Final Draft
of the original manuscript:

Lendlein, A.:
Fabrication of reprogrammable shape-memory polymer actuators for robotics
In: Science Robotics (2018) American Association for the Advancement of Science

DOI: 10.1126/scirobotics.aat9090

Science Robotics - Focus article

Fabrication of Reprogrammable Shape-Memory Polymer Actuators for Robotics

Andreas Lendlein[1,2*]

[1]Institute of Biomaterial Science, Helmholtz-Zentrum Geesthacht, Kantstr. 55, 14513 Teltow, Germany
[2]Institute of Chemistry, University of Potsdam, 14476 Potsdam, Germany
[*]Email: Andreas.Lendlein@hzg.de

Abstract
Shape-memory polymer actuators, whose actuation geometry and switching temperatures are reprogrammable by physical fabrication schemes, were recently suggested for robotics with the option for self-healing and degradability.

Main text
Combining materials with tailored fabrication schemes is an efficient and powerful approach to create (multiple) functions, such as actuation and self-healing, in material systems and thus is a promising strategy for addressing grand challenges in robotics [1]. With the ability of shape-memory polymer actuators (SMPAs to bend, twist, or contract fully reversibly upon cyclic temperature changes [2,3], the next generation of reprogrammable, adapting robots seems to be approaching. A prospect of what can be achieved is shown by a twisted, non-continuously responding SMPA that reversibly turns an arrow sign between three different positions in the hand of a manikin [4]. SMPAs are especially interesting for the next generation of soft robots, which attracted attention with their ability to stretch, squash and climb and their soft touch.

Segments of soft robots are typically actuated by pneumatic actuation or fluidic elastomer actuators [5]. Metallic shape-memory alloys working as tendons with variable lengths can be found as actuators in soft robot designs, although these are not really soft materials. Classical polymeric shape-memory materials are not suitable as actuators because of their one-way character. Heat-shrinkable films or tubes from shape-memory polymers contract upon a temperature increase but do not revert to the original expanded state when cooled again. This one-way effect results from the underlying mechanism and was the major limitation of this technology for decades.

Classical shape-memory polymers comprise two components. The permanent shape (here: shrunk state) is determined by netpoints, whereas switching domains are able to temporarily fix a second shape by “freezing” a polymer deformation. The thermo-sensitivity is related to a thermal transition temperature, T_{trans}, associated with switching domains. At $T > T_{trans}$, the material can be elastically deformed. For $T < T_{trans}$ the flexibility of the network chain segments forming the switching domains is decreased, for example, by vitrification or crystallization. In this way, the polymer´s shape is solidified. For implementing the shape-memory effect, the polymer network is heated to $T > T_{trans}$, deformed, and cooled under stress to $T < T_{trans}$. Releasing the external stress leads to the temporary shape.
In this mechanism, the geometry of the shape change and the capability for recovering the memorized shape are both associated with the switching domains. The recovery of the

original shape is driven by entropy gain of recoiling polymer chains in the softening switching domains when heated; at the same time, the information of the geometry of the movement is deleted.

The separation of these two functions and their assignment to two different domains were key to realizing the first freestanding SMPAs [2]. Two chemically different, crystallisable segments were covalently incorporated into a polymer network system. The melting temperature ranges associated with the two domain types formed by these segments are well separated. The crystallites with the higher *T*m's determine the geometry of the reversible shape change. They build a skeleton following the polymer´s phase morphology, keeping the chains of the second segment type in an oriented conformation. The oriented segments associated with the lower T_m range are actuating units because of a crystallization-induced elongation in the direction of orientation when cooled from the molten state. Reheating leads to a melting-induced contraction, which is supported by entropy gain.

The reversible actuation capability in a determinable geometry emerges from cleverly matching the polymer network architecture with a programming process, which is a thermo-mechanical treatment (Fig. 1a). For this purpose, the polymer is heated to T_{reset}, which is higher than the T_m range of the geometry-determining crystallites, and substantially deformed in the direction of actuation, for example, bending, twisting or stretching, to gain a high degree of segment chain orientation in the deforming parts of the polymer sample (Fig. 1b). Cooling to T_{low} results in crystallization of both segment types and finally in shape B, when the external load is removed. Reversible shape changes are obtained by repeating a heating / cooling cycle between T_{high} (between T_m ranges of both crystallite types) and T_{low} (Fig. 1c).

A remarkable feature of SMPAs is their reprogrammability into other shape-changing geometries, which is possible even after many actuation cycles by following the programming scheme in Fig. 1a.
Besides the geometry of movement, the switching temperature could be made programmable in temperature-memory polymer actuators [6]. In these materials, the two segments for geometry determination and actuation consist of the same repeating unit, in this case, an ethylene unit. A high variability of segment chain length, realized by blending copolymers of the same type but differing in their comonomer ratio, enabled an extraordinary broad melting temperature range. The switching temperature programming procedure pursues the goal to split the crystallites into two cohorts for geometry determination ($T_m > T_{sep}$) and actuation capability ($T_{sep} > T_m > T_{low}$) (see movie S1).
The concept of using only one type of segment according to the chemistry of the repeating unit is also applicable for other SMPAs, for example, poly(ε-caprolactone) [3].
The sophisticated, noncontinuously responding SMPA described at the beginning contains two types of actuator units, whose thermo-sensitivity is associated with well-separated temperature intervals [4].

The reprogrammability of actuation geometry and switching temperatures of SMPAs by physical fabrication schemes is a highly desirable feature for the next generation of adaptable soft robots. The technology's translational potential recently became apparent when a reversible shape-memory effect was realized with commercially available copolymers and blends as starting materials. Shaping and polymer-analogous chemistry

were performed in an integrated process, ensuring high efficacy. Semi-interpenetrating polymer networks, obtained by incomplete cross-linking, exhibited pronounced self-healing capability [7]. Although the materials showed impressive performance in several hundred actuation cycles without any change in their mechanical behaviour, the self-healing could prolong their lifetime.
In the future, advances can be expected from the application of 3D printing techniques following the example of classical shape-memory polymers [8, 9]. Triggers other than temperature changes could enable remote control or autonomous operability of soft robots, for example, by harvesting energy through sunlight or agitation [10]. Reprogrammable actuators might be the key to truly adaptive soft robots, which are not only highly stretchable but real morphing transformers.

References

[1] G.-Z. Yang, J. Bellingham, P. E. Dupont, P. Fischer, L. Floridi, R. Full, N. Jacobstein, V. Kumar, M. McNutt, R. Merrifield, B. J. Nelson, B. Scassellati, M. Taddeo, R. Taylor, M. Veloso, Z. L. Wang, R. Wood, The grand challenges of Science Robotics. *Sci. Robotics* **3**, eaar7650 (2018).

[2] M. Behl, K. Kratz, J. Zotzmann, U. Nöchel, A. Lendlein, Reversible Bidirectional Shape-Memory Polymers. *Adv. Mater.* **25**, 4466-4469 (2013).

[3] O. Dolynchuk, I. Kolesov, D. Jehnichen, U. Reuter, H.-J. Radusch, J.-U. Sommer, Reversible Shape-Memory Effect in Cross-Linked Linear Poly(ε-caprolactone) under Stress and Stress-Free Conditions, *Macromolecules* **50**, 3841-3854 (2017).

[4] M. Farhan, T. Rudolph, U. Nöchel, W. Yan, K. Kratz, A. Lendlein, Noncontinuously Responding Polymeric Actuators. *ACS Appl. Mater. Interfaces* **9**, 33559−33564 (2017).

[5] D. Rus, M. T. Tolley, Design, Fabrication and Control of Soft Robots. *Nature* **521**, 467−475 (2015).

[6] M. Behl, K. Kratz, U. Nöchel, T. Sauter, A. Lendlein, Temperature-Memory Polymer Actuators. *Proc. Natl. Acad. Sci. U. S. A.* **110**, 12555−12559 (2013).

[7] M. Farhan, T. Rudolph, U. Nöchel, K. Kratz, A. Lendlein, Extractable Free Polymer Chains Enhance Actuation Performance of Crystallizable Poly (ε-caprolactone) Networks and Enable Self-Healing. *Polymers* **10**, 255 (2018).

[8] M. Zarek, M. Layani, I. Cooperstein, E. Sachyani, D. Cohn, S. Magdassi, 3D Printing of Shape Memory Polymers for Flexible Electronic Devices. *Adv. Mater.* **28**, 4449-4454 (2016).

[9] H. Yang, W. R. Leow, T. Wang, J. Wang, J. Yu, K. He, D. Qi, C. Wan, X. Chen, 3D Printed Photoresponsive Devices Based on Shape Memory Composites. *Adv. Mater.* **29**, 1701627 (2017).

[10] M. Wehner, R. L. Truby, D. J. Fitzgerald, B. Mosadegh, G. M. Whitesides, J. A. Lewis, R. J. Wood, An Integrated Design and Fabrication Strategy for Entirely Soft, Autonomous Robots. *Nature* **536**, 451−455 (2016).

Acknowledgement

A.L. acknowledges K. Schmälzlin for the support on graphical presentation. **Funding:** The work was supported by the Helmholtz-Association through program-oriented funding.

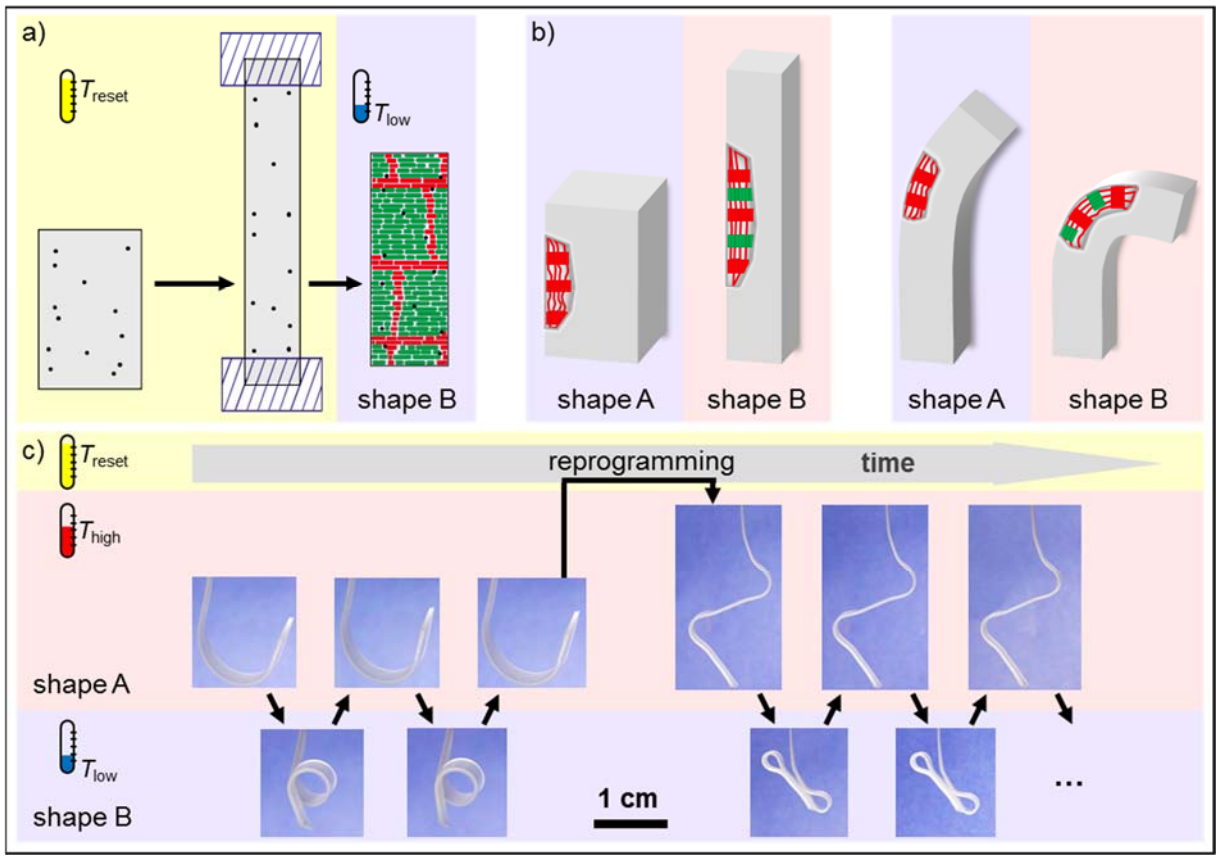


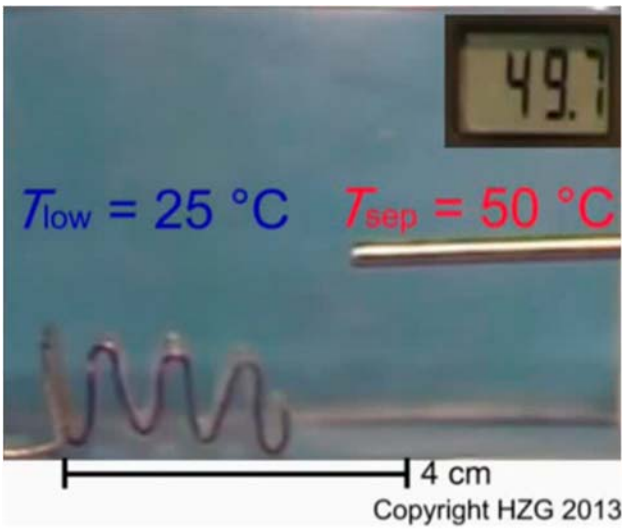
Fig. 1: Shape-memory polymer actuators (SMPA). (a) Programming is an essential part of the SMPA fabrication and includes polymer deformation at T_{reset} and cooling under stress to T_{low}. Removing the external load results in shape B. Geometry-determining units: red; actuation units: green (b) A high degree of segment chain orientation is created in the deforming parts of the polymer sample during programming. The spatial anisotropy of the chain orientation within the sample determines the actuation geometry, for example, stretching (left) or bending (right). (c) Cyclic heating and cooling between T_{low} and T_{high} leads to reversible shape change following the geometry of the deformation applied during programming. Reprogramming is a special capability of SMPAs, whose actuation geometry can be adjusted after substantial numbers of actuation cycles. CREDIT: (a) and (c) are reprinted from [2] with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim (© 2013), in adapted version.

Supporting Information - Science Robotics - Focus article

Fabrication of Reprogrammable Shape-Memory Polymer Actuators for Robotics

Andreas Lendlein[1,2*]

[1]Institute of Biomaterial Science, Helmholtz-Zentrum Geesthacht, Kantstr. 55, 14513 Teltow, Germany
[2]Institute of Chemistry, University of Potsdam, 14476 Potsdam, Germany
[*]Email: Andreas.Lendlein@hzg.de



File: Lendlein_VideoS1.m1v

Movie S1. Reprogrammable switching temperature in a temperature-memory polymer actuator. The movie demonstrates the temperature-memory actuation capability of a ribbon (80 × 20 × 0.9 mm) from crosslinked poly[ethylene-*co*-(vinyl acetate)]s, which was inked at its edges with blue color to enhance visibility contrast. A concertina-like appearance was created by folding at T_{reset} = T_{prog} = 90 °C, cooling to T_{low} = 25 °C, and heating to T_{sep}. The concertina shifted reversibly between an expanded concertina (shape A) at T_{sep} = 50 °C, 65 °C, 75 °C and a contracted concertina (shape B) at T_{low} whereby the degree of expansion increased with T_{sep}. Movie is taken from [6].

Reference

[6] M. Behl, K. Kratz, U. Nöchel, T. Sauter, A. Lendlein, Temperature-Memory Polymer Actuators. *Proc. Natl. Acad. Sci. U. S. A.* **110**, 12555−12559 (2013).