Supporting Information

Behl et al. 10.1073/pnas.1301895110

SI Materials and Methods

Methods 1. (c)PEVAs were prepared by mixing 100 - x g poly [ethylene-*co*-(vinyl acetate)] with a VA-content of 28 wt% (EVAX3175, cPEVA31), of 35 wt% (EVAX150, all from DuPont, cPEVA35) and x g (x = 0; 0.5; 1.0; 2.0; 5.0) dicumyl peroxide (Sigma-Aldrich) in a twin-screw extruder (EuroPrismLab, Thermo Fisher Scientific) at 110 °C and 50 rpm. The blends were compression molded into films with 1mm thickness and subsequently crosslinked at 200 °C and 20 bar for 25 min. cPEd20 was prepared by mixing 98 g low density polyethylene (Lupolen 1800 H, Lyondel) and 2 g dicumyl peroxide, other conditions were the same as described for cPEVA. Crosslinked polystyrene (cPS) was obtained from styrene copolymerized at 80 °C with 2.0 mol% divinyl benzene and 1 mol% benzoyl peroxide (Sigma-Aldrich).

cPCLBA was synthesized by thermally induced copolymerization of poly(ε-caprolactone)diisocyantoethyl dimethacrylate (38.8 wt%) with 60.4 wt% *n*-butyl acrylate (Sigma-Aldrich) and 0.8 wt% 2,2′-azoisobutyronitrile at 80 °C for 72 h. Poly(ε-caprolactone)diisocyantoethyl dimethacrylate was obtained from the reaction of poly(ε-caprolactone) (M_n 8,300 g·mol^{-1}) with 2-isocyantoethyl methacrylate according to the procedure described in (1). cPCLBA provided a $T_{g,mix}$ at −63 °C and a ΔT_m, which ranged from 5 °C to 60 °C with the peak at 50 °C.

Methods 2. The macroscopic change in sample length during the actuation should be reflected on the nanoscale by changes of the longperiods, which is the average distance between two crystalline lamellae consisting of a crystalline and an amorphous part. As long as the sample's macroscopic dimensions do not change, a doubling of the crystallinity should result in a reduction of the longperiod by 50% anticipating constant lamellar thickness at both temperatures. Accordingly, an increase of crystallinity of 50% by formation of additional crystalline lamellae in a part of the amorphous region (in-between the existing skeleton) would result in a decrease of the longperiod by one third. If the macroscopic sample changes its length because of actuation this has to be considered on the nanoscale of longperiods to the same extent. Applying this model on cPEVA20d20 for which an increase of crystallinity of 60% and a macroscopic length change of 12% were obtained during cooling from 75 °C to 25 °C, a longperiod of 10.7 nm could be calculated for shape B starting from a longperiod L (T_{sep}) of 15.4 nm for shape A. This estimate corresponds within the experimental margin of error to the experimentally determined longperiod L(T_{low}) of 11.4 nm for shape B.

1. Kumar UN, Kratz K, Wagermaier W, Behl M, Lendlein A (2010) Non-contact actuation of triple-shape effect in multiphase polymer network nanocomposites in alternating magnetic field. *J Mater Chem* 20(17):3404–3415.

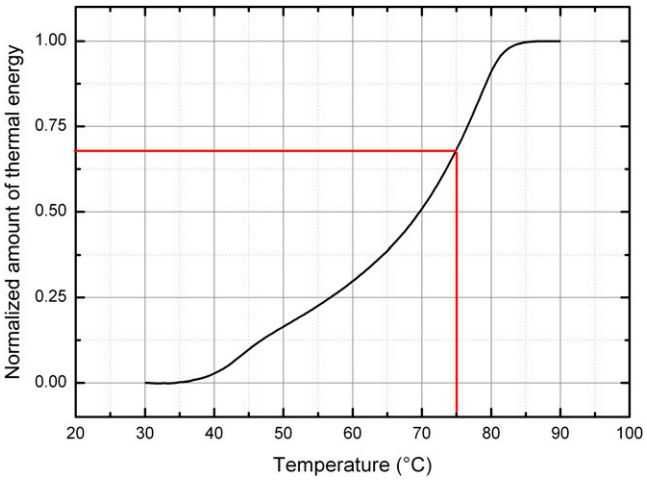


Fig. S1. Differential scanning calorimetry (DSC) investigations of cPEVA with 20 wt% vinyl acetate. Normalized amount of thermal energy of first heating as a measure for the crystallinity at T_{sep}.

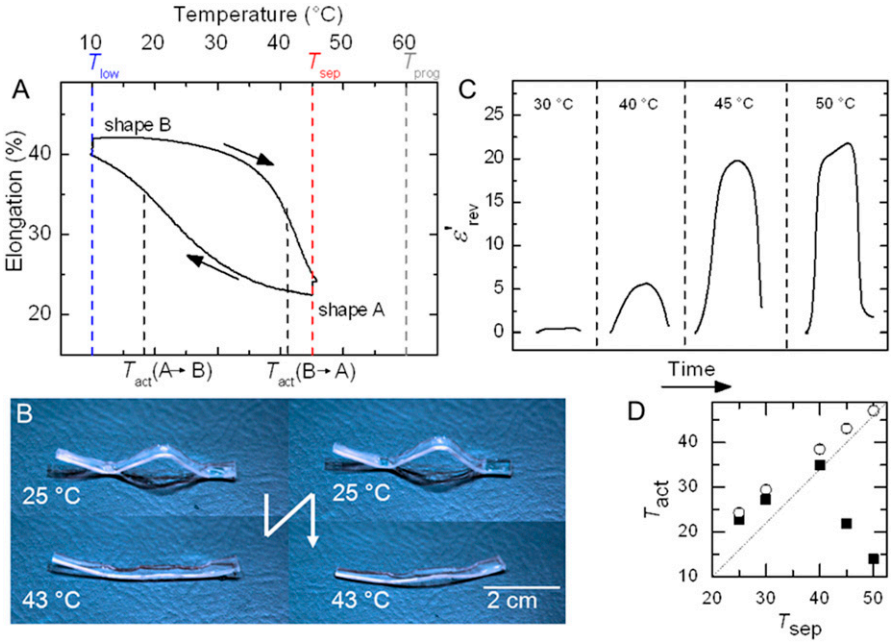
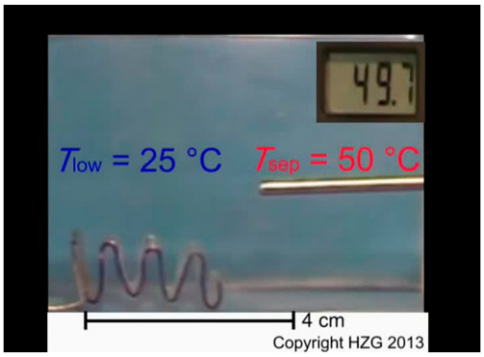


Fig. S2. Thermally controlled, programmable actuator capability of a polyester-based copolymer network. (*A*) A temperature-memory actuation was observed from a cPCLBA sample between $T_{low} = 10$ °C and $T_{sep} = 45$ °C after programming with $\varepsilon_{ssp} = 150\%$ at $T_{prog} = 60$ °C, cooling to $T_{low} = 10$ °C and heating to $T_{sep} = 45$ °C. (*B*) After deformation at $T_{prog} = 60$ °C and heating to $T_{sep} = 43$ °C a polymer ribbon from cPCLBA reversibly changes its shape between an almost flat shape at $T_{sep} = 43$ °C and a concertina like shape at $T_{low} = 0$ °C (ice water, image recorded at room temperature). (*C*) ε'_{rev} as a function of time for T_{sep}, which was varied from 30 to 50 °C. (*D*) Correlation between T_{sep} and the actuation temperatures upon cooling T_{act}(A→B) and heating T_{act}(B→A) in actuation cycles. [T_{act}(A→B): filled squares, T_{act}(B→A): open circles].

Table S1. Influence of the vinyl acetate comonomer content on the actuation capability of cPEVA for optimized programming parameters

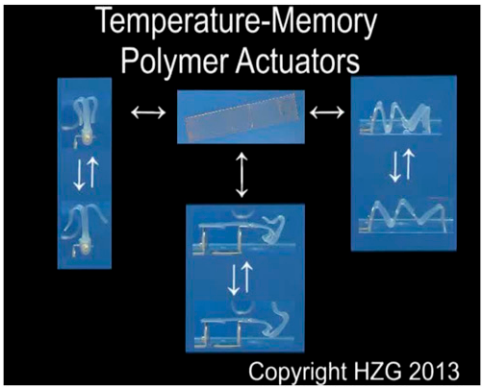
Sample ID*	ε_{ssp}, %	T_{sep},°C	T_{low}, °C	ε'_{rev}, %
cPEd20	250	95	25	—
cPEVA10d20	250	85	25	6
cPEVA20d20	150	75	25	8
cPEVA31d20	150	60	0	12
cPEVA35d20	50	50	0	4

See *SI Materials and Methods, Methods 1* for material synthesis.
*cPEd20: cross-linked low-density polyethylene, cPEVAXXd20 cross-linked poly[ethylene-*co*-(vinyl acetate)] in which XX represents the vinyl acetate fraction in wt% and d20 indicates 2.0 wt% of dicumyl peroxide used for cross-linking.



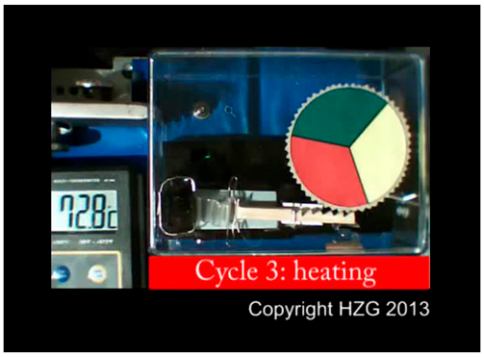
Movie S1. Programmable temperature-memory actuator. The movie demonstrates the temperature-memory actuation capability of a cPEVA ribbon (80 × 20 × 0.9 mm), which was inked at its edges with blue color to enhance visibility contrast. A concertina-like appearance was created by folding at T_{prog} = 90 °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 S1



Movie S2. Demonstration of the programmable, temperature-memory actuation capability of cPEVA. A ribbon (80 x 20 x 0.9 mm) from cPEVA is initially in a fixation device appearance, which reversibly shifts between an open shape at T_{sep} and a closed shape at T_{low}. The sample is later programmed into a caterpillar-like appearance, which reversibly changes between an expanded and a contracted concertina. Finally, the sample is deformed into a butterfly-like shape, which reversibly folds and unfolds its wings. Parameters of experiment: T_{prog} = 90 °C, T_{sep} = 75 °C, T_{low} = 25 °C.

Movie S2



Movie S3. Programmable, temperature-memory actuator in a heat engine with adjustable rotation rate. The heat engine is operated between T_{sep} = 75 °C and T_{low} = 25 °C. The colored disc rotates counterclockwise.

Movie S3