo-3d-bioprinter

# Demo





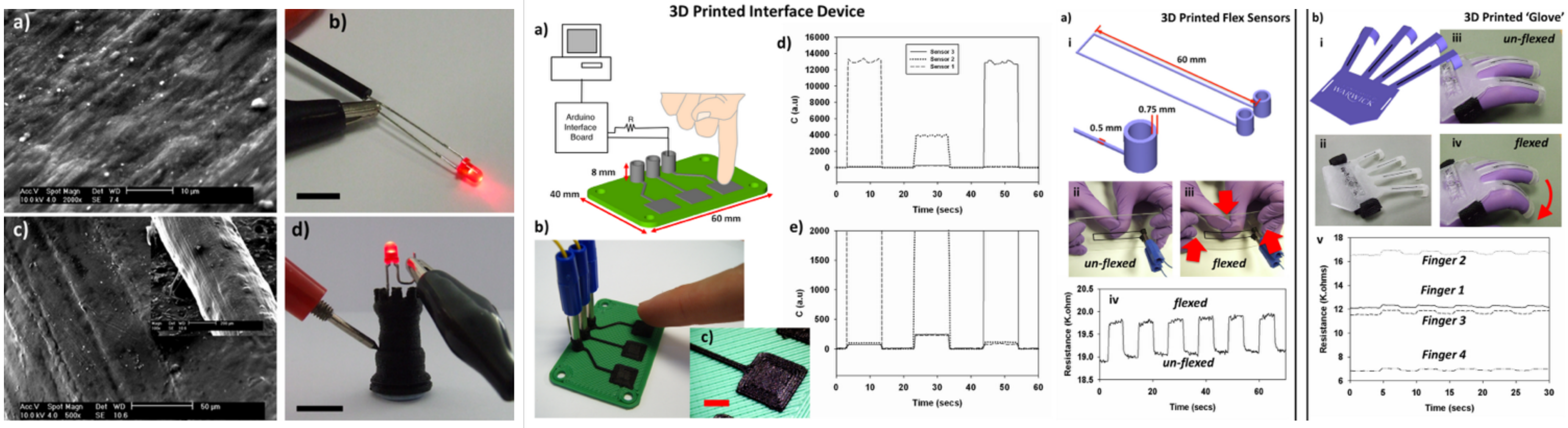




http://reprap.org/wiki/Polycaprolactone

# Potentials

## Conductive and Printable

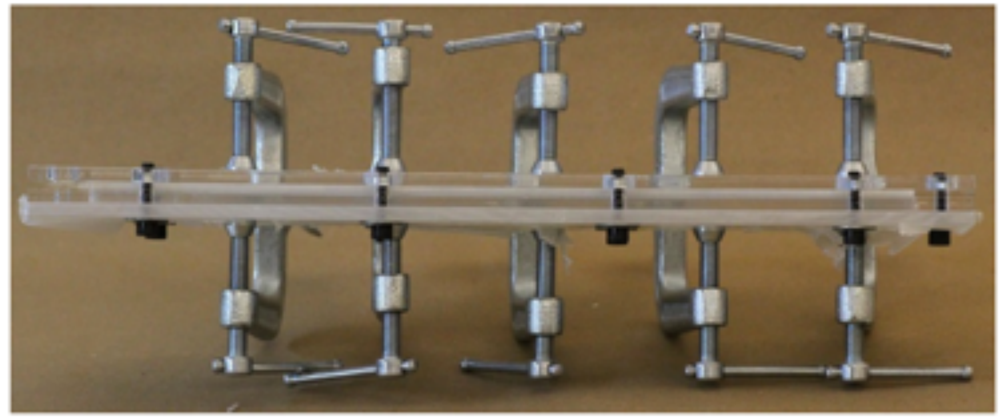
PCL can be mixed with carbon black to make a printable conductive filament called carbomorph, as described in this paper: A Simple, Low-Cost Conductive Composite Material for 3D Printing of Electronic Sensors.



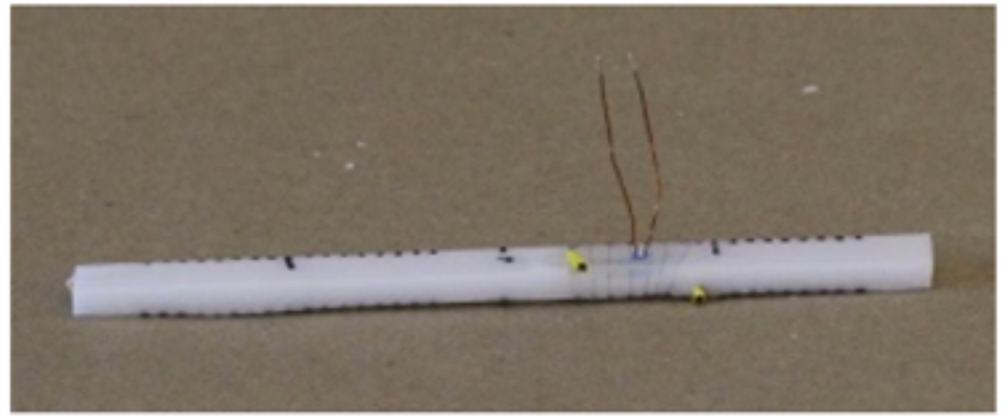

A Simple, Low-Cost Conductive Composite Material for 3D Printing of Electronic Sensors. Simon J. Leigh, Robert J. Bradley, Christopher P. Purssell, Duncan R. Billson, David A. Hutchins, November 21, 2012DOI: 10.1371/journal.pone.0049365

## Stiffness Change

(a) PCL pellets are melted in a hot water bath.



(b) The molten PCL is pressed into a mold to make $12.5 \times 5.0mm$ bars. Bars are cut into $152.4mm$ lengths when removed from the mold.



(c) Each bar is marked and wrapped with Nichrome wire at 1 revolution per 3.2mm. A thermistor is embedded into the center of the Nichrome wire wrap.

M. A. McEvoy, N. Correll (2014): Shape Change Through Programmable Stiffness. International Symposium on Experimental Robotics (ISER), Springer Verlag, Marrakech, Morocco, 2014.

# Stiffness Change

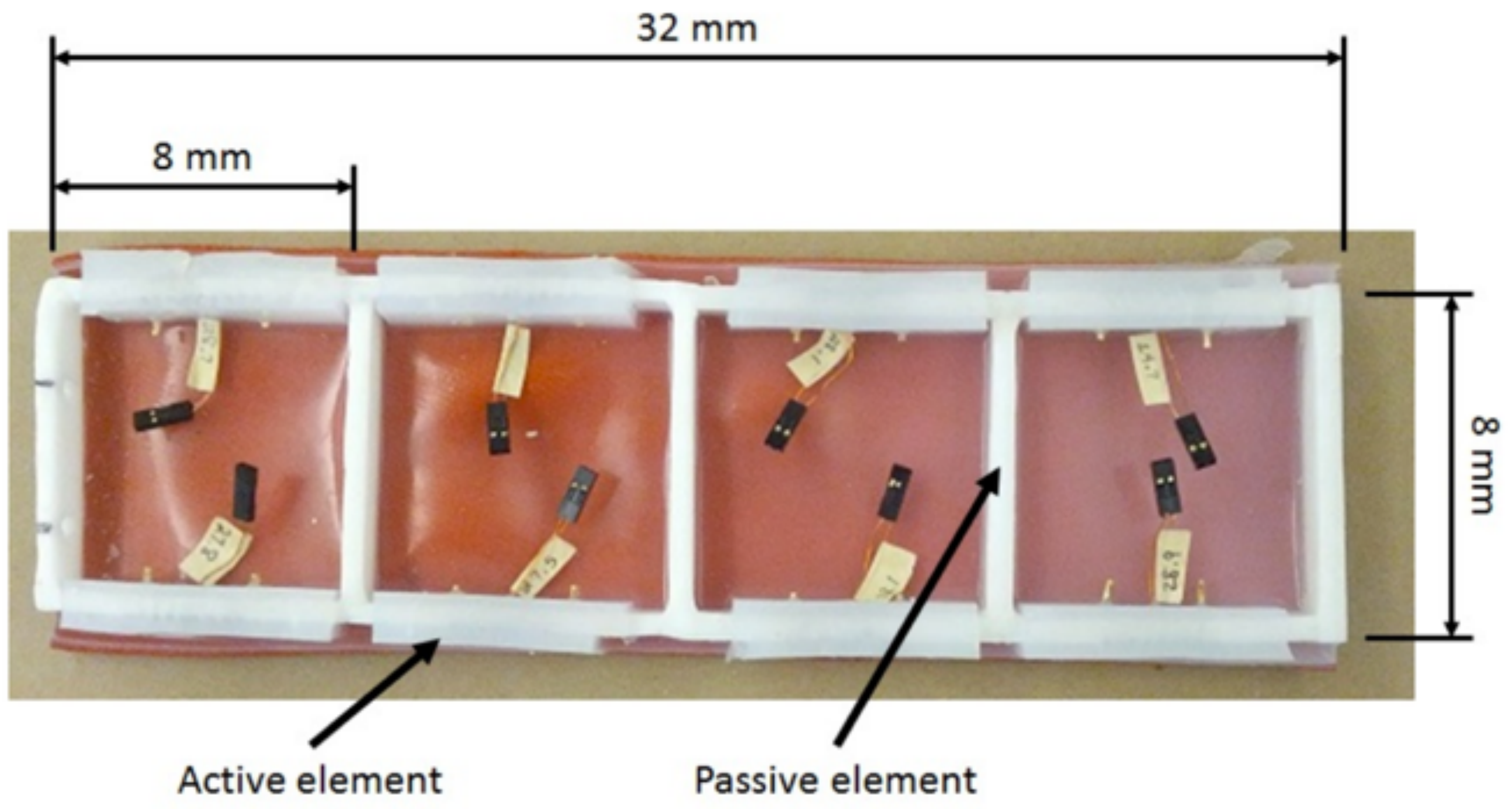
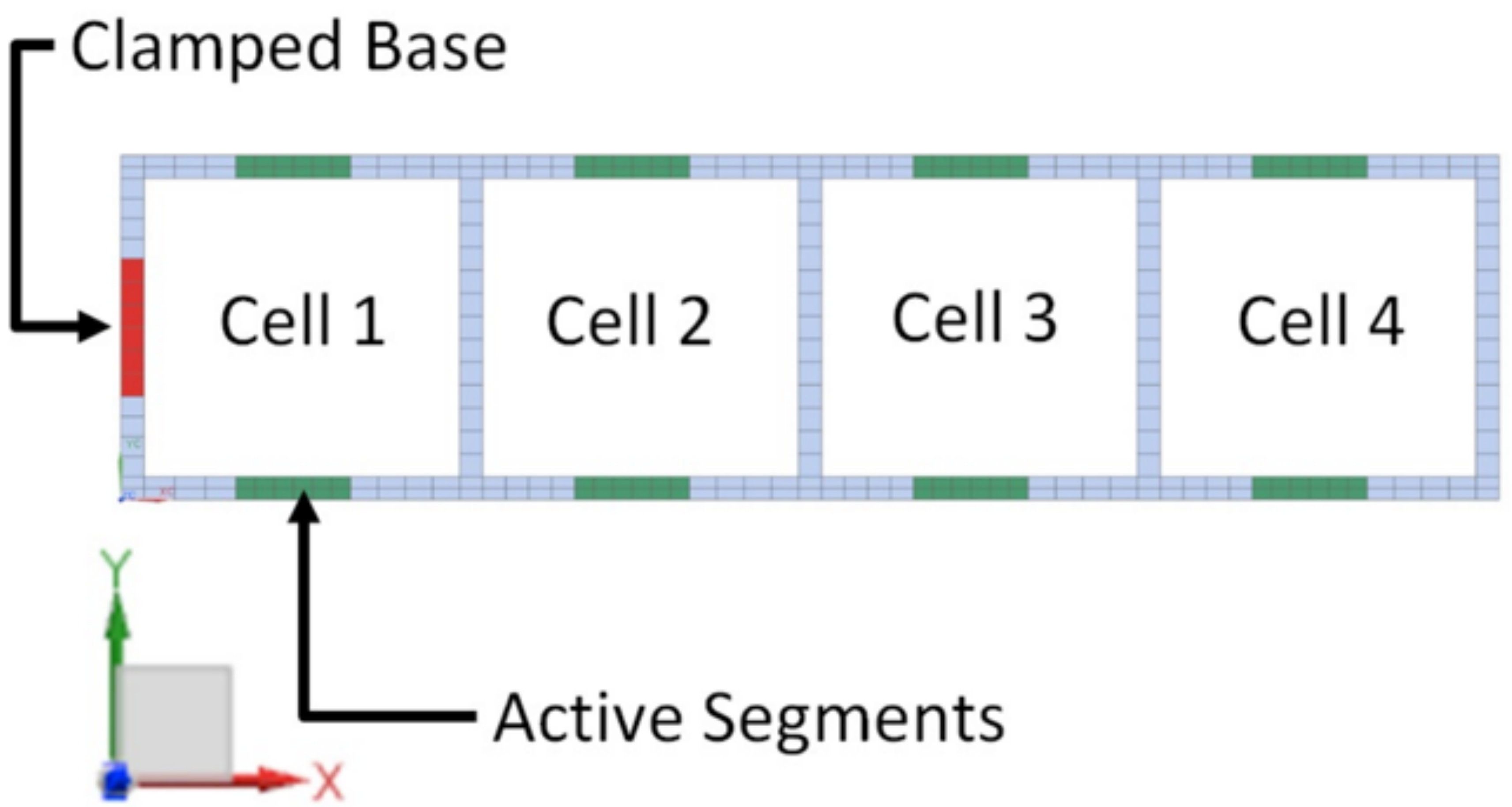
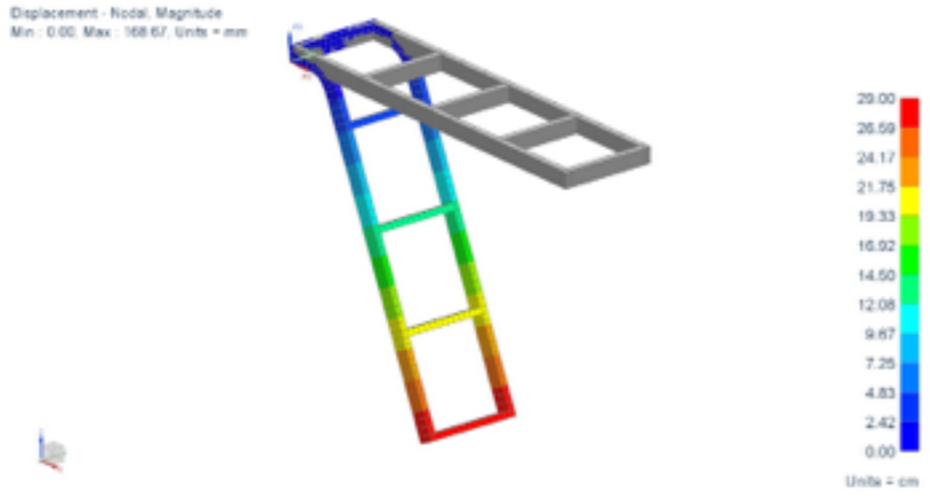



Fig. 2: Individual bars are welded together with an air gun then coated with silicon. This ensures that the sections of PCL that are heated to melting are contained.

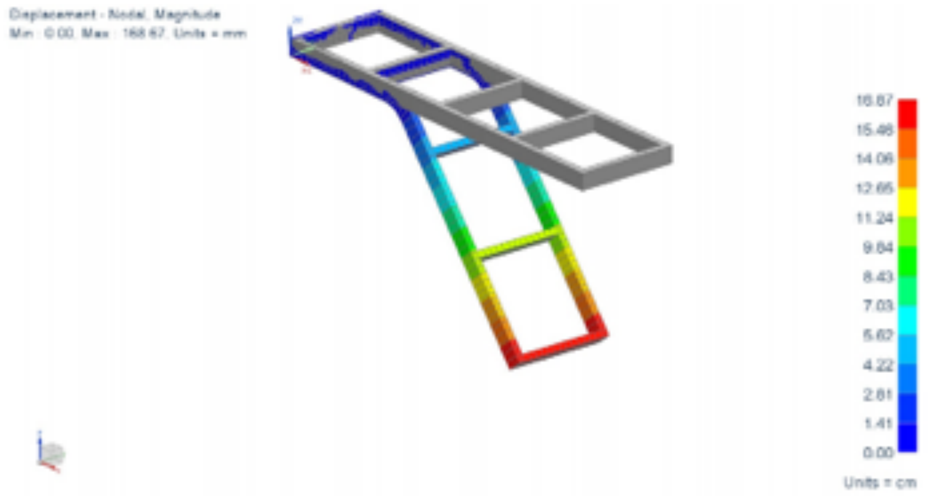



M. A. McEvoy, N. Correll (2014): Shape Change Through Programmable Stiffness. International Symposium on Experimental Robotics (ISER), Springer Verlag, Marrakech, Morocco, 2014.

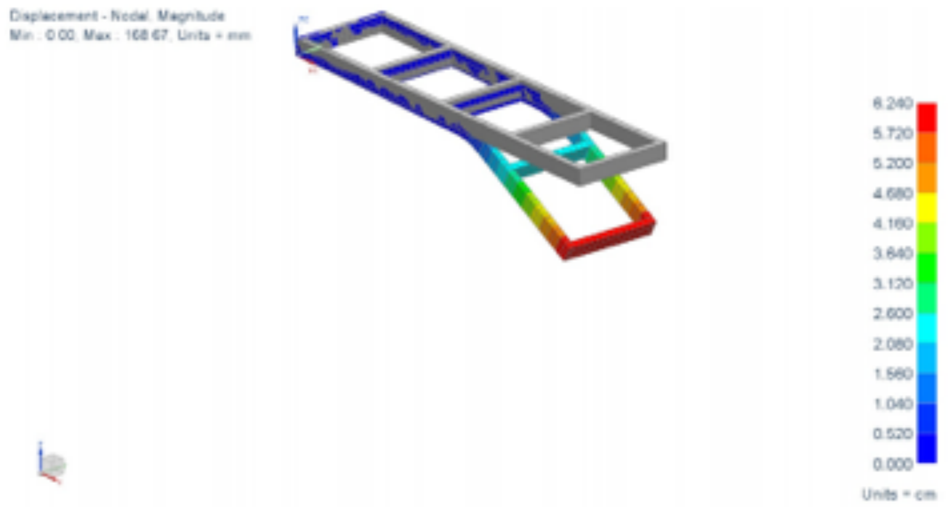
## Stiffness Change



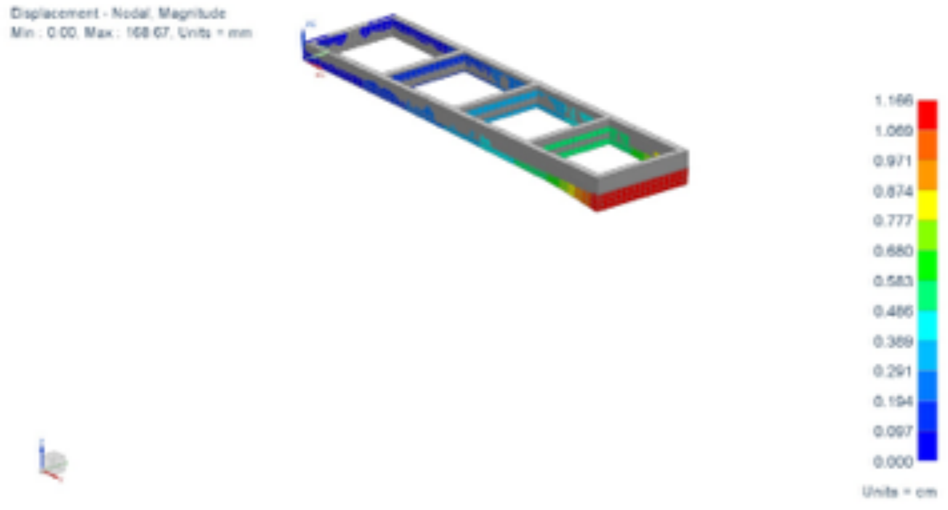
(a) The 4x1 test beam with both segments in cell 1 activated.



(b) The 4x1 test beam with both segments in cell 2 activated.



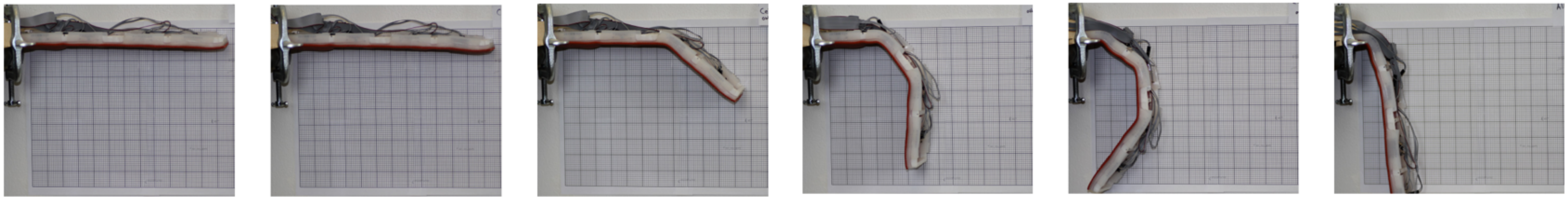
(c) The 4x1 test beam with both segments in cell 3 activated.



(d) The 4x1 test beam with both segments in cell 4 activated.

M. A. McEvoy, N. Correll (2014): Shape Change Through Programmable Stiffness. International Symposium on Experimental Robotics (ISER), Springer Verlag, Marrakech, Morocco, 2014.

## Stiffness Change



(a) Initial configuration: the 4x1 test beam with all of the cells inactive, i.e. all of the PCL bars are at room temperature.

(b) Initially the 4th cell is activated to 50 °C and the others are left at room temperature.

(c) The 4th cell is allowed to cool and the 3rd cell is activated to 50 °C.

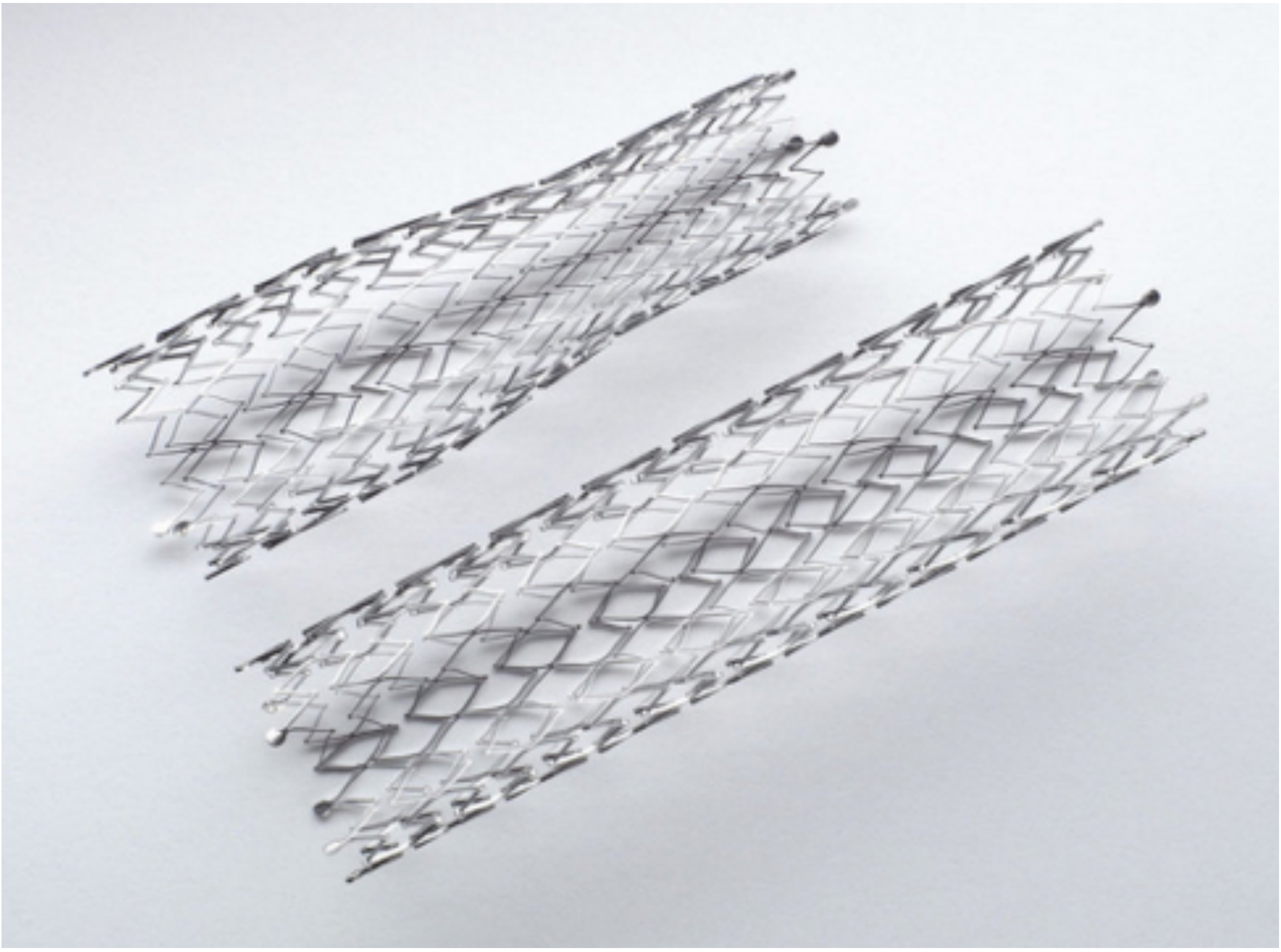
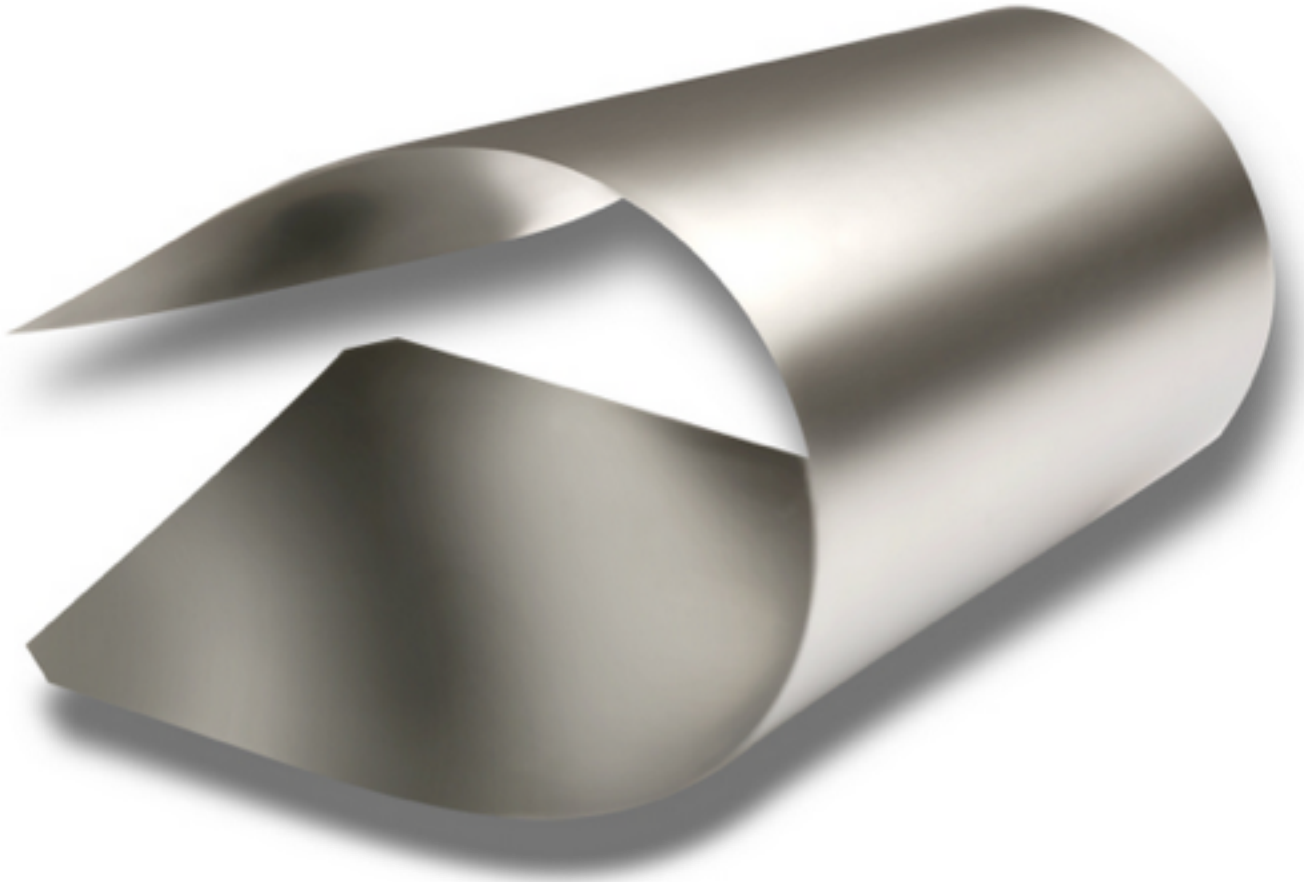
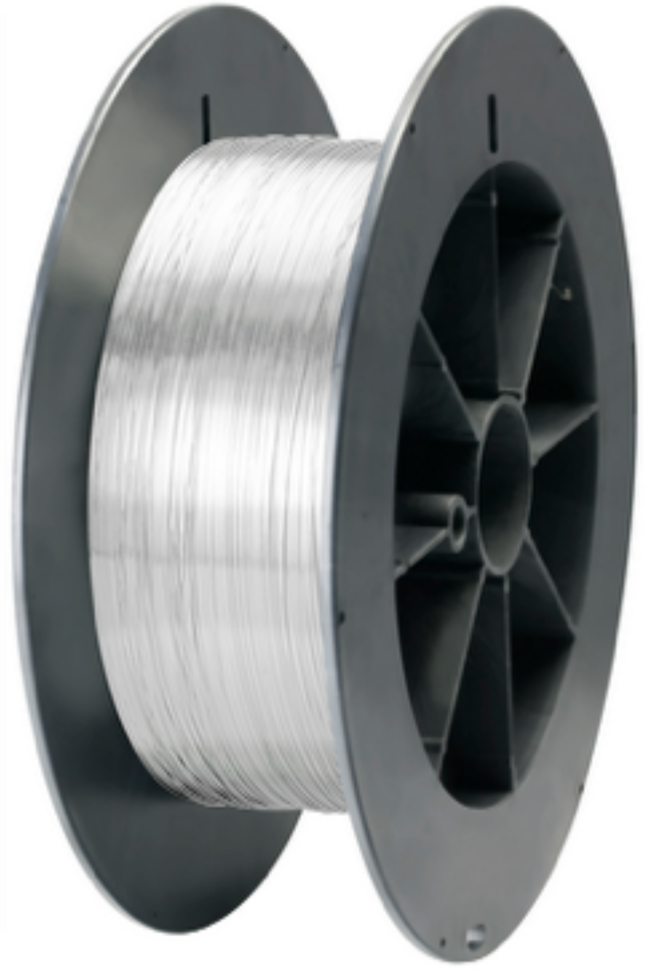
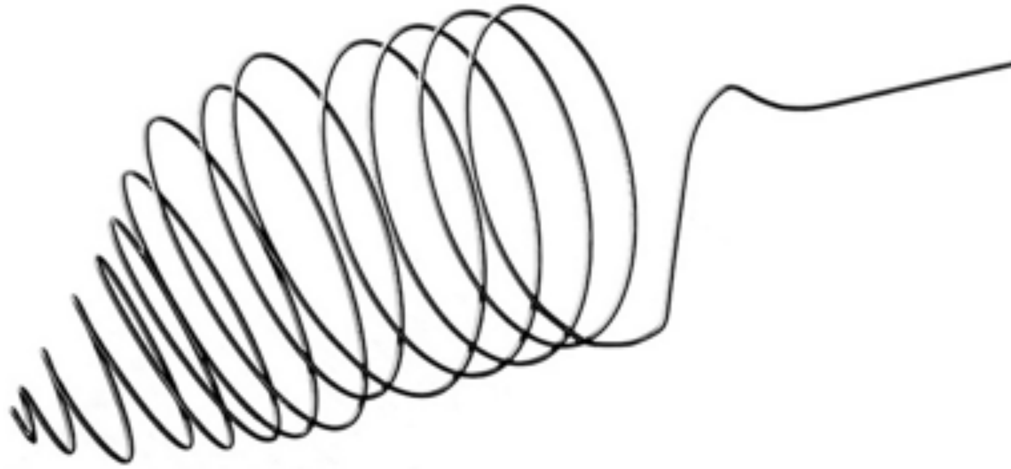
(d) Next, the 3rd cell is allowed to cool and the 2nd cell is activated to 50 °C.

(e) Lastly, the 2nd cell is allowed to cool and the 1st cell is activated to 50 °C. This geometry is only possible to achieve with distributed local control schemes.

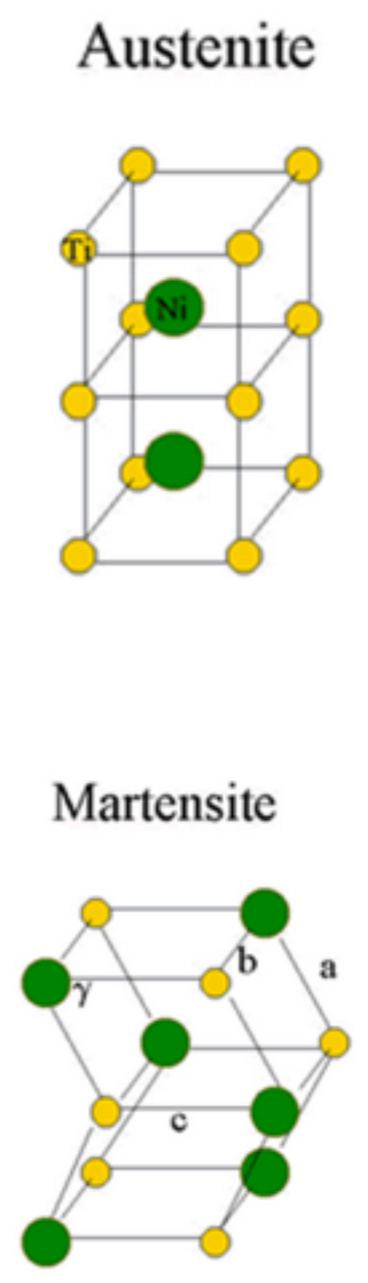
(f) Compare with all of the elements activated, demonstrating the conformation that arises with global simultaneous activation of all elements.

M. A. McEvoy, N. Correll (2014): Shape Change Through Programmable Stiffness. International Symposium on Experimental Robotics (ISER), Springer Verlag, Marrakech, Morocco, 2014.

SMA

# Principles


Austenite
Ti
Ni
Martensite
b
a
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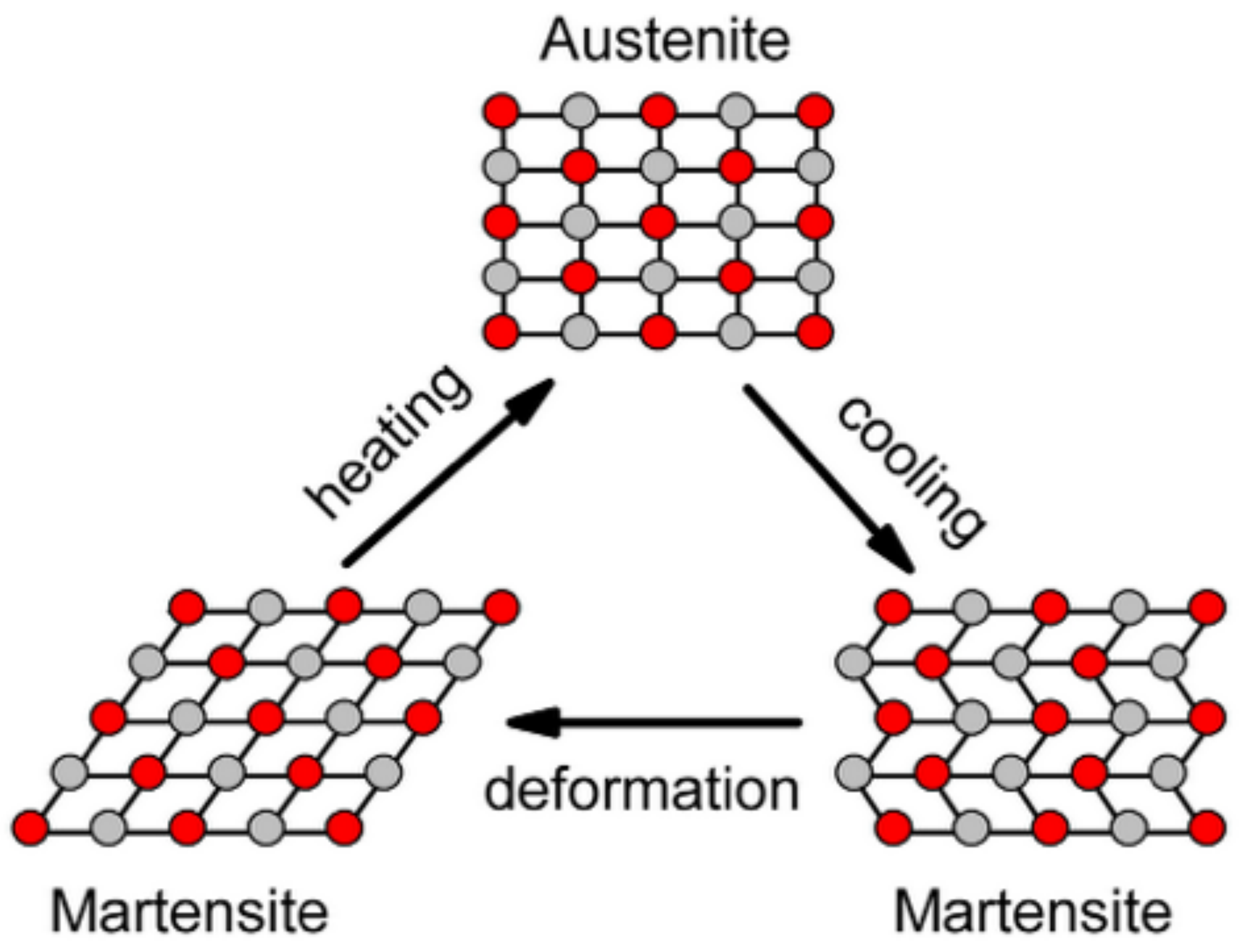
c


Austenite
heating
cooling
deformation
Martensite
Martensite

Sangbae Kim; Hawkes, E.; Kyujin Cho; Joldaz, M.; Foleyz, J.; Wood, Robert, "Micro artificial muscle fiber using NiTi spring for soft robotics," Intelligent Robots and Systems, 2009. IROS 2009. IEEE/RSJ International Conference on , vol., no., pp.2228,2234, 10-15 Oct. 2009

# demo: make your own Nitinol spring

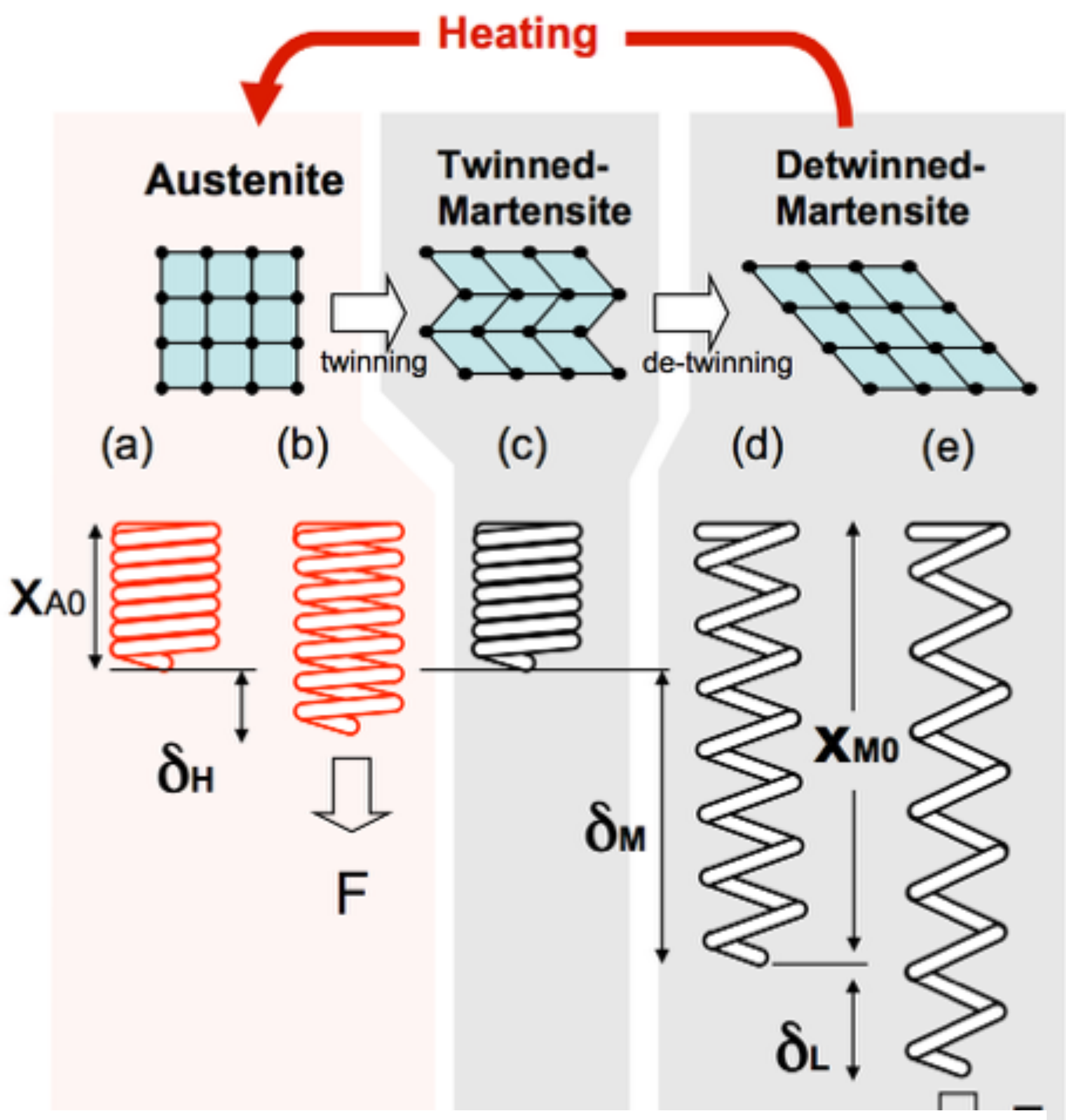
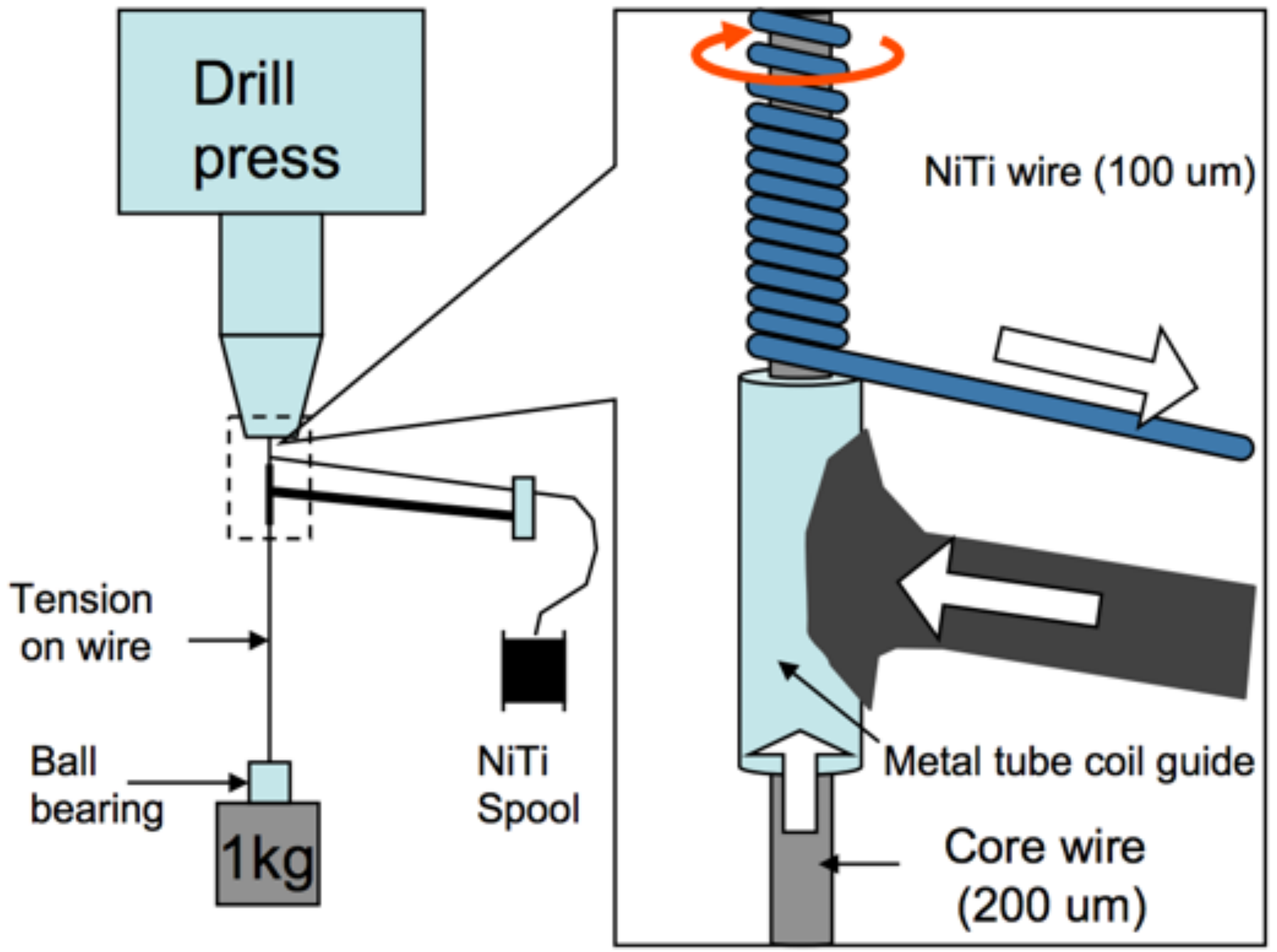
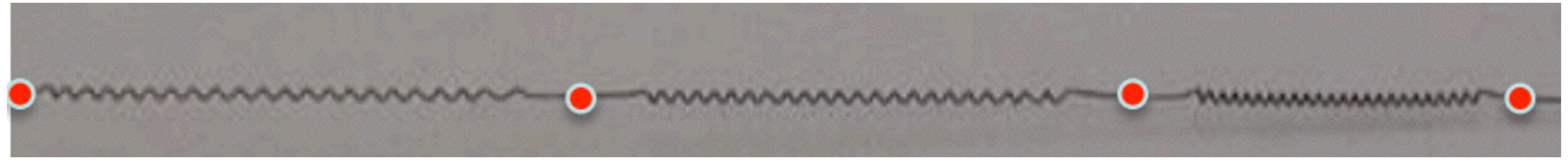


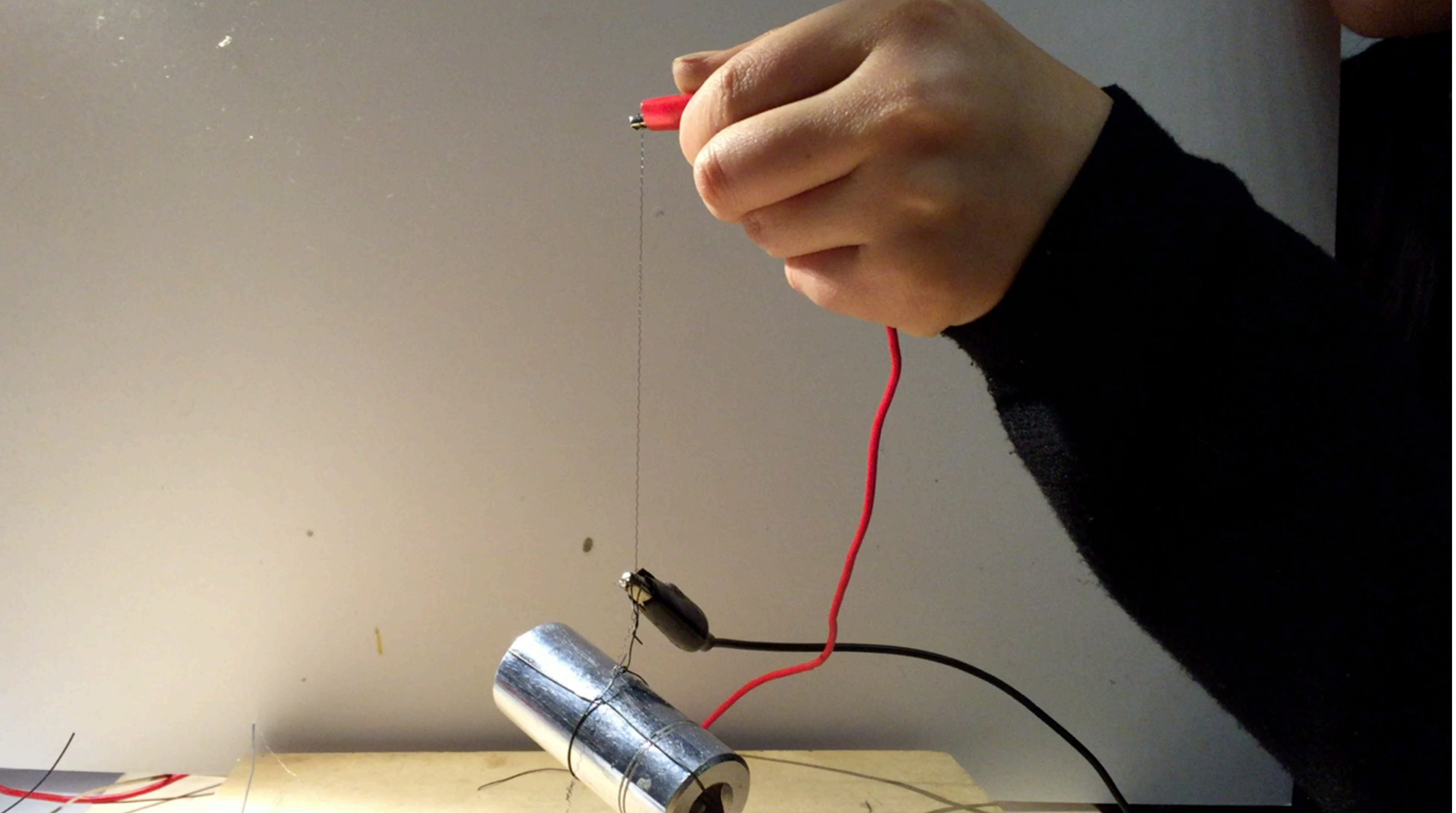

Fig. 2: Five representative states of NiTi spring actuator. (a)-full austenite without load, (b)-full austenite with load, (c)-twinned martensite without load, (d)- fully detwinned martensite without load, (e)-fully detwinned martensite with load.



Sangbae Kim; Hawkes, E.; Kyujin Cho; Joldaz, M.; Foleyz, J.; Wood, Robert, "Micro artificial muscle fiber using NiTi spring for soft robotics," Intelligent Robots and Systems, 2009. IROS 2009. IEEE/RSJ International Conference on , vol., no., pp.2228,2234, 10-15 Oct. 2009

DEMO



## embed material computation

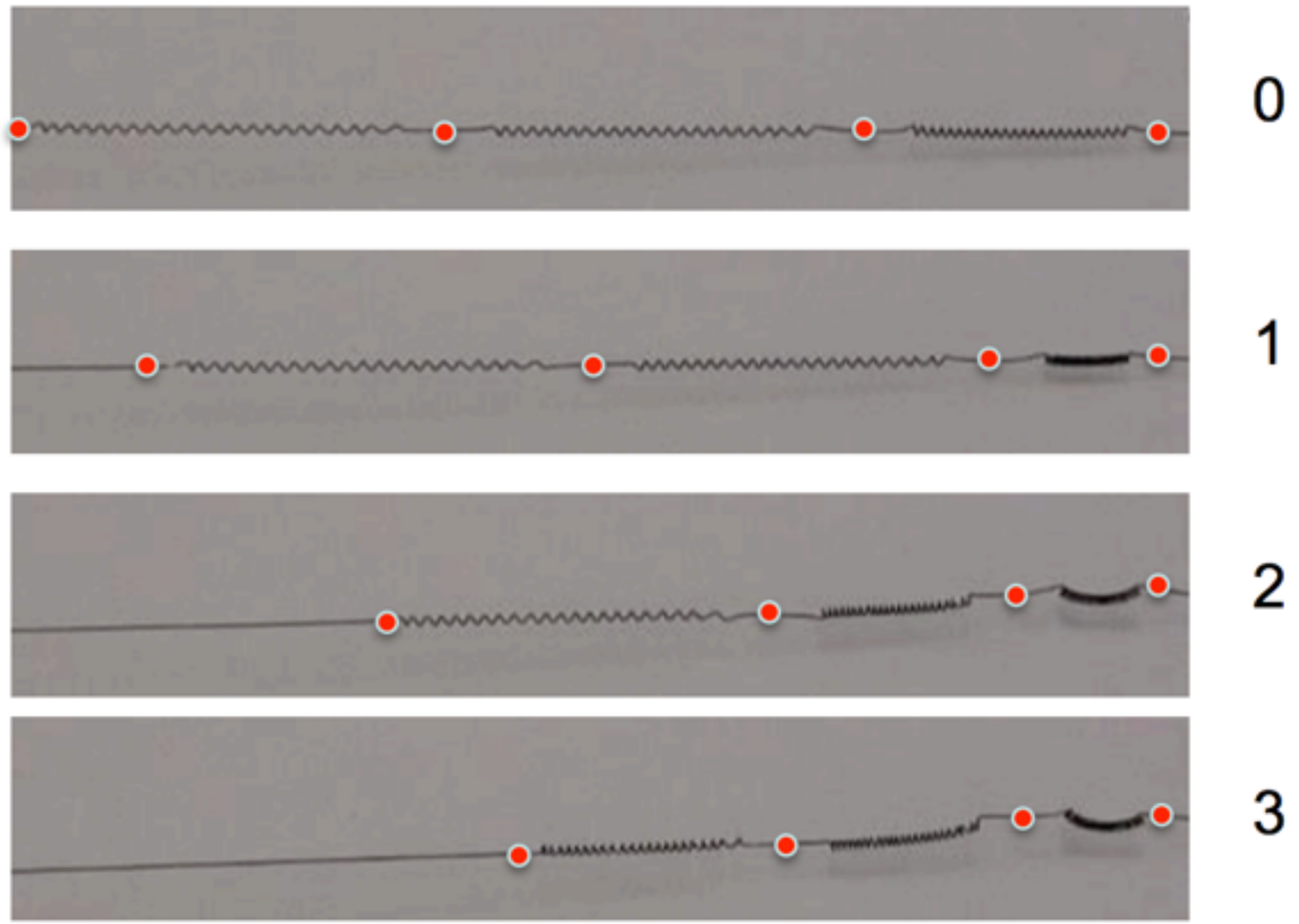
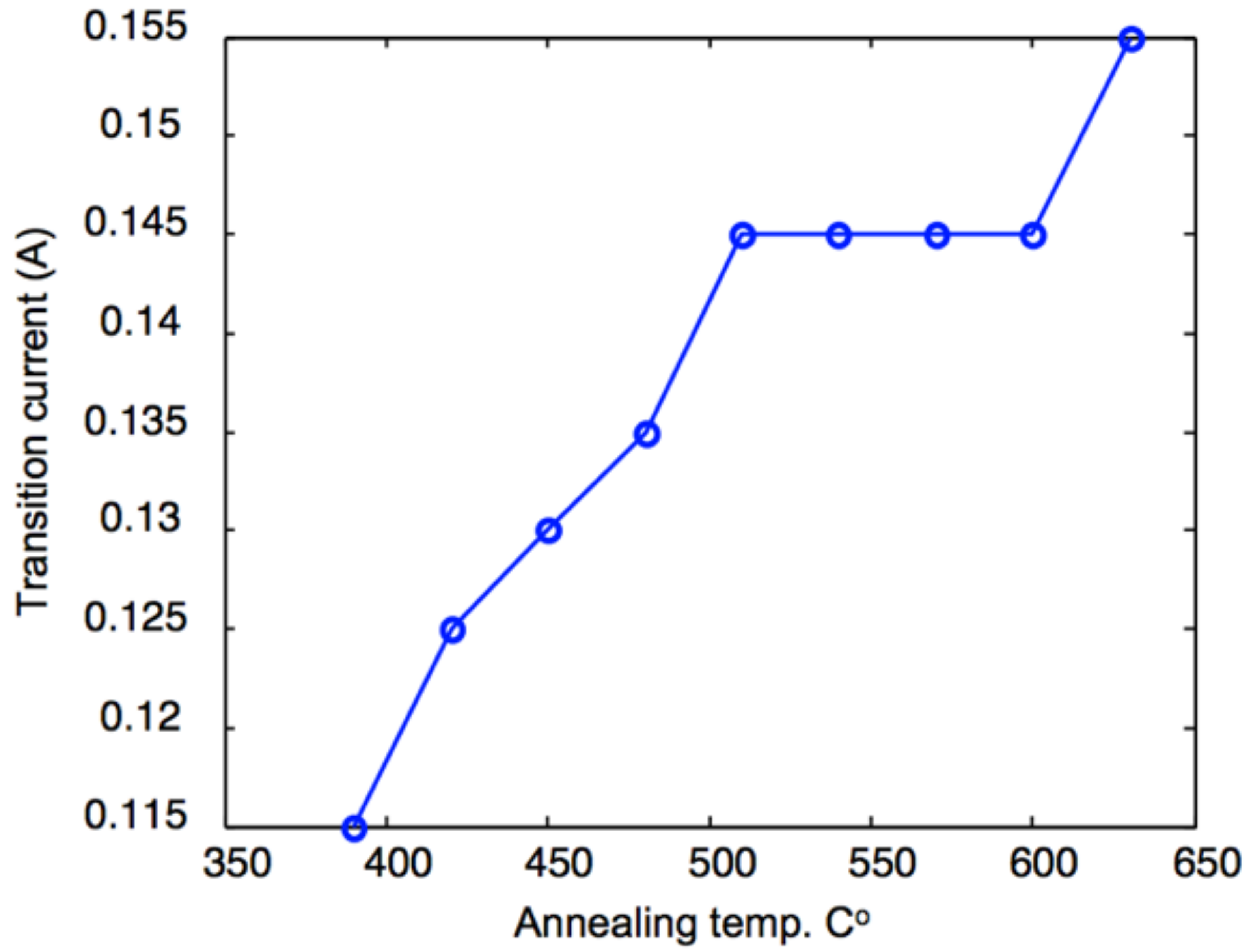
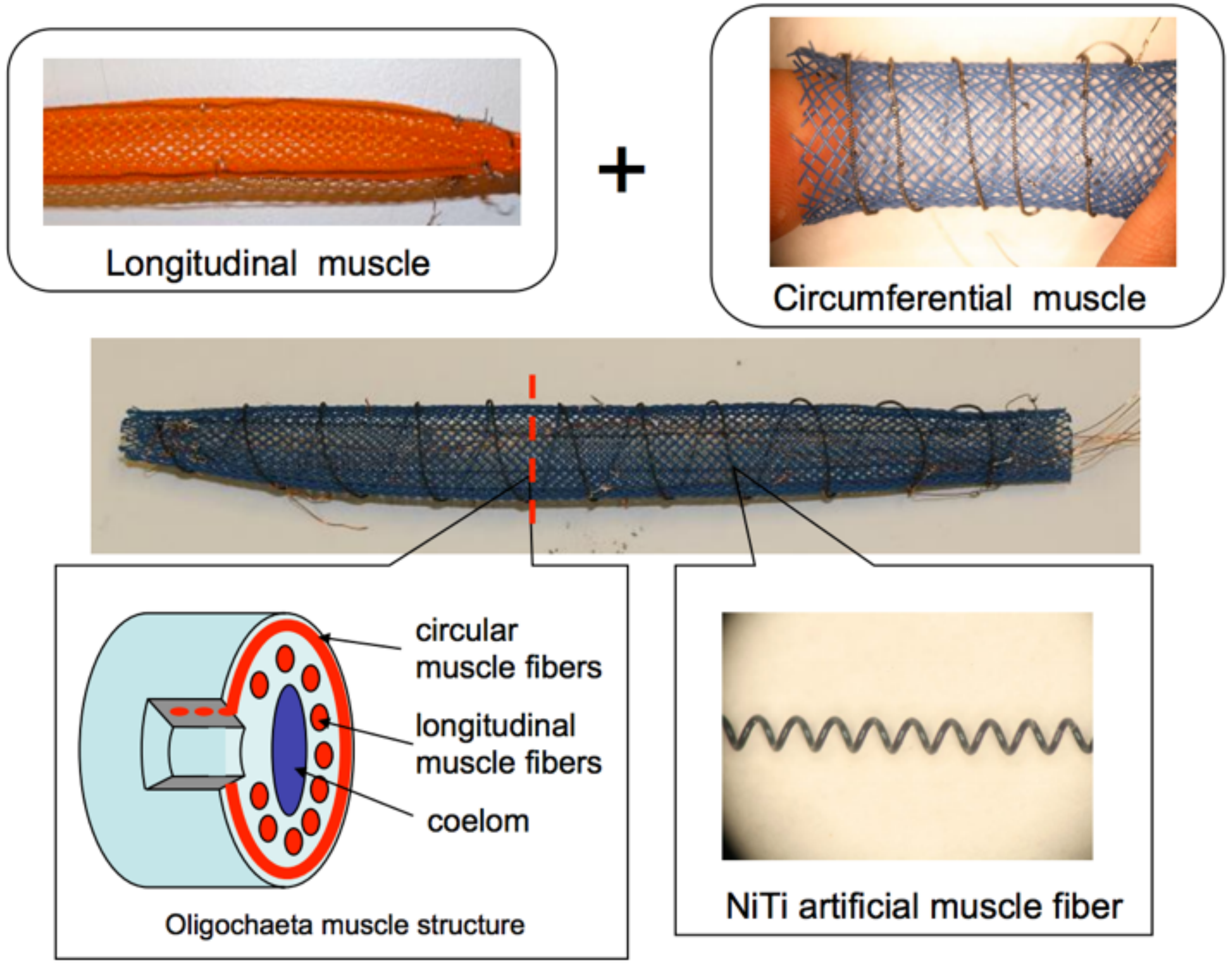


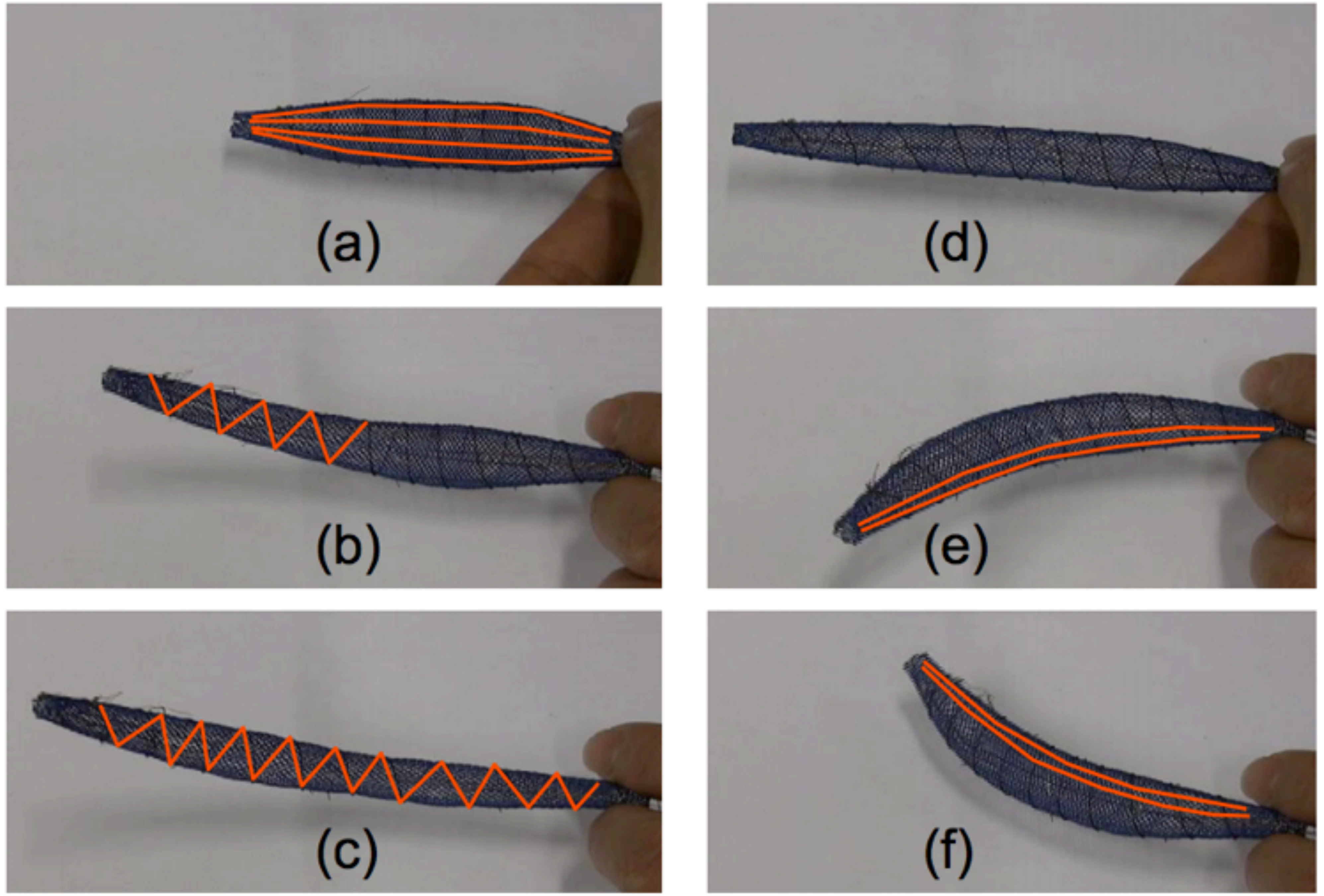

Fig. 10: Each spring segment is annealed at different temperatures and transitions at different current.




Sangbae Kim; Hawkes, E.; Kyujin Cho; Joldaz, M.; Foleyz, J.; Wood, Robert, "Micro artificial muscle fiber using NiTi spring for soft robotics," Intelligent Robots and Systems, 2009. IROS 2009. IEEE/RSJ International Conference on , vol., no., pp.2228,2234, 10-15 Oct. 2009

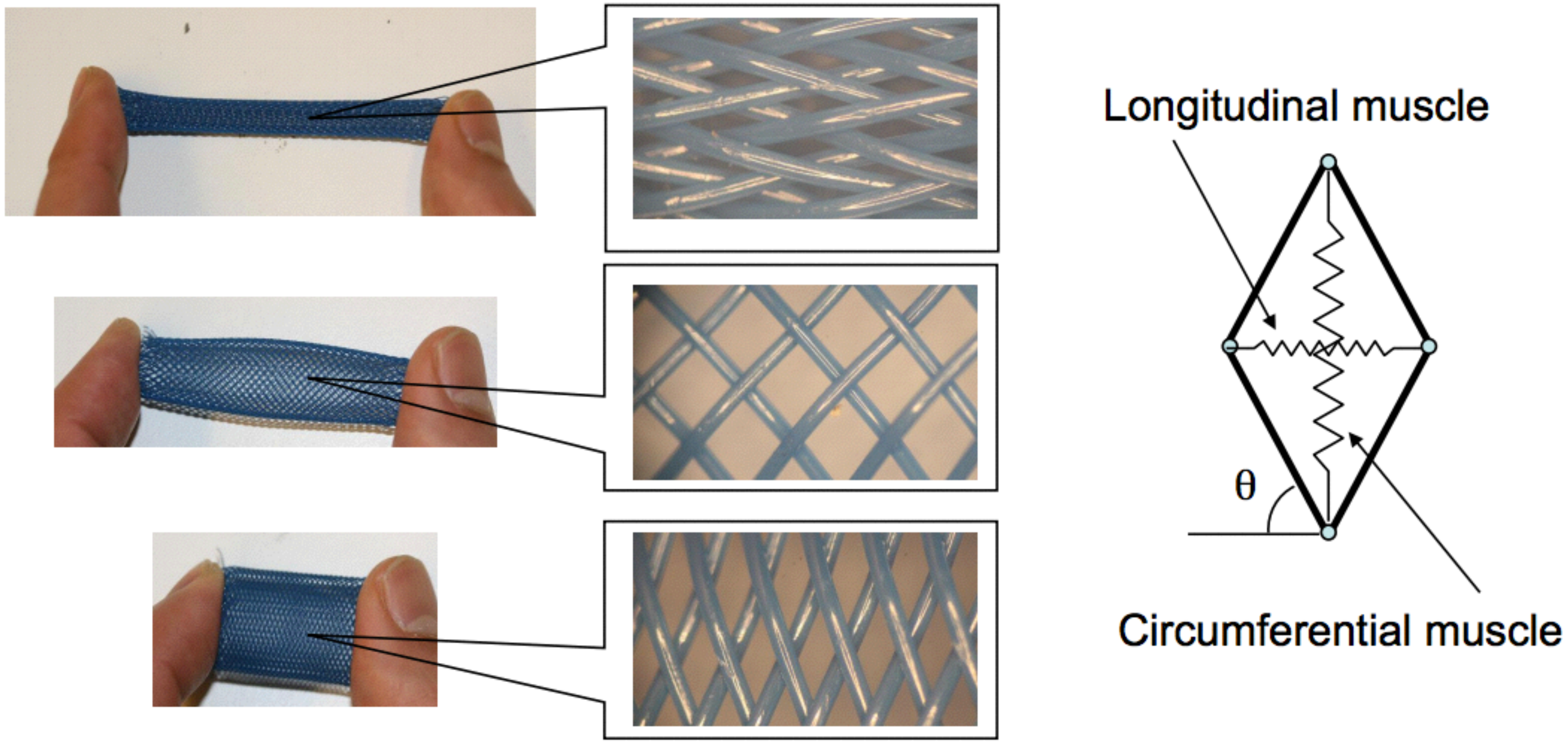
## design complex material system



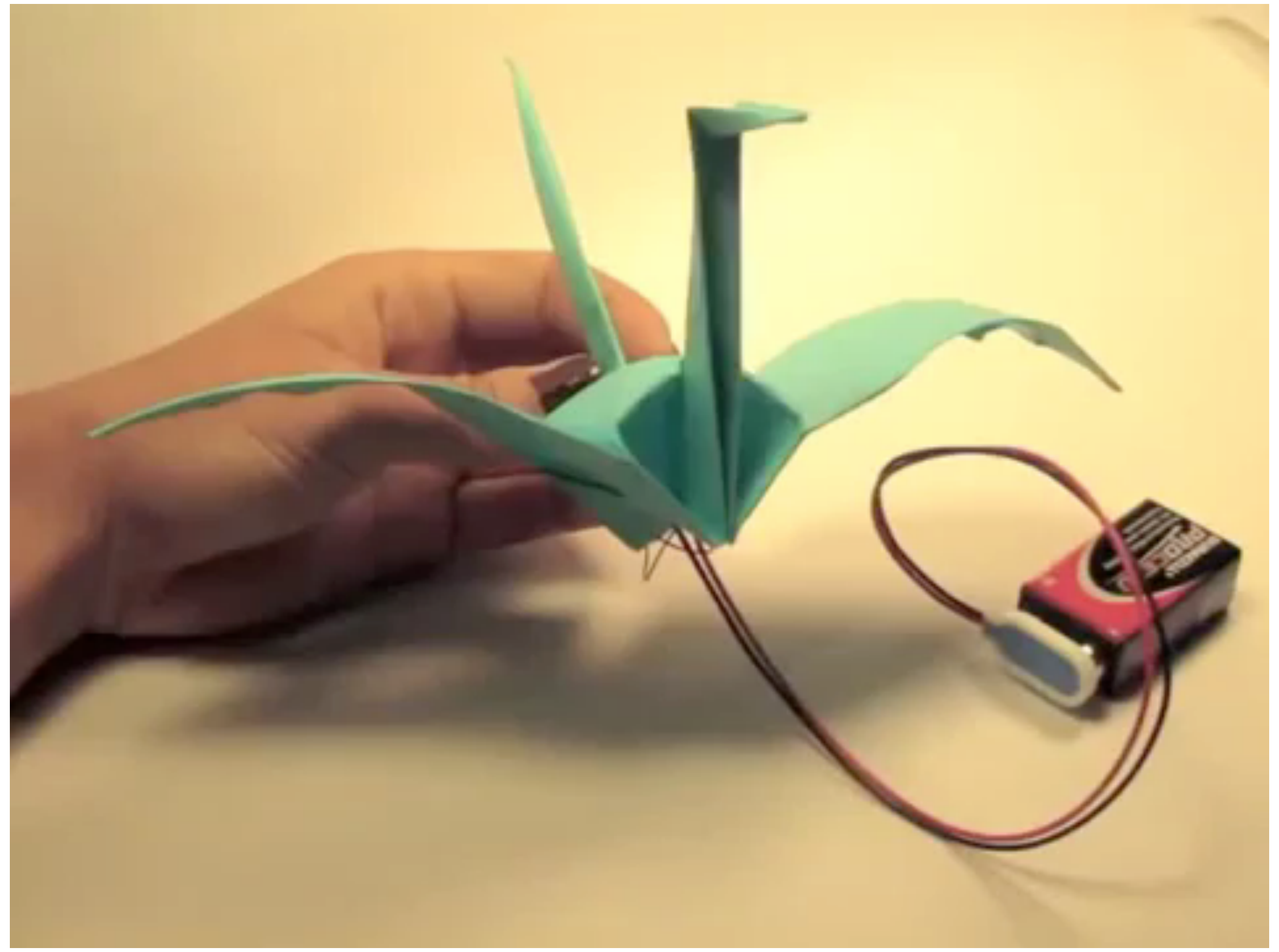



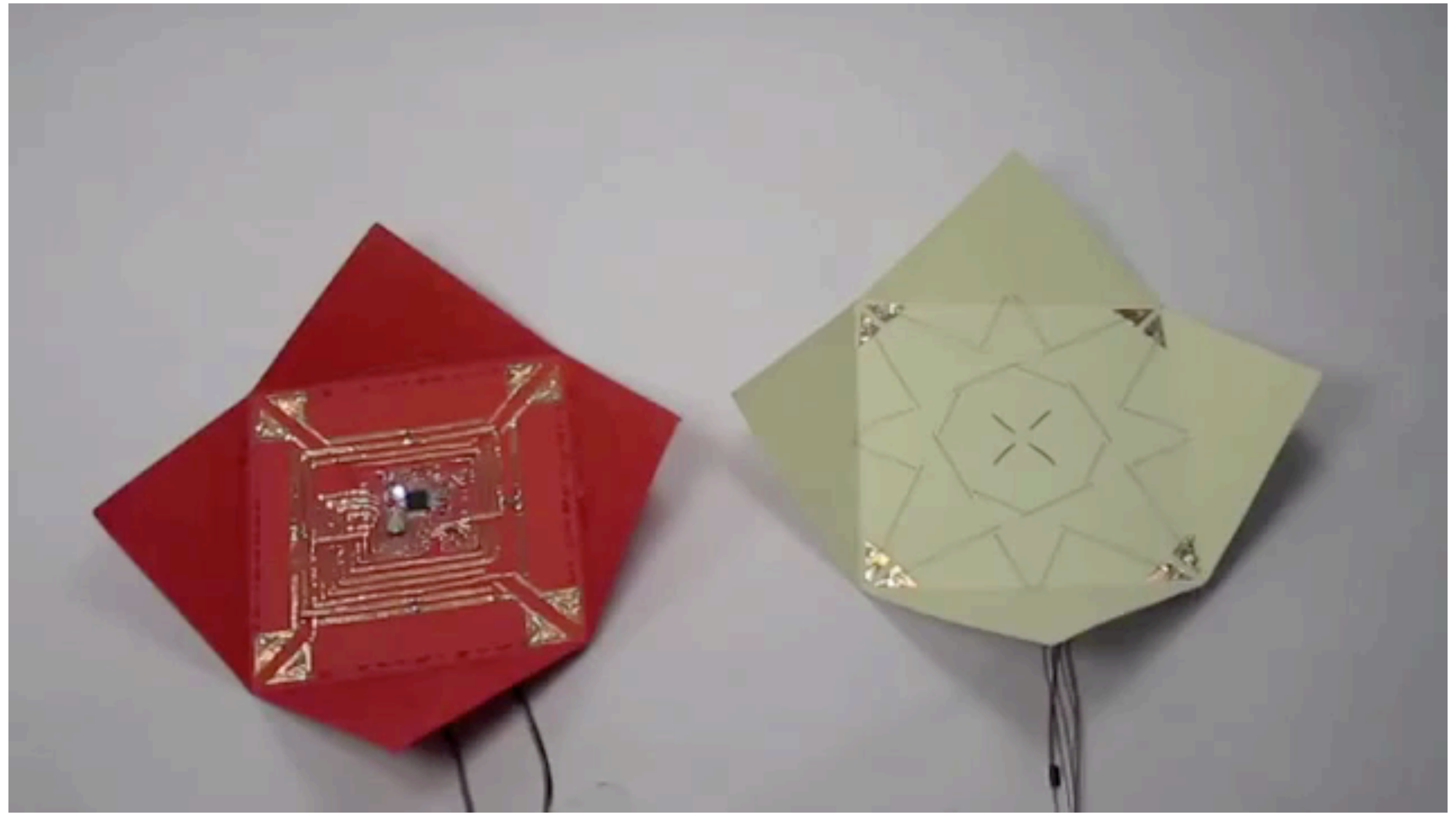

Sangbae Kim; Hawkes, E.; Kyujin Cho; Joldaz, M.; Foleyz, J.; Wood, Robert, "Micro artificial muscle fiber using NiTi spring for soft robotics," Intelligent Robots and Systems, 2009. IROS 2009. IEEE/RSJ International Conference on , vol., no., pp.2228,2234, 10-15 Oct. 2009

## utilize composite material structure



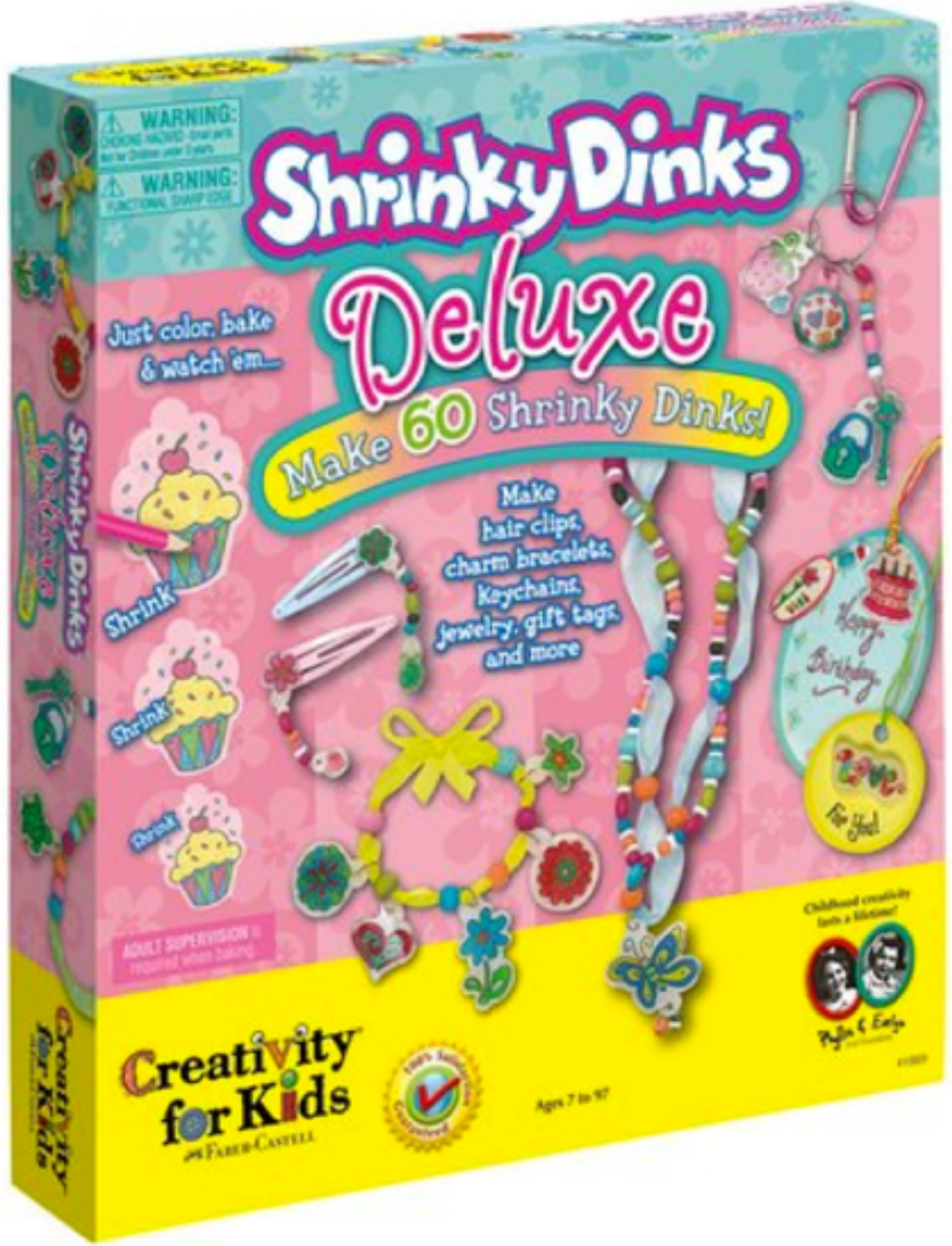

Sangbae Kim; Hawkes, E.; Kyujin Cho; Joldaz, M.; Foleyz, J.; Wood, Robert, "Micro artificial muscle fiber using NiTi spring for soft robotics," Intelligent Robots and Systems, 2009. IROS 2009. IEEE/RSJ International Conference on , vol., no., pp.2228,2234, 10-15 Oct. 2009



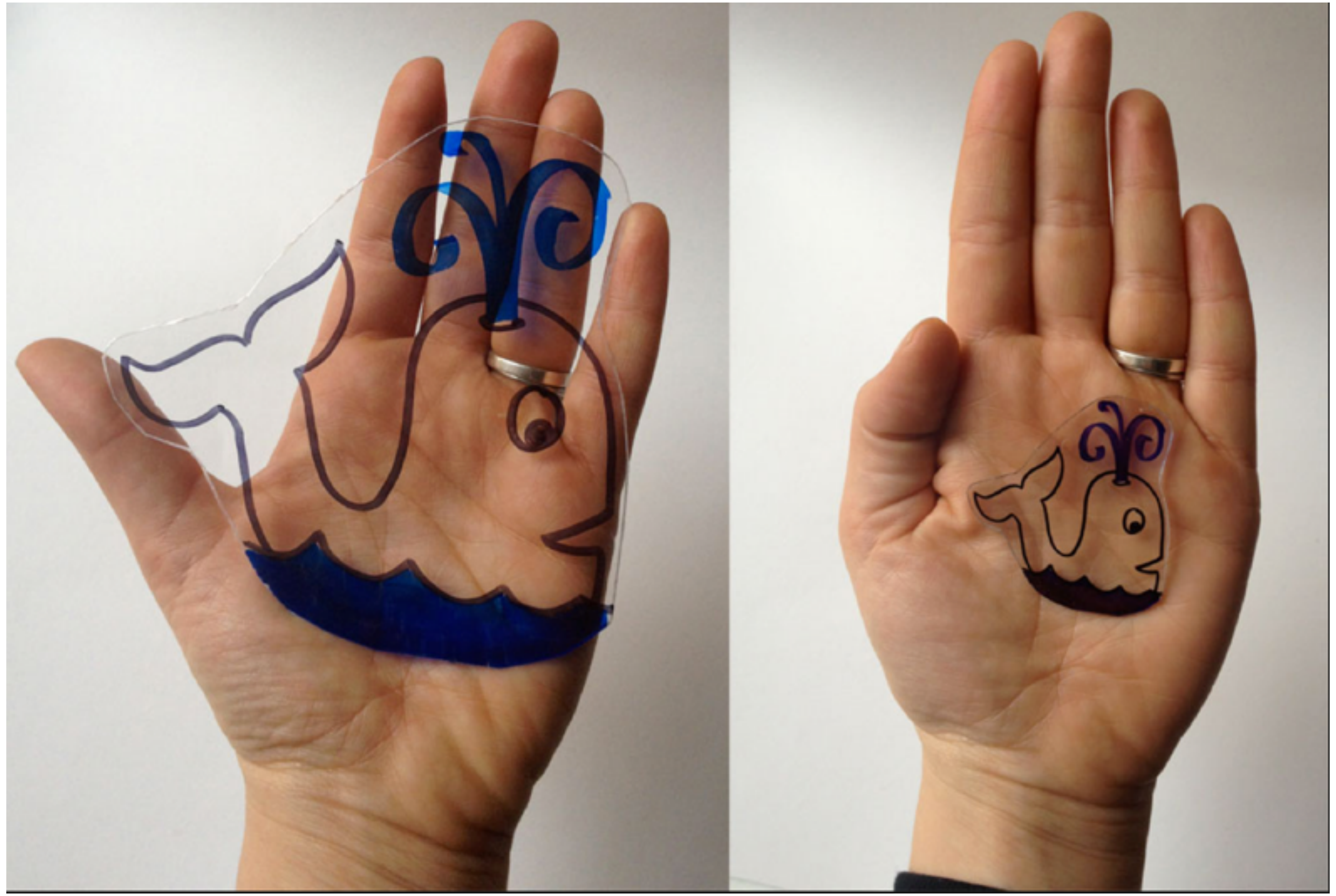


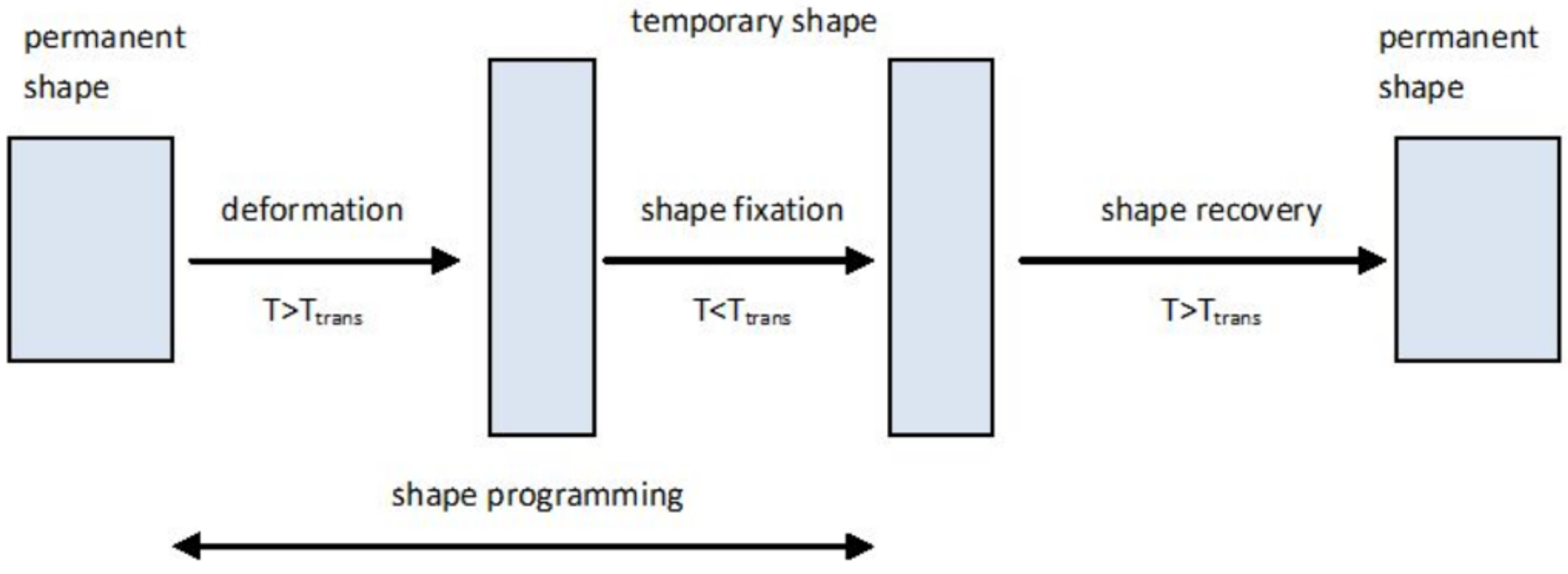
Collective Work from Jie Qi, MIT Media Lab.

# Pre-strained Polystyrene (Shrinky-Dinks)



Shrinky Dinks
Deluxe
Make 60 Shrinky Dinks!
Just color, bake & watch 'em...
Make hair clips, charm bracelets, keychains, jewelry, gift tags, and more
Shrink
Shrink
Shrink
Creativity for Kids

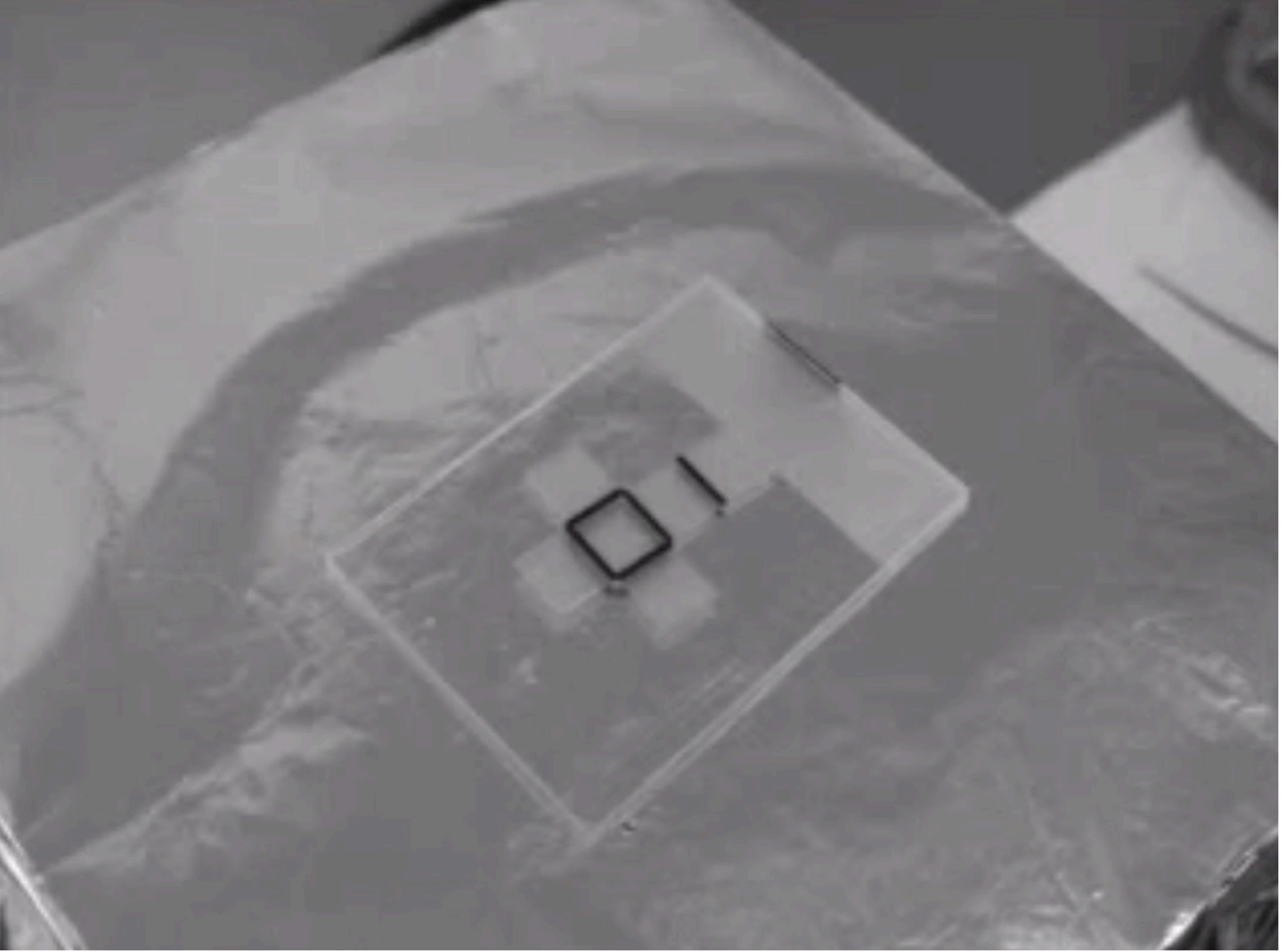





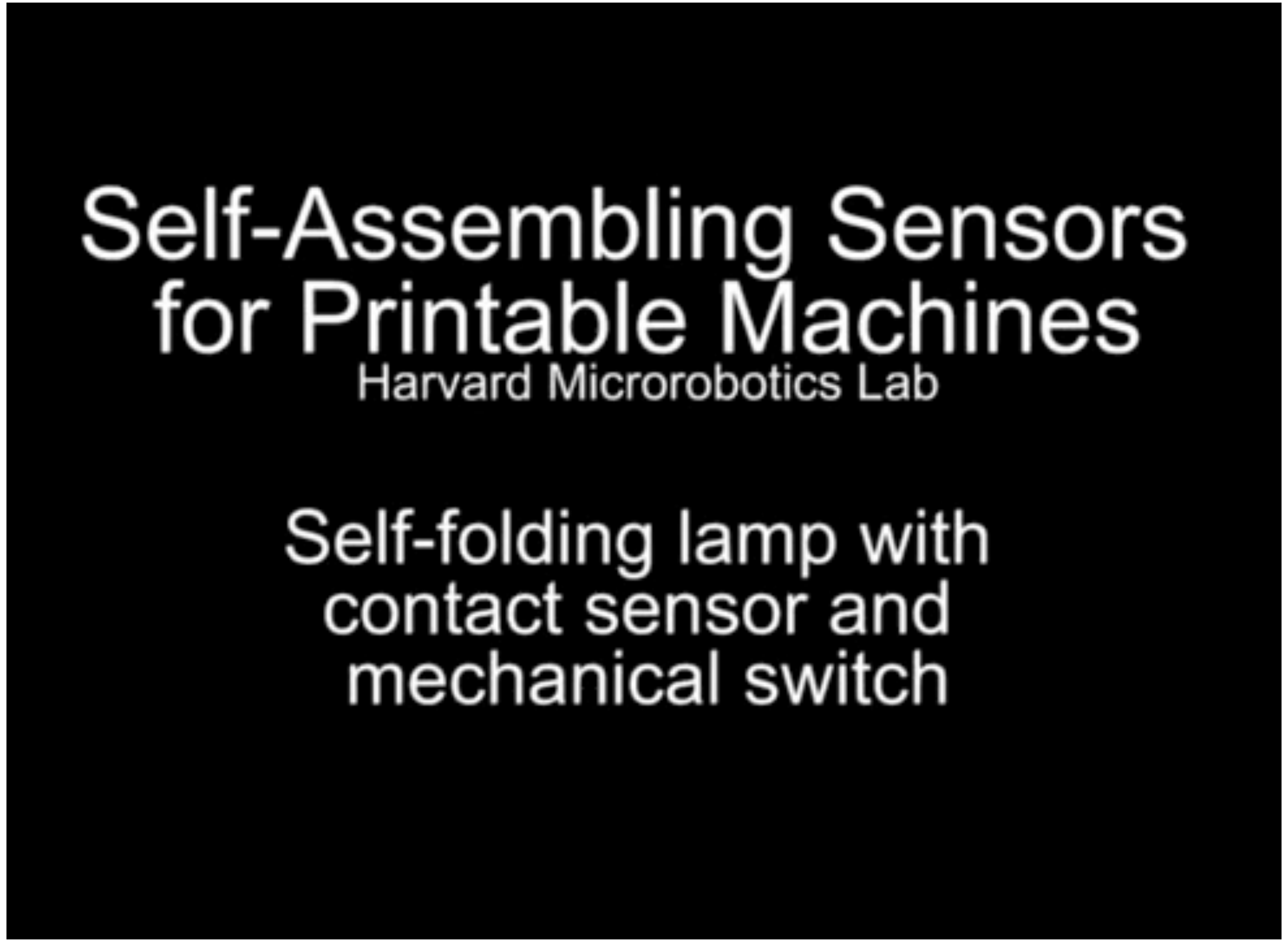

The sheets are made of optically transparent, pre-strained polystyrene (also known as Shrinky-Dinks) that shrink in-plane if heated uniformly

Prestressed polymer sheets are essentially shape memory materials that are fabricated by heating the polymer above Tg, stretching, and subsequently cooling below Tgto preserve the deformed shape. As a consequence of such processing, the stress stored temporarily in the sheets releases rapidly when heated above the Tg(e.g., sheets of Shrinky Dinks contract in plane by 50–60% in both the x and y dimensions;

# Demo

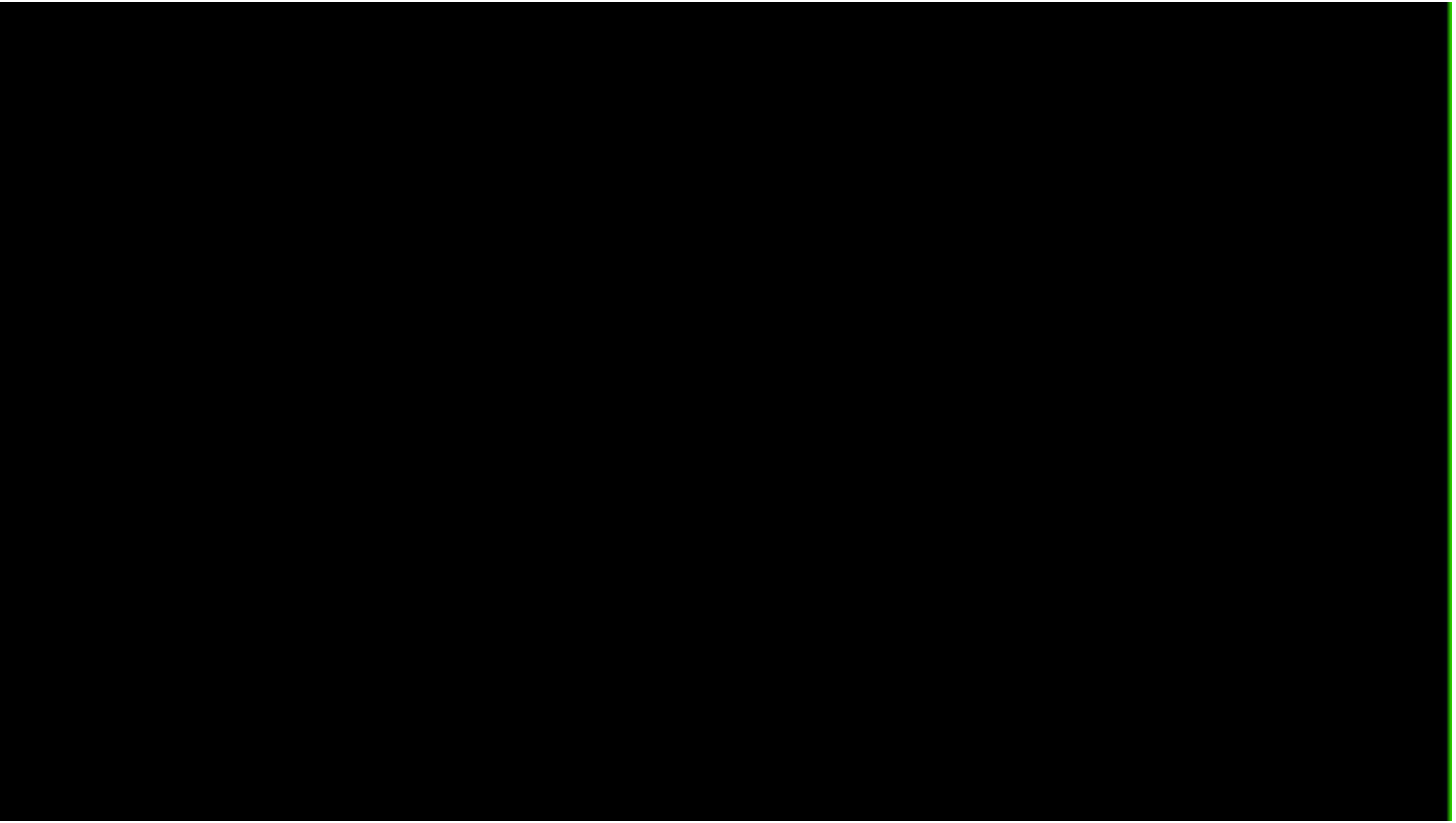


Self-folding of polymer sheets using local light absorption. Y Liu, J K Boyles, J Genzer and M Dickey. Soft Matter, 2011


Samuel Felton. Harvard Microrobotics Lab

Self-folding of polymer sheets using local light absorption. Y Liu, J K Boyles, J Genzer and M Dickey. Soft Matter, 2011



Kentaro Yasu and Masahiko Inami. 2012. POPAPY: instant paper craft made up in a microwave oven. In Proceedings of the 9th international conference on Advances in Computer Entertainment (ACE'12), Anton Nijholt, Teresa Romão, and Dennis Reidsma (Eds.). Springer-Verlag, Berlin, Heidelberg, 406-420.


Joanne Lo and Eric Paulos. 2014. ShrinkyCircuits: sketching, shrinking, and formgiving for electronic circuits. In Proceedings of the 27th annual ACM symposium on User interface software and technology (UIST '14). ACM, New York, NY, USA, 291-299.

# Overview: Stimuli Responsive Polymer

NATURE MATERIALS DOI: 10.1038/NMAT2614

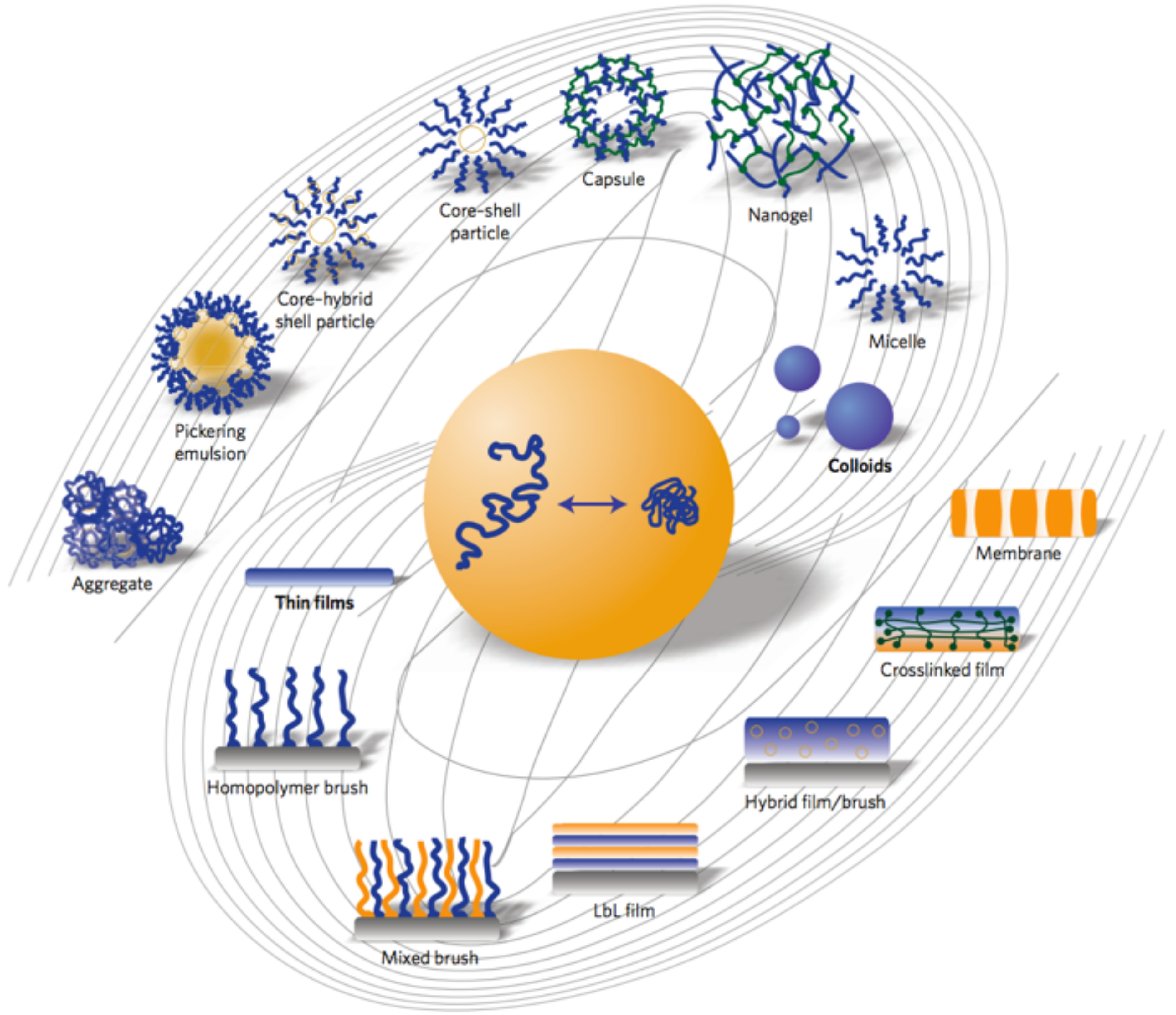



**Figure 1 |** 'Galaxy' of nanostructured stimuli-responsive polymer materials. These materials rely on the phase behaviour of macromolecule assemblies in thin films (polymer brushes, multilayered films made of different polymers, hybrid systems that combine polymers and particles, thin films of polymer networks, and membranes that are thin films with channels/pores), and nanoparticles (micelles, nanogels, capsules and vesicles, core-shell particles, hybrid particle-in-particle structures, and their assemblies in solutions and at interfaces in emulsions and foams).

# A Brief Review of Stimulus-active Polymers Responsive to Thermal, Light, Magnetic, Electric, and Water/Solvent Stimuli

HARPER MENG AND JINLIAN HU*

*Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Kowloon, Hong Kong*

## Thermal Reactive Polymer

With glass or melting transition acting as the switch, many polymer systems are reported to possess shape memory effect (SME). These SMPs usually have a physical cross-link- ing structure, crystalline/amorphous hard phase, or chemical cross-linking structure to store internal stress and a low temperature glass or m ing transition.

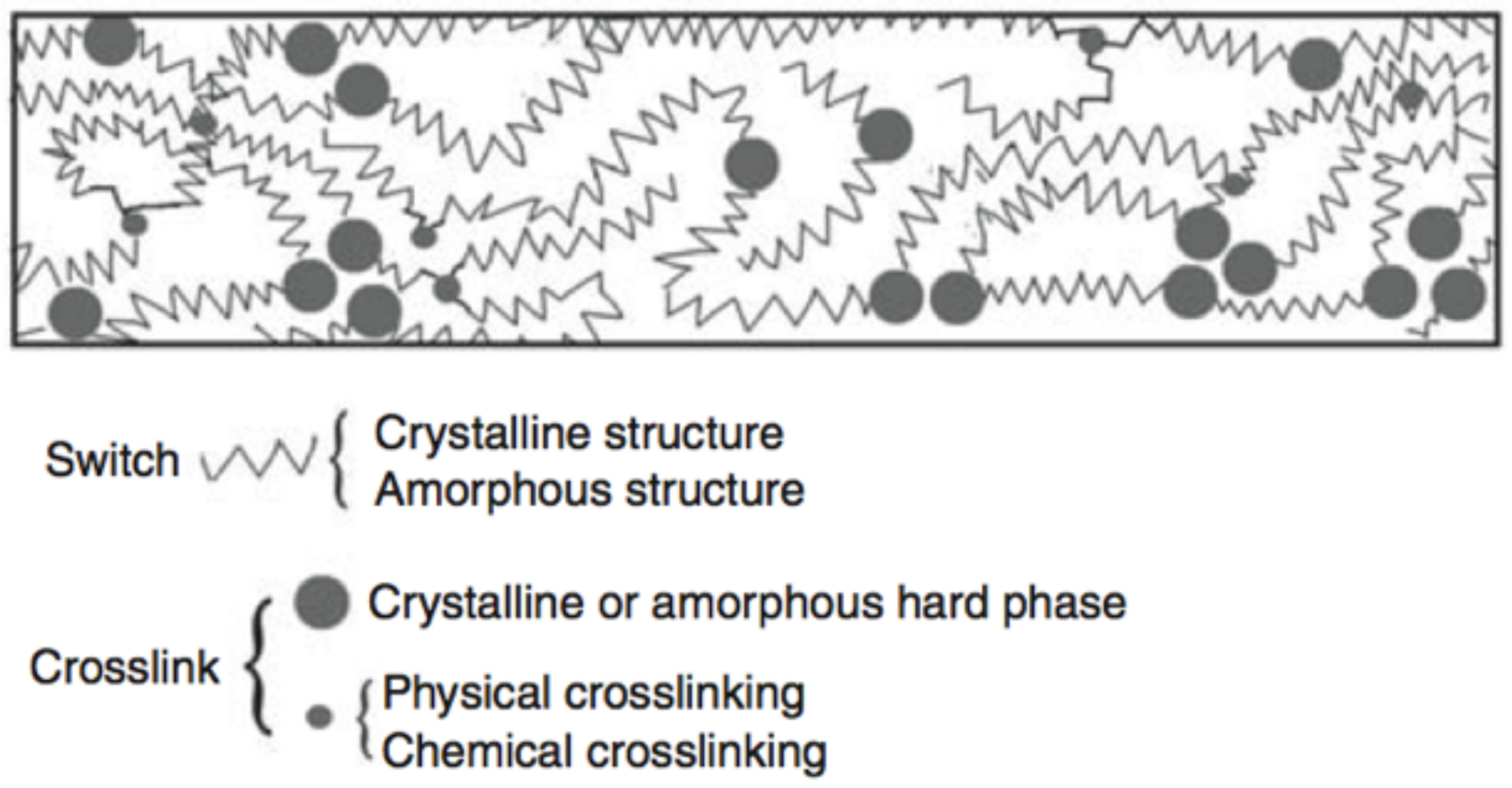



**Figure 1.** *The molecular mechanism of thermal-active SME.*

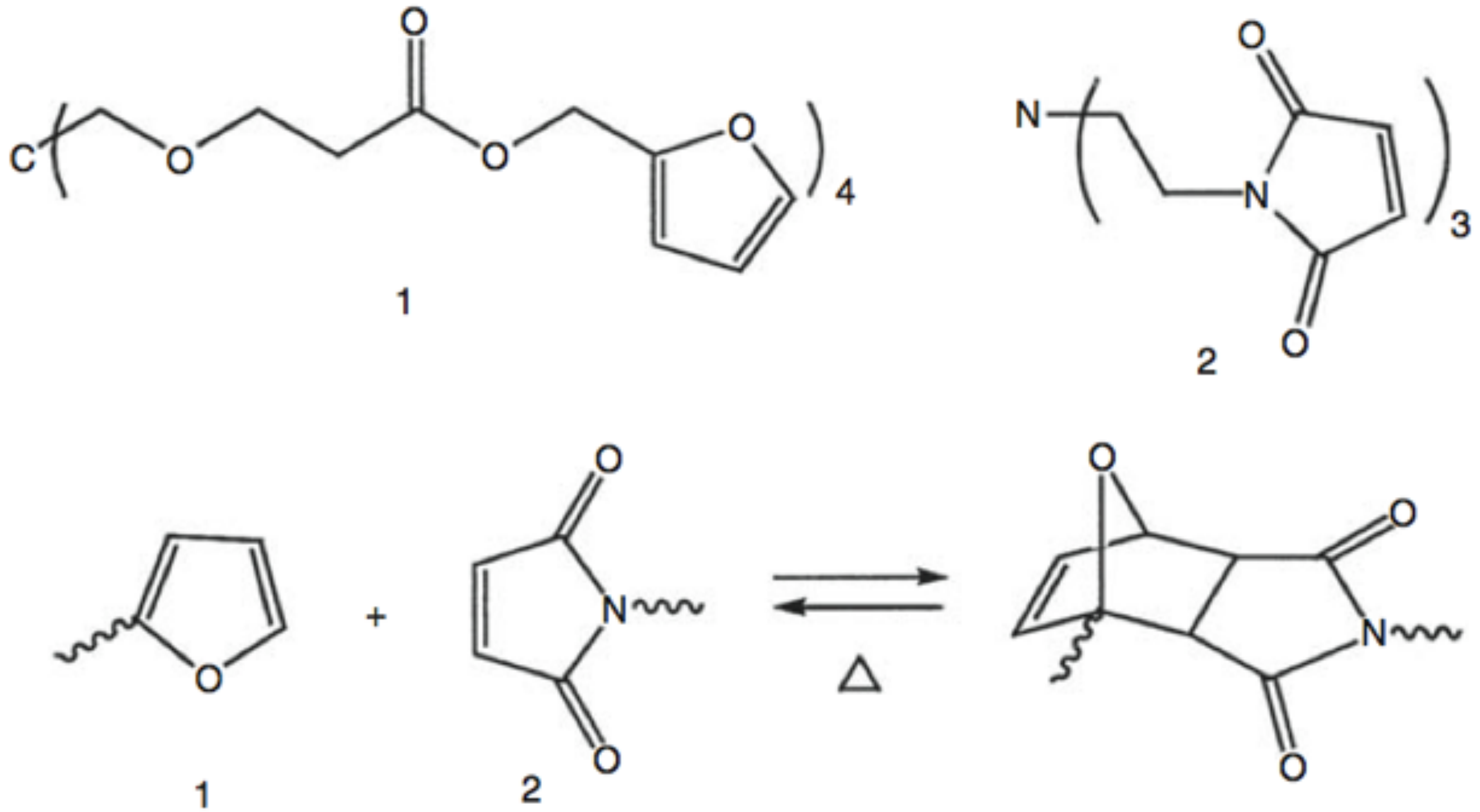



**Figure 3.** *A thermally reversible cross-linked structure. Reproduced with permission from The American Association for the Advancement of Science.*

## Thermal Reactive Polymer

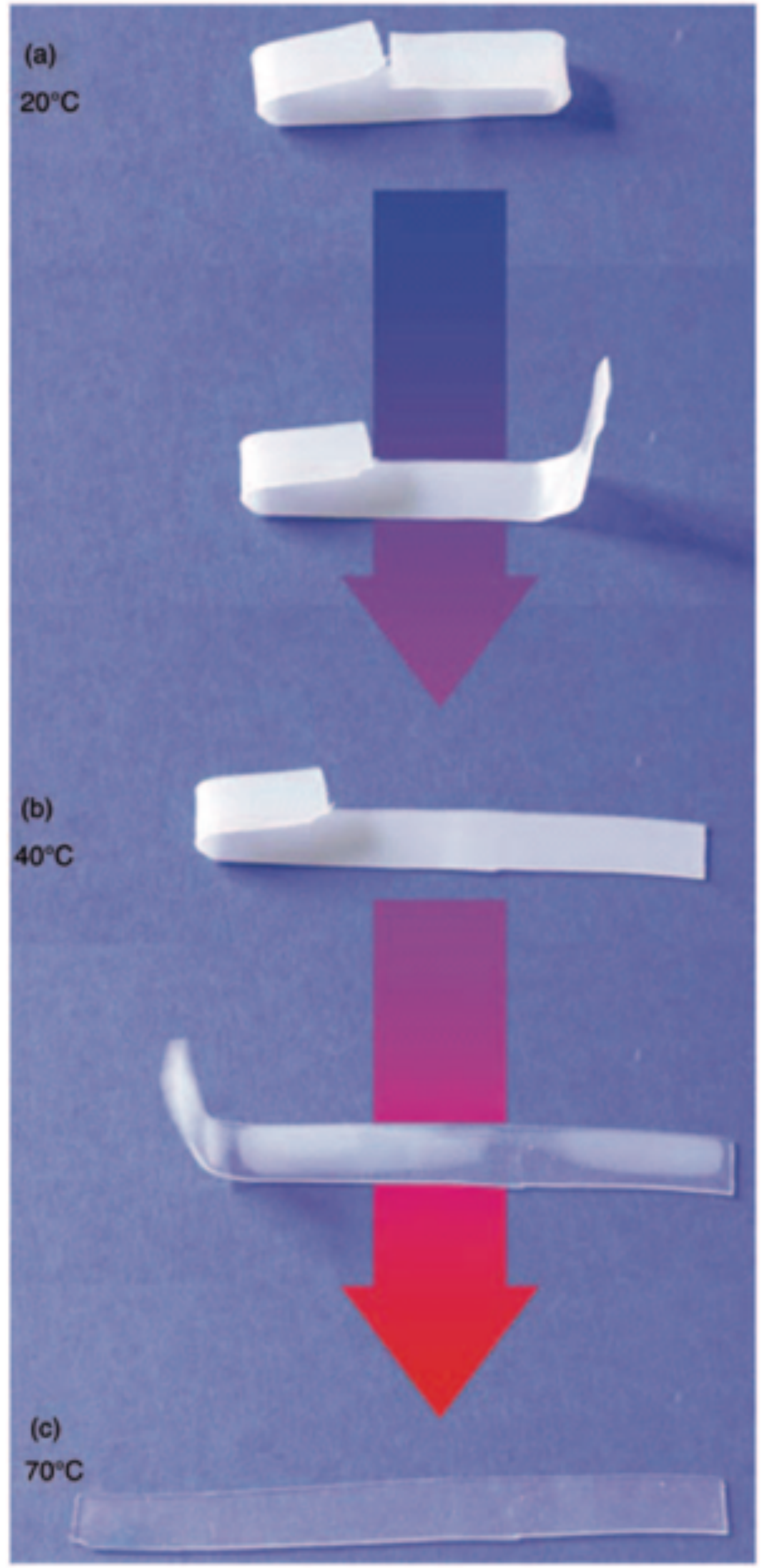



***Figure 6.*** *Triple-shape effect of a polymer network with two melting transition temperatures as two shape memory switches. The series of photographs demonstrates the recovery of shapes (b) and (c) by subsequent heating to 40°C and 70°C (from top to bottom). Shape (a) had been created before by heating the sample (flat film) to 70°C, deforming the left end of the sample and cooling to 40°C (resulting in shape (b)), finally cooling to 20°C while keeping the right side of the polymer film deformed. Reproduced with permission of The Royal Society of Chemistry, http://dx.doi.org/10.1039/b702524f.*

# Electroactive Polymer

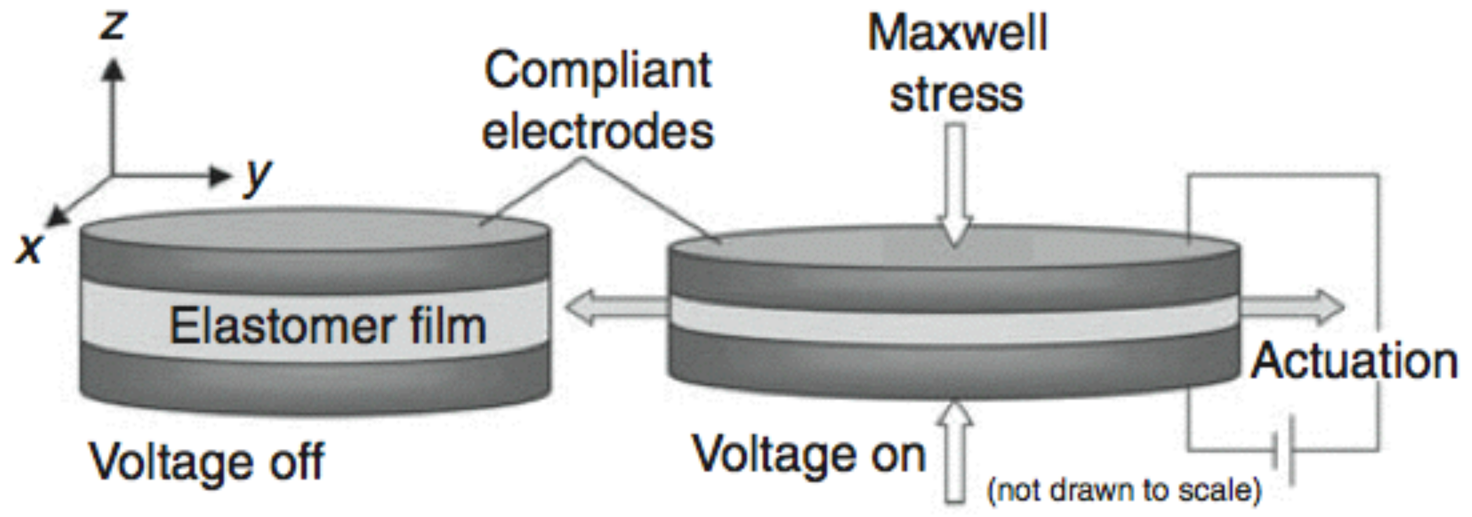
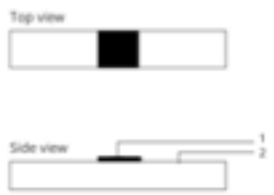
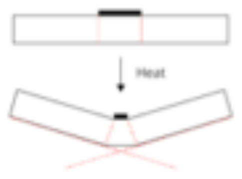
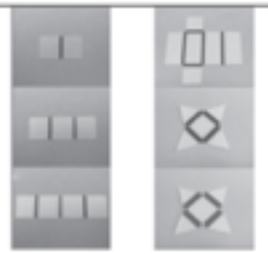
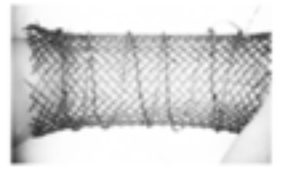
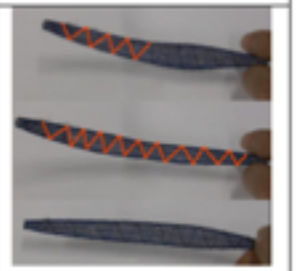
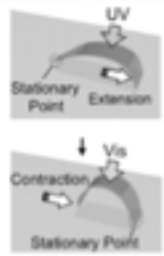
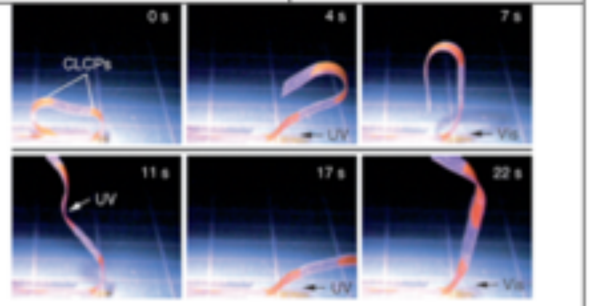
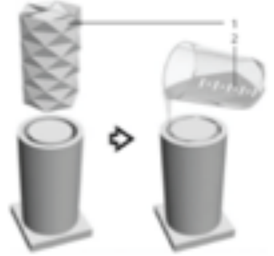
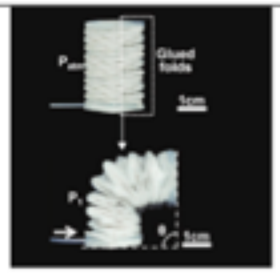
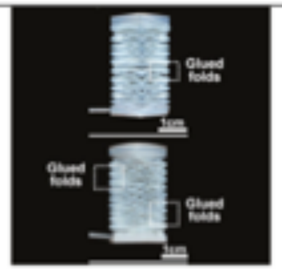
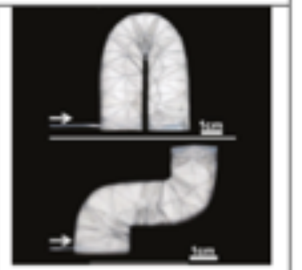
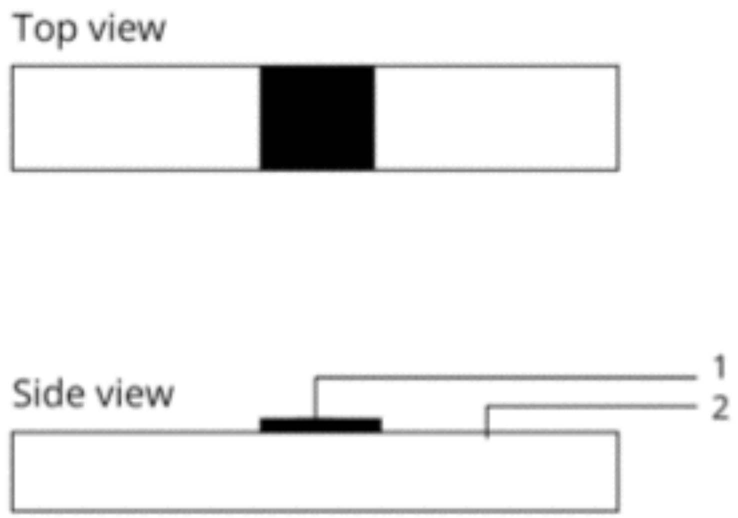
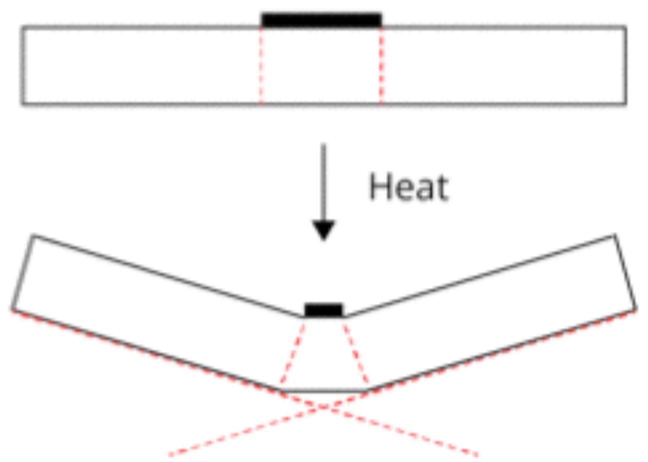
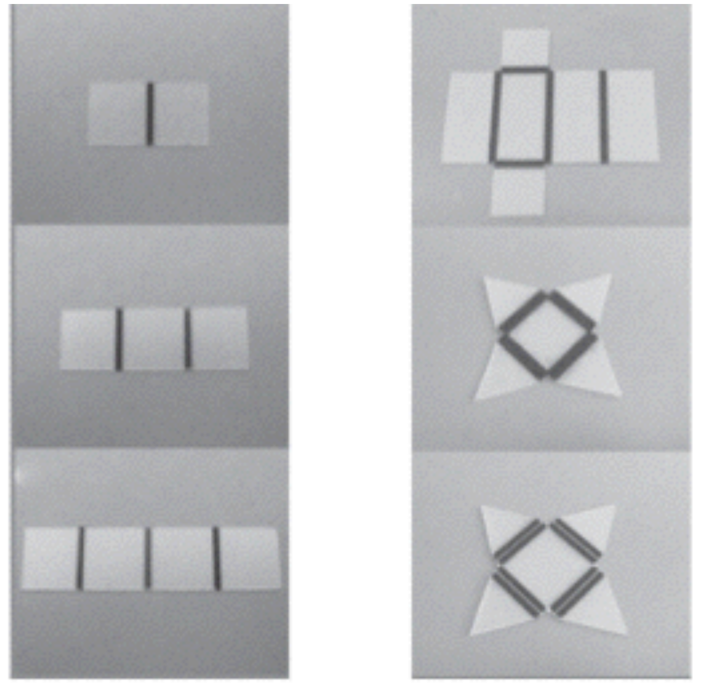
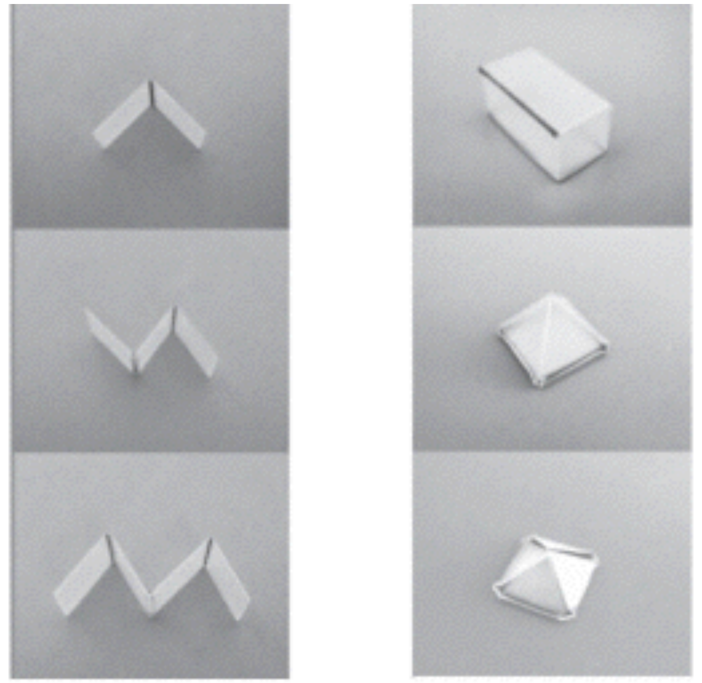
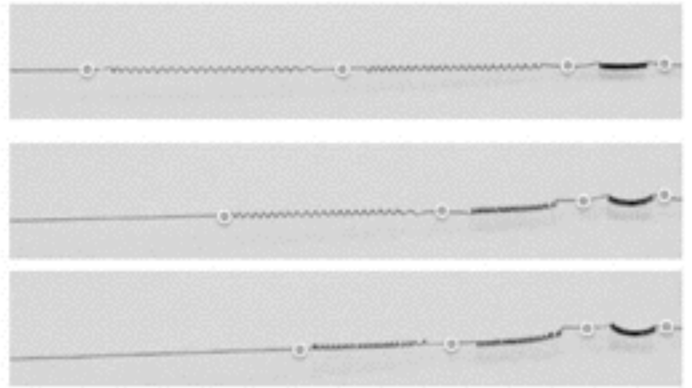
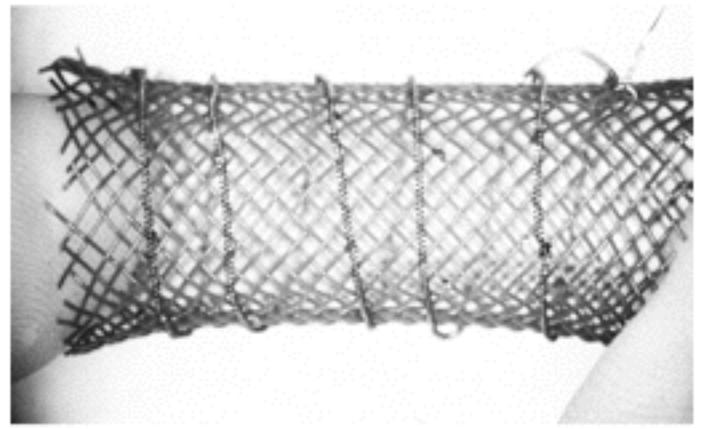
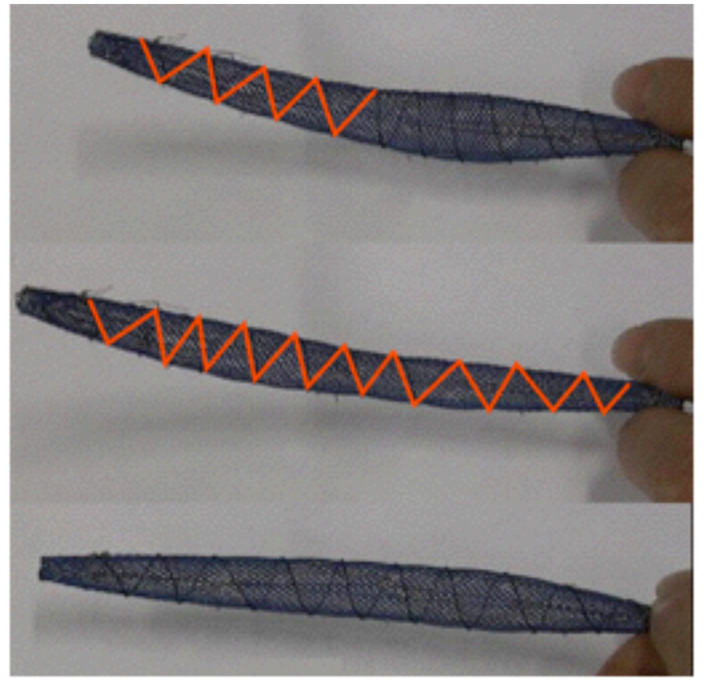
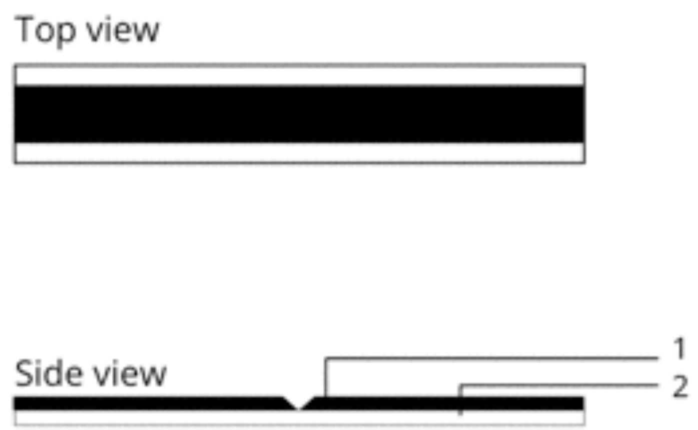
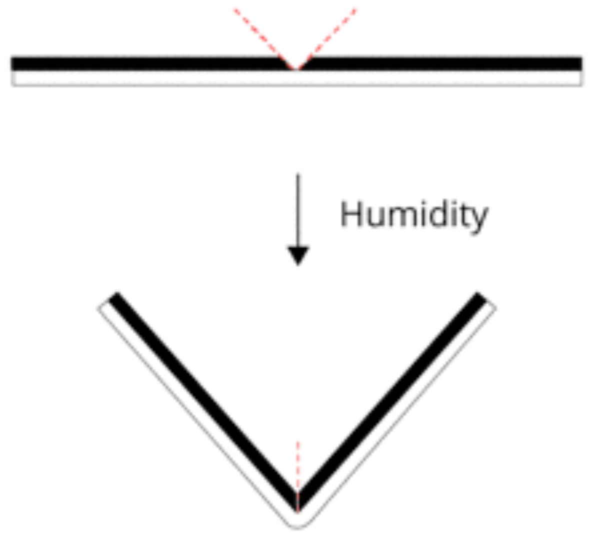


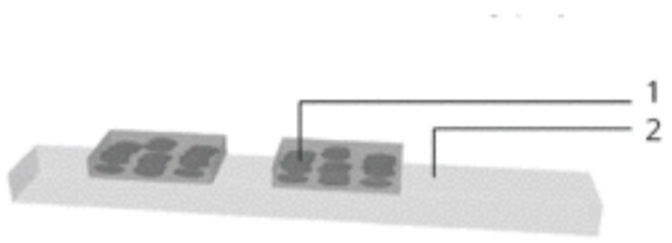

***Figure 17.*** *The dielectric elastomers actuate by means of electrostatic forces applied via compliant electrodes on the elastomer film. Reproduced with permission from Elsevier, http://dx.doi.org/10.1016/j.sna.2009.01.002.*

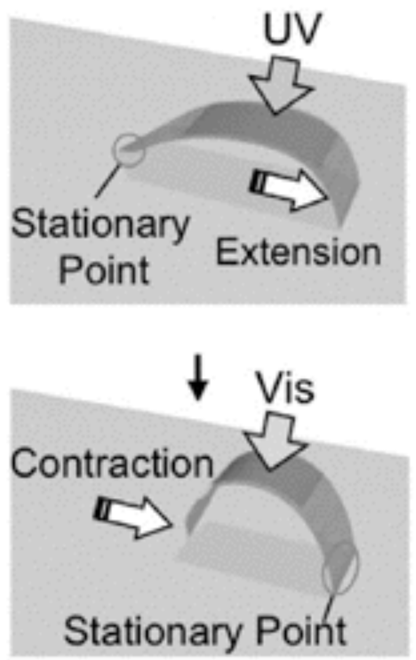
| Applied Stimuli | Direct Stimuli (Energy Source) | Material Computation Example | | | |
|---|---|---|---|---|---|
| | | Material Composition | Computation Principles | Material Geometry and Structure | Shape Change Output |
| Uniform external stimuli: Light | Heat |  1. White thermal prestrained polymer sheets 2. Black ink |  Anisotropy in light absorption; bending angle is related to ink width and shrinking rate. |  |  **Self folding polymer**[4] |
| Uniform internal stimuli: Current | Heat |  3 sections of Nitinol coil annealed at different temperature: 370°C, 480°C and 630°C. |  Each segment expands and contracts at different current. |  |  Micro muscle robot[3] |
| Uniform external stimuli: Humidity | Humidity |  1. Rigid plastic 2. Swelling polymer |  Angle limiter set by rigid material defines the folding angle under water. |  |  4D printing[8] |
| Uniform or discrete external stimuli: UV Light | UV Light |  1. Azobenzene Layer (photomobile polymer) 2. PE film |  Crosslinked LC elastomer extends under UV plastic film beneath does not. |  Photomobile robot[2] | |
| Uniform internal stimuli: Positive air pressure | Air pressure |  1. Paper origami 2. Elastomer |  Pressured air flows towards the side with lower tensile strength. |  |  Elastomeric Origami[5] |

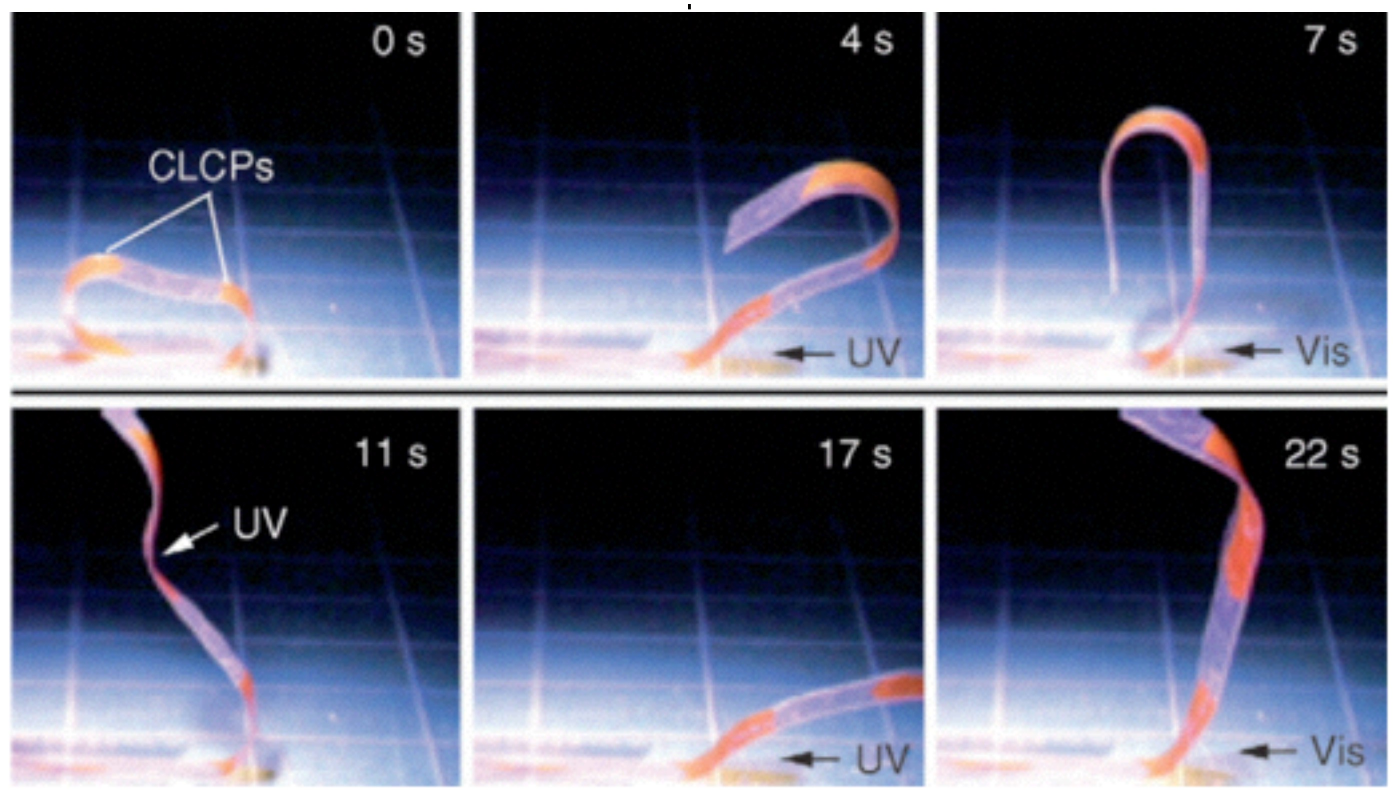
| Applied Stimuli | Material Composition | Computation Principles | Material Geometry and Structure | Shape Change Output |
| --- | --- | --- | --- | --- |
| **Uniform External:**<br>**Light** |  <br>1. White thermal prestrained polymer sheets<br>2. Black ink |  <br>Anisotropy in light absorption; bending angle is related to ink width and shrinking rate. |  | <br>**Self folding polymer**[4] |

| Applied Stimuli | Material Composition | Computation Principles | Material Geometry and Structure | Shape Change Output |
| --- | --- | --- | --- | --- |
| Uniform Internal:<br>Current |  <br>3 sections of Nitinol coil annealed at different temperature: 370°C, 480°C and 630°C. | <br>Each segment expands and contracts at different current. |  | <br>**Micro muscle robot**[5] |

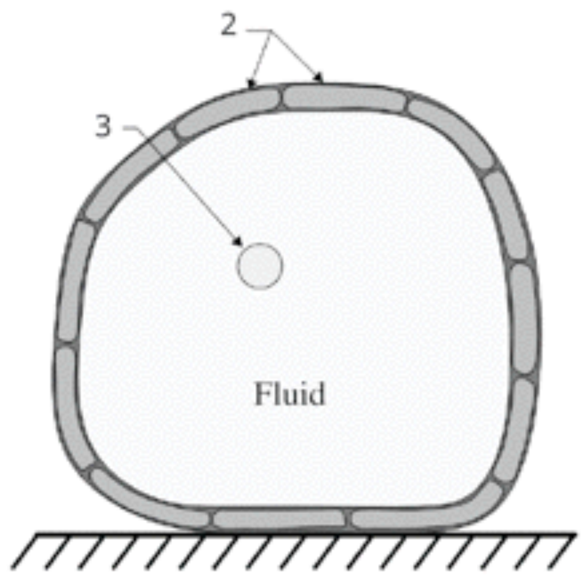
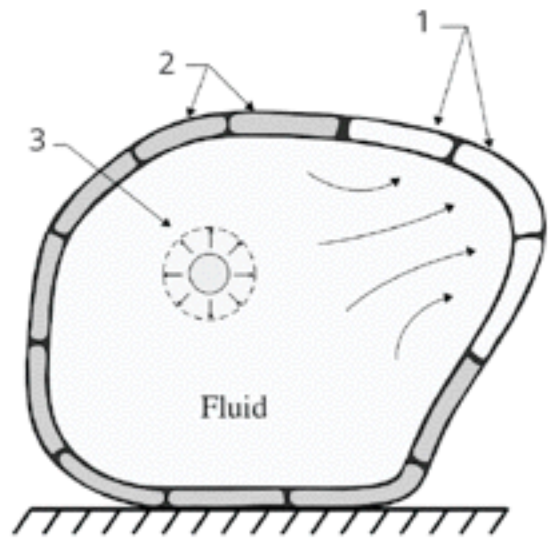
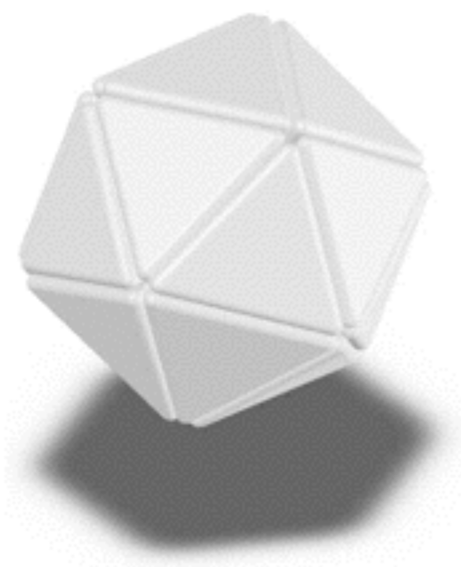
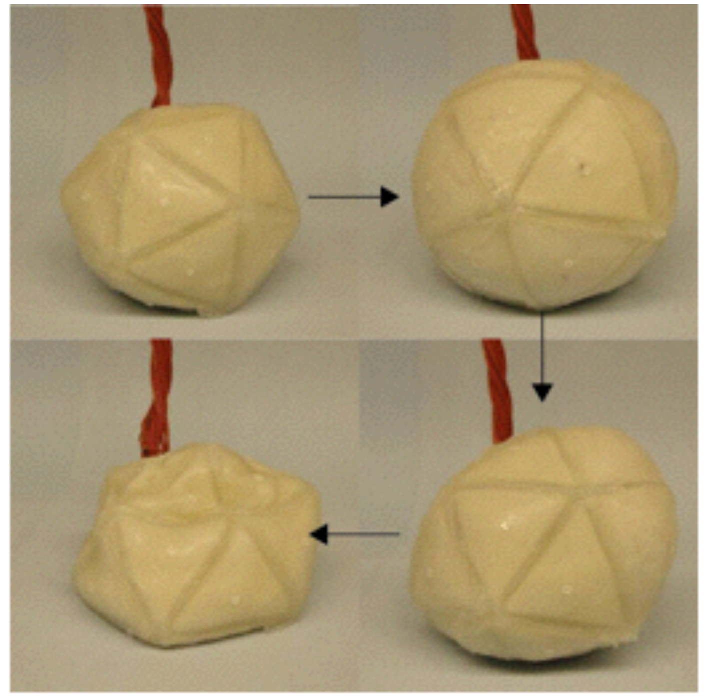
| Applied Stimuli | Material Composition | Computation Principles | Material Geometry and Structure | Shape Change Output |
| --- | --- | --- | --- | --- |
| Uniform External: Humidity |   1. Rigid plastic |   Angle limiter set by rigid |  |  |

<table>
<tr><th>Applied Stimuli</th><th>Material Composition</th><th>Computation Principles</th><th>Material Geometry and Structure</th><th>Shape Change Output</th></tr>
<tr>
<td>Discrete External:<br><br>Light</td>
<td>

1. Azobenzene Layer (photomobile polymer)<br>2. PE film</td>
<td>

Crosslinked LC elastomer extends under UV plastic film beneath does not.</td>
<td>

**Photomobile robot**[4]</td>
<td></td>
</tr>
</table>

| Applied Stimuli | Material Composition | Computation Principles | Material Geometry and Structure | Shape Change Output |
|---|---|---|---|---|
| Uniform Internal:<br>Positive Air Pressure<br>Discrete Internal:<br>Negative Air Pressure | <br>1. Unjammed cell<br>2. Jammed cell<br>3. Expanded actuator | <br>Negative air pressure reconfigure stiffness distribution through jamming separate cells |  | <br>**Jamming Skin**[9] |