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Multifunctional Shape-memory Polymers

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1. Abstract

The thermally-induced shape-memory effect (SME) is the capability of a material to change its shape in a predefined way in response to heat. In shape-memory polymers (SMP) this shape change is the entropy-driven recovery of a mechanical deformation, which was obtained before by application of external stress and was temporarily fixed by formation of physical crosslinks. The high technological significance of SMP becomes apparent in many established products (e.g. packaging materials, assembling devices, textiles and membranes) and the broad SMP development activities in the field of biomedical as well as aerospace applications (e.g. medical devices or morphing structures for aerospace vehicles). Inspired by the complex and diverse requirements of these applications fundamental research is aiming at multifunctional SMP, in which SME is combined with additional functions, is proceeding rapidly. In this review different concepts for the creation of multifunctionality are derived from the various polymer network architectures of thermally-induced SMP. Multimaterial systems, such as nanocomposites, are described as well as one component polymer systems, in which independent functions are integrated. Future challenges will be to transfer the concept of multifunctionality to other emerging shape-memory technologies like light-sensitive SMP, reversible shape changing effects or triple-shape polymers.

2. Introduction

Shape-memory polymers (SMP) can be deformed by application of external stress and fixed in a second, temporary shape.¹⁻¹¹ This temporary shape is stable until an appropriate stimulus is applied to the shaped body, which induces the recovery of the original shape. The movement occurring during recovery is predefined as it reverses the mechanical deformation, which leaded to the temporary shape (see Fig. 6 for an example of the macroscopic SME) and can be used for self-deploying sun-sails or antenna, morphing wing structures, heat-shrinkable packaging materials or wrinkle free fabrics.¹²⁻¹⁶

So far, the most extensively investigated group of SMP were thermally-induced SMPs, which are triggered by heat. SME is induced when a certain switching temperature T_{sw} is exceeded. Enabling the shape-memory effect (SME) requires the combination of a suitable molecular polymer network architecture and morphology with a tailored processing and programming technology. The latter is named "dual-shape creation process" (DSCP). During DSCP thermally-induced SMP are deformed in the amorphous state to an elongation ε_m by application of external stress. When cooled below the thermal transition temperature T_{trans} of

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switching domains, these domains solidify, forming physical crosslinks. As these additional crosslinks dominate the netpoints determining the permanent shape, they enable the temporary fixation of an elastic deformation, which can be recovered by reheating.

In cyclic, stimuli-specific mechanical tests, which consist of the DSCP and the recovery of the original, permanent shape, shape-memory properties can be quantified. Different test protocols have been developed. DSCP as well as the recovery process can be performed under constant strain or constant stress conditions e.g. in a tensile tester equipped with a thermochamber. In strain-controlled DSCP the sample is deformed to ε_m and held constant at this deformation while the temporary crosslinks are formed during cooling. Afterwards the external stress is released. In the stress-controlled DSCP the sample is deformed to ε_m and is held constant at the stress σ_m obtained after reaching ε_m , while the sample is cooled for temporarily crosslinking. Furthermore, DSCP can be varied between cold stretching of the sample ($T < T_{trans}$) or a temporary heating ($T > T_{trans}$) and subsequent cooling.

After DSCP the recovery process is conducted, which can be performed under constant strain or stress-free conditions.^{1, 17-19} The tensile stress σ as a function of temperature is determined in the recovery processes under constant strain, while the deformation ε as a function of temperature is measured in recovery processes under stress-free conditions. From each cycle consisting of DSCP and recovery, the SME is quantified by determining the shape fixity ratio $(R_{\rm f})$ and the shape recovery ratio $(R_{\rm r})$. $R_{\rm f}$ describes the ability of the switching domains to fix a mechanical deformation, while R_r is a measure for the ability of the material to memorize its permanent shape. Quantification of the thermally-induced SME includes the determination of the switching temperature T_{sw} from stress-free recovery as inflection point as well as the temperature $T_{\sigma,max}$ at which maximum stress is developed from constant-strain experiments.²⁰ Besides triggering by heat,²¹⁻²⁷ appropriate stimulation of SME was realized by light.^{28, 29} Irradiation with IR-light³⁰, application of electrical fields³¹, exposure of alternating magnetic fields³²⁻³⁴ or immersion in water³⁵ enabled indirect actuation of the thermally-induced SME. Furthermore, SMP were developed, which generate high stresses.^{36, 37} The ability of complex movements was realized in triple-shape polymers allowing the thermally-stimulated predefined movement from a shape (A) to a shape (B) and from there to a third shape (C).³⁸⁻⁴⁰ When DSCP and recovery process were conducted under constant stress a reversible change of shape could be obtained. ^{41, 42} In this manuscript we will focus on the thermally-induced SME.

Often complex requirements for properties (e.g. elasticity and thermal properties) and functions in addition to SME need to be fulfilled to meet the application derived specific. An example is the application of SMP in intelligent implants. Implants, which can be inserted into the body in a compressed temporary shape through a small incision as required for minimally-invasive surgery, change to their application relevant shape when heated to body temperature. In this application spectrum shape-memory alloys were already shown to be successful.^{43, 44} A second surgery for explantation can be avoided when such materials are additionally hydrolytically degradable. For this purpose multifunctional SMP are required.^{45, 46} When an on-demand remote actuation of the SME is desired, the SMP must be sensible to a stimuli not requiring direct contact.

SMP are polymer networks, in which netpoints determine the permanent shape and being connected by chain segments. These chain segments must allow a certain orientation upon application of external stress to obtain the required deformability, which increases with growing length and flexibility of these chains. The netpoints can either be of physical or chemical nature. While covalent bonds can be realized by suitable crosslinking chemistry, physical crosslinking requires a polymer morphology consisting of at least two segregated domains. Here, the domain providing the highest thermal transition T_{perm} is acting as netpoints (hard domains) while the chain segments forming the domains with the second highest thermal transition T_{trans} are acting as molecular switches (switching domains). By forming additional reversible crosslinks under conditions relevant for the particular application these molecular switches must be able to fix the deformed shape temporarily. In addition to switching domains, which fix the temporary shape by solidification, these switches can be functional groups, which are able to reversibly form and cleave covalent crosslinks based on a reversible chemical reaction.

The shape recovery in SMP is driven by the entropy elasticity of the switching segments, which are forming the switching domains. In the amorphous, rubber-elastic state polymer chains display a random coil conformation, which is the state of highest entropy in accordance with the Boltzmann Equation.⁴⁷ If a tensile stress is applied the polymer chains become oriented and loose entropy. When the external stress is released the sample recovers its original length, gaining back the entropy. The solidification of the switching domains prevents this immediate recovery of the polymer chains. Here, the entropy can only be regained when the switching domains are softened again. Although the underlying principle of entropy gain is known, complex theoretical models for a more detailed description of the processes occurring during SME are required.⁴⁸⁻⁵³



Figure 1: Different architectures for a) shape-memory polymers and b) multifunctional materials.

Polymer networks having covalent crosslinks are examples for single molecules capable of a thermally-induced dual-shape effect SME (Fig. 1a top). Depending on the desired polymer network morphology as well as the synthesis strategy, netpoints of covalent SMP networks can be created during synthesis starting from low molecular weight (co)monomers or by post processing methods. Chemical crosslinking after polymer processing can be realized by polymer analogous reaction, e.g. induced by addition of radical initiators to polymers or by exposure to energy rich irradiation (γ -radiation, neutrons, e-beam).⁵⁴⁻⁵⁹ Crosslinking of linear or branched polymers as well as (co)polymerization / poly(co)condensation of one or several (co)monomers, whereby at least one has to be tri-functional, enables the creation of covalently crosslinked SMP from low molecular weight starting materials.⁶⁰⁻⁶⁵

Polymer networks can be formed containing more than one type of chain segments, e.g. the horizontal and vertical polymer chains segments of the covalent polymer network (Fig.1A top) might be different. This enables the integration of several functions in the polymer network as each of the used chain segment types might contribute a specific function(s) to the material, e.g. segment chains can form the switching domains being essential for the thermally-induced SME, while other segment chains can enable the adjustment of the

elasticity in the temporary shape. Besides a polymer network structure, linear or branched multifunctional molecules can be created, which actively change their shape on the molecular level by conformational changes. Such molecules can also be equipped with further functional groups resulting in multifunctionality. The conformational changes are obtained by integration of segments, which favor the folding of the macromolecule or which are capable to from helices under certain environmental conditions, as well as segments which can establish intermolecular hydrogen-bonds contributing to the elastic stabilization of the polymer chain when stress is applied.

(Multi)block copolymers are thermoplastic SMP, in which different domains are formed as a result of phase separation resulting in a certain polymer morphology (Fig 1a middle). Here, the domains with the highest T_{trans} provide the domains acting as netpoints, which determine the permanent shape, while the domains with the second highest T_{trans} are acting as switching domains.

Furthermore, SMP can be designed as multimaterial systems (Fig. 1a bottom). (Multi)block copolymer as well as the covalent polymer networks can be used as components forming multimaterial dual-shape polymers. The preparation of binary blends from two polymers by a physical process is an efficient method for the creation of multimaterial systems, in which the properties of the resulting binary polymer blends can be systematically varied. Often one blend component is a (multi)block copolymer providing the SMP matrix. The second blend component is used for the modification of the properties of one or both domains, e.g. by formation of a mixed amorphous phase whose T_g depends on the weight ratio of both components.

The covalent polymer network approach to create multimaterials is applied in interpenetrating polymer networks (IPN). Here, two polymer networks not being covalently linked to each other. IPN can be obtained by two crosslinking processes occurring sequentially or both at the same time by using two different, not interfering chemical reactions forming the two different networks.^{66, 67} Each polymer network provides permanent netpoints contributing to the permanent shape.

Besides the change of shape, several other properties of the SMP are changing during SME. On the one hand property changes are occurring directly related to the thermal transition. These changes occur also in the case when the SMP was not programmed. An example is the change in permeability when the phase transition occurs. While below T_{trans} the switching segments are stiff, preventing diffusion of low molecular weight molecules (e.g. water) through the polymer matrix, at T > T_{trans} the polymer chains segments become flexible, enabling permeation of small molecules through the polymer matrix. This effect can be utilized for breathable thermosensitive fabrics.⁶⁸ Another example is the change of enthalpy caused by melting or crystallization of switching segments at $T_{\text{trans}} = T_{\text{m}}$, which can be utilized in phase change materials enabling compensation of small changes of the environmental temperature.

On the other hand, property changes are caused by the change of the conformation of the switching segments from an oriented to a random coil conformation, when T_{trans} is exceeded. Moreover, the mechanical properties change from an anisotropic characteristic to an isotropic behavior.⁶⁴ In addition, when crystallizable switching segments were used for the fixation of the temporary shape, the SMP display a different behavior in the interaction with polarized light depending on the orientation of the crystallites.^{69, 70}

Driven by potential applications, such as intelligent implants or textiles, the question arises whether SME of polymers can be combined with different functions, which are not directly linked to SME. Examples of such functionality combinations are electrical-conductivity and SME, change of color and SME, or degradability and SME.⁷¹⁻⁷³ Multifunctionality is the targeted combination of material functions which are not linked with each other.⁴⁵ The development of such multifunctional materials is posing a highly interesting challenge for fundamental research. Several approaches have been explored for creating multifunctionality, involving one component polymer systems as well as multimaterial systems, e.g. combining two polymers or a polymer and inorganic (nano)particles (Fig. 1b). An example for a single macromolecule, in which several functionalities have been integrated into the polymer structure are polymer networks, in which an additional functionality e.g. hydrolytical degradability was obtained by insertion of easily hydrolysable bonds (Fig. 1b top).⁷⁴⁻⁷⁶ Multifunctional one component polymer systems were realized as multiblock copolymers, in which the additional functionality has been incorporated in one or both segments (Fig 1b middle).^{73, 77, 78} In multimaterial systems the additional functionality, e.g. electrical conductivity, results from the integration of an additional material (e.g. carbon nanotubes) in a polymer network or multiblock copolymer (Fig 1b bottom).^{9, 79, 80}

In this review suitable polymer network architectures capable of a thermally-induced SME are introduced. Here, we begin with covalent polymer networks, explain thermoplastic one component polymer systems and finally describe multimaterial systems consisting of at least two different components. The thermal and elastic properties will be elucidated with respect to the molecular architecture as well as the functions linked to property changes occurring at T_{trans} including permeability, transparency, elastic properties, dielectric properties and

enthalpy. After discussing multifunctionality as a general principle in material sciences, the concept of multifunctional SMP will be outlined. First multimaterial systems will be described and categorized and afterwards the concept of one component systems with multifunctionality explained. Finally, both concepts will be compared and suggestions for future developments as well as potential applications will be given.

3. Thermally-induced One-way Dual-shape Effect in Polymers

3.1 Polymer Network Architectures

In the following, suitable polymer network architectures capable of thermally-induced SME will be presented beginning with covalent polymer networks as single molecule systems, followed by thermoplastic (multi)block copolymers as example of one component SMP from several molecules of the same type and finally multimaterial systems with SME. Details of properties from covalent SMP can be found in recent reviews.^{3, 4, 7}

Various types of thermal transitions T_{trans} associated to the switching domains are suitable as switching transition. The reversible solidification of the switching domains can be related to a melting transition ($T_{\text{trans}} = T_{\text{m}}$), a liquid crystalline transition ($T_{\text{trans}} = T_{\text{LC}}$) or a glass transition ($T_{\text{trans}} = T_{\text{g}}$). While in most cases melting and liquid crystalline phase transitions are assigned to relatively small temperature intervals the glass transition often covers a broad temperature interval. Liquid crystalline transitions can cover a temperature interval between 1 and 5 K, melting transitions mostly extent over a temperature range between 15 and 20 K. Accordingly, thermally-induced SMP can be classified according to the different types of switching transition T_{trans} .

Furthermore, the location of the switching segment within the polymer network, e.g. contributing to the overall elasticity or as a side chain, has a significant influence on the SME.



Figure 2: Examples for polymer network architectures suitable for exhibiting a shapememory effect (molecular switches: red; netpoints: grey): A) polymer networks consisting of switching segments linked by covalent netpoints, B) AB-polymer network, C) polymer network having side chains as switching segments, D) multiphase polymer network consisting of ABA triblock chain segments linked by covalent netpoints. Nomenclature: **N** indicates SMP network, **M**: one phase SMP network, **B**: biphasic SMP network, **G**: biphasic SMP network with grafted switching segments, **T**: biphasic SMP network obtained from triblock copolymers. Last one/two letter indicates thermal transition of phase(s): **A** glassy/amorphous, **C** crystalline, **LC** liquid crystalline phase.

Four different examples of polymer network architectures with covalent netpoints suitable to exhibit a SME are displayed in Fig. 2. The polymer network in Fig. 2A comprises one kind of switching segment and netpoints. Such a material consists in its temporary as well as in its permanent shape of only one phase in case T_{trans} is a T_g .^{59, 81, 82} Amorphous SMP networks with $T_{\text{trans}} = T_g$ (Cat. N-M-A) from low molecular weight monomers could be obtained by copolymerization of styrene with divinylbenzene. In this model system the influence of the degree of crosslinking on the thermomechanical properties had been investigated.⁸¹ T_{g} increased from 55 °C to 81 °C with increasing the amount of the crosslinker from 0 to 4 wt%, accompanied with an increase of the gel content from 0% to 80%. In a copolymer network from styrene and benzo-cyclo-butene, in which the latter is crosslinking the styrene chains, T_g could be substantially increased to a value of 165 °C, and enabled SME of nanoindents.⁸³ When the switching segment is crystallizable or liquid crystalline, the amorphous polymer network will become semicrystalline upon cooling below T_{trans} in its temporary shape and will consist of two different phases.^{58, 76, 84, 85} The photopolymerization of poly(Ecaprolactone)acrylate macromonomers having polyhedral oligosilsesquioxane (POSS) moieties located precisely in the middle of the network chains built polymer networks with $T_{\text{trans}} = T_{\text{m}}$ based on T_{m} of the oligo(ϵ -caprolactone) segments.⁸⁶ In such polymer networks having a POSS content of 47 wt% a second rubbery plateau could be determined, which had been associated to the physical interactions of the POSS moieties.

Main-chain smectic-C elastomers with $T_{\text{trans}} = T_{\text{LC}}$ (**Cat. N-M-LC**) could be exemplarily obtained by the reaction of tetrafunctional silanes, forming the netpoints, with oligomeric silanes, which work as spacers and to whom two distinct benzoate-based mesogenic groups have been attached.⁸⁷ These elastomers displayed a SME in contrast to other liquid crystalline elastomers, which displayed a shape-changing behavior. A comparison between SMP and shape-changing polymers has been recently given.^{2, 8} In shape-changing liquid crystalline elastomers, a macroscopic movement of the polymer is obtained by the alignment of the LC moieties. This molecular movement is amplified and converted into the macroscopic movement. In contrast, the SME in LC-elastomers is triggered by the thermal transition of the LC domains, which are acting as switching domains. Another subset of this SMP category (Fig. 2A) are polymer networks from crosslinked starlike hydroxytelecheles.^{63-65, 88, 89} Here, the hydroxytelecheles themselves are forming the netpoints. The chain segments of the starlike hydroxytelechelic oligomers are built by two arms from two different telechels linked by a junction unit.

The polymer network architecture (Fig. 2B) consists of two different kinds of chain segments linked by netpoints. Both types of polymer chain segments connect two netpoints and in this way contribute to the overall elasticity of the polymer network.^{38, 40, 74, 76} If both kinds of network chains are immiscible, a multiphase polymer network will be formed by phase segregation. The nomenclature is N-B-X-Y, with N indicating SMP network, B biphasic polymer network and X/Y indicating the thermal transition of phase(s): A glassy/amorphous, C crystalline, LC liquid crystalline phase. As an example, AB copolymer systems with $T_{\text{trans}} = T_{\text{m}}$ having two crystalline switching domains were synthesized by polycondensation of PCL diol and poly(ethylene glycol) (PEG) with 4,4'-(adipoyldioxy)dicinnamic acid as a chain extender. These photosensitive copolymers could be crosslinked by UV irradiation ($\lambda > 280$ nm) to show shape-memory properties (Cat. N-B-C-C). Thermal analysis displayed one or two melting peaks associated to $T_{m,PCL}$ or/and $T_{m,PEG}$ depending on the mol% of each phase. In addition, T_{trans} was shown to be a function of the mol% of PCL segment incorporated in the polymer network.⁹⁰ In AB-polymer networks providing to amorphous phases (Cat. N-B-A-A) the required phase separation is a challenge.91

In addition to the components of polymer network Fig.2A the polymer network architecture shown in Fig. 2C contains side chains having a dangling chain end.^{39, 60-62} Here, the side

chains do not contribute to the overall elasticity of the polymer network, as they are only connected to one netpoint (**Cat. N-G-C-C**). The nomenclature is **N-G-X-Y**, with **N** indicating SMP network, **G** biphasic polymer network with grafted switching segments and **X/Y** indicating the thermal transition of phase(s). The overall elastic behavior is determined by the network chains linking two netpoints. If the physical netpoints formed during programming have sufficient strength to block the entropy driven elastic recovery, both segments will be able to act as switching segments and are capable to stabilize the temporary shape by aggregation and solidification.

Polymer networks formed by ABA triblock chain segments are based on triblock copolymers, which were obtained by polymerizing the A blocks onto a block B, e.g. by ring-opening polymerization of lactones with a precursor for block B, having two telechelic groups. Here block B serves as a macroinitiator (**Cat N-T-A-C**). The nomenclature is **N-T-X-Y**, with **N** indicating SMP network, **T** biphasic polymer network obtained from triblock copolymers and **X/Y** indicating the thermal transition of phase(s). Finally, polymer networks can be formed by subsequent modification of the ABA triblocks with reactive groups capable of polymerization reaction.⁹² Depending on the miscibility of the different blocks a multiphase morphology can be achieved (Fig. 2D). If mixed phases are formed, these can act as switching domains in the same way as phases formed by only one segment type.⁹²



Figure 3: Categories of thermoplastic SMPs. **A** With crystalline hard domains and crystalline switching domains (**T-C-C**), **B** with amorphous hard domains and amorphous switching domains (**T-A-A**,). Nomenclature: **T** indicates thermoplastic SMP, **A** a glassy/amorphous, **C** a crystalline/liquid crystalline phase.

Linear block copolymers are an important group of physically-crosslinked SMP. In contrast to covalent crosslinked SMP, their permanent shape can be altered by heating above T_{perm} with

 T_{perm} being a T_{g} , a T_{m} , or a T_{LC} . A key requirement for such thermoplastic SMP is the formation of at least two segregated phases. Therefore, the different blocks of the copolymers have to be immiscible and of a minimum length in order to obtain a microscopic phase segregation. The switching segments provided by the domains could amorphous or crystalline phase as well, yielding the categories **T-A-A**,³² **T-A-C**,^{93, 94} **T-C-A**,⁹⁵⁻¹⁰⁰ and **T-C-C**,^{17, 73, 77, 101-109}. The nomenclature is **T-X-Y**, in which **T** indicates a thermoplastic SMP, **X** the phase proving the switching domains and **Y** the phase providing the hard domains, with **X/Y** indicated as **A** a glassy/amorphous and **C** a crystalline/liquid crystalline phase.

Thermoplastic SMP could be synthesized by direct coupling of pre-synthesized polymer blocks with a low molecular weight junction unit, by applying the prepolymer method, or by melt blending. When macrodiols are used as oligomeric building blocks, called precursors, diisocyanates, diacid dichlorides or phosgene are applied as low molecular weight junction unit.

The prepolymer method enabled production of thermoplastic polyurethane elastomers on an industrial scale. Here, the reaction of hydroxytelechelic oligoesters or -ethers with an excess of a low molecular weight diisocyanate yielded isocyanate-terminated prepolymers. By addition of low molecular weight diols or diamines, so called chain extenders, these prepolymers were further coupled. In this way shape-memory polyurethanes (SMPU) or polyureas were obtained as phase-segregated block copolymers whereby the prepolymer segments are forming the switching domains. In addition, each polymer chain contained segments of high polarity containing a high concentration of urethane and urea bonds. They formed domains exhibiting a high thermal transition temperature due to their high intermolecular interaction. Therefore, these domains represented the hard domains. While the length of the hard segment blocks was adjusted by the ratio of the prepolymer to diisocyanate/chain extender the length of the switching segments resulted from their synthesis method and is determined in the first step. In addition, side chains can act in thermoplastic SMP as switching segments as well.¹¹⁰



Figure 4: Multimaterial Systems Consisting of Several Different Molecules. A) Binary blends of multiblock copolymers forming a SMP (**B-C-C**), B) Interpenetrating polymer network (IPN) forming a SMP. Nomenclature: **B**: blend, **C**: crystalline phase providing T_{trans} **C**: crystalline phase providing T_{perm} **N**: polymer network, **I**: interpenetrating network, **C**: crystalline phase providing $T_{trans,1}$ **C**: crystalline phase providing $T_{trans,2}$.

Only a few examples of blends exhibiting SME have been reported so far although blends can be produced with high efficiency. The nomenclature will be denoted as B-X-Y with B indicating a blend, X phase providing T_{trans} , Y phase providing T_{perm} , with X/Y having A a glassy/amorphous, C a crystalline/liquid crystalline phase. Most examples of binary SMblends utilized a thermoplastic SMP as one component. The second component was either a commodity polymer to lower the costs while pertaining a certain level of SME or a component to adjust T_{trans} of the SMP by forming a mixed phase. An example is the blending of poly(vinyl chloride) with polyesterure thanes allowing the adjustment of T_{trans} by obtaining a mixed T_{g} .¹¹¹ Here, the poly(vinyl chloride) provided the hard domains by physical entanglements, which were enhanced by the hard segments of the polyesterurethane resulting in reduction of the hysteresis during shape recovery. The crystallization of the poly(ε caprolactone) segments of the polyesterurethane was hindered, these segments formed a mixed phase with poly(vinyl chloride). The resulting mixed amorphous phase acted as switching phase (Cat. B-A-C). In binary blends of shape-memory polyesterurethanes with phenoxy resins the polyurethane provided the hard domains, responsible for the fixation of the permanent shape. The domains of the polyurethane associated to a $T_{\rm g}$ acted as switching domains. The phenoxy resin displayed only one thermal transition, which was a glass transition. When a binary blend was formed, the soft segment of the polyurethanes and the phenoxy resin formed a mixed phase, whose $T_{\rm g}$ could be varied by the blend composition (Cat. B-A-C). T_{sw} of the blends could be varied by adjusting the blend composition in the range from -2 °C to 80 °C.^{111, 112}

Recently, a binary polymer blend exhibiting a SME could be prepared, in which the segments providing the switching domains and the segments forming the hard domains were contributed by two different bend components and therefore not covalently connected to each other (Fig. 4A).⁷⁸ As the switching segment and the hard segment were non-miscible, the same mediator segment type was incorporated in both multiblock copolymers to promote their miscibility (**Cat. B-C-C**). T_{sw} was shown to be almost independent from the blend composition, while the mechanical properties could be varied systematically over a broad range by the weight ratio of the two polymer components.

Another type of multimaterial system capable of SME are interpenetrating networks (IPN) (see Fig. 4B). The nomenclature will be denoted as I-X-Y with I indicating a interpenetrating polymer network (IPN), **X** phase providing $T_{\text{trans},1}$, **Y** phase providing $T_{\text{trans},2}$, with **X/Y** having A a glassy/amorphous, C a crystalline/liquid crystalline phase. Such IPNs can be obtained simultaneous polymerization and polycondensation of low molecular weight monomers or macromonomers capable of netpoint formation. The generated netpoints of both polymer networks determine the permanent shape. Both switching segments are immiscible, both contribute to the switching domains. Depending on the weight ratio of the two IPN components and the resulting polymer network morphology, an IPN can be created, in which both polymer networks contribute to the overall elasticity. Nevertheless, the entanglements and the netpoint density of one polymer network influence the elasticity of the other. An example for an IPN synthesized in the reaction sequence polymerization and afterwards polyaddition reaction is synthesized from a blend of PEG dimethacrylate (PEG-DMA) with star-shaped poly[(rac-lacide)-co-glycolide] (Cat. I-C-A). First the PEG-DMA was photopolymerized and afterwards the polyesterurethane network was formed using isophorone diisocyanate.⁶⁷ T_{trans} could be adjusted between -23 °C and 63 °C and R_{f} and R_{r} were reported to be above 93%.

4. Additional Functions Directly Linked with SME

4.1 General Principle of Using Functions Being Linked to Each Other

Besides the SME, the processes occurring during the shape change (phase transition, change in conformation of switching segments) cause changes in other macroscopic properties, e.g. permeability, elastic performance, transparency to light or change in enthalpy. The changes in properties occurring in a SMP can differ depending of the type of T_{trans} , which can be a T_{g} , a T_{m} or a T_{LC} . The change of these additional functionalities needs to be considered when selecting SMP for a specific application. But *vice versa*, depending on the intended application, T_{trans} can be selected in a way that the requirements for such additional functionalities will be met. In the following we will describe the changes occurring at T_{trans} including permeability, transparency, elastic properties, dielectricity and enthalpy.

4.2 Change in Permeability



Figure 5. Water vapor permeability of two polyester polyurethanes with $T_{\text{trans}} = T_{\text{g}} = 25 \text{ °C}$ (TSPU(a)) or $T_{\text{trans}} = T_{\text{m}} = 50 \text{ °C}$ (TSPU(b)) as a function of temperature.¹¹³

It was demonstrated for polyurethanes of category **T-A-A** ($T_{trans} = T_g$) that the temperature dependency of diffusion properties could be controlled by the choice of the switching segment building block.¹¹⁴ Thermoplasts having soft segment building blocks of a more hydrophobic character such as poly(butylene adipate) or poly(tetramethyleneoxide) displayed a lower diffusion rate for water. In contrast, in thermoplasts built from more hydrophilic building blocks such as poly(propylene oxide) or poly(ethylene oxide) the diffusion rate for water was considerably higher. Furthermore, in such amorphous polyurethanes the diffusion rate above T_g of the switching segment providing domains ($T > T_{trans}$) is sufficiently higher compared to the diffusion rate below T_{trans} . When T_{trans} is selected to be around body temperature, this effect can be used to control the diffusion of water vapor are only generated in a moderate way. In this situation the ambient temperature remains below T_{trans} of the fabric preventing the person from cooling out. When the person is more actively, more heat as well as water vapor are generated. In this situation the generated heat increases the ambient temperature $T > T_{trans}$ so that the vapor can evaporate through the garment. By the choice of T_{trans} of the switching

segment the permeability can be controlled as shown in Fig. 5.¹¹³ In thermoplastic SMPs of type **T-C-A** ($T_{\text{trans}} = T_{\text{m}}$) the differences in diffusion behavior are even more pronounced, as the crystalline domains are preventing diffusion more effectively.¹¹³

In thermoplastic SMPs of type **T-C-C** ($T_{trans} = T_m$) the situation differs as the hard segments forming domains remain crystalline, when the polymer is heated above T_{trans} . In a polyesterurethane, in which poly(ε -caprolactone) provided the switching domains and the polyurethane from a diisocyante and butane diol built the hard domains, it was demonstrated by time resolved FT-IR that water first penetrated into the switching domains while forming hydrogen bonds with the C=O groups.¹¹⁵ Afterwards hydrogen bonds between the C=O groups of the hard domains were formed. In the last step, hydrogen bonds between the C=O groups and the N-H groups were formed. The additional free volume obtained by the diffusion of water would lower T_g and influences in this way the elastic properties.

The opposite direction of the effect was demonstrated for commercially available polyurethanes ^{35, 116, 117} and its composites with carbon nanotubes ¹¹⁸ by lowering T_g below environmental temperature. In this way the SME could be actuated indirectly. In all cases the temporary shape has been programmed by conventional DSCP for thermally-induced SMP. A shape recovery could be obtained, when the materials were immersed into water whereas moisture diffused into the polymer sample and acted as plasticizer. In the polymers and composites based on polyurethanes the T_g was lowered from 35 °C to a temperature below ambient temperature. The lowering of the glass transition temperature depended on the moisture uptake, which was a function of immersion time. In time dependent immersion studies, a lowering of T_g between 0 and 35 K was realized, accompanied with a water uptake between 0 and 4.5 wt%. Because of this low solvent uptake, the SMP differs substantially from SMP hydrogels.⁸

4.3 Change in Transparency

In single molecule SMPs with $T_{\text{trans}} = T_{\text{m}}$ or T_{LC} (categories N-M-C, N-M-LC, N-B-C, N-B-A-LC, N-T-A-C) and one component materials with SME (thermoplasts of category T-A-C) the thermally-induced SMP is accompanied with a tremendous change of optical properties in terms of transparency. In such materials only the domains contributing to the fixation of the temporary shape are crystallizable. While the domains are crystalline at T < T_{trans} and in this way scattering the light leading to opaqueness, these domains become amorphous at T > T_{trans} . Fig.6 visualizes the change in transparency during SME.



Figure 6: Photo series demonstrating the change of transparency for two different poly(ε -caprolactone) based SMP. At T < T_{trans} the materials are in their temporary shape. When the thermally-induced SME is triggered by heating to T > T_{trans} the SMPs recover their permanent shape. a) Covalent polymer network from poly(ε -caprolactone)dimethacrylate (category N-M-C). At T < T_{trans} the material is opaque as the crystalline domains fixing the temporary shape are scattering. When heated to T > T_{trans} the crystalline domains are molten and the material is transparent. b) In contrast, in one component SMP, a multiblock copolymer form poly(ε -caprolactone) and polypentadecadolactone (category T-C-C) materials remains opaque as the hard domains forming segments maintain their crystallinity.

4.4 Change in Elastic Properties

As the E modulus is correlated with the flexibility of the polymer chain segments, the solidification or the softening of the chain segments reduces or increases flexibility, resulting in stiffer or softer materials. The extent to which this effect is pronounced depends on the SMP architecture. Consequently, the change in the elastic properties during softening/solidification of the switching domains need to discussed. Furthermore, it has to be asked if ε_b is influenced by the conformation of the switching segments. Lastly, the kinetics of the softening of the switching domains need to be considered for a temporal description of the change in elastic properties.

In covalent polymer networks with a one-phase architecture and in AB-polymer networks with T_{trans} provided by the second phase (categories N-M-A, N-M-C, N-M-LC and N-B-A-C), a tremendous decrease of E modulus can be determined, accompanied by a decrease in ε_b . In contrast, in covalently crosslinked SMP with an AB-polymer network architecture with T_{trans} provided by the first phase (category N-B-C-A), as well as in thermoplastic SMP of all categories (T-A-A, T-A-C, T-C-A, T-C-C, B-C-C), the decrease in the elastic properties is less pronounced, because in the covalent SMP networks the second phase and in the thermoplastic SMP the required hard segment forming domains provide mechanical strength. Nevertheless, as in these SMPs the polymer chain segments associated to T_{trans} do not contribute the elasticity in the same way after exceeding T_{trans} , ε_b decreases as well but with a lower extent compared to N-M-A, N-M-C, N-M-LC systems.

The influence of the switching segments conformation was investigated in covalent polymer networks with $T_{\text{trans}} = T_{\text{g}}$ after applying a predeformation. Here, it was demonstrated that ε_{b} of pre-strain samples decreased, while the overall elongation at break $\varepsilon_{\text{b,tot}}$, summarizing the pre-strain and the determined ε_{b} remained almost constant.⁶⁴

Besides programming, the kinetics of the softening of the switching domains influences the recovery process of polymer networks as the thermal transition of the switching domains can extend over a narrower or broader temperature interval.



In Fig. 7 the characteristic strain ε during shape recovery of covalently crosslinked one phase SMP networks (**Cat. N-M-C** and **N-M-A**) with $T_{\text{trans}} = T_{\text{m}}$ (Fig. 7a) and $T_{\text{trans}} = T_{\text{g}}$ (Fig. 7b) are presented. In general, the graphs of both systems are looking similar. Nevertheless, the differences of both systems become obvious when the first derivative of strain is considered. The first derivative of strain for SMP networks with $T_{\text{trans}} = T_{\text{m}}$ (**Cat. N-M-C**) displays a sharp peak (Fig. 7a). In contrast, the first derivative of strain for SMP networks with $T_{\text{trans}} = T_{\text{g}}$ exhibits a broader peak (Fig. 7b). Furthermore, in such SMP with $T_{\text{trans}} = T_{\text{g}}$ the width of the peak can be influenced by the heating rate: the faster the heating rate is the broader the peak becomes. Consequently, these clearly visible differences in the thermomechanical properties of the polymer systems reflect in the SME of such systems. An example are polymer networks with $T_{sw} = T_g$. In such polymer networks the temperature range of the strain recovery can be influenced by the heating rate. With lower heating rates the strain recovery starts and ends at lower temperatures, and the temperature intervals during recovery get smaller with decreasing heating rates.⁷⁵

4.5 Change in Color Indirectly Caused by Change in Orientation of Polymer Chain Segments

A reorientation of the polymer chain segments occurs when the thermally-induced SMP is heated above T_{trans} . In the temporary shape the polymer chain segments are in oriented configuration due to the applied deformation. When heated above T_{trans} the polymer chain segment obtain their entropically favored random coil conformation. An interesting function of the material could be created, if this conformational change would be visible macroscopically. Visualization and amplification was obtained by incorporating fluorescent, oligo(*p*-phenylene vinylene) dye particles, whose absorption spectrum was in the wavelength range of visible light, into a semicrystalline, covalently crosslinked SMP matrix via guest diffusion.⁷² The SMP was prepared by crosslinking poly(cyclooctene) in a free radical process.^{41, 59} Swelling of the cross-linked PCO with a solution of the dye at 50 °C yielded in PCO/dye blends. The thermal analysis suggested that the dye molecules did not exert a remarkable influence on the morphology and the thermal transitions of the polymer. The dye's color change was caused by a reversible aggregation-deaggregation of the dye molecules that occurs at T_{trans} of the SMP. Exposure of these phase-separated blends to $T > T_{\text{m}}$ of the PCO lead to dissolution of the dye molecules, and therefore caused a pronounced change of their absorption and fluorescence color. The optical changes were reversible; *i.e.*, the aggregate absorption and emission were restored upon cooling below $T_{\rm m}$. In thermo-mechanical investigations during deformation at $T_{high} = 75$ °C (Fig. 8a) the sample (1.5 mg mL⁻¹ PCO/dye) exhibited green (monomer) fluorescence due to complete dispersion of the dye molecules above $T_{\rm m}$ of PCO. Upon cooling and fixing, $T_{\rm low} = 5$ °C, the color of the sample changed from green (monomer) to orange (excimer) fluorescence (Figure 8b), indicating that the large free volume (low crystallinity, $X_c = 28\%$) and low T_g (-50 °C) allowed for the selfassembly of dye molecules into nano-scale aggregates regardless of the limited diffusion of dye molecules in a highly stressed environment.⁴¹ The temporarily fixed shape formed by removal of the applied stress could be recovered to the original permanent shape by heating to 75 °C, whereby the fluorescence color changed to green (Fig. 8c) again, indicating the molecularly dispersed state of the dye in the PCO network. The color was dictated by the phase behavior, independent of the mechanical state of the SMP. Such color changing SMP systems could have technological applications exploiting the unique photomechanical behavior as system having the ability to monitor a stress change, or enabling SMPs whose repeated transitions can be easily monitored even when the shape change is small.⁷²



Figure 8: Photographs of the SME of a 1.5 mg mL⁻¹ PCO/dye sample (illuminated with 365 nm UV light) during (a) deformation (75 °C, 600 kPa), (b) cooling/fixing (5 °C, 600 kPa), (c) unloading (5 °C, 4 kPa), and (d) recovery (75 °C, 4 kPa).

4.6 Change in Dielectric Properties

As dry polymers are generally poor conductors of electricity, they can be regarded as insulators. The application of an electric field on polymers having groups, which act as permanent dipoles, will result in alignment of the dipoles along the field. The favored random orientation of the dipoles can be regained when the electric field is released. In polymers the dipoles are usually a part of the whole polymer chain segment resulting in a fractional resistance of the dipoles. Consequently, a time gap between the release of the electric field and the recovery of the original random orientation occurs. A sinusoidally varying voltage for

the generation of an alternating electrical field is applied in dielectric thermal analysis (DETA).



Figure 9: Dielectric constant as a function of temperature for a polymer (w = const). Light grey, contribution from the electrons, middle grey contribution from pendant groups, dark grey, contribution from the polymer backbone, black contribution from crystalline dipoles. taken from ¹¹⁹

During the application of the field the electrons within the atoms of the polymer try to move towards the positive charge, while the nuclei try to move towards the negative charge, resulting in distorted orbitals as the electrons can not leave the vicinity of the nuclei. As the electrons have a low mass, their movements is not affected by the frequency and the temperature, in contrast to the nuclei. As polymers have high masses, their mobility as well as the mobility of the dipoles is strictly hindered. In amorphous polymers, in which the polar structures are located in pendant groups, heating will gain mobility with increasing temperature so that an increased dielectric constant is also expected. But the increasing temperature results in an increased Brownian motion, allowing more random motion. Both facts are equalizing each other, so that the dielectric constant is almost constant, until another from of mobility becomes available. When the system is further heated, the polymer backbone is able to gain mobility at T_g , thus the dielectric constant will increase. Again, after this step, the dielectric constant will remain almost constant again because increase in dielectric constant and increase in Brownian motion will flatten each other. As electron motion is independent from the polymer structure, the contribution of the electrons will be the same of structural identical polymers for the amorphous and the crystalline part. An expected contribution of crystalline polymer from a dipolar structure is neglectable, as the electrons of the crystalline part are not free to move. However, once a whole lamellar of the crystalline

domains has sufficient mobility and is able to rotate, the dielectric constant will increase further. This is the case at T_m , assuming no bulky pendants or branchings are preventing rotation. In conclusion, crystalline SMP with $T_{trans} = T_m$ have a higher dielectric constant compared to SMP with $T_{trans} = T_g$, while the overall change of the dielectric constant is higher in case of $T_{trans} = T_g$ compared to $T_{trans} = T_m$.

4.7 Change in Enthalpy

In SMP with $T_{\text{trans}} = T_{\text{m}}$ the SME is accompanied by a phase transition. When in a material a phase transition occurs, a significant change in enthalpy occurs. Water is a very abundant example for such a phase transition, which crystallizes at 0 °C, changing from liquid to the solid phase. During this crystallization a latent heat of 335 kJ·kg⁻¹ is spread to the environment, while during cooling in the liquid state from 42 °C to 41 °C a sensible heat of 4 kJ·kg⁻¹ is dissipated to the environment. During melting and heating this heat flux is reversed. During this crystallization as well as melting the temperature of the "water" remains constant. Materials, in which the difference in enthalpy occurring at T_{m} respectively T_{cryst} can be utilized, involve alloys, hydrated inorganic salt, linear long chain hydrocarbons such as paraffin, polyethylene glycol and fatty acids (capric, lauric, palmitic and stearic acids). A certain requirement of this utilization is a large heat of fusion as well as a small temperature range between the solidification point and the T_{m} .

In alloys the change in enthalpy can be utilized in various optical data storage systems such as CD-R, DVD-RAM or Blueray discs and nonvolatilve memories.^{120, 121} These alloys display two remarkable features: On the one hand, they show a very fast crystallization behavior and on the other hand a property contrast between the amorphous and the crystalline state.¹²² In the crystalline state they provide a high reflectivity and a low resistance, while in the amorphous state they owe low reflectivity and high resistivity.¹²³ When the alloy is cooled below T_m , the crystallization tendency increases with decreasing temperature while ate the same the atomic mobility decreases, hindering crystallization. Thus the ideal temperature for crystallization is between T_g and T_m . This can be used for optical or electrical data storage by pulsing the material in the amorphous state with a low energy laser or current pulse so the material crystallizes. When the crystalline material is pulsed with a short high energy laser or current the amorphous state can be regained. The resulting differences between the reflectivity of the crystalline state and the amorphous state as well as between the current states can be

used for storing information digitally. Recently, multifunctional alloys combining the large difference in enthalpy and magnetism were reported.¹²⁴

In organic substances the differences in enthalpy at T_{trans} were mostly investigated for usage in energy storage systems. Although their energy storage capability is lower compared to allow and other inorganic systems, they offer the advantage of a better availability and processability. While the usage of liquid paraffin embedded in silicone pillows, which crystallizes upon kinking a metal plate, as used in pocket warmers, is a fairly trivial but quite comfort application of utilizing the change in enthalpy, more sophisticated applications involve intelligent thermal insulation materials for buildings or textiles. The idea of materials displaying a large difference in enthalpy used as thermal insulation material in a building is that energy during the temperature change from night to day is stored in the material performing the enthalpy transition, which is a part of the insulation, while the room climate is kept constant for a longer time and thus reduces the need of extra cooling by air conditioning. During the temperature change from day to night the stored energy is released, thus the need for extra heating is reduced. As in this way the energy consumption for the air condition cooling as well as for the central heating, which both are mostly powered by fossil sources, can be reduced, a contribution to the saving of the limited resources can be made. In textiles the change in enthalpy can be used in a similar way. Here, the body climate is to be controlled during activities such as sports, providing comfort to the wearer.⁶⁸

Materials, in which the difference in enthalpy is utilized, are named phase-changing materials or phase-change materials. While the terminus "phase-change material" refers usually to alloys ¹²⁵ showing the phase-changing properties accompanied by change in reflectivity and resistivity, the terminus phase-changing materials (PCM) is more general. The presented application of PCM require creation of multimaterial systems, as these application demands other functionalities such as scratch or wear resistance, which can not be met by the PCM. For organic PCM processing in fibers¹²⁶, coatings¹²⁷, multi-layers or microcapsules^{128, 129} had been successfully demonstrated. Furthermore, PCM of organic substances display a limited heat-conductivity.¹³⁰ The application of the PCM capability with the SME feature in textiles would enable wrinkle free fabrics, which are able to control the body climate. In this way multifunctional materials would be obtained.

5. Multifunctionality of Shape-memory Polymers

5.1 Multifunctional Materials

First examples of multifunctional materials have their origin in the field of metallic alloys.¹³¹ Here, the multifunctionality refers to the aspect, that the alloy itself provides a structure, which is the basic functionality and to which additional functions might be added by incorporating further components.¹³² While similar results could also be obtained by macroscopic organization of structural materials incorporating different functions by processing techniques such as coating,¹³³ the development is driven by the motivation that a higher functional integration can be obtained and in this way a cost reduction could be achieved. In general, such multifunctional materials are realized as composites¹³⁴ or hybrid structures¹³⁵ of several distinct material phases, in which each phase contributes a different but necessary function.

Typical functions are strength¹³⁶, elasticity, degradability, electrical-conductivity¹³⁷⁻¹⁴⁰ or – insulation¹³⁸, thermal conductivity^{136, 140} or protection, energy storage, magnetism¹³⁷ or magnetic shielding, radiation protection¹⁴¹, light emission¹³⁹, self-healing, or actuation¹⁴². The multifunctional character of such composite materials might be even enhanced, if a hierarchical organization of the functions would be obtained by an organization of the structured composites in layers, in which each sublayer contributes with its multifunctionality.¹⁴³

Beyond the integration as multimaterial system or on the morphological level in single component materials, the final goal of multifunctional materials are materials that are truly integrated even on the molecular level.¹⁴⁴ "When it is a question of multifunctionality, nature always makes use of 'giant molecules', when single molecules have to be used for very different functions as structural complexity affords functional specifity" according to Ringsdorf.¹⁴⁵ In nature, in a singular system viability and stability, surface recognition and specific local interaction, function dependent structural regulation and self-replication can be combined. Furthermore, in enzymes as an example of multifunctional macromolecules, it is an important characteristic of a multifunctional material that the functions have to be independent.¹⁴⁶ Functions such as specific local interaction can be mimicked in multifunctional polymers by application of synthetic chemistry.^{147, 148} Such multifunctional polymers could be created by the targeted polymerization of specific monomeric precusors¹⁴⁹ or combination of suitable building blocks in blockcopolymers^{148, 150}. Besides multifunctional materials realized in a multimaterial approach, functions which could be implemented on the molecular level were non-linear diffraction¹⁵¹, conductivity¹⁵², ionic transport¹⁵³, or actuation¹, ¹⁵⁴. Additionally, the entry of the molecular level enables functions such as paramagnetism,

insulating properties, and infrared (IR) transparency to be changed simultaneously as atomic spin-relaxation processes get involved.¹⁵⁵

In chemistry the term functionality is also correlated to a reactive group so that multifunctionality is often referred to polymers having several different or several of the same reactive groups in one molecule.¹⁵⁶ Such reactive groups are an example for a functionality on the molecular level. When such polymers having several of the same reactive groups are able to react with ligands, presenting a multiple acceptor unit, the polymers are also name multivalent. Here, multifunctionality differs from the understanding of material sciences, in which a functionality origins from the bulk material. Thus, the hierarchical organization of different reactive groups in different subunits, each responsible for a certain function, enables multifunctional materials.¹⁵⁷⁻¹⁵⁹ Finally, not every function, which is integrated in a polymer, might be required for each application, therefore multifunctional polymers cover the aspect of universality, so that they contribute only with the relevant functions to the specific application.¹⁶⁰

As all actively moving polymers, serve as structural polymers and in addition provide the capability of actuation upon stimulation they can be referred to be multifunctional. Nevertheless, according to our understanding, SMPs having multifunctionality provide one or several functionalities in addition to the structural function and the SME. Therefore, multifunctional SMP can be obtained by addition of independent functions such as electrical conductivity, thermal conductivity or hydrolytical degradability. Multifunctionality can be obtained by the integration of various functions in multimaterial systems on the nano- or micro level, such as in composites, multifibers, or multilayer constructs, as well as single material systems combining the different functions on the molecular level, such as enzymes, polymeric prodrugs or actively moving polymers (shape-memory effect, shape-changing capability).

In this chapter the various aspects of multifunctional SMP will be discussed with a focus on the additionally added functions besides SME. Following at first the concept of alloys, multifunctional SMP by multimaterial approaches will be presented. Afterwards, SMP in which the different functionalities are combined on the molecular level will be introduced, beginning covalent polymer networks proceeded by thermoplastic multiblock copolymers. Finally, SMP obtained by a combination of a multimaterial and an integration of functionalities on the molecular level will be described (Fig. 1).

5.2 Multifunctional SMP by Multimaterial Approaches

The application of the multi-material approach offers opportunities for combination of functions by processing of different components into a single body structure with the advantage that no new material needs to be synthesized.^{136, 140, 161-163} Since polymer composites are built up from discrete phases consisting of a polymer matrix with other domains, they are particularly suited for exploitation towards multifunctionality.^{164, 165} Using the multi-material approach, new functions such as unique electrical, magnetic properties as well as radio-opacity and bio-functionality can be added to SMP by incorporating small amount of active fillers in polymer matrix. In most cases the pure SMP can be thermallyactuated by increasing the environmental temperature (direct heating). Mixing SMP with magnetically or electrically active fillers, extended the range of suitable stimuli. Composites from SMPs and carbon fillers, such as carbon black (CB) or carbon nanotubes (CNTs) can be actuated through an electric field.^{31, 166} Owing to their unique properties, especially CNTs are promising for various applications such field-effect transistors or solar cells.¹⁶⁷⁻¹⁶⁹ Similarily the SMP composites (SMC) containing a small amount of magnetic particles, such as iron oxide or nickel zinc ferrite can be inductively actuated by applying an alternating magnetic field.^{32, 33} The latter approach has the advantage for potential applications in wireless/remote operation. Also incorporation of small amounts of filler to SMP lead to an improvement in material properties, such as modulus, strength, heat resistance etc.^{18, 170} Functionalized with drugs, SMP can work as efficient drug delivery systems. Drug loaded SMP stents can be implanted by minimally invasive surgery and will lead to an improved strain recovery capacity for larger devices in smaller delivery instrumentations. Also an improved biological tolerance could be expected when using biocompatible SMP materials. ^{171, 172} Such combinations of the shape-memory function with other material functionalizations are expected to open new application fields of SMPs. Different functions resulting from adding functional fillers to SMP-matrices are discussed below.

5.2.1 Magnetic sensitivity

SMPs with magnetic functionality obtained by incorporating magnetic particles in a SMP matrix are another emerging class of multifunctional materials. The magnetic particles improved the mechanical properties and also enabled the induction of the SME in an alternating magnetic field.¹⁷³ In general, the incorporated magnetic particles consisted of

iron/ironoxide, nickel, or cobalt compounds and could generate heat in an alternating magnetic field by hysteresis losses, eddy current losses and/or other relaxational losses depending on the nature and size of the particle.¹⁷⁴ Nano-sized particles can generate a sufficient amount of heat required for induced SME at high magnetization frequency. Thus the remote actuation of SMPs was demonstrated by incorporation of silica coated magnetite nanoparticles in thermoplastic SMP.³² The thermoplastic material consisted of an aliphatic polyetherurethane (TFX) from methylene bis(*p*-cyclohexyl isocyanate), butanediol and polytetrahydrofuran. In Fig. 10 the magnetically induced uncoiling of a corkscrew-like spiral of a composite from TFX and 10 wt% magnetic nanoparticles is shown exemplarily. Similarly, incorporation of magnetite nanoparticles into polymerization of poly(*ε*-caprolactone) dimethacrylates enabled the realization of this strategy of indirect heating for polymer networks based SMP nanocomposites.¹⁷⁵ Recently, the remote activation of methacrylate-based SMP networks with varying amount of magnetite nanoparticles was reported.¹⁷⁵



Figure 10: Magnetically-induced shape-memory effect of thermoplastic composite consisting of Fe(III)oxide nanoparticles in a silica matrix and polyetherurethanes. Taken from ³²

Certain ferromagnetic particles with an appropriate diameter generate heat by only hysteresis loss mechanism and enable an innate thermoregulation caused by the Curie temperature (T_C). These ferromagnetic particles are able to heat a material up to T_C (i.e.; the ferromagnetic material becomes paramagnetic and loses its ability to generate heat via a hysteresis loss mechanism).^{33, 176} By selecting a ferromagnetic particle material with a T_C within safe medical limits, the danger of over heating in *vivo* applications can be eliminated. T_C of nickel zinc ferrite magnetic particles (Ni_{1-x}Zn_xFe2O4) (III) can be varied in a wide range. T_C decreases from approximately 370 °C to 150 °C by increasing zinc substitution (x) from 0.4 to 0.75.^{33, 177} A prototype of a therapeutic device having a complex shape was prepared from Ni Zn ferrite particles (10 wt%) embedded in a SMPU matrix.³³ The first prototype was a flowershaped endovascular thrombectomy device that can be used for stroke treatment. The second prototype device was an expandable SMPU foam device for potential application in aneurysm embolization. Both devices are presented in their collapsed and deployed forms in Fig. 11.



Figure 11: Collapsed and actuated SMPU composite (10 wt% NiZn ferrite) for: a) flower shaped device; and b) foam device (taken from ³³)

5.2.2 Radio-frequency (RF) Sensitivity

SMC functionalized with the sensitivity to radio-frequency (RF) can be developed by the dispersion magnetoelectroelastic (MEE) particles into a SMP matrix. MEE materials are a class of adaptive materials that exhibit coupling between elastic strain, and magnetic and electric potential. This coupling leads to significant interactions between the elastic, electric, and magnetic fields. For example, as a MEE material undergoes elastic deformation, some of the induced strain energy is converted into electrostatic and/or magnetic potential. Conversely, immersing a MEE material in an electromagnetic field can cause some of the field energy to be converted into strain, producing a finite strain in the material.¹⁷⁸

RF-energy induced shape change in epoxy-based thermoset SMPs, filled with MEE particles (diameter 38 to 106 μ m) was reported. The thermoset obtained by curing of epoxy groups at room temperature served as SMP matrix. This SMP is characterized by a T_g of 59 °C (Cat. N-

M-A).¹⁷⁸ The MEE particles consisted of a near single crystal of terbium, iron, and dysprosium-d of nominal composition $Tb_{0.3}Dy_{0.7}Fe_{1.92}$.¹⁷⁸ The RF-energy-induced thermal response of the epoxy-based thermoset SMP cylinders containing 0.0, 10.0, and 15.0 vol.% MEE particles were measured to determine the effect of particle loading level on energy coupling efficiency. Maximum temperatures of approximately 30 °C, 65 °C, and 100°C were recorded for specimens containing 0.0, 10.0, and 15.0 vol% MEE particles, respectively by exposure to an RF frequency of 1.4 MHz. The RF actuation of SME in the epoxy-based SMC with 10 wt% of MEE particles is illustrated in Fig. 12. The transition from a bent (temporary shape) to the flat beam (permanent) occurred in approximately 90 s by RF excitation (1.4 MHz and 14 W).



Figure 12: Series of photographs demonstrating the shape-recovery of thermoset SMP beam with 10 vol% MEE particle content. Taken from 178

5.2.3 IR sensitivity

The IR-light possesses wide emission spectra and unique heating effect in a non-contact manner, therefore actuating SMP materials with IR-light could realize the applications of SMP.¹⁷⁹ In a laser-activated polyurethane medical device feasibility of this concept has been demonstrated successfully.¹⁸⁰⁻¹⁸² As the required energy was quite high in such devices, heat transfer between the heat source and the SMP needed to be enhanced. Functionalization of SMP with the capability of a higher heat transfer was realized by the incorporation of conductive fillers, such as conductive ceramics, carbon black, and carbon nanotubes.^{183, 184} The incorporation of particles also influenced the mechanical properties: incorporation of microscale particles resulted in increased stiffness and recoverable strain levels^{185, 186} and could be further enhanced by the incorporation of nanoscale particles.¹⁸⁷



Figure 13: Comparison of the stress recovery before (left) and after (right) remote actuation by infrared irradiation. Neat polymer (M) bends and does not recover. In contrast, a 0.57 vol.% (1 wt.%) CNT nanocomposite (PCN) (20 mm \times 4 mm \times 0.4 mm, deformed 300%) contracts and exerts ~ 19 J to lift a 60 g weight (moving bottom clamp) 3.3 cm with ~588 N of force on exposure to infrared irradiation (arrow indicates moving direction). Taken from ⁷¹

To achieve an enhanced photothermal effect, the molecular structure of the particles has to be considered. Polesterurethanes reinforced with CNTs or CB of similar size displayed an increased $R_{\rm f}$.⁷¹ The CB reinforced materials actuated by IR-radiation provided between 20% and 30% of the stress achieved by heat actuation while almost 100% could be observed for CNT SMP nanocomposites (SMC-CNT). This effect had been attributed to a synergism between the anisotropic CNTs and the crystallizing polyurethane switching segments. By exposing to near-IR radiation, the SMC-CNT deformed to 300% exerted ~ 19 J to lift a 60 g weight more than 3 cm (Fig. 13). In contrast, the heating efficiency of CB reinforced polymer by exposure to IR-radiation was much less and the necessary exposure time and power required was greater than for SMC-CNT.⁷¹

5.2.4 Radio-opacity

SMP materials could be used in a variety of different medical devices and diagnostic products as deployable elements of implants from vascular grafts to components of cardiac pacemakers and artificial hearts.¹⁷¹ In most of these medical applications proper device placement inside the human body is a prerequisite. Imaging techniques like X-ray allow physicians to monitor the location and as well as proper function of implants non-invasively.^{171, 172, 188} A certain requirement is radio-opacity of the implant, which can be easily achieved in the case of metallic implants. In contrast, most polymeric materials are translucent for X-rays. The most common technique for functionalization of SMPs with X-ray contrast properties is the incorporation of radio-dense fillers such as heavy element oxides or salts. For instance, bone cement, used in orthopedic surgery for fixation of hip and knee prostheses, is made radio-

opaque through addition of zirconium oxide (ZrO_2) , barium sulfate (BaSO₄) or tantalum (Ta).^{189, 190} High loading filler fractions are often required to achieve good X-ray visibility, with filler fractions between 40 and 60 wt% not being uncommon.



Figure 14: Fluoroscopic image of 3 vol% tantalum-filled SMP coils with varying diameter immersed under 50 cc's of water. The three coils had coil diameters of 10 mm, and wire diameters of 0.25 (uppermost), 0.45 (lower left), and 0.088 mm (lower right). Taken from¹⁸⁸

SMC containing 3 vol% (50 wt%) of Tantalum powder, have been developed to exhibit the function of radio-opacity in combination with SME. Furthermore, these radio-opaque SMC might be suitable materials to be used as coil implants for treatment of intracranial aneurysm. X-ray diffractometer tests showed that tantalum filler increased the radio-opacity of the material, although in medical imaging X-rays of lower energy would be used. Fig. 14 shows an X-ray image of the tantalum filled SMP coils. When the SMC were actuated in an aneurysm model, the SMC coils deployed demonstrating that typical hemodynamic forces did not hinder the shape-recovery process. The SMP coils were stable inside the aneurysm dome and did not compact or migrate within the cavity.¹⁸⁸

Similarly radio-opaque SMC have been fabricated by co-extrusion of biomedical grade polyether urethane (PEU) and barium sulfate (BaSO₄) micro-particles. It was demonstrated

that $BaSO_4$ particles improved the mechanical properties of the PEU without disturbing the SME.¹⁹¹

5.2.5 Electrical conductivity

Incorporation of electrically conductive materials such as conducting polymers, carbon black, carbon nanotubes, carbon nanofibers etc enabled electrically conductive SMP.^{9, 31, 71, 166, 192, 193} The fillers significantly reduced the electric resistivity and resulted in conductive SMPs. Furthermore, when an appropriate current is applied, joule heating occurred and was used for the actuation of the SME indirectly. An important group among these multifunctional SMPs are composites from SMPs and CNTs. Low concentrations of CNTs can significantly enhance the mechanical and thermal properties, impart unique electrical and magnetic properties as well as improve the shape-memory behavior of the polymer matrix.^{192, 194, 195} CNTs have an anisotropic nature enabling a percolative behavior at low volume fractions in the SMP matrix. Possible applications of such SMC-CNTs are electroactive actuators for controlling microaerial vehicles.¹⁹⁶ However, CNTs are strongly affected by van der Waal's forces, which give rise to the formation of aggregates and then makes dispersion of CNTs in polymer matrix difficult. The compatibility and interfacial adhesion as well as homogenous distribution of CNTs in a polymer matrix could be achieved by surface modification in nitric acid and sulfuric acid mixture.³¹ Generally, inclusion of CNTs in SMPs, such as thermoplastic elastomers can significantly modify polymer behavior, impart new or enhance characteristic properties from the associative networking of the nanoelements.

The impact of CNTs (average diameter 100 nm; length > 10 µm) on the thermal, mechanical and electrical behavior of thermoplastic SMPU (Cat T-A-C) was investigated.⁷¹ The SME for this SMC was actuated thermally, optically and electrically. The Joule heating caused by the finite resistivity of the nanocomposite enabled current induced actuation. By applying electric current, the CNT nanocomposites (16.7 wt. % CNT) deformed to 100% exerted ~ 6 J to lift a 60 g weight 1 cm as shown in figure 15. The resistivity of the nanocomposite was directly related to the concentration of CNT, its aspect ratio and orientation distribution (which was dependent on deformation history).¹⁹⁷ The critical concentration of the CNT was also a function of the percolation threshold ($\varphi_c \sim 0.5-1.0 \text{ vol}\%$).⁷¹ R_f and the recovery of constraint stress of a nanocomposite with 2.9 vol% (5 wt%) CNT was higher than pristine SMPU or SMPU filled with 20 wt% of carbon black (CB).



Figure 15: Electrically stimulated stress recovery of 10.2 vol.% (16.7 wt%) CNT nanocomposite (20 mm \times 4 mm \times 0.4 mm, deformed 100%), exerting \sim 6 J to lift a 60 g mass 1 cm. To maintain sufficient Joule heating, the current was increased with increased recovery, as CNT nanocomposites are piezoresistive. (taken from ref. ⁷¹)

The enhanced recovery characteristics were thought to be associated with the synergism between the anisotropic CNTs and the crystallizing switching segments of the polymer. The extent of CNT orientation in the direction of deformation (tube axis parallel with applied stress) increased with increasing CNT concentration. In conjunction, the polymer crystallite fraction was a function of CNT concentration. The addition of CNTs also slightly increased initial polymer crystallinity by serving as heterogeneous nucleation sites.¹⁹⁸ Simultaneous X-ray diffraction–deformation experiments revealed a complex interplay between crystallization of switching segments, their alignment and the orientation of CNTs during elongation.⁷¹ On removal of the stress, the CNT alignment relaxed and the partial crystallinity remained constant. Heating the constrained composite resulted in melting of the crystallites without substantial change in CNT alignment.

For improving particle-matrix interaction in SMC surface modified multi-walled CNTs (MWCNTs), with 10-20 nm diameter and 20 μ m length were incorporated in a SMPU matrix.³¹ The effects of surface modified MWCNTs on the mechanical and electrical properties of the SMC were discussed. The composites (SMP-MWCNTs) made with surface modified MWCNTs displayed improved mechanical properties, and the modulus and stress at 100% elongation increased with increasing surface modified MWCNT content. Nevertheless, the surface modification decreased the electrical conductivity of the nanotubes. This was attributed to the fact that the acid treatment of the surface lead to an increase in the numbers of defects in the lattice structure of carbon-carbon bonds. The electrical conductivity was in the order of 10⁻³ S·cm⁻¹ for a composite with 5 wt% modified-MWNT. A high voltage of 60 V was required to heat the SMC-MWCNTs above the T_{sw}.^{199, 200} A sample, having a permanent shape of a rectangular strip was deformed and fixed into a helix-like temporary shape. The original permanent shape of the sample was recovered almost completely within 10 sec when

an electric field of more than 40 V was applied.³¹ The SMC with untreated MWCNT resulted in higher temperatures than that of the composite with modified MWCNT under application of a voltage level. A homogenous distribution of MWCNT in SMPU could be reached by mixing the MWCNT with the prepolymer mixture prior to the addition of butane diol acting as chain extender. In general, this procedure, called *in-situ* polymerization, provides a good opportunity of interaction between the polymer chains and nanofillers. Highly conductive SMPU actuators were developed by application of *in situ* polymerization of SMPU in the presence of surface modified MWCNT.¹⁹⁶.¹⁹⁴

SMC with the additional functionality of electrical conductivity and in which the conductive filler is polymeric, had been achieved by the use of conductive polypyrrole (PPy) as a coating layer of SMPU.²⁰¹ The presence of PPy increased the electric conductivity of the composites and a percolation threshold at 10 wt% loading of PPy layer was achieved. The electrical conductivity was increased from 0.053 to 0.09 S⁻cm⁻¹ as the percolation threshold was reached. At 20 wt% loading of PPy under a 40 V electric potential, 85% to 90% strain recovery rate was achieved in 20-30 s with bending mode. In case of lower loading, the sample took higher time to recover original shape. This was explained by the combination of increased switching segment crystallinity, tensile strength, and elongation at break at lower PPy content and the loss of the integrity of the PPy network during deformation. The effect of incorporating a combination of MWCNTs and/or PPy to SMPU was also investigated.²⁰² The highest electrical conductivity (0.098 S cm⁻¹) and the highest shape recovery rate (90 to 96%) were achieved for the samples containing 2.5 wt% PPy (coating layer) and 2.5 wt% of dispersed MWCNTs within the SMPU matrix. The conductivity of this composite was high enough to enable an electroactive shape recovery by heating above T_{sw} of 40-48 °C due to melting of PCL switching segment domain in PU.

In SMPU composites of carbon nanofibers (CNF), oxidized carbon nanofibers (ox-CNF), and CB the influence of the type of particle fillers on the resistive heating of nanocomposites was explored.^{203, 204} SMPU composites with crystalline switching segments were synthesized in a low-shear chaotic mixer and in an internal mixer. The switching segment crystallinity was reduced in the presence of CNF and ox-CNF. For the CNF/SMPU composites prepared in the chaotic mixer, the electrical percolation occurred at 4 wt% with electrical conductivity of $\sim 10^{-5}$ S cm⁻¹, while the composites prepared in a Brabender internal mixer remained insulators ($\sigma \sim 10^{-11}$ S cm⁻¹) at up to 7 wt% CNF. The resistivity of composites of CNF and ox-CNF showed weak dependence on strain, while that of the composites of CB increased by several
orders of magnitude with imposed tensile strain. Resistive heating induced heating was demonstrated in CNF/SMPU composite with 5 wt% filler content at an applied voltage of 300 V.

The combination of CB nanoparticles and short carbon fibers in a styrene based thermoset SMP created a highly conductive SMC. Using 5 wt% CB and 2 wt% short carbon fibers, an impressive electrical conductivity of 2.3 S cm⁻¹ was reported.⁷⁹ A typical example of electrically induced SME for nanocomposites with 5 and 2 wt% CB and SCF, respectively is shown in Fig. 17. Only 50 sec are required to reach a complete recovery from the temporary to the permanent shape by heating the sample up to 65 °C upon application of an electric field. The shape transition at 25 V was documented with a digital camera (Fig. 16).²⁰⁵ R_r was dependent on the magnitude of the applied voltage and the electrical resistivity of the composites.



Figure 16: Series of photographs showing the macroscopic SME of SMP/CB/SCF composite containing 5 wt% CB and 2 wt% SCF. The permanent shape is a plane stripe and the temporary shape was fixed as right-angled shape. Taken from ref.²⁰⁵

In addition, such partially conductive SMC were investigated by the dispersion of micron sized nickel particles (3 -7 μ m) in a commercially available SMPU (Diaplex MS-5510). The Ni particles dispersed in SMPU solution were able to align in the form of conductive chains under a weak static magnetic field (0.03 T) before curing. The electric conductivity of the SMPU was proposed to be significantly improved in the chain direction of the Ni particles, which could be more suitable for joule heat induced shape-recovery at low electrical voltage. Joule heating of samples containing 10 vol% Ni raised the specimen temperature above T_g inducing strain recovery (bending mode) in 90 s. Instead of using only Ni particles, small amount of Ni particles forming chains inside polymers with randomly distributed CB were

also proposed.²⁰⁶ The aligned Ni chains served as conductive channels to bridge CB aggregates. Consequently the electrical conductivity was significantly increased while keeping the other properties constant.



Figure 17: Resistivity *vs* volume fraction of CB with/without 0.5 vol% of Ni. Red symbol, right after fabrication; blue symbol, one month later. The inset Fig. illustrates how the resistance was measured. Taken from ref. 206

The effect of CB concentration on the resistivity of SMPU/CB/Ni (aligned or chained) and SMP/CB/Ni (random, without alignment by magnetic field), as well as SMPU/CB is demonstrated in Fig. 17. Obviously, the random distribution of Ni (0.5 vol%) slightly reduced the resistivity of the composites. The aligned Ni obtained the chain shape in the magnetic field, reduced the electrical resistivity by a factor of ten. This remarkable reduction in the electrical resistivity was the result of the conductive chains, which served as conductive channels to bridge those small isolated CB aggregations. The reduction in resistivity was dramatic with low concentration of CB and then decreased in its magnitude with increasing the concentration of CB. SME induced by Joule heating demonstrated that for SMPU/CB/Ni (chained) composite with approximately 10 vol.% CB and 0.5 wt.% Ni, a temperature of 80 °C was reached, which was much higher than the T_g of switching domain of the SMPU, so that almost full recovery was observed within 120 sec. The temperature of SMPU/CB sample was the lowest; about 45 °C only, slightly higher than the T_g of the switching segment of SMPU, hence, the shape recovery was small. For sample SMP/CB/Ni (random), the temperature reaches around 65 °C and the shape recovery was not completed after 120 sec.

5.3 Multifunctional SMP by Integration of Functionalities in one-component materials

In the multimaterial systems presented so far, typically one component contributed one function, e.g. SME by the matrix polymer and radio opacity by the inorganic particles; a concept, which followed the approach of multifunctional metallic alloys. The high variability in the chemical structure of macromolecules raises the question if several functionalities can be integrated on the molecular level, e.g. a SMP obtained by the chemical coupling of semiconducting, polymeric building blocks.

As explained in chapter 1, the research field of multifunctional materials is frequently motivated by the requirements of certain applications. In biomedical applications the SME can be used to insert a bulky implant or instrument in a compressed temporary shape minimally invasively in the body. The question arising immediately is how to get the implant removed again as it is necessary in many cases. A suitable method is the disintegration of the hydrolytic degradation resulting in soluble degradation products, which can be metabolized and/or excreted. As the SMP material itself needs to be degradable, the function SME and biodegradation have to be integrated on the molecular level. Furthermore, the material needs to be non-toxic, compatible to the surrounding tissue and no toxic degradation products should be released.²⁰⁷⁻²¹⁷

Functionalization of SMP with hydrolytically degradability requires incorporation of hydrolytically cleavable groups into the polymer chain segments of the SMP. This could be achieved by the usage of either hydrolytically degradable polymeric building blocks as chain segments into the polymer networks or in thermoplasts, or the incorporation of easily hydrolyzable bonds into the chain segments as weak links.^{218, 219} An example for the latter was the ring-opening polymerization of ε -caprolactone with digylcolide.

Two different hydrolytic degradation mechanisms have to be considered in hydrolytically degradable polymers: surface or bulk degradation. In polymers showing surface degradation the cleavage of the hydrolyzable bonds is faster than the diffusion of water into the polymer matrix. In contrast, bulk degrading polymers are initially swollen in water followed by hydrolytic chain cleavage. This process of bulk degradation of polymer networks can be subdivided into three steps: swelling and induction period (1), reduction of molecular weight accompanied by reduction of mechanical strength (2), and mass loss (3).^{64, 220}



Figure 18: Tensile tests of amorphous polymer hydrolytically degradable SMP networks at room temperature, 37 °C and 70 °C in air and water.

A key requirement for the investigation of hydrolytically degradable SMP is an accurate determination of the SMP network composition.^{221, 222} The influence of swelling on the mechanical properties of degradable SMP was investigated in urethane networks based on poly[(*L*-lactide)-*co*-glycolide] with $T_{\text{trans}} = T_g$ (**Cat. N-M-A**). In tensile tests (Fig. 18), the dry material exhibited a yield point in the stress–strain curves at T < T_g . An *E* modulus of 685 MPa and an ε_b of 195% were determined. At $T > T_g$, the dry network showed rubber-elasticity with $\varepsilon_b = 505\%$ and no yield point. Tensile tests of pre-incubated samples having an initial water uptake of 0.5 – 1% revealed elastic behavior with a lower *E* modulus and a higher ε_b compared to dry samples. In stress-controlled DSCP R_f and R_r was determined for dry and aqueous environment. Values of R_f of typically more than 90% were obtained, whereby R_{f,H_2O} was higher than R_{f,air}. In contrast, R_{r,H_2O} was significantly lower in aqueous environment compared to the dry state, in which $R_{r,air}$ 100%. Additionally, T_{sw} was clearly reduced in water.

In phosphate buffer solution at pH 7.0 and 37 °C the degradation behavior of different SMP networks was investigated. In Fig. 19a the mass loss as a function of time (72 weeks) of polymer networks oligo-(*\varepsilon*-caprolactone)dimethacrylate, from from poly(*E*caprolactone)dimethacrylate and *n*-butyl acrylate, and oligo-[(*E*-caprolactone)-coglycolide]dimethacrylate with different glycolide content is depicted, representing SMP according categories N-M-C and N-B-A-C, as well as N-M-C with a higher amount of hydrolysable groups.⁷⁶ In all these SMP networks, hydrolysis of the ester bonds in the main drives the hydrolytic degradation. SMP from $oligo(\varepsilon$ -caprolactone)dimethacrylate and from $poly(\varepsilon$ -caprolactone)dimethacrylate copolymerized with *n*-butyl acrylate displayed mass losses of only 10 % during 72 weeks. The number of easily hydrolyzable bonds was

substantially increased by the introduction of glycolide units in the copolyester segment. Consequently, an accelerated mass loss was determined. In case of polymer networks from oligo-[(*ɛ*-caprolactone)-*co*-glycolide]dimethacrylate with a glycolide content of 9 wt% an induction period of 20 weeks can be observed. After 53 weeks a total mass loss of 15% was detected. When the glycolide content was increased to 13 wt% an induction of 20 weeks was determined as well. In contrast to the system with only 9 wt% of glyocolide, after 58 weeks a total mass loss of 60% was observed. Furthermore, polymer networks with a glycolide content \geq 14 wt% displayed a decrease in crystallinity of the polymer network. This should result in an additional acceleration of degradation, as water penetrates faster into amorphous than in crystalline parts.⁷⁶

Hydrolytic degradation of amorphous SMP with $T_{\text{trans}} = T_g$ were investigated in copolyesterurethane networks based on oligo[(*rac*-lactide)-*co*-glycolide]. Within 100 to 150 days the polymer networks were degraded up to > 90% (Fig. 19b).⁶⁴ In the degradation experiments the copolyesterurethane networks from oligomeric telechelics having M_n around 10 k showed an induction period of 120 days. When the crosslink density of such networks was increased by creating oligomers with $M_n = 1$ kD an induction period of 100 days was determined. In these copolyesterurethane networks with M_n of the oligomers = 1 kD the densely crosslinking prevented a fast diffusion of water into the core of the network. The copolyesterurethane network with M_n of the oligomers = 5 kD exhibited an induction period of 50 days.

Besides covalent polymer networks as hydrolytically degradable SMP thermoplastic SMP with tailored degradability had been prepared and were investigated for their degradation properties.^{73, 77, 223-225} Prominent examples were polyesterurethane multiblock copolymers having poly(ε -caprolactone) segments providing the switching domains and poly(*p*-dioxanone) or polydepsipeptide segments providing the hard domains.



Figure 19: a) Hydrolytic degradation of polymer networks from ε -caprolactone based on different acrylate networks (\circ : poly(ε -caprolactone)dimethacrylate, \blacklozenge : poly(ε -caprolactone)dimethacrylate and *n*-butyl acrylate, \bigtriangleup : poly[(ε -caprolactone)-*co*-glycolide]dimethacrylate (9 wt%), \blacksquare : poly[(ε -caprolactone)-*co*-glycolide]dimethacrylate (13 wt%)); b) hydrolytic degradation of copolyesterurethane networks (M_n of macrotetraoles: \blacktriangle :1 kD, \blacksquare : 5 kD, \diamond : 10 kD)

a) Permission requested from American Chemical Society, USA;

b) Permission requested from Wiley InterScience, UK

5.3 Multifunctional SMP by Combinations of Multimaterial and Molecular Integration Approaches

Following the two concepts introduced above, it is quite understandable that the number functionalities could be further increased, by combinations of multimaterial and molecular integration approaches. As the number functionalities, which might interfere with each other should increase with the number functionalities, this approach is promising. Multifunctional SMPs based on this combined approach were realized as hydrolytically degradable SMPs containing magnetic particles or drugs. In the following we will describe these two examples,

whereby we will focus on the interaction between the newly obtained functionality and the SMC.

The magnetic sensitivity and biodegradability can be combined together in SMC by using a biodegradable SMP as matrix material along with magnetite nanoparticles as filler. Magnetite nanoparticles are typically used as a biomedical material because of their favorable biocompatibility and availability. A biodegradable multiblock copolymer (PDC), with poly(pdioxanone) as the hard segment and $poly(\varepsilon$ -caprolactone) as the switching segment can be used as SMP (Cat. T-C-C) matrix in these magneto-active SMC. PDC had a crystallizable switching segment and had been developed for medical applications. T_{trans} of PDC is T_{m} associated to PCL-domains, which is only slightly higher than body temperature to avoid any damage to surrounding tissue when heated to induce the SME.³² Similarly, another family of magneto-active and biodegradable SMC can be produced by using crosslinked poly(Ecaprolactone) (Cat. N-M-C) as matrix material with integrated magnetic nanoparticles.¹⁷⁵ PCL represents favorable biocompatibility, non-toxicity and drug permeability and had been recommended for clinical applications. The in vitro degradation of SMC consisting of crosslinked poly(*e*-caprolactone) and Fe₃O₄ nanoparticles had been recently studied.²²⁶ Changes in mechanical properties, molecular weight and gel fraction were used to trace degradation behavior of the specimens. A decreasing tendency in recovery ratio with degradation time was observed for all the samples. Also an increase in degradation rate was observed with the addition of Fe₃O₄ in composites because of the hydrophilicity of the nanoparticles. On the basis of degradation results, the authors also proposed a mechanism of PCL degradation to illustrate the effect of degradation on shape-memory.²²⁶

The aim to develop a drug loaded, degradable stent (Fig. 20) or anchorable drug release system stimulated the design of a multi material system based on a degradable SMP matrix.²²⁷ SMP networks with $T_{\text{trans}} = T_{\text{g}}$ (Cat. N-M-A) and $T_{\text{trans}} = T_{\text{m}}$ (Cat. N-M-C) were selected as matrices, whereby three different SMP network architectures were realized based on i) oligo[(ε -caprolactone)-*co*-glycolide]dimethacrylate (CG-DMA) telechelics, which were crosslinked by photopolymerization (Cat. N-M-C),^{228, 229} ii) star-shaped oligo[(ε caprolactone)-*co*-glycolide]tetroles (oCG) (Cat. N-M-C) or oligo[(*rac*-lactide)-*co*glycolide]tetroles (oLG) (Cat. N-M-A) crosslinked by low molecular weight aliphatic diisocyanates,^{230, 231} and iii) branched oligo(ε -caprolactone)octols (oCl) crosslinked by low molecular weight aliphatic diisocyanates (Cat. N-M-C).⁷⁰

When drugs were incorporated in SMPs of Cat N-M-C based on CG-DMA with varying polymer chain segment length, SME actuated in air was not influenced by drug loading, and a quantitative shape recovery was obtained. When the experiments were conducted in an aqueous environment, a small change in T_{sw} was observed. In SMP with smaller M_n drug incorporation (by swelling) led to a decrease of $R_{\rm f}$ from 86 to 76%, while drug incorporation (in situ) resulted in a R_f of only 62%. In contrast, R_r values were not influenced by drug loading. This different behavior had been attributed to changes in the crystallization behavior of the switching segments, thereby reducing $R_{\rm f}$. In branched oCl networks a similar behavior was observed, although less pronounced, as the polymer chain segment length was higher. In SMPs with drug loadings of 10 wt% a decrease of R_r was determined for networks with a degree of polymerization of 10 and 20. In contrast, $R_{\rm f}$ increased slightly for networks with a degree of polymerization of 10 and decreased when degree of polymerization was 20. SMPs of this class with a higher drug loading were too brittle for a determination of SMC. A similar trend could observed based be in **SMPs** on oligo[(e-caprolactone)-coglycolide]dimethacrylate.

In general, it was demonstrated for the above mentioned material system that the three specified requirements, e.g., i) the incorporation of drugs independent of their hydrophilicity did not influence the SMC, ii) a diffusion-controlled release could be enabled, which was independent from the biodegradation, and iii) the programming and shape recovery process, which the device experienced during minimally invasive implantation did not change the drug release, can be fulfilled. For details about the relationship between drug loading and degradation as well as drug release before and after actuation of the SME, the interested reader is kindly referred to recent review.²³²



Figure 20: Illustration of the principle of an SMP urether stent from oCG-DMA derived network. Permission requested from Wiley-VCH Verlag GmbH & Co. KGaA

6. Conclusion and Outlook

The thermally-induced SME of polymers has been explained as macroscopic effect and the molecular mechanism as well as the related morphological changes were discussed. Suitable polymer network architectures were presented, starting from single macromolecule systems over one-component SMPs up to multimaterial SMP systems, such as blends and interpenetrating networks. Examples polymers were given for each class and their synthesis is briefly described. As the SME is mainly based on the polymer network architecture and the related morphology, a variety of (co)monomers can be used as starting materials in the synthesis of SMP and on this way broad spectrum of material properties can be realized for SMP.

In addition to the tailoring of elastic and thermal properties applications often require the SME to be combined with additional functions, such as electric conductivity, stimuli-sensitive

permeability or certain magnetic properties. Two approaches have to be distinguished when several functions are combined in one material: the functions can be dependent on each other or independent.

A combination of functions depending on each other is obtained when conformational or morphological changes occurring during the shape-memory effect form the basis for the additional function(s). These changes involve the phase transition of the switching domains and the change in the conformation of the switching segments from an oriented to a random coil conformation. A prominent example is the combination of water vapor diffusability in combination with SME, which is broadly applied in breathable and wrinkle-free fabrics.

Multifunctinality as a combination of functions being independent from each other can be achieved by the formation of multimaterials systems. In this approach each material component contributes a certain function. Multifunctional SMP could be obtained by combining a SMP matrix material with different particulate fillers. The prepared (nano)composites are an interesting versatile and low-cost approach for the generation of multifunctional SMP, as realized for the combination of electric conductivity and SME.

Multifunctionality could even be integrated in one component materials by combining SME with hydrolytic degradability. For this purpose easy hydrolysable chemical bonds were incorporated in polymer networks and thermoplastic SMP. By controlling number und distribution of these weak links in the material the degradation rate could be adjusted independently from the shape-memory properties. The integration of different functions in a one component system is a scientific challenge and will also stay a fascinating topic of fundamental research in the near future. An example could be the integration of electric conductivity by suitable polymer building blocks.

Furthermore the concepts for creating multifunctionality could be transferred to recently achieved novel shape-memory capabilities such as light-sensitive SMP, polymer having a reversible shape changing capability or triple-shape polymers.

7. References

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Figure captions:

Figure 1: Different architectures for a) shape-memory polymers and b) multifunctional materials.

Figure 2: Examples for polymer network architectures suitable for exhibiting a shapememory effect (molecular switches: red; netpoints: grey): A) polymer networks consisting of switching segments linked by covalent netpoints, B) AB-polymer network, C) polymer network having side chains as switching segments, D) multiphase polymer network consisting of ABA triblock chain segments linked by covalent netpoints. Nomenclature: **N** indicates SMP network, **M**: one phase SMP network, **B**: biphasic SMP network, **G**: biphasic SMP network with grafted switching segments, **T**: biphasic SMP network obtained from triblock copolymers. Last one/two letter indicates thermal transition of phase(s): **A** glassy/amorphous, **C** crystalline, **LC** liquid crystalline phase.

Figure 3: Categories of thermoplastic SMPs. **A** With crystalline hard domains and amorphous or crystalline switching domains (T-A-C, T-C-C), **B** with amorphous hard domains and amorphous or crystalline switching domains (T-A-A, T-C-A). Nomenclature: T indicates thermoplastic SMP, A a glassy/amorphous, C a crystalline/liquid crystalline phase.

Figure 4: Multimaterial Systems Consisting of Several Different Molecules. A) Binary blends of multiblock copolymers forming a SMP (**B-C-C**), B) Interpenetrating polymer network (IPN) forming a SMP. Nomenclature: **B**: blend, **C**: crystalline phase providing T_{trans} **C**: crystalline phase providing T_{perm} **N**: polymer network, **I**: interpenetrating network, **C**: crystalline phase providing $T_{trans,1}$ **C**: crystalline phase providing $T_{trans,2}$.

Figure 5. Water vapor permeability of two polyester polyurethanes with $T_{\text{trans}} = T_{\text{g}} = 25 \text{ °C}$ (TSPU(a)) or $T_{\text{trans}} = T_{\text{m}} = 50 \text{ °C}$ (TSPU(b)) as a function of temperature.¹¹³

Figure 6: Photo series demonstrating the change of transparency for two different poly(ε -caprolactone) based SMP. At T < T_{trans} the materials are in their temporary shape. When the thermally-induced SME is triggered by heating to T > T_{trans} the SMPs recover their permanent shape. a) Covalent polymer network from poly(ε -caprolactone)dimethacrylate (category **N-M-C**). At T < T_{trans} the material is opaque as the crystalline domains fixing the temporary shape are scattering. When heated to T > T_{trans} the crystalline domains are molten and the material is transparent. b) In contrast, in one component SMP, a multiblock copolymer form poly(ε -caprolactone) and polypentadecadolactone (category **T-C-C**) materials remains opaque as the hard domains forming segments maintain their crystallinity.

Figure 7: Influence of polymer network architecture on recovery of ε as a function of temperature. a) --- Recovery of strain ε of a covalently crosslinked SMP network based on poly[(ε -caprolactone)-*co*-glycolide]dimethacrylate (**N-M-C**) at a heating rate of 2 K:min⁻¹; — First derivation of ε of poly[(ε -caprolactone)-*co*-glycolide]dimethacrylate network.⁷⁶ b) -- -- Recovery of strain ε of a covalently crosslinked SMP based on oligo[(*L*-lactide)-*ran*-glycolide] (**N-M-A**) at a heating rate of 3 K:min⁻¹; — First derivation of ε of polymer network from oligo[(*L*-lactide)-*ran*-glycolide].⁷⁵

Figure 8: Photographs of the SME of a 1.5 mg mL⁻¹ PCO/dye sample (illuminated with 365 nm UV light) during (a) deformation (75 °C, 600 kPa), (b) cooling/fixing (5 °C, 600 kPa), (c) unloading (5 °C, 4 kPa), and (d) recovery (75 °C, 4 kPa).

Figure 9: Dielectric constant as a function of temperature for a polymer (w = const). Light grey, contribution from the electrons, middle grey contribution from pendant groups, dark grey, contribution from the polymer backbone, black contribution from crystalline dipoles.

Figure 10: Magnetically-induced shape-memory effect of thermoplastic composite consisting of Fe(III)oxide nanoparticles in a silica matrix and polyetherurethanes. Taken from ³²

Figure 11: Collapsed and actuated SMPU composite (10 wt% NiZn ferrite) for: a) flower shaped device; and b) foam device (taken from 33)

Figure 12: Series of photographs demonstrating the shape-recovery of thermoset SMP beam with 10 vol.% MEE particle content. Taken from ¹⁷⁸

Figure 13: Comparison of the stress recovery before (left) and after (right) remote actuation by infrared irradiation. Neat polymer (M) bends and does not recover. In contrast, a 0.57 vol.% (1 wt.%) CNT nanocomposite (PCN) (20 mm \times 4 mm \times 0.4 mm, deformed 300%) contracts and exerts ~ 19 J to lift a 60 g weight (moving bottom clamp) 3.3 cm with ~588 N of force on exposure to infrared irradiation (arrow indicates moving direction). Taken from ⁷¹

Figure 14: Fluoroscopic image of 3 vol% tantalum-filled SMP coils with varying diameter immersed under 50 cc's of water. The three coils had coil diameters of 10 mm, and wire diameters of 0.25 (uppermost), 0.45 (lower left), and 0.088 mm (lower right). Taken from¹⁸⁸

Figure 15: Electrically stimulated stress recovery of 10.2 vol.% (16.7 wt%) CNT nanocomposite (20 mm \times 4 mm \times 0.4 mm, deformed 100%), exerting \sim 6 J to lift a 60 g mass 1 cm. To maintain sufficient Joule heating, the current was increased with increased recovery, as CNT nanocomposites are piezoresistive. (taken from ref.⁷¹)

Figure 16: Series of photographs showing the macroscopic SME of SMP/CB/SCF composite containing 5 wt% CB and 2 wt% SCF. The permanent shape is a plane stripe and the temporary shape was fixed as right-angled shape. Taken from ref. ²⁰⁵

Figure 17: Resistivity vs volume fraction of CB with/without 0.5 vol% of Ni. Red symbol, right after fabrication; blue symbol, one month later. The inset Fig. illustrates how the resistance was measured. Taken from ref.²⁰⁶

Figure 18: Tensile tests of amorphous polymer hydrolytically degradable SMP networks at room temperature, 37 °C and 70 °C in air and water.

different acrylate networks (\circ : poly(ε -caprolactone)dimethacrylate, \blacklozenge : poly(ε -caprolactone)dimethacrylate and *n*-butyl acrylate, \bigtriangleup : poly[(ε -caprolactone)-*co*-glycolide]dimethacrylate (9 wt%), \blacksquare : poly[(ε -caprolactone)-*co*-glycolide]dimethacrylate (13 wt%)); b) hydrolytic degradation of copolyesterurethane networks (M_n of macrotetraoles: \blacktriangle :1 kD, \blacksquare : 5 kD, \bullet : 10 kD)

a) Permission requested from American Chemical Society, USA;

b) Permission requested from Wiley InterScience, UK

Figure 20: Illustration of the principle of an SMP urether stent from oCG-DMA derived network. Permission requested from Wiley-VCH Verlag GmbH & Co. KGaA

Figure	1
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N-M-A	N-B-A-A	N-G-C-C	N-T-A-C
N-M-C	N-B-A-C		
N-M-LC	N-B-C-A		
	N-B-A-LC		

Cat T-C-C	Cat T-A-A
T-C-A	T-A-C













Figure 9





Figure 11



Figure 12














Figure 17



Figure 18







Figure 20

