

Shape-Memory Polymers Designed in View of Thermomechanical Energy Storage and Conversion Systems

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Andreas Lendlein* and Matthias Heuchel

Effective temporary shape fixation by strain-induced formation of supramolecular nanostructures enables high energy density one-way shape-memory polymers.

Many sustainable or resilient, wireless technologies such as soft robots, artificial muscles, etc., require local energy storage or conversion of energy from their environment into motion. The capability of active movements, such as a one-way shape-shift or reversible shape changes, can be implemented in polymers by thermomechanical programming as shape-memory function. Stored mechanical energy can be locally released by exposure to heat in one-way shape-memory polymers (SMPs) by entropy driven recoiling. In this respect, Bao and coworkers designed an amorphous one-way shape-memory polymer optimized in its recoverable mechanical stress level when programmed at 300% deformation.¹

Stored mechanical energy can be locally released by exposure to heat in one-way shape-memory polymers (SMPs) by entropy driven recoiling.

A one-way shape-memory polymer is capable of temporarily fixing a mechanical deformation and reverting to its original shape when exposed to heat.² The programming process of implementing the temporary shape together with the thermally induced recovery builds the shape-memory cycle. It begins with heating a material sample to a temperature T_D , at which point it is deformed to a certain strain ϵ_m . While maintaining the applied stress, the sample is cooled below the thermal transition temperature associated with its switching domains. After the external stress is removed in

the cooled state, the sample maintains a significant amount of fixed strain ϵ_f and thereby stores elastic deformation energy. Most of the elastic strain energy can be recovered if the sample is heated again above a characteristic switching temperature T_{sw} . The sample returns to a strain ϵ_p , which is close to the original shape. The amount of the recoverable elastic energy of the SMP sample is limited by the amount of reversible (elastic) work. This work can be calculated from the stress–strain $\sigma(\epsilon)$ relationship of the material at the relevant temperature. In a cold drawing protocol of the programming process, the sample is deformed to ϵ_m at T_D below the thermal transition temperature T_{sw} associated with switching domains. As the thermally induced shape-memory effect (SME) is a one-time, irreversible effect, the sample does not return to the temporary shape upon cooling.

Bao and coworkers demonstrate the potential of their SMP as a thermomechanical energy storage system by lifting weights;¹ the principle is presented in Figure 1a. The polymer sample is stretched at an ambient temperature. Instead of returning to the original length, it retains the elongated shape at a low temperature, and in this way stores elastic deformation energy. Only when heated above a characteristic switching temperature T_{sw} would the molecular mobility of the stretched chains be high enough, and chain segments return into their entropically favored random coils. As a result, the sample contracts when the stored elastic energy is released, e.g. a weight can be lifted. For a further cycle, the one-way SMP sample has to be loaded again. The stored

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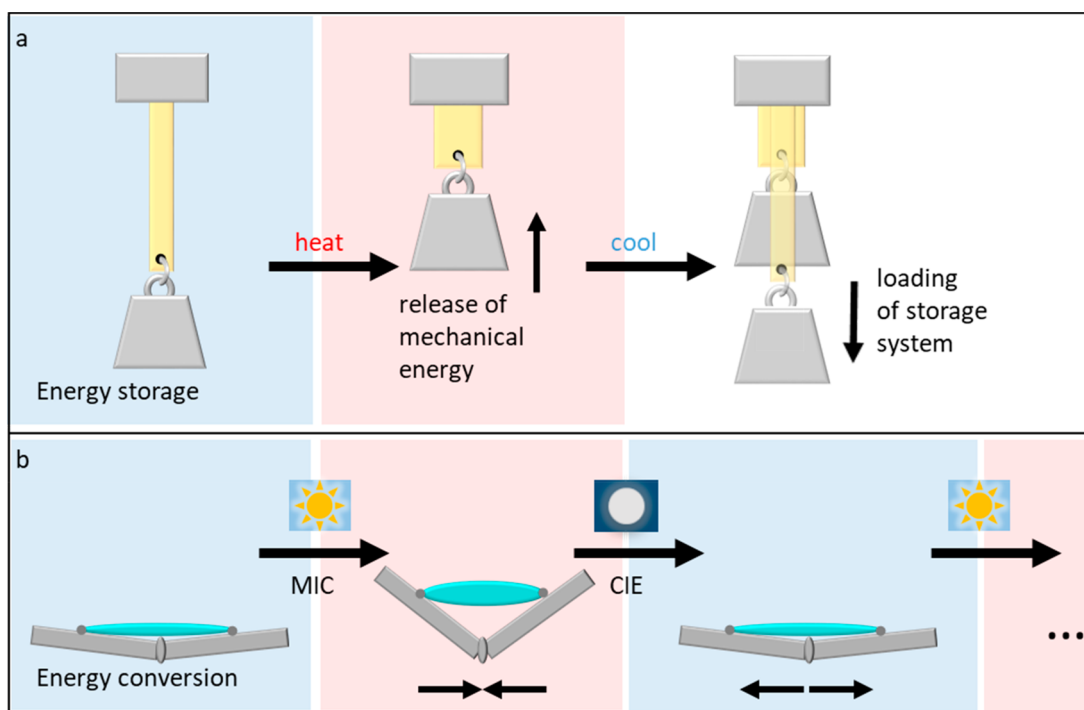


Figure 1. Principles of thermomechanical energy storage and conversion systems based on SMPs. (a) A programmed SMP sample can lift a weight when heated above a characteristic switching temperature T_{sw} by releasing the stored elastic deformation energy in a one-way process. (b) As artificial muscle, a SMPA material may reversibly bend a joint by MIC during heating and CIE upon cooling.

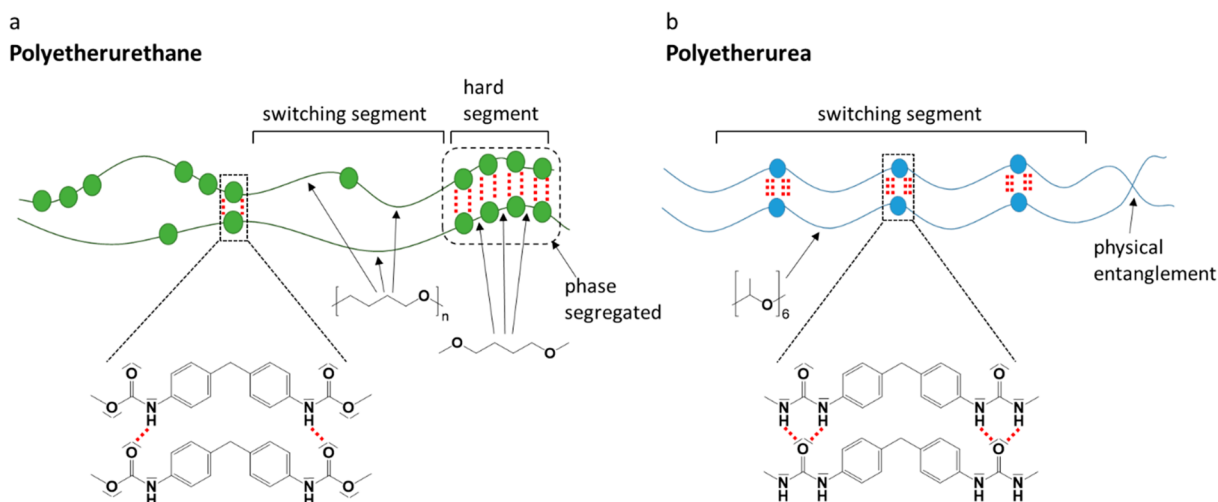


Figure 2. Comparison of the chemical structure of (a) shape-memory polyetherurethane with (b) the polyetherurea PPG-MPU introduced in ref 1. Red dots indicate hydrogen bond interactions between urethane or urea groups on neighboring chains.

energy density of typical SMPs is $<1 \text{ MJ}\cdot\text{m}^{-3}$.³ For higher energy values in a given sample volume, alternative material concepts should be investigated, as in the SMP created by the Bao group.

The next task certainly would be to turn the energy storage/release processes into a reversible, continuous sequence of events and realize a thermally controlled actuator. Conversion of thermal energy of heat/cold (day/night) cycles into oscillating motion can be realized by shape-memory polymer actuators (SMPAs) through crystallization and melting in domains of oriented chain segments (actuating units).²

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The actuation behavior of SMPAs is enabled through macroscale deformation under temperature control, whereby the macromolecular orientation of actuation units and

the skeleton structure of geometry-determining units are dictated in the polymers. Crystallization and melting of the actuation units directly contribute to the reversible movement. The entropy gain after melting lead to melt-induced contraction (MIC). In the opposite direction, the crystalline induced elongation (CIE) during cooling extends the sample size in the orientation direction of the chain segment of the actuating units. Cross-linked networks based on semicrystalline polymers are capable of reversible actuation⁴ and are suitable for a reversible muscle-like movement, as shown in Figure 1b. If the temperature rises significantly, the energy stored in the orientation of the actuating units can be released. In this sense, SMPAs can also serve as energy storage systems.

PPG-MPU, the SMP created by Zhenan Bao's lab, uses a glass transition as thermal switch. A typical example for established amorphous SMPs are polyetherurethanes composed of switching and hard segments, which form a phase-segregated morphology.⁵ While the switching segment is usually an oligoether (e.g., polytetrahydrofuran, PTHF), the hard segments constitute urethane groups (for instance, derived from methylene diphenyl diisocyanate, MDI) and a short chain extender such as 1,4 butanediol (Figure 2a). The hard domains contribute strength and rigidity to the material through physical cross-links. The switching segments provide elasticity and store the deformation energy if the material is stretched.

PPG-MPU consists of polypropylene glycol (PPG) and methylene bisphenylurea (MPU) units in the backbone (Figure 2b). In contrast to the polyether urethane with PTHF of varying chain length between MDI units, in PPG-MPU, the length of the PPG backbone chains between MPU units is fixed (six repeat units). This symmetry has important consequences. Under uniaxial strain (see Figure 4 of ref 1), the polymer chains align into stable supramolecular nanostructures consisting of long, fibril shaped regions (length $>10\ \mu\text{m}$, width $\sim 100\ \text{nm}$) that are parallel to the strain. These long fibrils comprise stacked layers of nanofibers (diameter 8 nm) oriented perpendicular to the strain and are separated by an amorphous material. On the next lower hierarchical size level, the nanofibers are composed of multiple aligned nanorods—formed from stacked urea–urea hydrogen bonds (0.45 nm) between MPU units on the chain, a supramolecular assembly concept, which was discovered by the Bao team earlier.⁶ The supramolecular nanostructures, induced by strain, trap stretched PPG backbone chains (length $\sim 2\ \text{nm}$) in an elongated state. This state has to be stabilized. The constant PPG backbone chain length helps to align urea groups of neighboring chains. This is the prerequisite for the formation of a multivalent interaction between several MPU units of these neighboring chains (Figure 2b).⁷ This

interaction is much stronger than the interaction between MDI-derived urethane groups (Figure 2a) in a polyetherurethane. So, the combination of constant PPG chain length and high H-bond interaction between urea groups enables the specific energy density of $19.6\ \text{MJ}\cdot\text{m}^{-3}$, which is a remarkable performance for a one-way SMP. Both one-way SMPs and SMPAs might play an important role in the realization of autonomous systems and contribute to sustainable and resilient technical solutions such as soft robots or living machines. Consequently, the next challenge will be exploring whether a reversible shape-memory actuator material can be realized based on the molecular design presented by Bao's team.

Author Information

Corresponding Author

Andreas Lendlein – Institute of Active Polymers, Helmholtz-Zentrum Hereon, 14513 Teltow, Germany; Institute of Chemistry, University of Potsdam, 14476 Potsdam, Germany; orcid.org/0000-0003-4126-4670; Email: Andreas.Lendlein@hereon.de

Author

Matthias Heuchel – Institute of Active Polymers, Helmholtz-Zentrum Hereon, 14513 Teltow, Germany

Complete contact information is available at:

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Notes

The authors declare the following competing financial interest(s): A.L. is coinventor on patents in the field of polymer-based shape-memory materials and fibers.

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