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Shape-memory polymers with multiple transitions: complex actively moving polymers

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Qian Zhao,^{ab} Marc Behl^{ac} and Andreas Lendlein^{*ac}

Shape-memory polymers (SMPs) are able to perform shape transitions in a pre-defined pathway in response to suitable external stimuli such as heat, magnetism, electricity, moisture, or light. Most of the SMPs are dual-shape materials, which enable a single shape transition from a temporary to a permanent shape. Recently, triple-shape polymers (TSPs), which are capable of accomplishing two shape transitions, as well as multi-shape polymers with shape changes have been introduced including temperature-memory polymers (TMPs) with tunable multiple shape transitions. Different concepts for obtaining multi-shape polymers are introduced and the sophisticated structural design concepts in combination with tailored shape-memory creation processes (SMCPs) are explained. Future opportunities emerge in alternative actuation methods and exploration of potential applications.

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Introduction

The intense research activities in this field over the last decade have turned shape-memory polymers (SMPs) into an important class of actively moving materials.^{1–5} Upon application of an external stimulus, SMPs are able to change their shape in a predefined way. Such a shape-memory capability requires the deformation of the material into a temporary shape by application of external stress before. This process is called ‘shape-

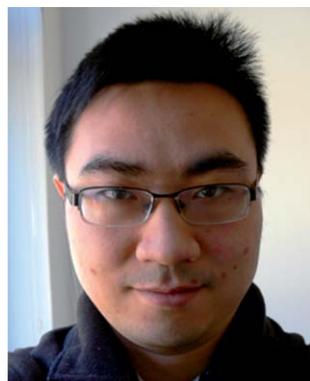
memory creation process’ (SMCP) or ‘programming’. In most cases the stimulus, which is required for the actuation of the SME, needs to be applied during programming as well. Termination of the stimulus fixes the temporary shapes. When the stimulus is applied again, the SMP reverses the pre-defined pathway applied during the SMCP. SMPs differ from another class of actively moving polymers, which is called shape-changing polymers (SCPs). SCPs deform only as long as the stimulus is applied.^{6–10} The shape-memory effect (SME) of the SMPs can be induced by various external stimuli such as heat, magnetism, electricity, moisture, and light.^{4,11–15}

Dual-shape polymers (DSPs) are the most often investigated type of SMPs. They contain only one type of switching domains enabling one shape transition, which can be activated in response to the stimulus. DSPs are able to transform from a temporary shape (A) to the permanent shape (B). Recently,

^aCenter for Biomaterial Development, Institute of Polymer Research, Helmholtz-Zentrum Geesthacht, Kantstr. 55 14513 Teltow, Germany. E-mail: andreas.lendlein@hzg.de

^bDepartment of Chemical and Biological Engineering, Zhejiang University, 310027 Hangzhou, China

^cJoint Laboratory for Biomaterials and Regenerative Medicine, Kantstr. 55, 14513 Teltow, Germany



Qian Zhao received his doctor's degree from Zhejiang University, China in 2009. Then he worked for Zhejiang University as a postdoctoral researcher for two years. Currently, he holds a postdoctoral position at the Active Polymers Department in the Institute of Polymer Research at Helmholtz-Zentrum Geesthacht in Teltow, Germany. His current research interest is stimuli-sensitive polymer materials especially shape-memory polymers.



Marc Behl received his diploma in Chemistry from the University of Wuppertal and his doctor's degree from Johannes Gutenberg University, Mainz. Currently, he is the head of the Active Polymers Department in the Institute of Polymer Research at Helmholtz-Zentrum Geesthacht in Teltow, Germany. His primary research interests are design, synthesis, and characterization of materials capable of active movement with a focus on shape-memory polymers.

triple-shape polymers (TSPs) have been explored.^{16,17} They are able to switch from a first shape (A) to a second shape (B) and further to a third shape (C). This concept has been extended in some cases to a fourth (D) or a fifth (E) shape. Therefore, the recovery process of the multi-shape polymers (MSPs), which exhibit two or more shape transitions, can provide more complex shape changes when compared to DSPs providing only a single shape transition. This functionality is desirable for applications requiring adjustable complex shapes, such as smart implants or surgical devices. In this review we first explain the fundamentals of DSPs as a basis for the concept of triple- and multi-shape polymers. Various activation methods, which are applicable to induce the transitions, will be discussed as well. Finally, future perspectives for fundamental research as well as potential applications are outlined.

Dual-shape polymer-SMPs with single shape transition

The SME is not an intrinsic material property but a function of a material. It requires the combination of a suitable molecular polymer network architecture providing a sufficient elastic deformability and a tailored SMCP. Generally, SMPs provide a polymer network architecture consisting of switching segments, which are interconnected by netpoints determining the permanent shape. The netpoints can be chemical (covalent) bonds or intermolecular interactions, such as crystallites.¹ In addition to the netpoints, the domains formed by switching segments, which are sensitive to the particular external stimuli, must be capable of fixing the temporary shape on demand by forming additional reversible crosslinks. These additional temporary crosslinks can be of physical nature (e.g., crystallization or vitrification of the switching segments)¹ or of chemical nature (reversible covalent bonds, e.g., photo-reversible cyclo-addition formed by cinnamic or cinnamylidene acetic acid



Andreas Lendlein is Director of the Institute of Polymer Research at Helmholtz-Zentrum Geesthacht in Teltow, Germany and a Member of the Board of Directors of the Berlin-Brandenburg Centre for Regenerative Therapies (BCRT). He is a professor at the University of Potsdam and an Honorary Professor at Freie Universität Berlin as well as a Member of the Medical Faculty of Charité University Medicine Berlin.

He completed his Habilitation in Macromolecular Chemistry in 2002 at RWTH Aachen University and received his doctoral degree in Materials Science from the Swiss Federal Institute of Technology (ETH) in Zürich in 1996. His current research interests include (multi)functional polymer-based materials, biomaterials and their interaction with biological environments as well as the development of medical devices and controlled drug delivery systems especially for regenerative therapies.

groups).^{18,19} Fig. 1 displays some important examples of polymer network architectures providing different types of combinations from netpoints and switching segments. Although not all-embracing, this classification shows a guideline for designing the architecture of SMPs. A typical SMCP is shown in Fig. 2 for the thermally-induced SME, which is the most extensively investigated SME. The switching segments provide a transition temperature (T_{trans}), which is typically determined by dynamic thermomechanical analysis (DMA) or differential scanning calorimetry (DSC) measurements. For crystalline segments, T_{trans} is accordingly a melting temperature (T_{m}), for liquid crystalline segments a clearing temperature (T_{cl}), and for vitrifiable segments a glass transition temperature (T_{g}). When the SMP is heated to a temperature T_{high} above T_{trans} , the switching segments become flexible and the polymer material can be elastically deformed by the application of external stress. The temporary shape is obtained by cooling the material to a temperature T_{low} below T_{trans} , at which the switching segments

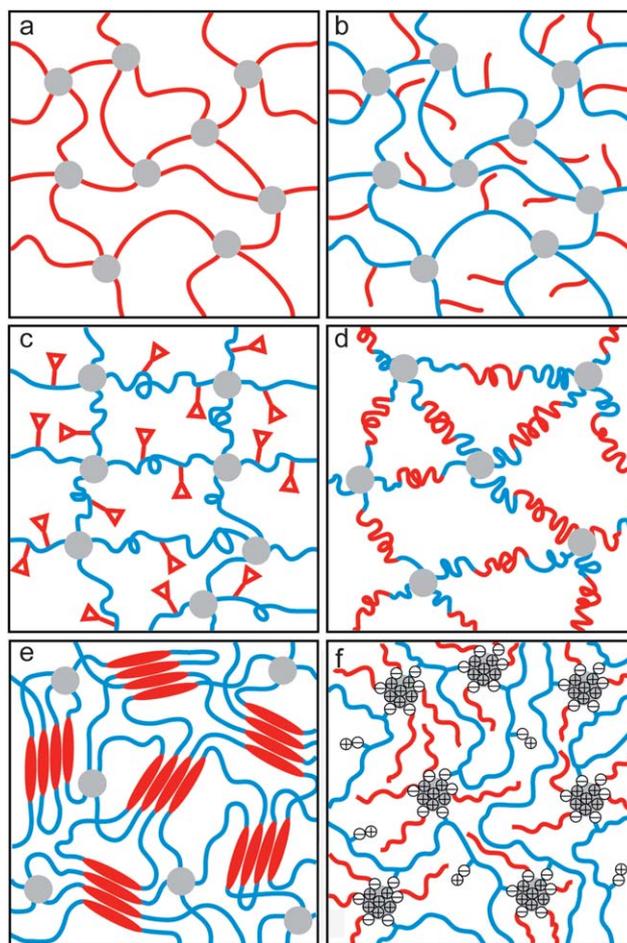


Fig. 1 Examples for polymer network architectures suitable for exhibiting a SME (molecular switches: red; netpoints: gray): (a) switching segments linking netpoints, (b) side chains as switching segments, (c) functional groups as molecular switches capable of reversibly forming a covalent bond, (d) ABA triblock segments linking netpoints, (e) liquid-crystalline polydomains enabling fixation and (f) assembly of ionic switching segments and ionomers containing ion-rich domains as netpoints. (a) to (d) were taken from ref. 20, with kind permission of Springer Science+Business Media.

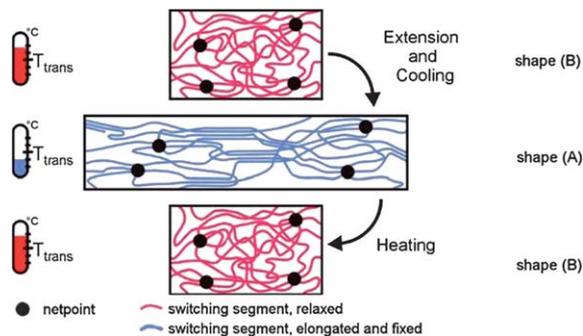


Fig. 2 Molecular mechanism of the thermally-induced SME. T_{trans} is the thermal transition temperature of the switching phase (taken from ref. 1) © WILEY-VCH Verlag GmbH, 69451 Weinheim, Germany, 2002.

solidify to provide new physical crosslinks, and releasing the external stress. If the material is heated over T_{trans} , the permanent shape is recovered as the deformed switching segments recoil into the initial state to retain the highest state of entropy. The temperature, at which the sample shows the highest recovery rate, is defined as a switching temperature (T_{sw}). In addition to T_{trans} , the shape fixity ratio (R_f) and the shape recovery ratio (R_r) are another two important quantities, which are used to describe the shape-memory properties. R_f quantifies the ability of the material to fix a certain mechanical deformation ϵ_m in the programming process. R_r quantifies the ability to recover the permanent shape after programming. R_f and R_r are calculated from the strain values obtained in the cyclic, thermomechanical tensile or bending tests.

The stimuli for actuating the SME can be generally classified into heat, (alternating) magnetic field, electric current, moisture, light, *etc.* However, except the intrinsically light-induced SMPs,^{18,19} all other reported SMPs were indirectly thermally actuated SMPs.^{2,20} In these systems, magnetism, electricity or light is absorbed by functional molecular groups or additives (particles or fibers) and then converted into heat, thereby causing a temperature increase of SMPs. This increase in temperature then induces the SME of the SMPs or their composites indirectly, once T_{sw} of the sample bulk is exceeded. In addition, the SME can also be triggered by indirectly lowering T_{trans} .

Direct thermally-induced dual-shape effects

Thermally-induced SMPs whose SME is induced by direct application of heat have been widely investigated.^{4,12} However, studies on optimization of the function are still a topic of current interest in order to overcome limitations such as low recovery stress or transition temperature, and to match the wide-spreading application requirements. In this context, we present some recent developments of SMPs.

SMPs are able to store large changes in strain in their temporary shape. However, this large recoverable change in strain is usually associated with a low recovery stress due to their relatively low elastic modulus (E), especially at a temperature above the T_{trans} of the switching domains. The E values of shape-memory metallic alloys are typically around 200–400 MPa

and can reach up to 800 MPa, while the E values of most SMPs are lower than 10 MPa above T_{trans} .^{21–23} Recovery stress is the stress, which the sample develops during shape recovery under constraint conditions and gives a measure of the load the sample could apply during the shape transition and in this way act against outer constraints. In spite of the large recovery stress, shape-memory alloys suffer from rather low recoverable strains. The reported maximum adoptable strain was 13.5%.²⁴ Conclusively, the combination of large recovery stress and large recoverable strain is a challenge for shape-memory polymers.

Recovery stress depends on the E modulus of the deformed SMPs at T_{high} .²² Since recovery always occurs above T_{sw} , which is related to T_{trans} , a high value for the E modulus at temperatures above T_{trans} is required. Otherwise, recovery stress would still be low even if the material possesses a very high E modulus below T_{trans} .⁵ Different strategies have been followed to enhance the recovery stress such as the incorporation of reinforcing fillers, *e.g.* carbon nanotubes and silica nanoparticles,^{4,12,22} variation of the programming parameters, *e.g.* the temperature T_d at which the deformation is applied during programming,²² or adjustment of the crosslinking density, *e.g.* by variation of the crosslinker contents or the molecular weights of the oligomers used for crosslinking.

Commonly, incorporation of nanoparticles into SMPs resulted in an increase of E below and above T_{trans} .^{22,25–27} When about 20 wt% carbon nanotubes (CNTs) were embedded in neat polyvinyl alcohol (PVA) to prepare CNT–PVA fibers,²² the fibers generated a large recovery stress, which was two orders of magnitude higher than the stress generated by conventional SMPs. These fibers could be stretched up to 800% of their original length. However, the addition of the nanoparticles resulted in a broadened T_g . The achieved recovery stress was as high as 130 MPa when the temperature at which the deformation was applied (T_d) was as low as 70 °C. In contrast, the recovery stress was less than 40 MPa, if a T_d of 180 °C was applied.

In CNT–PVA, it was also noticed that the recovery stress can be significantly influenced by the programming parameters. When the samples were pre-programmed at different T_d s (70 °C, 90 °C, 120 °C, 150 °C, and 180 °C) and were subsequently heated from room temperature to 230 °C at a rate of 5 °C min^{−1}, the maximum recovery stress of the CNT–PVA fibers occurred at the maximum recovery stress temperature $T_{\sigma,\text{max}}$, which was basically equal to T_d . This phenomenon is called temperature memory effect (TME) as the materials memorize the temperature, at which they were deformed recently.

The E modulus can be significantly enhanced when the crosslinking density is increased. However, an increased crosslinking density also reduces the elongation at break. A straightforward approach is therefore the increase of crosslinking density after the shape recovery. This was demonstrated for a polymer network created from star-shaped thiol oligomers, which were crosslinked with star-shaped oligomers having terminal vinyl groups. After an initial crosslinking, which enabled the programming and the shape-recovery, the sample was finally cured, which increased the crosslinking density and in this way the E modulus.²⁸

Another approach to increase the E modulus as well as the stress at recovery is the incorporation of nanoparticles as covalent netpoints. A recently reported example is a SMP consisting of modified SiO_2 as netpoints and PEG switching segments.^{25,26} The SiO_2 nanoparticles are functionalized with sulfonic acid and afterwards mono-amine group terminated PEG was tethered through electrostatic attraction to the particles to form organic-inorganic hybrids with hydroxyl groups at the ends of tethered PEG chains.²⁵ The prepared nanoparticles were subsequently reacted with hexamethylene diisocyanate (HDI) to obtain crosslinked polymer networks. At a moderate particle content of 16 vol%, the E of the shape-memory hybrid can reach more than 100 MPa above T_{trans} . This principle could be transferred to SiO_2 nanoparticles grafted with poly(ϵ -caprolactone) (PCL).²⁶ After linking the applied nanoparticles with 4,4'-methylenediphenyl diisocyanate (MDI), SMP networks with high recoverable strains (up to 600%) and an enhanced mechanical strength with an E modulus of almost 700 MPa were obtained. However, the nanoparticles need to be carefully selected. When a nanoclay was used as netpoint providing material, to which PCLs were tethered, the E modulus was only around 12 MPa.²⁷

In summary, incorporation of particles, increase of cross-linking density, as well as usage of macroscopic covalent netpoints are useful ways to increase the E modulus. Especially, the latter holds promise for multifunctional materials, which provide more functionalities except the shape-memory functionality.

Indirect thermally-induced dual-shape effects

The thermally-induced dual-shape effect is usually directly triggered by increasing the environmental temperature by application of a heater or addition of hot gas or liquid. However, these heating methods might not be applicable to all cases, especially when not all parts of the DSP device are accessible or when heating of the environment would cause harm, *e.g.* in an organism. Another important application for indirect heating is the situation when the device needs to be heated *e.g.* in a non-heat conducting environment or in a very cold surrounding such as space or aerospace.

A straightforward approach for indirect heating is the application of heat by light in the form of irradiation with IR-light, radio frequency, or microwaves. The interaction with the light source and in this way the heat transfer can be enhanced by the incorporation of fillers so that multifunctional materials are created. In addition, this enables additional heating sources such as electrical current or alternating magnetic fields. Both types are common that they can be turned on or off on demand. In addition to these indirect heating methods, another strategy to trigger the DSE indirectly is lowering the T_{trans} by diffusion of a low molecular weight plasticizer such as H_2O into the polymer or by dissolving the switching segments. Here we shortly introduce indirectly thermally-induced SMPs with single transition, which were categorized by the method of indirect actuation.

Irradiation of DSPs with infrared (IR) light was a first demonstration of the indirectly triggered DSE without

increasing the environmental temperature and was used to activate polyurethane-based medical devices.^{29,30} A laser was required as a light source to provide a sufficient amount of heat energy. The required high energy could be reduced by enhancing the heat transfer by incorporation of conductive fillers such as carbon nanotubes³¹ or gold nanorods.³² In the case of the latter, when irradiation with near-IR wavelengths is applied, the heating can be performed transdermally.³² More recently, laser light with a visible wavelength of 532 nm was used to trigger the DSE of a composite of PCL and gold nanoparticles.³³ Shape recovery of the composite could be controlled locally in the region exposed to the laser because heat release by gold nanoparticles upon absorption of light only locally increased the temperature of the polymer with poor thermal conductivity (Fig. 3). Moreover, the shape recovery process could be stopped immediately at any stage upon turning off the light. Therefore, multiple intermediate shapes of the material could be obtained. These two benefits can hardly be achieved by directly heating. Similarly, radio frequencies³⁴ and microwave frequencies³⁵ were applied to heat the DSPs (or their composites) indirectly to trigger the DSE.

The incorporation of magnetic nanoparticles (Fe_2O_3 , Fe_3O_4 , Ni, *etc.*) into DSPs enabled the actuation of the DSE by alternating magnetic fields. Once a sufficient amount of heat energy is generated by the nanoparticles at a high magnetization frequency, the magnetically-induced DSE occurs. The first magnetically-induced DSE was realized by incorporating silica coated Fe_2O_3 nanoparticles with diameters of 20–30 nm into thermoplastic DSP matrices.³⁶ The DSE of the nanocomposites, which showed a homogeneous distribution of the nanoparticles, could be induced by remote actuation applying an alternating magnetic field. The required bulk temperature of the DSP–nanocomposite was achieved when the applied magnetic field strength or the nanoparticle content was sufficiently high. The magnetically-induced recovery procedure of a coiled sample is exemplarily shown in Fig. 4. Similarly, composites of DSP thermosets with Fe_3O_4 nanoparticles had been prepared.^{37,38}

When electrically conductive materials such as conducting polymers, carbon black, carbon nanotubes, carbon nanofibers, or metal powders were incorporated into the SMPs, the



Fig. 3 Photographs showing a spatially selective shape recovery process at room temperature by separate laser exposures on four sections of an AuNP-loaded XbOCL film stretched to 100% deformation (successively from the bottom section to the top section), with the film stepwise lifting a load 350 times its weight. Reproduced from ref. 33 with permission from The Royal Society of Chemistry.

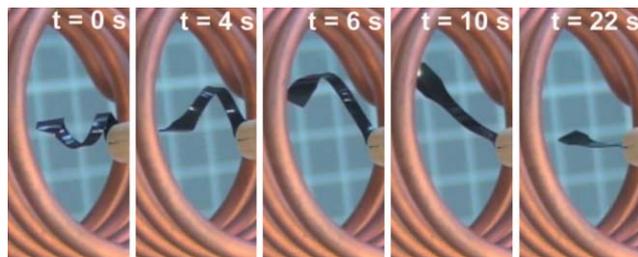


Fig. 4 Magnetically-induced shape-memory effect of the thermoplastic composite consisting of Fe(III) oxide nanoparticles in a silica matrix and poly-etherurethanes. Taken from ref. 36. Copyright 2006 National Academy of Sciences, USA.

dual-shape effect could be actuated indirectly by the application of an appropriate current.^{4,12–14,31} In this way, a certain degree of conductivity could be reached in the dual-shape polymers, which generally are isolators like all polymers. The internal Joule heating generated from the conductive fillers due to the application of the current could induce the thermal dual-shape effect indirectly. In this way, external heating could be avoided.

A third indirect actuation of the SME can be obtained by using low molecular weight molecules to lower T_{trans} of the SMP. When polyurethanes were immersed into water, the water molecules diffused into the amorphous switching domains. These water molecules acted as a plasticizer and increased the flexibility of the polymer chains. In this way, the T_g of the switching domain of the polyurethane was lowered by 35 K.³⁹ As a result, T_g could be lowered from a temperature above ambient temperature to a temperature below it. Once T_{trans} was decreased the SME occurred. The maximum water uptake of these polymers was 4.5% so that these materials were still considered to be polymers rather than hydrogels. Similarly, organic solvents or mixed solutions such as DMF⁴⁰ or ethanol⁴¹ can also induce this type of SME. A water-induced SME can also be achieved for SMPs containing crystallizable hydrophilic PEG switching segments.⁴² Here the PEG crystals were dissolved upon immersion in water and the SME occurred.

Triple- and multi-shape polymers with two or more shape transitions

Independent of the applied stimulus methods for inducing the DSE, all DSPs with a sharp, single thermal transition are characterized by only two independent shapes. Although intermediate shapes during the transition procedure could be achieved upon termination of a suitable stimulus, they are associated with the permanent shape and the SMCPs in which the temporary shape was created. In this way, once a temporary shape has been changed, all intermediate shapes will be changed as well. Moreover, the shape recovery process will not stop at an intermediate shape, if the exposure of the stimulus carries on. A transition from a temporary shape to an intermediate shape cannot be considered as a complete transition. Triple- and multi-shape polymers (TSPs) can perform even more shape transitions than dual-shape polymers after suitable SMCPs.¹⁷ For example, TSPs are able to switch from a first shape

(A) to a second shape (B) and from there to a third shape (C) during the recovery process.¹⁶ These polymers provided two independent transitions: from shape A to shape B and from shape B to shape C. For an ideal TSP ($R_f = 100\%$ and $R_r = 100\%$), shape B is independent from shapes A and C. In this way changing shape A through application of different SMCPs should not affect shape B, as shape B is only determined by the programming procedure and not affected by programming of shapes A and C. Although shape B can also be considered as an intermediate shape between shapes A and C, it is the termination of the recovery process from shape A to B as well as the beginning of the transition from shape B to shape C. In this way, shapes A, B and C are distinct from each other.⁴³ However, if both shape transitions are associated with the same part of the device, the total deformability/elongation at break needs to be considered. Fig. 5 visualizes an example for potential applications of a TSP.¹⁶ The TSP was manufactured into an intelligent fastener consisting of a plate with anchors that can potentially be used in assembly technology to fix a specific component. Firstly, the device is fixed into a compact form (A), which is easy to be handled. Upon increasing the environmental

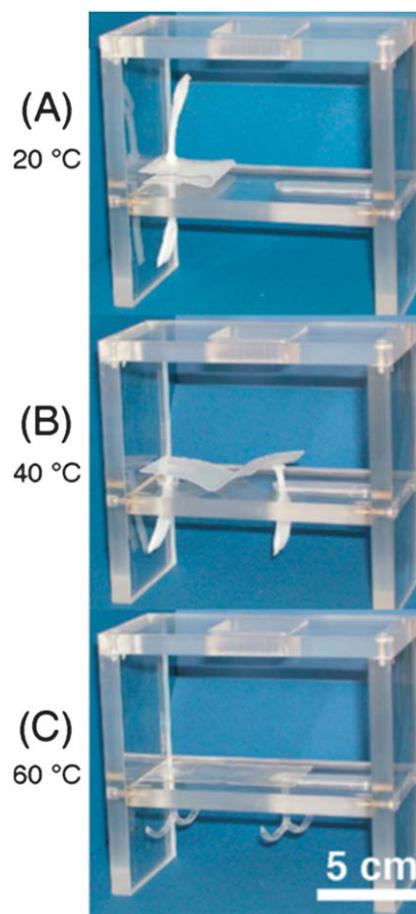


Fig. 5 Series of photographs illustrating the triple-shape effect by the example of a potential fastening system consisting of a plate with anchors. The picture series show the recovery procedure from the temporary shape A (A) to the temporary shape B (B), and subsequently to the permanent shape C (C). Taken from ref. 16. Copyright 2006 National Academy of Sciences, USA.

temperature, the bent plate unfolds so that the folded anchors are able to get through the narrow gap to be in the suitable position (B) followed by opening the anchors (C). This series of complex movements can hardly be achieved by a dual-shape polymer.

The following section presents an overview of SMPs, which are able to perform multiple transitions, classified by direct and indirect heating.

Triple-shape and multiple-shape effects induced by direct heating

In general, multiple transitions can be achieved by recovery processes in multi-phase SMPs with two (or more) distinct T_{trans} s or SMP with a single broad thermal transition region associated with the switching domains. Detailed introductions are presented below, including the triple-shape effect (TSE), and the quadruple-shape effect (QSE).

TRIPLE-SHAPE POLYMERS. As a structural concept for creating triple-shape polymers, two segregated switching domains with two T_{trans} s are required. The first discovered triple-shape polymers are multi-phase polymers, which were named MACL and CLEG.¹⁶ MACL was obtained as a copolymer network containing PCL segments with a $T_m = 50$ °C and poly(cyclohexyl methacrylate) (PCHMA) segments with a $T_g = 140$ °C. Both segments provided polymer chain segments forming links between netpoints and in this way both contributed to the overall elasticity of the polymer network. CLEG provided PEG segments and PCL segments with two segregated T_m s (34 °C and 50 °C respectively). In the CLEG system, only the PCL segments were crosslinking the poly(meth)acrylate backbone while the PEG segments were introduced as side chains. Although the two polymer systems were of different architectures, both of them possessed two domains, which were associated with two discrete T_{trans} s ($T_{\text{trans,A}}$ for the lower transition temperature and $T_{\text{trans,B}}$ for the higher one). In addition to providing two T_{trans} s and a suitable polymer network architecture, a suitable 'triple-shape creation process' (TSCP) is required to enable the two transitions of TSPs.

In order to create the two temporary shapes (shape A and shape B), most commonly, dual transitions of TSPs need to be enabled by a two-step programming procedure (2SPP). When a typical TSP with two T_{trans} s is programmed by 2SPP, the permanent shape (C) is at first deformed into a temporary shape (B) at a deformation temperature (T_{high}), which is above both T_{trans} s. Afterwards the TSP is cooled to a mediate temperature (T_{mid}) between $T_{\text{trans,A}}$ and $T_{\text{trans,B}}$ whereby the application of the external stress is maintained. The temporary shape (B) can be fixed by cooling below $T_{\text{trans,B}}$ due to the solidification of the switching domains associated with shape B. During the second programming step, this shape B is deformed to the other temporary shape (A) under maintenance of T_{mid} . Afterwards, the polymer is cooled to a temperature T_{low} , which is below both T_{trans} s. Shape A is then fixed by the solidification of the other switching domains, which contribute to $T_{\text{trans,A}}$. During the deformation process, thermo-mechanical conditions show a significant impact on the TSE of the obtained polymers.⁴⁴ Here

the order of the temperatures should be $T_{\text{low}} < T_{\text{trans,A}} < T_{\text{mid}} < T_{\text{trans,B}} < T_{\text{high}}$. Accordingly, two transitions of the TSP are enabled upon recovery, including transition A \rightarrow B, which is associated with $T_{\text{trans,A}}$, and transition B \rightarrow C, which is associated with $T_{\text{trans,B}}$. The described 2SPP, called 2SPP-I, is a conventional SMCP mostly used to create triple-shape capability. In addition, a 2SPP, called 2SPP-II, was reported including the following steps: heating to T_{high} , application of a first deformation, which is fixed by cooling to T_{low} , heating to T_{mid} , application of the second deformation, which is fixed by cooling to T_{low} again, and finally heating to T_{high} for recovery. 2SPP-II differs from 2SPP-I in such a way that here shape B is fixed at T_{low} while in 2SPP-I it is fixed at T_{mid} .¹⁹ An alternative TSCP method to achieve dual shape transitions in a TSP is a one-step programming procedure (1SPP), which is similar to the SMCP for dual-shape polymers.⁴⁵ Although during programming only a single-step deformation was applied at T_{high} , a TSE could be observed during reheating. The 1SPP requires that all segments, whose solidification is associated with the fixation of a single shape, contribute to the overall elasticity of the polymer network. Therefore not all TSPs are suitable for 1SPP. Examples, which are qualified for a 1SPP, are the MACL system or a copolymer network obtained from crosslinking of star-shaped PCL and poly(ω -pentadecalactone) (PPDL) precursors.⁴⁶ The high elasticity of the sample attributed to the deformability of the crystalline PPDL domains enabled a new programming of the TSE by a deformation at ambient temperature (cold drawing). This programming, named c1SPP, significantly shortened the time interval for programming. Moreover, shortcomings such as the low mechanical properties at T_{high} and thermal degradation that could potentially occur during programming can be avoided. 1SPP and c1SPP techniques do not only provide simpler ways for achieving a TSE but also enrich scientific understanding of the phenomenon. However, in c1SPP the directions of the applied deformations for programming the two temporary shapes cannot be independent. In this way, shape B, which has not been defined in an individual programming step, correlates with the shape recovery from shape A to shape C. Therefore the 2SPP is still the preferable TSCP when complex shape transitions need to be realized.

The TSCP is quantified in cyclic, thermomechanical experiments.⁴⁷ Such an experiment is shown in Fig. 6 for the MACL system, which was programmed by stress-controlled 2SPP-I. The sample was stretched at T_{high} from ϵ_c (shape C) to ϵ_B^0 . Then, the material was cooled to T_{mid} , which resulted in ϵ_{Bload} when external stress was maintained until the physical crosslinks were established. Upon release of the external stress, the sample retained the elongation ϵ_B (shape B). A second deformation step at T_{mid} , which leads to ϵ_A^0 , was correlated with ϵ_{Aload} after cooling to T_{low} while the external stress was maintained. After a sufficient time at T_{low} , the second temporary netpoints related to $T_{\text{trans,A}}$ determined the second temporary shape A (ϵ_A) without further application of external stress. In the recovery procedure, the recovery of shape B (ϵ_{Brec}) and shape C (ϵ_{Crec}) was triggered by heating to T_{high} . R_f and R_r of the different shape transitions can be calculated according to the following equations using the data obtained from the thermomechanical experiment.

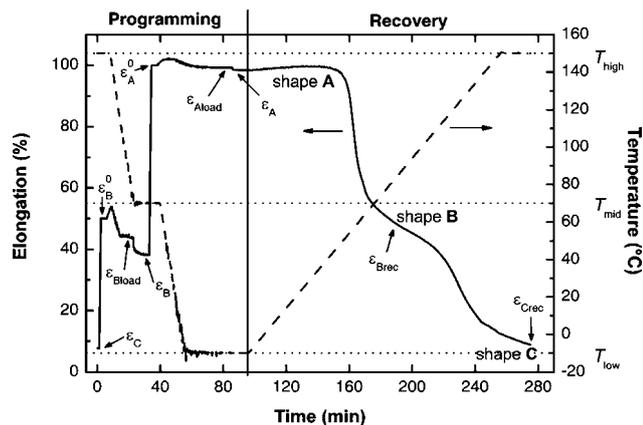


Fig. 6 Cyclic, thermomechanical experiment of MAEL(45) (fifth cycle) according to 2SPP-I as a function of time: solid line, strain; dashed line, temperature. Taken from ref. 16. Copyright 2006 National Academy of Sciences, USA.

$$R_f(C \rightarrow B) = (\varepsilon_B - \varepsilon_C) / (\varepsilon_{Bload} - \varepsilon_C) \quad (1-1)$$

$$R_f(B \rightarrow A) = (\varepsilon_A - \varepsilon_B) / (\varepsilon_{Aload} - \varepsilon_B) \quad (1-2)$$

$$R_f(C \rightarrow A) = (\varepsilon_A - \varepsilon_C) / (\varepsilon_{Aload} - \varepsilon_C) \quad (1-3)$$

$$R_r(A \rightarrow B) = (\varepsilon_A - \varepsilon_{Brec}) / (\varepsilon_A - \varepsilon_B) \quad (2-1)$$

$$R_r(B \rightarrow C) = (\varepsilon_B - \varepsilon_{Crec}) / (\varepsilon_B - \varepsilon_C) \quad (2-2)$$

$$R_r(A \rightarrow C) = (\varepsilon_A - \varepsilon_{Crec}) / (\varepsilon_A - \varepsilon_C) \quad (2-3)$$

$R_f(C \rightarrow B)$, $R_f(B \rightarrow A)$ and $R_r(A \rightarrow B)$, $R_r(B \rightarrow C)$ are quantifying each deformation step, while $R_f(C \rightarrow A)$ and $R_r(A \rightarrow C)$ are related to the overall R_f and R_r .

For the DSPs, which contain only one thermal transition, the elastic modulus decreases dramatically only around the transition region. Compared with the DSPs, the TSPs provide two thermal transitions. Therefore, a two-step decrease of the elastic modulus can be observed for the TSPs (Fig. 7a). Each step of the loss can be attributed to the each separated T_{trans} . In the temperature region between the two T_{trans} s, the elastic modulus remains almost constant. This platform relates to the temporary shape B.

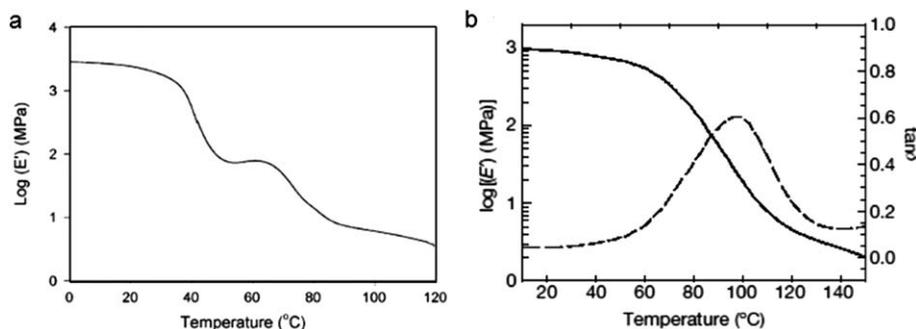


Fig. 7 Dynamic mechanical analysis curves for (a) a triple-shape polymer bilayer (taken from ref. 52, © 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim) and (b) a temperature memory polymer. Reprinted by permission from Macmillan Publishers Ltd: Nature, ref. 64, Copyright 2010).

The most common way to incorporate two T_{trans} s within a network is covalently linking two switching segments whose segregated domains provide discrete T_m and/or T_g .^{16,43,45,46,48} Recent examples include side-chain liquid crystalline polymer networks,^{49,50} in which the liquid crystalline solidification of the side chains and the vitrification of the polymeric backbone acted as molecular switches to trigger the TSE. In another approach, TSPs were prepared by incorporating grafted ureidopyrimidone (UPy) groups providing reversible hydrogen bonding with a $T_{trans,B}$ of around 60 °C as well as another switching segment with $T_{trans,A} = T_g$.⁵¹ Fig. 8 shows some typical chemical structures of these triple-shape polymers, as well as schemes for variation of the network structure at the molecular level during the shape recovery within the cyclic thermomechanical experiment. The triple-shape properties of these systems were of high efficiency, whereby the preparation of the materials requires sophisticated chemistry skills. Therefore, bilayers, fibers in a matrix, as well as utilization of the amorphous phase of semi-crystalline polymers have been explored, which seemed to be more facile to realize.

Bilayers prepared by macroscopically combining two epoxy thermoset layers with two well-separated T_g s enabled a macro-phase-separated TSP composite with two T_{trans} s.⁵² The TSE could be performed by bending deformations and was tunable by changing the thickness ratio of the two layers. Similarly, two layers of shape-memory polyurethane networks crosslinked by chemically modified silica nanoparticles with two separated T_g s were incorporated into a triple-shape bilayer.⁵³ However, the macroscopically asymmetrical structure of the triple-shape bilayers may lead to unexpected strains once a certain stress level is exceeded.

In addition to bilayer structures also fibers in a matrix were investigated as an alternative geometry to combine two kinds of dual-shape polymers with two T_{trans} s.⁵⁴ Non-woven thermoplastic PCL nanofibers (average diameter < 760 nm) were embedded into a shape-memory epoxy matrix, where the PCL fibers provided a T_m of around 55 °C while the epoxy matrix had a T_g from 20 °C to 45 °C.

Fabricating multi-material systems with different geometrical designs is a versatile approach to build functional TSPs.

Based on the principle that semi-crystalline polymers possess a crystalline and an amorphous phase, a poly(ester)

urethane) multi-block copolymer was synthesized from semi-crystalline poly(1,4-butylene adipate) (PBA-3500) as the soft segment phase (switching domain) and methylene bis(4-phenylisocyanate) (MDI) as the hard segment phase (permanent physical netpoints).^{55,56} The soft segment, which possesses a T_m of 34 °C as well as a T_g of -49 °C, contributed two T_{trans} s. Further investigation demonstrated that semi-crystalline PCL segments were also able to provide two transitions, which were associated with devitrification of PCL and melting of hitherto crystalline PCL, to actuate the TSE.⁵⁷

MULTIPLE-SHAPE POLYMERS. As the number of thermal transitions correlates with the number of shapes, which can be achieved in a shape-memory material, polymers, which possess *e.g.* three T_{trans} s, should be able to perform three shape transitions after a suitable quadruple-SMCP. This was demonstrated in a ternary blend of multi-phase polyolefins composed of nearly linear high density polyethylene (HDPE) with a T_m of

132 °C and two ethylene-1-octene copolymers (EOCs) with T_m s of 59 °C and 96 °C. Crosslinking was achieved by hydrogen abstraction from the saturated C-H bonds using 2,5-dimethyl-2,5-di(*tert*-butylperoxy)-hexane at 190 °C.⁵⁸ The resulting polymer network was capable of three shape transitions. In principle, incorporation of additional EOCs with different T_m s could further increase the number of transitions but this approach is limited by the number of well separated T_m s, which can be obtained in such a blend. Also for other polymer systems the chemical synthesis procedure becomes more and more challenging when several distinct T_{trans} s need to be incorporated into the material to obtain a multiple shape polymer.

Nevertheless, a virtue can be made of the necessity that when more and more phases are combined instead of several distinct T_{trans} s one broad T_{trans} is obtained. As generally there is no difference between the dual-shape programming of TMPs and

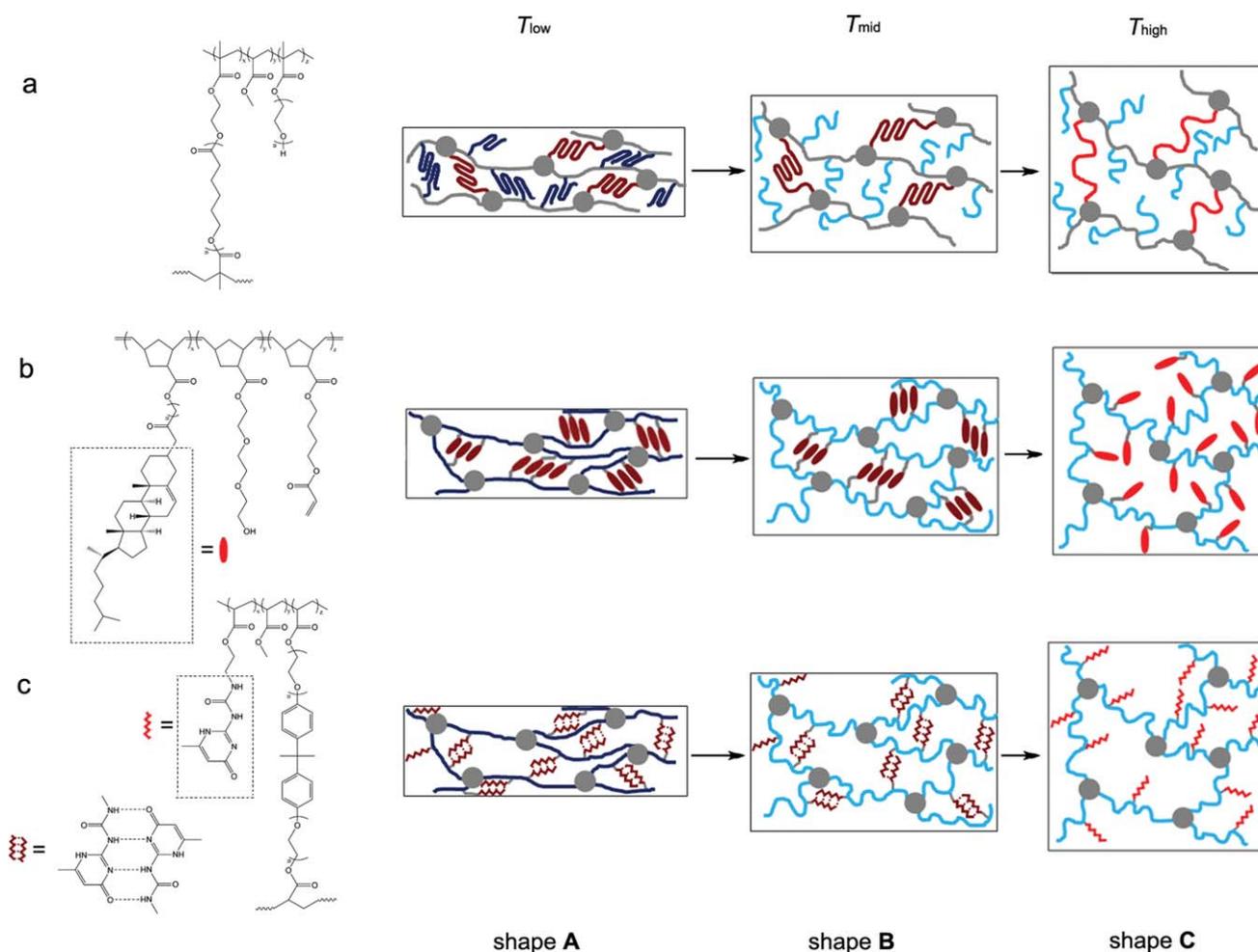


Fig. 8 Chemical structure as well as schematic representation of the changes in the polymer network structure at the molecular level of some selected examples of triple-shape polymers. (a) CLEG network,¹⁶ (b) side-chain liquid crystalline polymer networks,⁵⁰ and (c) UPy network.⁵¹ The switching segments related to $T_{trans,B}$ (PCL segments for (a), side-chain liquid-crystalline mesogens for (b), and hydrogen bonds based on UPy units for (c)) are colored in light red at T_{high} and in dark red at T_{mid} and T_{low} . The switching segments related to $T_{trans,A}$ (PEG segments for (a), polynorbornene backbone for (b), and poly(methyl acrylate) backbone for (c)) are shown in light blue at T_{high} and T_{mid} whereas in dark blue at T_{low} . The segments in light color represent that they are amorphous (flexible), while the segments in dark color represent that they are solidified to form temporary netpoints. The gray dots represent the permanent netpoints, and the gray lines visualize the amorphous polymer chain segments.

that of TSPs or multiple-shape polymers this broad T_{trans} can be used for the programming of multiple-shapes. A single broad thermal transition can be treated as an arrangement of an infinite amount of infinitely sharp transitions, which are continuously distributed. Each of these sharp transitions can be considered as a controlling unit (CU) with an associated T_{trans} .⁵ When the polymer is deformed at one of these T_{trans} s as $T_{\text{trans},i}$ (namely $T_d = T_{\text{trans},i}$), only CUs with T_{trans} s below $T_{\text{trans},i}$ are activated for the shape recovery. As T_{sw} would correlate with $T_{\text{trans},i}$ as well as T_{sw} and T_d would be almost identical, the selection of the appropriate T_d enables the adjustment of T_{sw} . This principle could be utilized for creating TSPs. Here, two suitable T_d s would be selected during a two-step TSCP. Such a TSP could be considered as a polymer network consisting of domains providing the sufficient elasticity and switching domains, whose elasticity is a linear function of the temperature.⁵⁹ Once the switching temperature of the transition domain is increased, the recovery driven by the entropy elasticity occurs. Therefore the system can also be understood as a modified Maxwell–Weichert model of two Maxwell units and a spring.⁶⁰ The applicability of TMPs as TSPs was shown for a norbornene-based copolymer with a broad T_g obtained by ring-opening metathesis polymerization (ROMP) of norbornene cholic acid (NCA) and norbornene triethylene glycol monomethyl ether (NTEG).⁶¹ The range of the broad T_g , as well as the hydrophilicity, solubility, and mechanical properties of the material, could be adjusted by changing the molar ratio of NCA and NTEG within the copolymer composition.

The applicability of TMPs for multiple-shape polymers was demonstrated for the thermoplastic perfluorosulphonic acid copolymer (trade name Nafion®), providing a polytetrafluoroethylene backbone and perfluoroether sulphonate side chains. Unlike the DSPs or the TSPs, the elastic modulus of these TMPs decreases gently in the broad thermal transition region (Fig. 7b). The phase morphology of such a perfluorosulphonic acid copolymer is rather complicated, however generally it is believed that these copolymers provide an ionic cluster phase and a crystalline phase. Two thermal transitions can be observed, a T_g extending over the temperature interval from ~ 40 °C to 150 °C as well as a second transition above 250 °C attributed to the ionic interactions. When deformations at T_d

58 °C, 70 °C, or 100 °C were applied, the maximum strain recovery occurred at a temperature around $T_{\text{sw}} \approx T_d$ (Fig. 9a).⁶²

Also (co)polymers featuring a broad melting temperature range (ΔT_m) contributed by crystallizable segments are capable of a TME (Fig. 9b).⁶³ PEVA copolymers, which are composed of crystallizable polyethylene segments and amorphous poly(vinyl acetate) segments, possess a relatively broad ΔT_m and two T_g s at -107 °C and 38 °C. The ΔT_m is tunable by variation of the ethylene content. When two PEVA copolymers containing different amounts of polyethylene segments were blended, the ΔT_m could even be extended to 100 °C, which was quite sufficient to perform tunable multiple transitions of the TMP (Fig. 8). Similar to the T_g -based TME for the ΔT_m -based TME, the observed $T_{\sigma,\text{max}}$ or T_{sw} was approximately equal to T_d .

It can be noticed that in the crystalline cPEVA the temperature interval between the different T_d s and in this way T_{sw} can be tighter when compared to the perfluorosulphonic acid copolymer, as T_m s are generally extending over a narrower temperature interval as T_g s. In addition, compared to other TSPs, the PEVA copolymer can be easily synthesized.

QUADRUPLE- AND QUINTUPLE-SHAPE EFFECTS BASED ON THE TMP. When three deformations were applied in an appropriate MSCP to such a TMP based on T_g or T_m a tunable quadruple-shape effect was obtained.⁶⁴ However, it must be said that in the cPEVA demonstrator the deformations were applied to different segments, while for the perfluorosulphonic acid copolymer they were applied to the same piece in the same direction. Nevertheless, also in a TMP used as a MSP providing a broad ΔT_m the deformations can be applied to the same part of the sample resulting in a multi-shape recovery of the same piece as demonstrated for polyesterurethane composed of poly(ϵ -caprolactone) and poly(ω -pentadecalactone) segments.⁶⁵

Vice versa, devices providing spatially separated T_g s, which can be created by suitable polymer synthesis, are also capable of a MSE. The post-curing of a pre-cured thermoset SMP on a hot stage with a linear temperature gradient resulted in a TMP possessing a range of T_g s distributed in a gradient fashion along the temperature gradient of the stage.⁶⁶ When the material was programmed at a T_d above the highest T_g of the intact SMP sample, the recovery of the sample sections occurred spatially according to their own T_g s when the ambient temperature

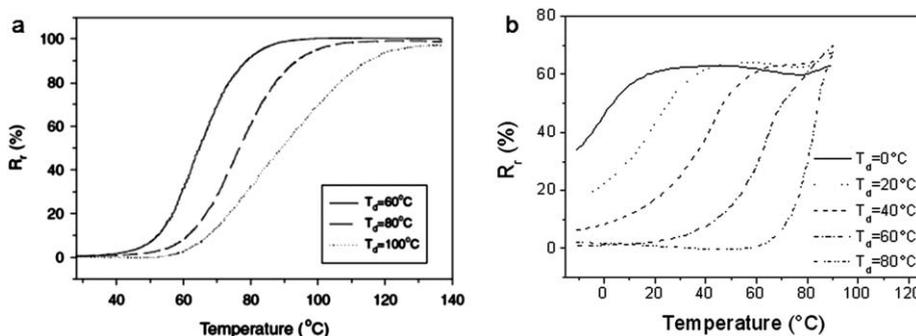


Fig. 9 (a) Stress-free recovery process of Nafion (taken from ref. 62, © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim) and (b) PEVA copolymer (calculated from data of ref. 63, © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

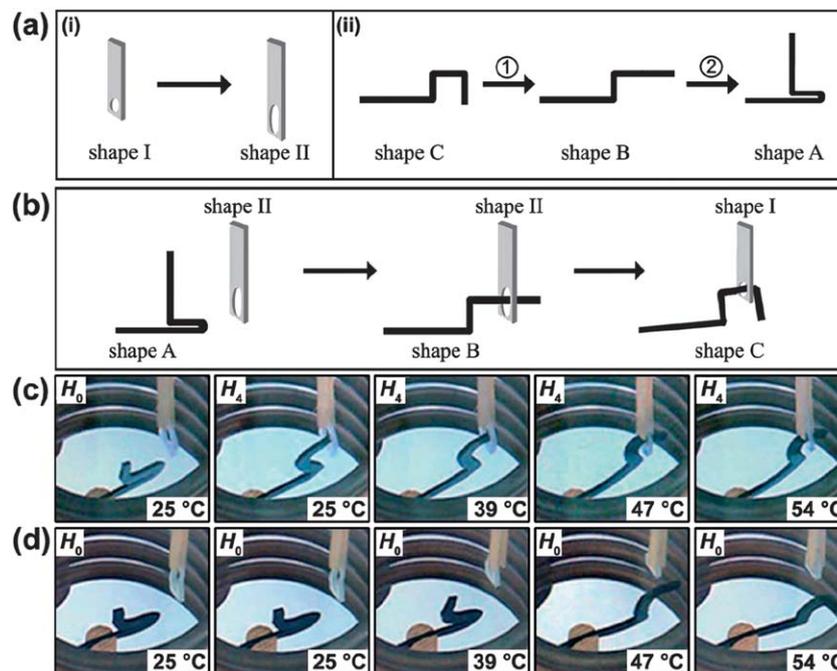


Fig. 10 Fixation device demonstrator consisting of a triple-shape nanocomposite with adjustable $T_{sw,app}$ as the active component. (a) Schematic representation of SMCPs applied for programming of the DSP counterpart (i) and the triple-shape nanocomposite hook (ii). (b) Working principle of the fixation device. Recovery images taken at different T_{env} s, (c) photograph series achieved by environmental heating at $H_4 = 20.2 \text{ kA m}^{-1}$ (protocol 1). (d) Recovery images obtained by protocol 2: environmental heating without magnetic field at $T_{env} = 25 \text{ }^\circ\text{C}$ (taken from ref. 70, © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

continuously increased. This SMP with a graded morphology can be considered as spatially distributed CUs providing continuously graded T_{trans} .

The combination of discrete T_{trans} as well as the utilization of a broad T_g for several T_{trans} s enabled a quintuple-shape polymer. Poly(methyl methacrylate)/poly(ethylene glycol) semi-IPN (PMMA/PEG semi-IPN) was prepared by *in situ* bulk homopolymerization and crosslinking of MMA in the presence of linear PEG.⁶⁷ The incorporation of PEG within the network did not only result in a broadened T_g of PMMA, but also introduced an additional $T_{trans} = T_m$ associated with the melting of PEG segments. The versatile approach of combining two very common polymers has enabled a quintuple-shape effect.

When the recovery curves of multiple-shape polymers based on TMPs are compared with those of triple/multiple shape polymer systems providing more distinct thermal transitions, it can be noticed that in the case of the first the recovery occurs soon after the previous shape transition had been passed while in the case of systems providing phase-segregated domains with individual T_{trans} more distinct shape recovery steps can be noticed.

Triple-shape and multiple-shape effects induced by indirect heating

In general, all stimuli capable of inducing the single transition of dual SMPs, which have been described in the former sections, could be applied to the multi-shape polymers. In this chapter we present an overview about indirectly thermally-induced polymers providing multiple shape transitions.

The incorporation of silica coated Fe_2O_3 nanoparticles into a TSP matrix such as the MACL network enabled the magnetically-induced triple-shape effect.⁶⁸ When the frequency of the alternating magnetic field was maintained constantly at 258 kHz, the nanocomposite was remotely heated at first to a $T_{mid} = 70 \text{ }^\circ\text{C}$ and secondly to a $T_{high} = 150 \text{ }^\circ\text{C}$ when the two magnetic field strengths (H) of 14.6 kA m^{-1} and 29.4 kA m^{-1} were applied. Similarly, a TSE of $\text{Fe}_2\text{O}_3/\text{CLEG}$ nanocomposites was also realized by magnetic heating.⁶⁹ The temperature difference between the environmental temperature and the bulk temperature of the material could be controlled by adjusting the applied H or the content of the incorporated nanoparticles. Upon combination of environmental heating (T_{env}) and magnetic heating, the apparent switching temperature ($T_{sw,app}$) could be easily and reversibly adjusted, avoiding complex chemical synthesis, novel programming methods, or material preparation.⁷⁰ The concept of magnetically adjustable $T_{sw,app}$ was demonstrated by a fixation device, which was composed of a triple-shape nanocomposite hook and a dual-shape polymer fixation counterpart with a $T_{sw} = 47 \text{ }^\circ\text{C}$ (Fig. 10). At a magnetic field strength of $H_4 = 20.2 \text{ kA m}^{-1}$, the hook could place and fix successfully inside the counterpart before it moved upwards, when T_{env} exceeded $47 \text{ }^\circ\text{C}$ (Fig. 10c). In contrast, the procedure failed when only environmental heating was applied (Fig. 10d).

As an additional function comparable to the TME, a magnetic-memory effect (MME) was discovered when magnetic nanoparticles were incorporated within TMP matrices.⁷¹ It could be shown that the magnetic field strength applied at deformation (H_d) was similar to the applied field strength under stress-free (H_{sw}) or constant-strain ($H_{\sigma,max}$) conditions (Fig. 11).

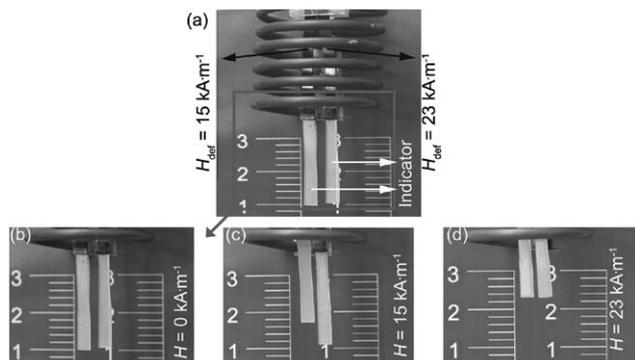


Fig. 11 Macroscopic demonstration of a MME in TMPU(15:1): (a) samples after deformation at $H_d = 15 \text{ kA m}^{-1}$ (left) and $H_d = 23 \text{ kA m}^{-1}$ (right) with a pure TMPU strip acting as an indicator. (b) Closer view of the indicator. (c) Shape change of left sample at $H_d = 15 \text{ kA m}^{-1}$. (d) Both samples recovered at $H_d = 23 \text{ kA m}^{-1}$ (taken from ref. 71, 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

In contrast to H -triggered multiple transitions of SMPs, radio-frequency (RF) was applied to induce multiple-SMEs as well.⁷² Based on the concept that Fe_2O_3 nanoparticles and CNTs can be selectively heated using two distinct RFs (296 kHz and 13.56 MHz), these two nanofillers were embedded into different regions of a polymer sheet, and after a suitable SMCP a multiple-transition performance could be achieved when one of the RFs was applied. When this system is compared to TSPs, the approach enables traditional dual-shape polymers to perform multiple-shape transition through combination of two independent single transitions and in this way broadens the design concepts to achieve multiple transitions.

Conclusion and outlook

Dual shape polymers are polymers providing netpoints and switching segments interconnecting the netpoints. The idea of an additional switching phase opened the field of triple and multiple-shape polymers and in this way the introduction of even more additional switching phases enables the opportunity for an additional shape transition. After quadruple polymers have been introduced recently the record is now at quintuple shape polymers. It can be assumed that the research field will still further progress. If the number of thermal transitions increases in this way, the transitions are getting closer and closer. In this context, the idea is born to utilize one broad thermal transition, which commonly is disliked in the classical polymer synthesis of engineering plastics. Such a broad thermal transition can be either a broad T_g or a broad T_m .

In fundamental research the field will develop towards multimaterial systems, layers, fibers in matrices and nanocomposites, which are the main focus. Conclusively, multi-shape materials become more and more easily available. Furthermore, they can be actuated indirectly by alternating magnetic fields; research in this direction is still in its infancy. For commercially relevant plastics the multiple-shape technology becomes interesting and in the next couple of years the first approaches towards applications have to be expected.

References

- 1 A. Lendlein and S. Kelch, *Angew. Chem., Int. Ed.*, 2002, **41**, 2034–2057.
- 2 M. Behl and A. Lendlein, *Mater. Today*, 2007, **10**, 20–28.
- 3 L. Sun, W. M. Huang, Z. Ding, Y. Zhao, C. C. Wang, H. Purnawali and C. Tang, *Mater. Des.*, 2012, **33**, 577–640.
- 4 J. Leng, X. Lan, Y. Liu and S. Du, *Prog. Mater. Sci.*, 2011, **56**, 1077–1135.
- 5 T. Xie, *Polymer*, 2011, **52**, 4985–5000.
- 6 M. Behl and A. Lendlein, *Soft Matter*, 2007, **3**, 58–67.
- 7 H. Y. Jiang, S. Kelch and A. Lendlein, *Adv. Mater.*, 2006, **18**, 1471–1475.
- 8 Y. Yu, M. Nakano and T. Ikeda, *Nature*, 2003, **425**, 145.
- 9 Y. Qiu and K. Park, *Adv. Drug Delivery Rev.*, 2001, **53**, 321–339.
- 10 A. Lendlein, M. Behl, B. Hiebl and C. Wischke, *Expert Rev. Med. Devices*, 2010, **7**, 357–379.
- 11 A. Lendlein and R. Langer, *Science*, 2002, **296**, 1673–1676.
- 12 M. Behl, M. Y. Razzaq and A. Lendlein, *Adv. Mater.*, 2010, **22**, 3388–3410.
- 13 L. Hsu, C. Weder and S. J. Rowan, *J. Mater. Chem.*, 2011, **21**, 2812–2822.
- 14 Y. Hu and W. Chen, *Macromol. Chem. Phys.*, 2011, **212**, 992–998.
- 15 P. T. Mather, X. F. Luo and I. A. Rousseau, *Annu. Rev. Mater. Res.*, 2009, **39**, 445–471.
- 16 I. Bellin, S. Kelch, R. Langer and A. Lendlein, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 18043–18047.
- 17 M. Behl and A. Lendlein, *J. Mater. Chem.*, 2010, **20**, 3335–3345.
- 18 A. Lendlein, H. Y. Jiang, O. Jünger and R. Langer, *Nature*, 2005, **434**, 879–882.
- 19 L. Wu, C. Jin and X. Sun, *Biomacromolecules*, 2011, **12**, 235–241.
- 20 M. Behl, J. Zotzmann and A. Lendlein, *Adv. Polym. Sci.*, 2010, **226**, 1–40.
- 21 E. Hornbogen, *Adv. Eng. Mater.*, 2006, **8**, 101–106.
- 22 P. Miaudet, A. Derre, M. Maugey, C. Zakri, P. M. Piccione, R. Inoubli and P. Poulin, *Science*, 2007, **318**, 1294–1296.
- 23 I. A. Rousseau, *Polym. Eng. Sci.*, 2008, **48**, 2075–2089.
- 24 Y. Tanaka, Y. Himuro, R. Kainuma, Y. Sutou, T. Omori and K. Ishida, *Science*, 2010, **327**, 1488–1490.
- 25 P. Agarwal, M. Chopra and L. A. Archer, *Angew. Chem., Int. Ed.*, 2011, **50**, 8670–8673.
- 26 Y. Zhang, Q. Wang, C. Wang and T. Wang, *J. Mater. Chem.*, 2011, **21**, 9073–9078.
- 27 F. Cao and S. C. Jana, *Polymer*, 2007, **48**, 3790–3800.
- 28 D. P. Nair, N. B. Cramer, J. C. Gaipa, M. K. McBride, E. M. Matherly, R. R. McLeod, R. Shandas and C. N. Bowman, *Adv. Funct. Mater.*, 2012, **22**, 1502–1510.
- 29 D. J. Maitland, M. F. Metzger, D. Schumann, A. Lee and T. S. Wilson, *Lasers Surg. Med.*, 2002, **30**, 1–11.
- 30 G. M. Baer, W. Small, T. S. Wilson, W. J. Benett, D. L. Matthews, J. Hartman and D. J. Maitland, *Biomed. Eng. Online*, 2007, **6**, 43.
- 31 H. Koerner, G. Price, N. A. Pearce, M. Alexander and R. A. Vaia, *Nat. Mater.*, 2004, **3**, 115–120.

- 32 K. C. Hribar, R. B. Metter, J. L. Ifkovits, T. Troxler and J. A. Burdick, *Small*, 2009, **5**, 1830–1834.
- 33 H. Zhang, H. Xia and Y. Zhao, *J. Mater. Chem.*, 2012, **22**, 845–849.
- 34 C. S. Hazelton, S. C. Arzberger, M. S. Lake and N. A. Munshi, *J. Adv. Mater.*, 2007, **39**, 35–39.
- 35 H. Du, Y. Yu, G. Jiang, J. Zhang and J. Bao, *Macromol. Chem. Phys.*, 2011, **212**, 1460–1468.
- 36 R. Mohr, K. Kratz, T. Weigel, M. Lucka-Gabor, M. Moneke and A. Lendlein, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 3540–3545.
- 37 M. Y. Razzaq, M. Behl, K. Kratz and A. Lendlein, *Mater. Res. Soc. Symp. Proc.*, 2009, **1140**, 185–190.
- 38 X. J. Yu, S. B. Zhou, X. T. Zheng, T. Guo, Y. Xiao and B. T. Song, *Nanotechnology*, 2009, **20**, 235702.
- 39 W. M. Huang, B. Yang, L. An, C. Li and Y. S. Chan, *Appl. Phys. Lett.*, 2005, **86**, 114105.
- 40 H. Lv, J. Leng, Y. Liu and S. Du, *Adv. Eng. Mater.*, 2008, **10**, 592–595.
- 41 Y. Zhao, C. C. Wang, W. M. Huang and H. Purnawali, *Appl. Phys. Lett.*, 2011, **99**, 131911.
- 42 Y. C. Jung, H. H. So and J. W. Cho, *J. Macromol. Sci. Phys.*, 2006, **45**, 453–461.
- 43 I. Bellin, S. Kelch and A. Lendlein, *J. Mater. Chem.*, 2007, **17**, 2885–2891.
- 44 J. Li and T. Xie, *Macromolecules*, 2011, **44**, 175–180.
- 45 M. Behl, I. Bellin, S. Kelch and A. Lendlein, *Adv. Funct. Mater.*, 2009, **19**, 102–108.
- 46 J. Zotzmann, M. Behl, Y. K. Feng and A. Lendlein, *Adv. Funct. Mater.*, 2010, **20**, 3583–3594.
- 47 W. Wagermaier, K. Kratz, M. Heuchel and A. Lendlein, *Adv. Polym. Sci.*, 2010, **226**, 97–148.
- 48 S. Chen, J. Hu, C.-W. Yuen, L. Chan and H. Zhuo, *Polym. Adv. Technol.*, 2010, **21**, 377–380.
- 49 S.-k. Ahn, P. Deshmukh and R. M. Kasi, *Macromolecules*, 2010, **43**, 7330–7340.
- 50 S.-k. Ahn and R. M. Kasi, *Adv. Funct. Mater.*, 2011, **21**, 4543–4549.
- 51 T. Ware, K. Hearon, A. Lonneckner, K. L. Wooley, D. J. Maitland and W. Voit, *Macromolecules*, 2012, **45**, 1062–1069.
- 52 T. Xie, X. C. Xiao and Y. T. Cheng, *Macromol. Rapid Commun.*, 2009, **30**, 1823–1827.
- 53 C. Y. Bae, J. H. Park, E. Y. Kim, Y. S. Kang and B. K. Kim, *J. Mater. Chem.*, 2011, **21**, 11288–11295.
- 54 X. F. Luo and P. T. Mather, *Adv. Funct. Mater.*, 2010, **20**, 2649–2656.
- 55 T. Pretsch, *Smart Mater. Struct.*, 2010, **19**, 015006.
- 56 T. Pretsch and W. W. Muller, *Polym. Degrad. Stab.*, 2010, **95**, 880–888.
- 57 M. Bothe, K. Y. Mya, E. M. J. Lin, C. C. Yeo, X. H. Lu, C. B. He and T. Pretsch, *Soft Matter*, 2012, **8**, 965–972.
- 58 I. S. Kolesov and H.-J. Radusch, *eXPRESS Polym. Lett.*, 2008, **2**, 461–473.
- 59 L. Sun and W. M. Huang, *Soft Matter*, 2010, **6**, 4403–4406.
- 60 M. Heuchel, J. Cui, K. Kratz, H. Kosmella and A. Lendlein, *Polymer*, 2010, **51**, 6212–6218.
- 61 Y. Shao, C. Lavigueur and X. X. Zhu, *Macromolecules*, 2012, **45**, 1924–1930.
- 62 T. Xie, K. A. Page and S. A. Eastman, *Adv. Funct. Mater.*, 2011, **21**, 2057–2066.
- 63 K. Kratz, S. A. Madbouly, W. Wagermaier and A. Lendlein, *Adv. Mater.*, 2011, **23**, 4058–4062.
- 64 T. Xie, *Nature*, 2010, **464**, 267–270.
- 65 K. Kratz, U. Voigt and A. Lendlein, *Adv. Funct. Mater.*, 2012, **22**, 3057–3065.
- 66 A. M. DiOrio, X. Luo, K. M. Lee and P. T. Mather, *Soft Matter*, 2011, **7**, 68–74.
- 67 J. Li, T. Liu, S. Xia, Y. Pan, Z. Zheng, X. Ding and Y. Peng, *J. Mater. Chem.*, 2011, **21**, 12213–12217.
- 68 U. N. Kumar, K. Kratz, W. Wagermaier, M. Behl and A. Lendlein, *J. Mater. Chem.*, 2010, **20**, 3404–3415.
- 69 U. N. Kumar, K. Kratz, M. Behl and A. Lendlein, *eXPRESS Polym. Lett.*, 2012, **6**, 26.
- 70 U. N. Kumar, K. Kratz, M. Heuchel, M. Behl and A. Lendlein, *Adv. Mater.*, 2011, **23**, 4157–4162.
- 71 M. Y. Razzaq, M. Behl and A. Lendlein, *Adv. Funct. Mater.*, 2012, **22**, 184–191.
- 72 Z. He, N. Satarkar, T. Xie, Y.-T. Cheng and J. Z. Hilt, *Adv. Mater.*, 2011, **23**, 3192–3196.