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Shape Memory Systems with Biodegradable Polyesters

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Outline

1. Introduction
2. Shape memory systems
 - 2.1. homopolymers and composites
 - linear
 - crosslinked
 - 2.2. copolymers and composites
 - linear
 - crosslinked
 - 2.3. polyester-containing polyurethanes and related composites

2.4. blends and composites

linear

crosslinked

2.5. polymers with thermosets

conetwork

semi interpenetrating network

interpenetrating network

3. Applications

4. Outlook and future trends

Acknowledgements

References

Abstract

Preparation, properties and applications of shape memory polymer (SMP) systems composed of or containing biodegradable polyesters have been surveyed in this chapter. SMPs are capable of memorizing one or more temporary shapes and recovering to the permanent shape upon an external stimulus that is usually heat. SMPs were classified in respect to their molecular structure (homopolymers, copolymers, blends) and architecture (conetwork, interpenetrating network) in this review. A further distinction was made whether the related system was linear (thermoplastic) or crosslinked (thermoset). The underlying mechanisms of shape memory actions are introduced and discussed. Emphasis was put to present the recent progress on shape memory biodegradable polyester systems and their potential for practical applications, especially in surgery. Attempt was made to deduce trends for future developments and applications.

Key words for indexing:

shape memory polymers, biodegradable polyesters, biobased polyesters, one-way shape memory, two-way shape memory, shape fixity ratio, shape recovery ratio, recovery stress, shape programming, shape memory copolymers, shape memory polyurethanes, conetwork, interpenetrating network (IPN). semi IPN, full IPN, dual-shape memory, triple-shape memory, multi-shape memory, thermo-responsive shape memory, electro-activated shape memory, magnetic field activated shape memory, shape memory nanocomposites, reversible crosslinking, Diels-Alder reaction, thermoset, photoset, suture, stent, self healing

1. Introduction

Growing environmental concerns and public awareness of the necessity of sustainable growth trigger the present research and development (R&D) works to produce and use biodegradable polymers, and especially those which are derived from renewable resources. Environmental issues are mostly related to dwindling of fossil fuels (crude oil, natural gas) as feedstock of petro-chemistry, carbon dioxide emission of the latter, and disposal problem of plastic waste. Biobased, biodegradable polymers are promising candidates to overcome the abovementioned problems when they are capable to replace the competing petroleum-based counterparts. Biodegradable polymers decompose to carbon dioxide, water and biomass under aerobic conditions, whereas the product range is enlarged by methane when decomposition takes place under anaerobic conditions. The decomposition itself is a rather complex process involving hydrolysis, microbiological attack, enzymatic cleavage, and thermal degradation. Nevertheless the controlling ester cleavage is mostly due to enzymatic attack [1]. Bio-based polymers originate from biomass (e.g. thermoplastic starch), synthesized by microorganisms (polyhydroxyalkanoates, PHAs, of bacterial origin) or produced by biotechnological routes from suitable monomers (e.g. polylactic acid, PLA, synthesized by ring opening polymerization from lactide). PHAs are real biopolymers, in fact, because they have been produced by living organisms. Note that biodegradable polymers can be produced from petrochemical sources, as well. Poly(ϵ -caprolactone) (PCL), polyesteramides, aliphatic and aromatic copolyesters belong to the “petro-based” biodegradable polymers. The above listing makes clear that the major part of biodegradable polymers are polyesters, and in particular, aliphatic polyester versions. A further peculiar feature of aliphatic polyesters is that practically all of their monomers can be synthesized from renewable resources [1].

Shape memory polymers (SMPs) and composites thereof are emerging smart materials in different applications, especially in biomedical, aerospace and construction engineering fields. SMPs may adopt one (dual-shape), two (triple-shape) or several (multi-shape) stable temporary shapes and recover their original or permanent shape (or other temporary shapes when not dual-shape type) upon the action of an external stimulus. The external stimulus may be temperature (set by direct or indirect ways), pH, water, light irradiation, redox condition etc. In most cases, however, the SMPs are thermosensitive or thermally activated ones. The “switching” or transformation temperature (T_{trans}), enabling the material to return to its permanent shape, is either linked with the glass transition (T_g) or the melting temperature (T_m). Therefore the SMPs are often subdivided based on their switch types into T_g - or T_m -based SMPs. As reversible “switches”, however, other mechanisms such as liquid crystallization/melting, supermolecular assembly/disassembly, irradiation-induced reversible network formation, formation and disruption of a percolation network, may serve [2]. The permanent shape is guaranteed by physical (entanglement, interpenetrating networks) or chemical network (composed of permanent or temporary covalent bonds) structures. The corresponding sites are also termed net points. The temporary shape is set by mechanical deformation above T_{trans} . In exceptional cases the deformation temperature may be below

T_{trans} . The macroscopic deformation applied is translated to conformational changes of the molecular chains or its segments. They are fixed by maintaining the deformation *via* cooling causing either vitrification (T_g -based) or crystallization (T_m -based versions). The strain energy, stored by this way, is released when the material is unloaded and heated above T_{trans} . Note that $T_{\text{trans}} > T_g$ or T_m . This heating triggers conformational rearrangements of the molecular chains or melting of the crystals, respectively, through which the permanent shape is restored. All what is disclosed above is related to one-way SMPs. This means that the external stimulus activates only the change from the temporary to the permanent shape (dual-shape variant) or from one temporary to the other one in multi-shape SMPs. Such one-way SMPs meet the requirements of many applications as it will be shown later. Nevertheless, considerable research efforts are devoted to produce two-way SMP systems which feature a reversible shape change on the basis of “on-off” switching of the external stimulus. A large body of works was already dealing with different SMPs, and the related knowledge is well summarized in recent reviews [2-6].

The shape memory (SM) properties are typically quantified by the shape fixity (R_f) and shape recovery ratios (R_r). R_f means the extent of fixing of the externally applied deformation in the temporary shape. Its value is 100% when the applied deformation, introduced above T_{trans} , is fully kept below T_{trans} in the temporary shape. The usual deformation modes are tension, bending and compression. R_r is the percentage of the recovery of the original shape when the material heated above T_{trans} subsequently. $R_r=100\%$ when the original shape of the material is fully restored. SM properties are usually determined in cyclic (one or more) thermomechanical tests performed under stress- or strain-controlled conditions. Figure 1 displays the course of a SM thermomechanical test. Apart from R_f and R_r , further SM characteristics, such as the temperature interval of recovery, recovery rate and recovery force, can be measured. The latter is assessed in strain-controlled mode, termed also constrained recovery. An excellent overview on the quantification of SM behaviour in cyclic thermomechanical tests was compiled by Sauter et al [7].

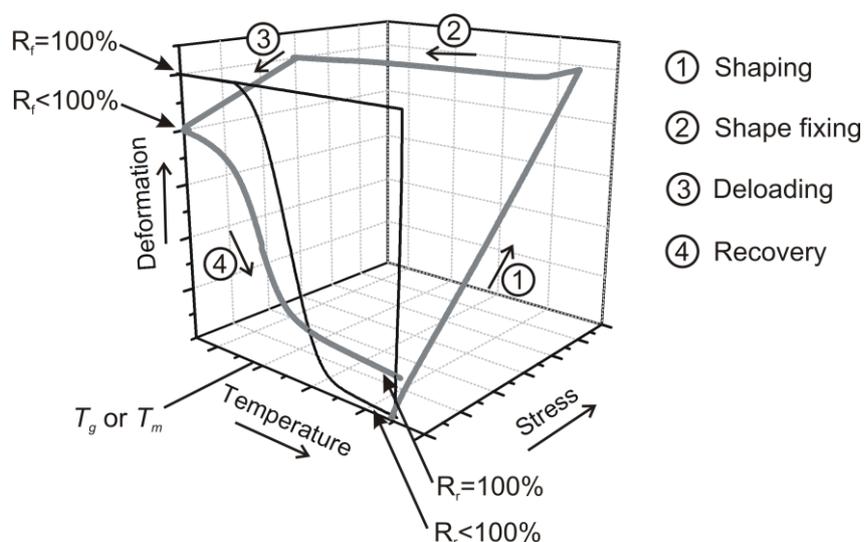


Figure 1: Single SM cycles of one-way SM polymers, schematically

SMPs and related composite systems are grouped differently. The classification may consider the SM mechanisms, the morphology, the type (one-way, two-way), the activation mode (e.g. thermal, photo, chemical sensitive) among others.

Biodegradable polymers play a prominent role in the family of SMPs. This is due to their biodegradability because in many of the medical applications the related “devices” with shape memory (SM) function (e.g. sutures, catheters, stents) should be present only temporarily in the human body. The other, not less important, aspect is that the switch temperature for shape programming (T_{trans}) can well be matched with that of the body.

Next we shall give an overview on SMP systems which are composed fully or partly from biodegradable polyesters. To give a comprehensive review is beyond our intention owing to large body of the related works available both in the open and patent literatures. On the other hand, the reader will get a structured overlook on the basic strategies followed to tailor the structure and performance of SMPs in order to meet the requirements of given applications.

2. Shape memory polymer systems

The grouping followed is according to the basic compositions of the SMPs treated, i.e. homopolymers, copolymers, blends and polymers with thermosetting resins. In order to deliver an adequate review, systems containing biodegradable polyesters are also included. Accordingly, polyurethane (PU) systems composed of polyester building blocks are also reported, though in a very concise manner. Further, each group of the above SMPs is divided into two subgroups, viz. linear and crosslinked versions. This subdivision is reasoned by the fact that the SM properties are generally improved by various crosslinking mechanisms.

2.1. homopolymers and composites

Linear

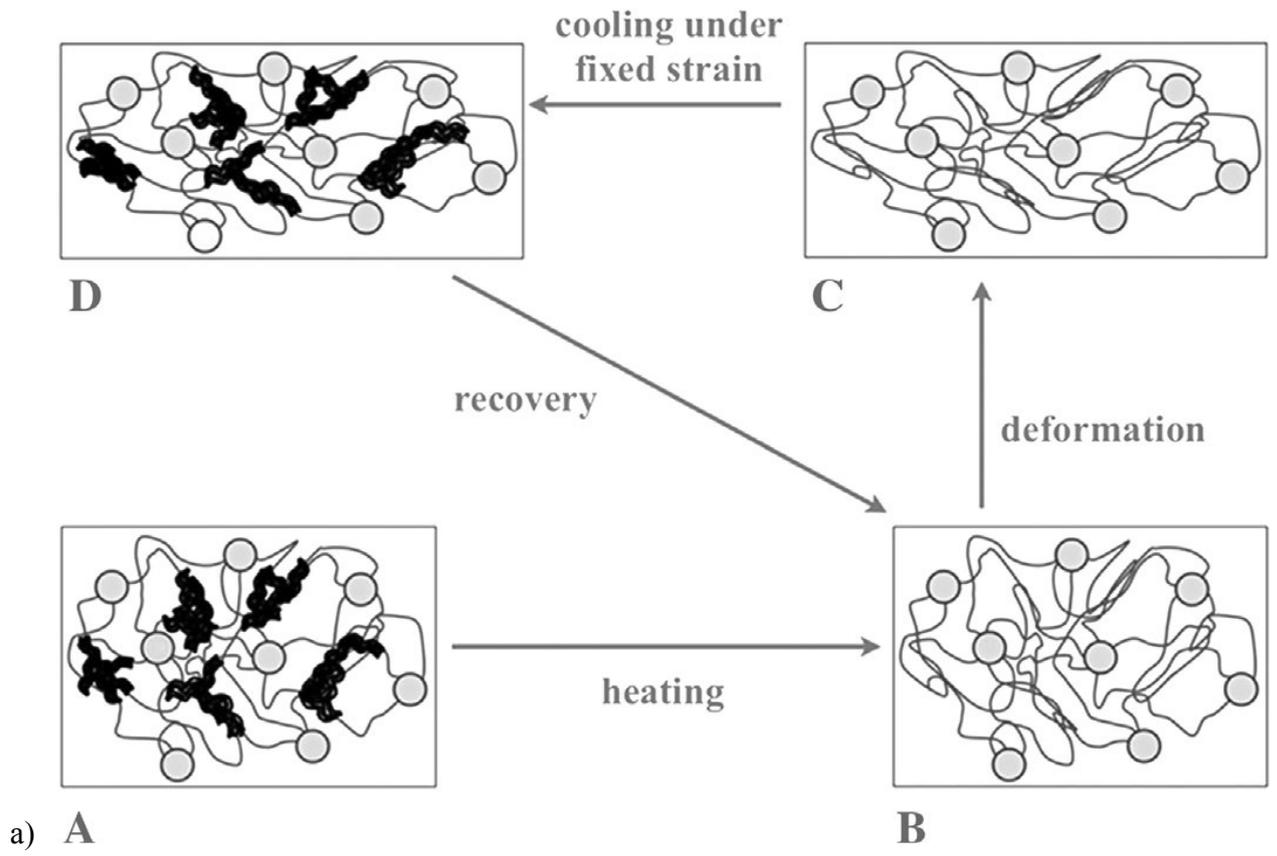
Semicrystalline poly(L-lactic acid) (PLLA or PLA) exhibits T_g and T_m in the ranges of 60-70 °C and 150-170 °C, respectively. Therefore in its uncrosslinked form the crystalline domains act as net points, whereas molecules in the amorphous phase work as switching segments. Accordingly, T_{trans} is usually slightly above the T_g . Wong *et al* [8] studied the shape recovery and recovery stress as a function of stretching ratio (≤ 400 %) and deformation temperature ($T_{\text{trans}}=85-120$ °C). As expected, R_r decreased with increasing stretching and T_{trans} . The drop in the recovery was attributed to strain-induced crystallization. The latter hampered the chain mobility in the amorphous phase yielding low R_r . To overcome this problem two approaches have been followed. Ghobadi *et al* [9] enhanced the amorphous chain mobility by plasticization with water (≤ 2 wt.%). Radjabian *et al* [10] used spun PLA filament, wound in helical form, for SM testing. The filament itself has a complex supermolecular structure which does not change substantially in the SM cycle. Thus, R_r did not change with T_{trans} (70-90 °C), but remained still modest (~ 50 %). By contrast, R_f decreased with increasing T_{trans} .

Crosslinked

It is intuitive that the net point function cannot be fulfilled properly by the crystalline domains evolving in slow crystallizing polymers, such as PLA and PCL. Slow crystallizing polymers are prone for cold crystallization above their T_g (annealing), which is, in addition, prominently influenced by the deformation of the amorphous chains [11]. Therefore research interest turned to crosslinked systems. In the corresponding crosslinked semicrystalline polymer T_m can be used as T_{trans} instead of the T_g . To use the melting/recrystallization transition instead of the glass/rubbery one is beneficial since the former transition is “sharper” (occurring in a smaller temperature range) and faster than the latter one. Recall that chemical (covalent or thermoreversible) or physical crosslinking (through phase segregated domains), and their combination, may replace those “net points” which were initially responsible for the permanent shape.

PLA is often plasticized in order to decrease its T_g to ambient temperatures. This, however, supports the cold crystallization that should be avoided. Moreover, the plasticizer is easily bleeding out. Both crystallization and plasticizer migration can be circumvented by suitable electron beam irradiation of plasticized PLA. The resulting elastomer-like material showed promising SM behavior [12].

Unlike PLA, the ductility of PCL is very high which predestinates it for SM applications. The T_g and T_m of PCL are at about $-50\text{ }^\circ\text{C}$ and $60\text{ }^\circ\text{C}$, respectively [13]. In order to make use of its T_m as T_{trans} (which is exclusively the case), PCL should be crosslinked by a suitable manner. Otherwise the chain entanglement serves for “keeping” the permanent shape. PCL was crosslinked by sol-gel chemistry by Pandini *et al* [14]. The related pathway contained the alkoxy silane end grouping of an α,ω -hydroxyl terminated PCL, followed by hydrolysis and polycondensation reactions of the terminal alkoxy silane groups. The created chemical crosslinks maintained the crystallization ability of PCL. The T_m and crystallization temperature (T_c) of PCL were, however, affected by the crosslinking degree. The resulting material showed both one- and two-way SM behaviors. Figure 2 displays the morphology changes during the one- and two-way SM cycles in this sol-gel crosslinked PCL.



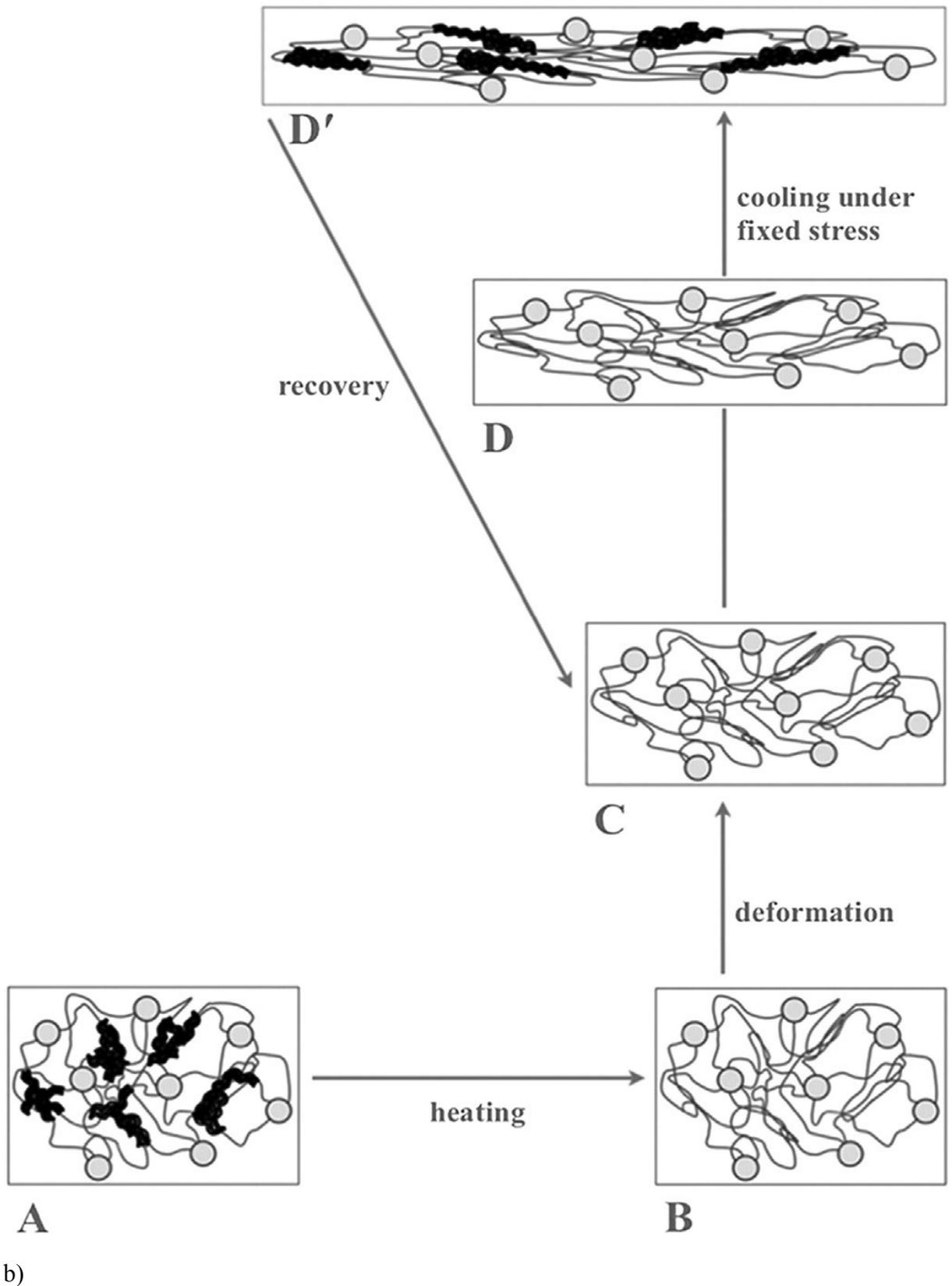


Figure 2: Schematic representation of the structural evolution in sol-gel crosslinked PCL during one- (a) and two-way (b) SM cycles. Notes: filled gray circles represent the sol-gel induced crosslinks, while black domains mark the crystalline PCL domains. During heating

T_m and upon cooling T_c are surpassed, and recovery took place above T_m . Both T_m and T_c rose with the crosslinking density of PCL ([14], reprinted with permission of Elsevier)

In a companion paper the same authors [15] prepared peroxide crosslinked PCL with different molecular architectures. PCL was terminated by methacrylate and crosslinked in its melt phase. The typical thermomechanical behavior of the corresponding SMP, showing two-way SM effect, is given in Figure 3.

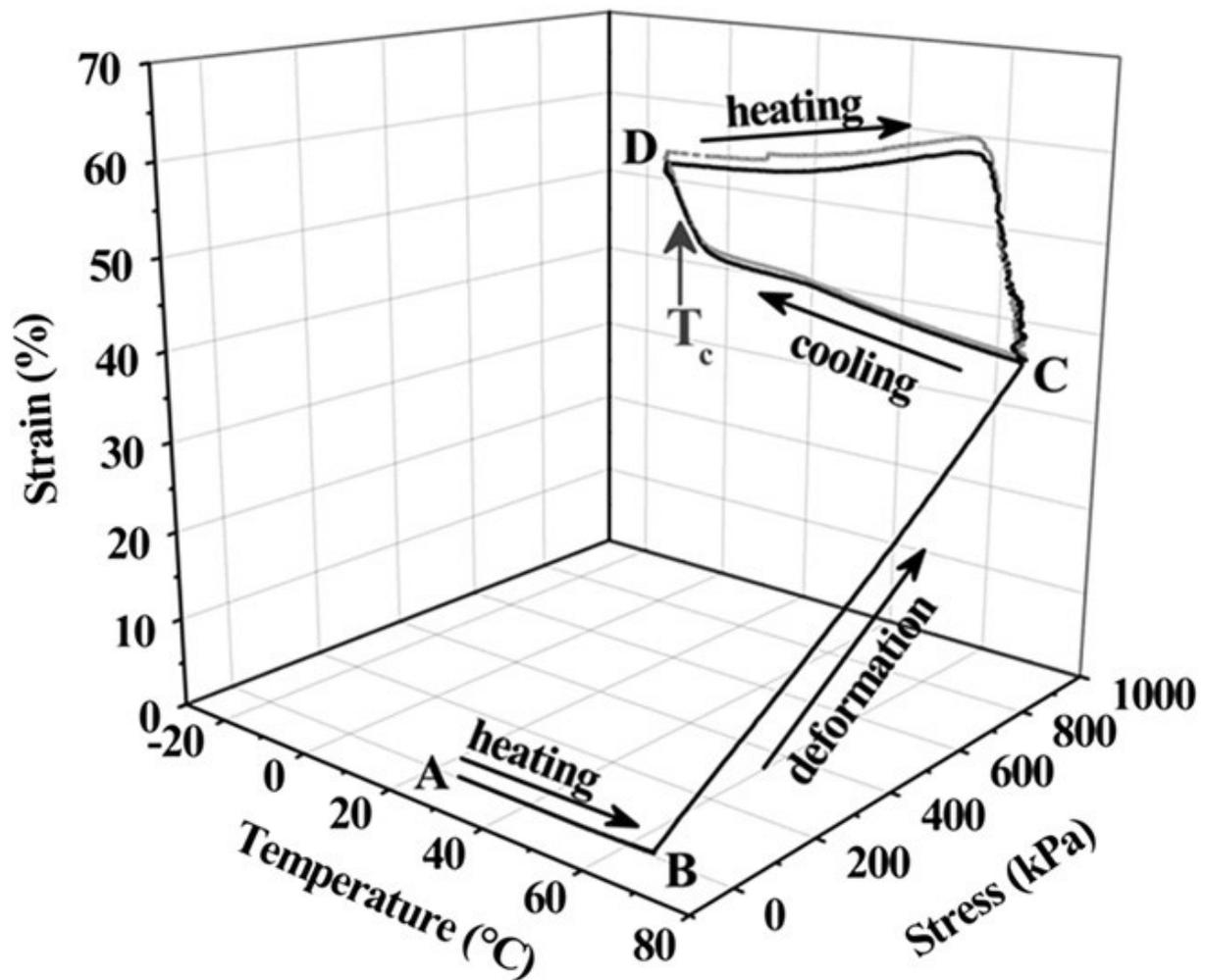


Figure 3: Typical thermomechanical cycle employed for the evaluation of the two-way SM effect in crosslinked PCL. For designation cf. Figure 2b ([15], reprinted with permission of Elsevier)

Polyhedral silsesquioxane (POSS) containing PCL with acrylate end groups were also synthesized and photocrosslinked. This approach allowed controlling the morphology of the resulting SMP in micro- and nanoscale whereby “compromising” the crystallizations of PCL

and POSS [16]. PCL can be crosslinked also by peroxide in the melt. When magnetic field-induced SM effect is the goal, PCL is usually filled with Fe₃O₄ (magnetite) nanoparticles [17]. To achieve electro-active SMPs conductive fillers, such as carbonaceous nanofillers, may be incorporated into the crosslinkable PCL. This was demonstrated by Xiao and coworker [18] who incorporated multiwall carbon nanotubes (MWCNT) in crosslinked PCL. Recall that although here the electric field is the external stimulus, it is translated into heat by the Joule effect. So, the corresponding nanofilled crosslinked PCL remains a thermoresponsive system. R_r changed parallel with that of the gel fraction for the crosslinked PCL. This fact corroborates the prominent influence of crosslinking on the SM performance.

Apart from photo- and peroxide crosslinking, radiation crosslinking methods can also be adapted. The group of Zhu [19-20] used γ -irradiation to crosslink PCL in presence and absence of various sensitizers and studied the SM behavior as a function of radiation dose and dosage rate. Recovery of the related PCLs were studied at $T=56$ °C. With increasing radiation dose the recovery temperature could be decreased due to a similar decrease in T_m . The higher was the molecular weight (MW) of PCL, the higher the crosslinking degree was [19]. Polyfunctional polyester acrylates proved to be suitable additives to enhance the crosslinking degree of PCL upon γ -irradiation [20].

ϵ -caprolactone diol oligomers can easily be converted into the related dimethacrylates which can be efficiently photocured [21]. During their SM programming T_m of the PCL segments served as T_{trans} . The latter could be changed between 30 and 50 °C *via* the MW of the PCL diol. The photosets showed excellent SM properties in multiple cycles. Thus, $R_f=86-97\%$ and $R_r=92-97\%$ data were measured after the 5th cycle.

A promising further tool to tailor the SM properties is given by the creation of thermoreversible crosslinks via Diels-Alder reactions. The beauty of this approach is that the thermoreversibility of the reaction allows us to recycle the corresponding polymer *via* remelting. As Diels-Alder reaction in the polymer synthesis mostly the cycloaddition, occurring between furan and maleimide groups, is preferred. This is due to the fact that the adduct forms, and the retro Diels-Alder reaction runs at rather low temperatures. Inoue *et al* [22] reported that the Diels-Alder type crosslinking of properly functionalized PLA yields good SM properties. Recall that here T_{trans} (=60-100 °C) is still linked with the T_g for PLA. The SM function was lost when the material was heated to $T\sim 160$ °C where the retro reaction, disconnecting the crosslinks, took place. Defize *et al* [23-24] synthesized star-shaped PCLs with furan, anthracene and maleimide end functionalities, respectively. The resulting SMPs showed excellent R_f and R_r values, even after 4 cycles, using T_m of the PCL as T_{trans} (=65 °C). The outstanding SM behavior was restored after recycling of the corresponding system. Note that recycling means here the cycloreversion, i.e. onset of the retro Diels-Alder reaction at $T\geq 105$ °C – cf. Figure 4. Note that the anthracene end functionalization, instead of furan, was foreseen to influence the kinetics of the adduct formation and its temperature stability.

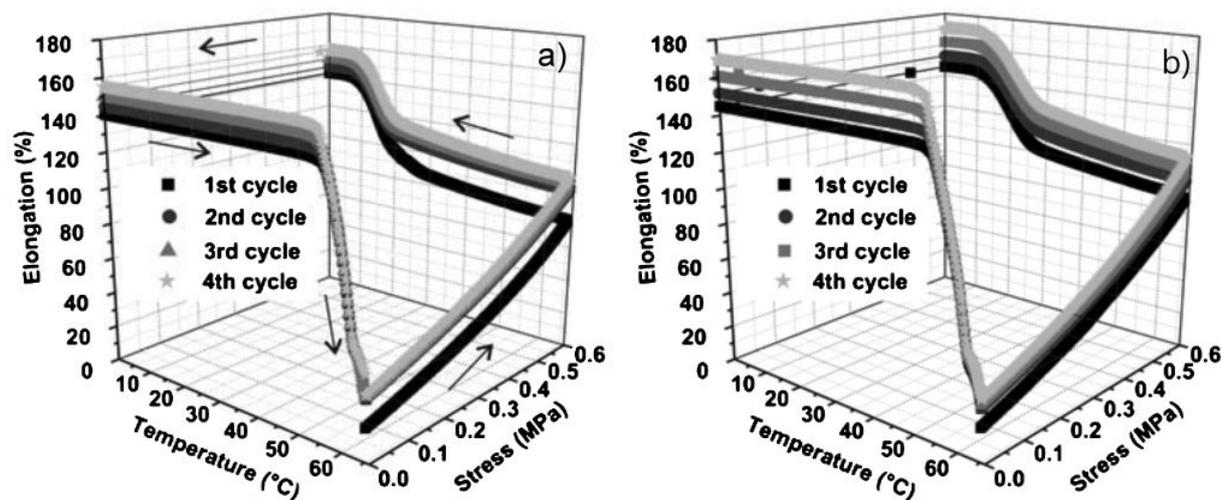


Figure 4: SM properties evaluated by thermomechanical cycling of the PCL crosslinked by Diels-Alder reaction before (a) and after recycling (b). Note: star-shaped PCLs bearing furan and maleimide groups, respectively, were reacted ([23], reproduced with permission of Wiley)

Peroxide crosslinked poly(propylene sebacate), synthesized from biorenewable resources, exhibited a T_m at about 50 °C serving as T_{trans} in the SM cycle. The value of T_m could be tuned by the peroxide crosslinking and boehmite nanofillers content yielding a temperature interval between 37 and 51 °C, which is close to the body temperature. Interestingly, the boehmite nanoplatelets contributed to a fast in vitro degradation of this polymer [25].

2.2. copolymers and composites

Copolymerization is the most widely used technique to control T_m and tune the biodegradability of polymers. Copolymerization thus widens the potential of SMPs for their biomedical applications.

Linear

Segmented copolymers of various architectures belong to the eldest family of SMPs. Research on SMPs started on polyurethane (PU) block copolymers as briefly described in the next section. Replacing urethanes by aromatic amide (aramide) groups is an actual research direction because isocyanates and amines, used for PU synthesis, may be toxic and carcinogenic, respectively. Rabani *et al* [26] prepared segmented copolymers with short hard amide and PCL soft segments. PCL diols of low MW (2-4 kDa) used as main building blocks. SM properties of the related copolymers were assessed in tensile tests whereby setting T_{trans} ($=19$ °C) $< T_m$. Though such deformation conditions for SM programming are unusual, they can be adapted, as well. Recovery was measured at T_m (~ 55 °C). Both R_f (60-80%) and R_r (75-100%) depended on the extent of deformation and number of the cycles of the SM

tests. The largest change in the SM behavior was observed after the first cycle, which is typical.

Linear poly(L-lactide-co- ϵ -caprolactone)s (PLACLs) were produced by Lu's team [27]. The lactide/lactone ratio was varied between 90/10 and 60/40 which was associated with a large change in the T_g (reduction from 54 to 14 °C). For shaping $T_{trans}=T_g+15$ °C, whereas for shape fixing $T=T_g-15$ °C were selected. R_f decreased (96-90%), whereas R_r increased (75-97%) with increasing caprolactone content of the copolymer.

Bacterial poly[(3-hydroxybutyrate)-co-(3-hydroxyvalerate)] (PHBV), exhibiting $T_g \sim -13$ °C and a broad melting range (37-115 °C), peaked at $T_m=94$ °C, showed also thermoresponsive SM behavior. For setting the temporary shape $T_{trans}>T_m$, while for shape fixing ambient temperature were used [28]. Poly(trimethylene carbonate-co-D,L-lactide) random copolymers were synthesized by Yang *et al* [29] to adjust the mechanical properties and biodegradability upon request. Poly(trimethylene carbonate) (PTMC) itself is an amorphous elastomer having a $T_g \sim -15$ °C, which is much too low for many SM applications. By copolymerization, the T_g could be enhanced. As $T_{trans} (=37$ °C) $>T_g (=22$ °C) was used for shaping (elongation to 150 %) and fixing occurred $T=0$ °C. R_r was found for 83%. Several works were devoted to synthesize terpolymers composed of lactide, glycolide and trimethylene carbonate. For their copolymerization usually stannous compounds are used which may be relatively toxic. Therefore these catalysts were replaced by low toxicity zirconium-based compounds. The T_g of the terpolymers, that was considered for selecting T_{trans} , was between 12 and 42 °C [30-31].

Linear, cyano functionalized polynorbornene having long PCL side chains showed good SM properties according to the report of Yang and coworkers [32]. This polynorbornene grafted by PCL along with the cyano groups in the main chain showed higher ductility and strength than the unmodified polynorbornene. Moreover, T_m of the phase separated PCL could be well used for T_{trans} in SM tests. It is worth noting that polynorbornene is one of the eldest SMP.

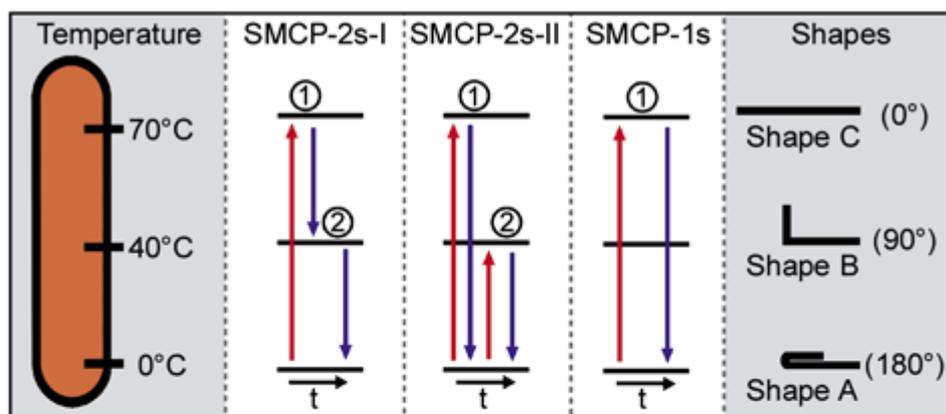
Inorganic fillers, such hydroxyapatite, carbon nanotubes (CNT), Fe_3O_4 , TiO_2 , are often incorporated as micro- and nanoscale fillers in SMPs to enhance the mechanical properties and trigger other types of actuation than directly thermal. Liu *et al* [33] succeeded to improve the SM behavior of PLACL using surface grafted TiO_2 nanoparticles. However, both R_f and R_r went through a maximum as a function of the TiO_2 content. Recall that in this amorphous PLACL T_g served for T_{trans} and shape fixing was owing to the entanglements physical network.

It is worth noting that filling and reinforcing with traditional materials usually improve the mechanical but often degrade the SM properties. The latter is typically a loss in ductility that hampers the deformability of the corresponding composite [34]. To overcome this problem Wang *et al* [35] reinforced PLACL by in situ produced micro- and nanofibers from poly(glycolic acid) (PGA). The authors generated the PGA fibers in PLACL through in line extrusion stretching. Attention should be paid to the fact, that this method basically follows the microfibrillar composite concept of Fakirov ([36] and references therein). The LA/CL ratio of 82/18 resulted in an amorphous PLACL with a T_g of 22 °C. For the temporary shape

$T_{\text{trans}}=T_g+15\text{ }^\circ\text{C}$, and for its fixing $T=T_g-15\text{ }^\circ\text{C}$ were selected. The PGA phase supported both shape fixing (restraining the molecular chain movement) and recovery (acting as additional net points).

Crosslinked

To prepare crosslinked systems various functionalization methods and crosslinking procedures may be chosen. Crosslinkable functional groups may appear as end or side groups, and even in the main macromolecular chains. The group of Lendlein functionalized oligomers composed of L-lactide and glycolide with UV-curable methacrylate end groups [37]. The comonomer ratio and length of the chain segments were varied in the experiments. The T_g values, used to choose T_{trans} , of the photocured random copolymers were between $T_g=50-55\text{ }^\circ\text{C}$. Schmidt [38] produced thermosets from oligomeric ϵ -caprolactone dimethacrylate and butyl acrylate by peroxide crosslinking. Into the network Fe_3O_4 nanoparticles were also embedded to trigger the SM function by electromagnetic activation. The magnetite particles in this case worked for the “remote” control of the temperature by transforming the electromagnetic energy to heat. T_m of the PCL segments ($43-49\text{ }^\circ\text{C}$) was selected as T_{trans} . Garle *et al* [39] modified PCL homo- and copolymers by cinnamate compound. The UV crosslinkable cinnamoyl side groups resulted in a crosslinked gel content of about 70 wt.%. SM transformation was governed by T_m of the PCL segments. Narendra Kumar and coworkers [40] elaborated a synthesis route for producing thermally and magnetically activated triple-shape memory polymers using methacrylate end functionalized crystallizable PCL ($T_m=55\text{ }^\circ\text{C}$) and polyethylene glycol (PEG) ($T_m=38\text{ }^\circ\text{C}$). The copolymer was cured by peroxide in presence and absence of silica coated magnetite nanoparticles. The outcome was a magnetically active SMP. For programming of the two temporary shapes the above T_m values were considered whereby adapting one- or two-step programming procedures – cf. Figure 5.



a)

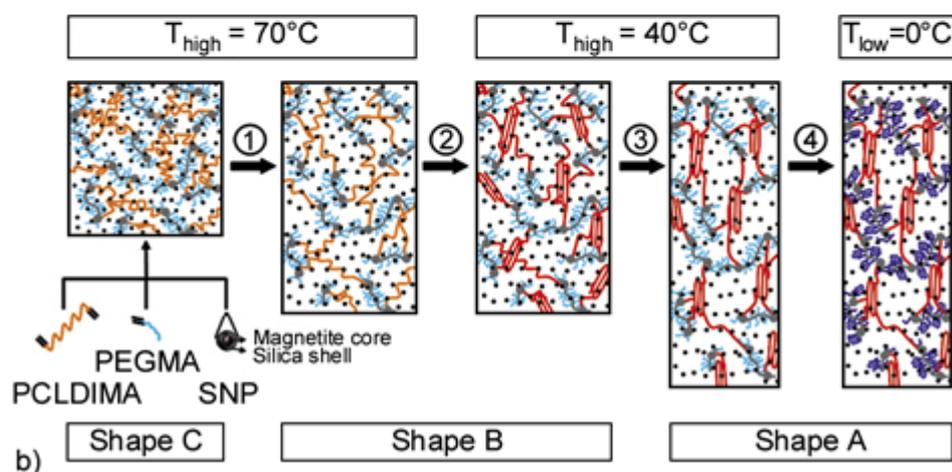


Figure 5: (a) Schematic representations of the different SM creation procedures applied for bending of the nanocomposites. Two-step programming methods: SMCP-2s-I, SMCP-2s-II, as well as single-step programming procedure: SMCP-1s. (b) Molecular mechanism for graft polymer network composites during SM creation procedure. Designations: PEGMA: methacrylate functionalized PEG, PCLDIMA: PCL dimethacrylate. Phase structure: orange:amorphous PCL chain segments, light blue: amorphous PEG chain segments, red: crystalline PCL chain segments, dark blue: crystalline PEG chain segments, grey: amorphous poly(methacrylate) chain segments.

The group of Nagata incorporated UV curable moieties directly into the main chain of the related polymers [41-43]. Thus, photocurable, biodegradable multiblock SMPs were prepared by polycondensation from PCL diol, PEG and 5-cinnamoyloxyisophthalic acid [41]. The latter compounds acted as UV crosslinker without any photoinitiator. The semicrystalline photosets exhibited $T_g \sim 60^\circ\text{C}$, and T_m in the range of $35\text{-}47^\circ\text{C}$. Both R_f and R_r values were reported above 90% when selecting tensile deformation between 100 and 300 % and $T_{\text{trans}}=37\text{-}60^\circ\text{C}$. A similar strategy was followed to produce photocrosslinked PCL [42] and copolymers [43] composed of ϵ -caprolactone and L-lactide whereby incorporating coumarin groups in the main chain. Coumarin is biodegradable and non toxic. Moreover, it participates in reversible crosslinking depending on the wavelength. Multiblock copolymers were also synthesized from PCL diol and PLA diol via polycondensation with cinnamic acid compound

[44]. Again, the latter was responsible for reversible photocuring that did not affect the crystallization of PCL but reduced that of PLA. Choosing $T_{\text{trans}}=40\text{-}60\text{ }^{\circ}\text{C}$, tensile elongations 100-500% and fixing temperature $22\text{ }^{\circ}\text{C}$, R_f and R_r data between 88 and 100% have been measured. The authors emphasized that reversible photocrosslinking may be a promising way to produce light-sensitive SMPs.

There are many possibilities to tailor the properties of SMPs via their block (segmented) architecture. Zhang et al [45] produced diacrylated PCL-polydimethylsiloxane-PCL macromers that have been photocured afterward. This development targeted the reduction of water sensitivity and improvement of the flexibility and surface properties of the polymer whereby maintaining the switch function of the PCL phase ($T_{\text{trans}}=80\text{ }^{\circ}\text{C}$). Note that PCL exhibits $T_g=-60\text{ }^{\circ}\text{C}$, whereas polydimethylsiloxane has a $T_g=-125\text{ }^{\circ}\text{C}$.

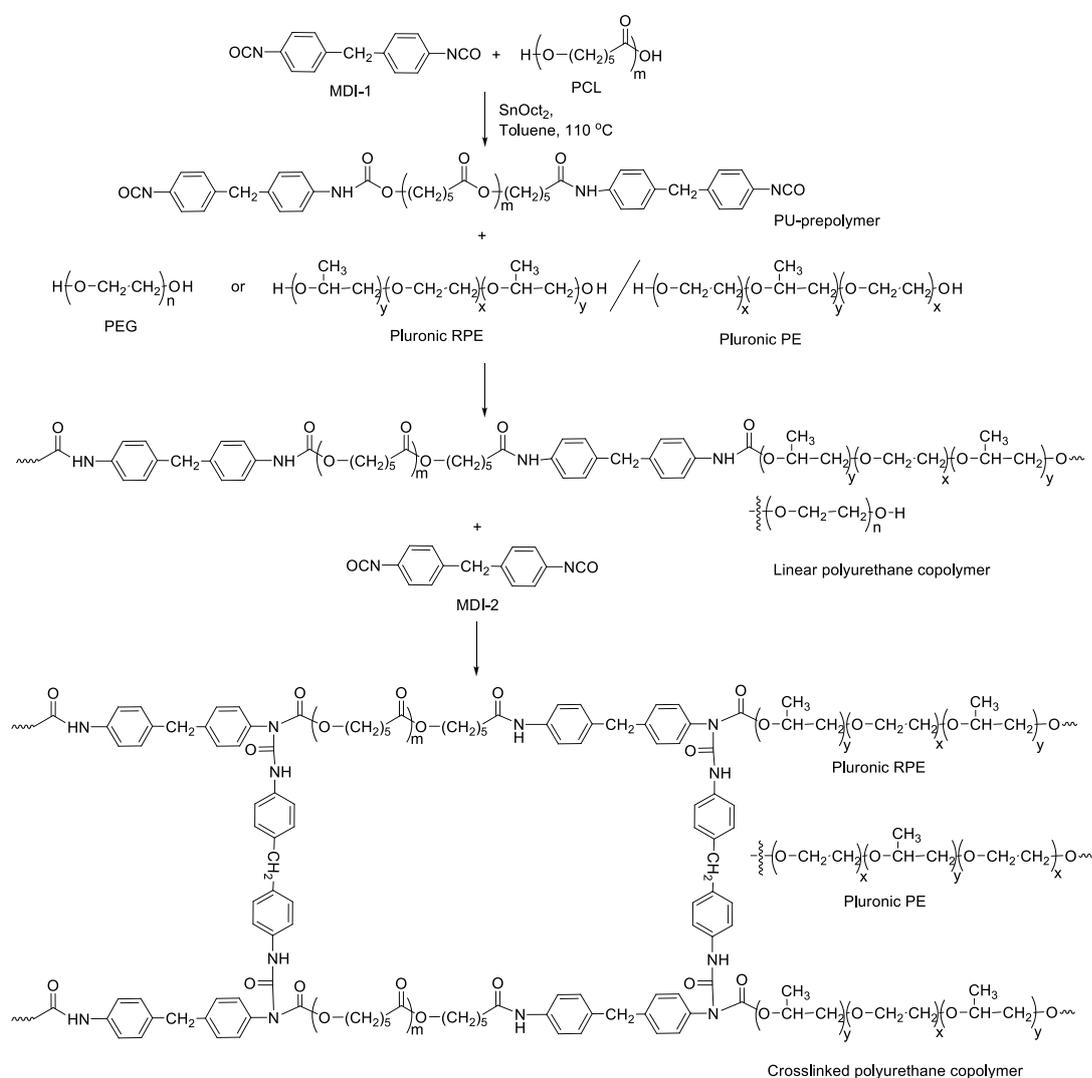
Biobased polyesters composed of 1,3-propanediol, sebacic acid and itaconic acid in various ratios showed excellent SM properties after crosslinking with peroxide. T_{trans} could be tuned by the composition between $12\text{ and }54\text{ }^{\circ}\text{C}$ [46].

The feasibility of Diels-Alder coupling was shown on the example of biodegradable polyester by Ninh and Bettinger [47]. In this case hyperbranched poly(glycerol-co-sebacate) with pendant furan groups was coupled with bifunctional maleimide crosslinker to produce an elastomeric material. POSS moieties may serve as crosslinking sites, as well. Ishida *et al* [48] have shown how a bacterial PHA, namely poly(3-hydroxyoctanoate-co-3-hydroxyundecanoate), can be crosslinked by POSS derivative making use of UV-assisted thiol-ene coupling. The thiol compounds were tetrathiol crosslinker and thiol functionalized POSS. A seldom used crosslinking technique is to create ionic clusters as net points through incorporation of ionic monomers in the main chain [49]. They can be, however, easily incorporated into polyesters in polycondensation reactions. The ionic aggregates may restrict the crystallization of the main chain or its segments. Consequently, creation of ionomers may be a reasonable approach to tune T_m of semicrystalline SMPs.

2.3. polyester-containing polyurethanes and related composites

PU-based systems are the most widely prepared and studied SMPs. Their development started in the 1990s by Hayashi and they are still in the focus of both industrial and academic interests [50]. This is, in particular, due to the highly versatile PU chemistry. The reason why we have inserted this brief section as a separate entry is that the polyols used for PU synthesis are typically biodegradable polyester-based ones. The interested reader might have already noticed that the ϵ -caprolactone chemistry plays an important role in the reported polyester-related SMPs. PCL diols are, however, traditional building blocks of PUs. Recently ϵ -caprolactone based oligomers with various molecular architectures became platform chemicals for PU and polyester syntheses [51]. The interest behind this development is due to the complete biodegradability, low T_g and relatively low T_m of PCL. PCL-based PUs are segmented polymers with excellent SM behaviors. The reaction of diisocyanate with low MW

diol chain extenders yields the hard, whereas the PCL chains give the soft segments. It is generally accepted that the exceptional shape memory behavior of such PUs is related to their phase segregated morphology. For thermoplastic version the hard phase is responsible for memorizing the permanent, whereas the soft one for the temporary shape and its fixing [52]. As a consequence, T_{trans} is linked to the T_m of PCL – cf. Figure 6. In crosslinked PUs, the crosslinked network guarantees the permanent shape and thus transitions related to the hard phase may also be involved in SM programming. The research on SM PUs has many similarities with that on SM polyesters. Peculiar attention was paid at the copolymer architecture. So, efforts were dedicated to modify both soft and hard phases in order to improve the SM performance. The ways followed cover the use of other polyester diols than PCL (for example PLA-based ones [53-54]), additional crosslinking via functional POSS [55], incorporation of nanofillers [56-57], creation of ionomers [58], and blending [59-60], as well.



a)



b)

Figure 6: Chemical pathway of the synthesis of multiblock linear and crosslinked SM PU by incorporating high MW PCL soft segment as switch phase (a), and demonstration of the shape memory effect setting $T_{\text{trans}}=80\text{ }^{\circ}\text{C}$ (b). Designations: MDI - methylene diphenyl diisocyanate, Pluronic® - different polyols under this trade name (K. Czifrák, S. Kéki, M. Zsuga and J. Karger-Kocsis: unpublished results, 2013)

2.4 blends and composites

Polymer blends may exhibit SM behavior irrespective of the miscibility of the blend components. One of the blend components should show the required transition (T_g - or T_m -related) and act as “switching” phase. The other, being elastic, is responsible for the permanent shape.

Linear

Because PLA is highly brittle, it has been blended with numerous polymers to improve its toughness. A “byproduct” of this research was the observation that some blends, in fact, showed SM feature. Lai and Lam [61] studied the SM performance of PLA/thermoplastic PU blends at 70/30 and 50/50 compositions. Thermoplastic PU was found in dispersed form at 70/30 ratio, while a bicontinuous phase structure was concluded for the PLA/PU=50/50. After deforming the specimens at $T_{\text{trans}}=25, 80$ and $120\text{ }^{\circ}\text{C}$, the recovery was assessed in the temperature range $T=20$ to $160\text{ }^{\circ}\text{C}$. Note that the selected T_{trans} data are below and above of the T_g of the PLA (ca. $80\text{ }^{\circ}\text{C}$). R_f , R_r and the recovery stress strongly depended on T_{trans} and recovery temperatures. With increasing T_{trans} R_f increased while an adverse trend was observed for R_r .

Zhang *et al* [62] demonstrated SM behavior for PLA toughened by a polyamide-12 based elastomer, that was incorporated up to 30 wt.%. For T_{trans} of the tensile loaded specimens room temperature was selected, which is in between the T_g of the polyamide elastomer ($T_g\sim 50\text{ }^{\circ}\text{C}$) and that of the PLA ($T_g=75\text{ }^{\circ}\text{C}$). Recovery was triggered at temperatures above the T_g of PLA.

Thermoplastic PU elastomer ($T_g\sim -35\text{ }^{\circ}\text{C}$) was blended with PLA in 10 wt.% with and without MWCNT with various surface treatments [63]. The latter was introduced in 10 wt.%

to achieve electroresponsive SM. For temporary shaping T_g of PLA was considered. R_f decreased with increasing number of the electroactivated thermal cycles. This was attributed to the formation of “frozen in” crystals in the dispersed PLA phase.

PLA/PCL blends in the compositions range of 100/0 to 60/40 were produced with and without additional MWCNT by Amirian *et al* [64]. The phase segregated blends exhibited two T_g and two T_m values. The latter increased with increasing amount of MWCNT. For $T_{trans}=T_g(PLA)+15$ °C, while for shape fixing $T_g(PLA)-15$ °C were chosen. R_f was measured at $T=70$ °C where the melting of PCL is also involved. As a consequence, both R_f and R_r decreased with increasing PCL content of the blends. R_f was marginally affected, while R_r went through a maximum as a function of the MWCNT content (0-3 wt.%) during the tensile deformation SM tests.

A novel approach should be credited to Luo and coworkers [65] to improve the SM performance of PCL. The cited authors prepared inclusion complexes between α -cyclodextrin and PCL. Through this host-guest complexation a peculiar physical network has been created with “naked” PCL segments as “switching” phase and cyclodextrin-PCL inclusion complex domains as net points. Both R_f and R_r were slightly reduced with the inclusion ratio (30-50%). The *in vitro* degradation of this new type of blend was faster than the reference PCL.

PCL worked as efficient switching phase also in styrenic thermoplastic rubbers, such as styrene-butadiene-styrene block copolymer [66]. R_f increased steeply before leveling off above 30 wt.% PCL content. An opposite tendency, almost a mirrored picture of the R_f course, was found for R_r as a function of the PCL content that was varied in the whole composition range. This behavior was traced to the actual morphology of the blends. As long as the thermoplastic rubber phase remained continuous excellent R_f and R_r data were measured.

Du *et al* [67] investigated effects of layered architecture and blend morphology on the SM behavior using thermoplastic PU and PCL. The PU/PCL ratios set were 75/25, 50/50 and 25/75, respectively. The layered structure was achieved by a special multilayer coextrusion technique. The layer thickness varied with the composition ratio whereby keeping the number of layers and the overall thickness of the multilayer film as constants. T_m of PCL served as T_{trans} ($=70$ °C) during shape creation that was fixed at $T=21$ °C. R_f of the multilayer film was the higher the lower its PCL content was, and it changed as a function of the thermomechanical cycles only marginally. The PU/PCL blend at 50/50 ratio outperformed the multilayer film with respect to R_f at the same PCL content. On the other hand, all other blends showed inferior R_f data to the multilayer film. Interestingly, R_r increased with increasing thermomechanical SM cycles, at least up to the 5th one. This may be an effect of recrystallization in confined space in both blends and multilayer films. The PU/PCL multilayer films demonstrated SM behavior comparable (at 50/50) to or better than those of the corresponding blends.

Crosslinked

Crosslinking is a useful tool to improve the SM behavior as already quoted. This technique has been adapted for PLA/PEG blends investigated in the range of 100/0 to 70/30. Crosslinking occurred by adding blocked polyisocyanate. T_g of the amorphous phase, composed of both PLA and PEG, served to select the T_{trans} . Both R_f and R_r increased with increasing amount of the polyisocyanate crosslinker. The crosslinking reduced also the recovery time of the corresponding blends [68].

2.5 polymers with thermosets

Combination of crosslinkable resins with biodegradable polyesters may result in various structures. Distribution of the polyester as dispersed phase in thermosets is the usual prerequisite of toughness improvement. The dispersion is generated by phase separation upon curing. Such systems may show SM properties though this is not yet reported for systems with biodegradable polyesters. Far more interesting are, however, those systems which feature conetwork, semi interpenetrating (semi IPN) and full IPN structures.

Conetworks

Conetworks are chemically crosslinked networks in which none of the constituents forms a continuous phase. This definition does not exclude however the possible presence of homocrosslinked domains. On the other hand, they differ markedly from the grafted IPN structure in which both phases are continuous and chemically coupled. Li *et al* [69] prepared conetwork structured thermosets by the peroxide induced copolymerization of methyl methacrylate and PCL dimethacrylate. The poly(methyl methacrylate)/PCL ratio was varied between 80/20 and 20/80. The related systems exhibited a single T_g that changed as a function of composition in a broad range ($T_g=110\dots-20$ °C). The broad T_g relaxation may be used to memorize multiple shapes via careful programming. The authors showed that the related conetwork may show quadruple SM, i.e. “remembering” to three temporary shapes. The energy stored in the whole T_g range can be partitioned into several parts for multi-shape programming as long as the partitioned energy during cooling is sufficient for shape fixing. Erden and Jana [70] modified SM PU with polybenzoxazine. The precured benzoxazine with its phenolic hydroxyl groups can react with the polyisocyanate whereby forming a conetwork with the polyurethane. Polybenzoxazine appeared in the PU matrix in phase segregated nanoscale domains. They can be treated as net points of a second fixing phase in addition to the hard segments of the PU. Recall that the latter, being net points, are responsible for the permanent shape of PU. Cocrosslinking with benzoxazine shifted the T_g of the corresponding systems toward higher temperatures. At the same time the recovery stress was doubled compared to that of the reference PU. Enhancing the recovery stress is a very actual research direction to meet the demand of sensors and actuators.

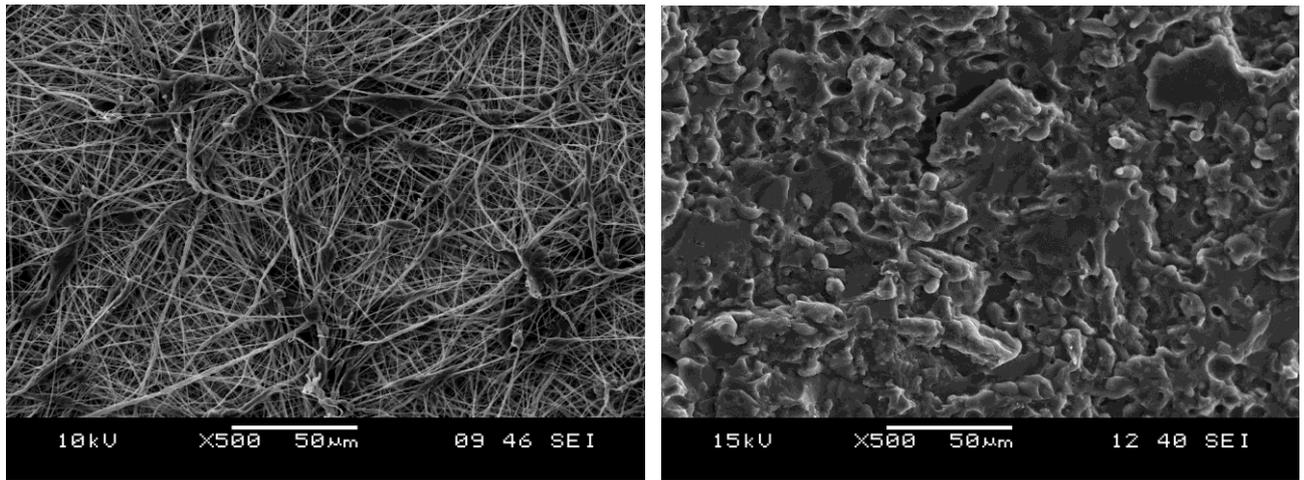
Epoxy (EP) -PCL conetworks were produced by the group of Hartwig [71-72]. Crystalline PCL domains, overtaking the role of “switch” phase, were covalently integrated into the cationically polymerized EP network. The EP/PCL ratio has been varied between 85/15 and 60/40. After deformation at $T_{\text{trans}}=70$ °C and fixing at $T=20$ °C, R_f of 100% was measured. In the companion paper the authors addressed the nucleation of the PCL phase [72].

semi interpenetrating network

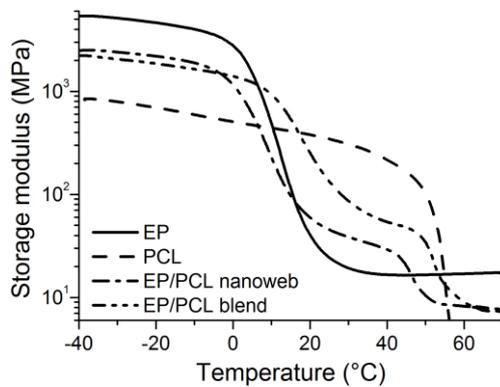
Unlike conetworks, semi IPNs are composed of two continuous phases from which one is of thermoplastic nature. It is intuitive that the related entangled structure should contribute to the onset of SM properties. This was confirmed recently [73]. It is worth noting that entanglement in semi and full IPN structures is usually not on molecular level though the latter system features one single T_g [74]. “Full” IPN denotes that both constituent continuous phases are crosslinked polymers. Semi IPNs may not only have SM, but also self healing properties. Though the term “shape memory assisted self healing” was coined by the Mather group [75], the concept should be credited to Karger-Kocsis [76].

The group of Mather [75] produced semi IPNs containing high MW PCL as thermoplastic and tetrathiol crosslinked low MW PCL diacrylate as thermoset phase. The linear/network PCL ratio was studied between 0/100 and 80/20. At 200% tensile deformation R_f increased slightly, whereas R_r decreased sharply with increasing amount of the thermoplastic PCL. Self healing was demonstrated on partially broken double edge notched tensile loaded specimen. Healing happened by wetting, diffusion and randomization of the linear PCL component above its T_m , *viz* at $T=80$ °C.

Quasi semi IPN structure can be produced by other ways. Such a structure is given when electrospun PCL nanofiber mat is infiltrated by EP followed by curing of the latter. This material showed triple shape behavior. For setting the two temporary shapes T_m of PCL and T_g of EP served. T_g of EP was below the T_m of PCL [77]. Fejős *et al* [78] not only confirmed this concept on the same material combination but compared the SM behavior with that of a “real” semi IPN structured EP/PCL at the same composition. The latter was generated in one-pot synthesis via phase segregation. The storage modulus *vs* temperature traces of the PCL nanoweb containing EP and semi IPN structured EP/PCL were similar (cf. Figure 7). The dynamic mechanical analysis (DMA) traces clearly show that both EP systems have a bicontinuous phase structure because their storage moduli do not drop at the T_g of EP which would happen for dispersed PCL. Instead of that, the moduli run in between those of the PCL and EP. The SM properties of the EP/PCL with semi IPN structure were somewhat better than that with the electrospun PCL nanofiber mat. Note that the semi IPN version should have self healing activity, which was, however, not yet tested.



a)



b)

Figure 7: Structure of the electrospun PCL nanoweb (left) and the semi IPN (right, fracture surface) (a), DMA traces of the electrospun PCL nanoweb containing EP, IPN structured EP/PCL and the parent PCL and EP (b). Notes: the PCL content in the EP/PCL combinations was 23 wt.%.

interpenetrating network

Full IPN structured thermosets are also suitable SMP systems. It was shown by Zhang *et al* [79]. The IPN structure was composed of crosslinked PU (polylactide-glycolide-based (PLAGA) diol crosslinked by polyisocyanate) and crosslinked PEG dimethacrylate (cured by UV irradiation). The content of the latter was varied between 0 and 50 wt.%. The IPNs were amorphous and exhibited a rather broad T_g range (T_g between -23 and 63 °C) that served for T_{trans} . Both R_f and R_r data were reported over 93 %.

3. Applications

Biodegradable polyester SMPs are mostly used in and developed for applications in the human body. That is the reason why many R&D works addressed the adjustment of T_{trans} , related to T_m or T_g , respectively, to the body temperature. The other aspect, usually covered in the related research, was the investigation of the *in vitro* biodegradability using phosphate buffered saline solutions. The medical applications of biodegradable polyesters are typically surgical sutures, catheters and stents. In many other medical applications, such as bone fixing, other polymers than polyesters are used.

Absorbable polymer sutures for wound closure appeared in the 1970s. These PGA-based sutures registered tremendous growth which is unbroken until now. Since the wound should be closed for healing, which can be easily triggered by a transition from temporary to permanent shape, the interest turned for smart sutures making use of the SM behavior. The attribute “smart” may be related to the antimicrobial and healing activities, set by the incorporation of suitable additives into the sutures [80-81].

Nowadays metallic stents, also from SM alloys, are widely accepted in the surgery. Their use is, however, associated with some complications due to the stiffness (Young’s moduli) mismatch between the metal and the tissue. The related “tissue trauma” is repeated when the stent is removed surgically after the disease has been cured. Biodegradable polymer stents have been getting focused attention due to the recognition that the stents are only temporarily needed in the body and they may have similar flexibility, elasticity as the body tissues [82-83]. PLA (T_{trans} linked with T_g) and PCL (T_{trans} linked with T_m) were used first as stent materials. The related T_g and T_m values are much higher than the body temperature, and thus their expansion was supported by hot liquid filled balloons. Instead of balloon-expandable, R&D works were devoted to self-expandable stents with SM function. Note that they should have sufficient elasticity to expand. Venkatraman *et al* [83] used poly(L-lactide-co-glycolide) (PLAGA) copolymers with various compositions and thus T_g values to produce single- and bilayer stents. They work aimed at enhancing the recovery stress and accelerating the shape recovery process. Stents with fast recovery at $T=37\text{ }^\circ\text{C}$ were also produced from poly(ϵ -caprolactone-co-D,L-lactide) which not only has the appropriate T_{trans} but also degrades better than the reference PLA [84].

4. Outlook and future trends

Biodegradable SM polyesters not only can biodegrade in the body but also have further beneficial properties such as easy shaping, tuning of the shaping temperature and adjustable degradation rate. Their disadvantages are mostly related to the relatively high shaping temperature (T_{trans}), slow recovery rate, and low recovery stress. These aspects remain in the forefront of the future R&D works. T_g manipulation by copolymerization and conetworking, T_m adjustment by copolymerization seem to be the right tools in this respect. Moreover, these methods may contribute also to achieve controllable degradation of the corresponding SMPs.

Creation of conetwork and IPN structures may markedly enhance the recovery rate and stress. Semi IPN structured systems may exhibit a further function, namely self healing, which would widen the application field of SMPs. To enhance the recovery stress biodegradable polyester-based composites will be developed. Exploring various thermo- and photoreversible reactions to ensure easy thermoplastic-type recycling of the SMPs is an actual and challenging task. Biodegradable SM polyesters are predestinated to medical use. The related development will be fuelled by the needs of scaffolding materials, and stents in particular.

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References

- [1] Bikiaris, D.N. (2013) Nanocomposites of aliphatic polyesters: An overview of the effect of different nanofillers on enzymatic hydrolysis and biodegradation of polyesters. *Polymer Degradation and Stability*, **98** (9), 1908-1928.
- [2] Hu, J., Zhu, Y., Huang, H., Lu, J. (2012) Recent advances in shape–memory polymers: Structure, mechanism, functionality, modeling and applications. *Progress in Polymer Science*, **37** (12), 1720-1763.
- [3] Behl, M., Razzaq, M.Y., Lendlein, A. (2010) Multifunctional shape-memory polymers. *Advanced Materials*, **22** (31), 3388–3410.
- [4] Mather, P.T., Luo, X., Rousseau, I.A.(2009) Shape Memory Polymer Research. *Annual Review of Materials Science*, **39**, 445–471.
- [5] Xie, T. (2011) Recent advances in polymer shape memory. *Polymer*, **52** (22), 4985-5000.
- [6] Huang, W.M., Zhao, Y., Wang, C.C., Ding, Z., Purnawali, H., Tang, C., Zhang, J.L. (2012) Thermo/chemo-responsive shape memory effect in polymers: a sketch of working mechanisms, fundamentals and optimization. *Journal of Polymer Research*, **19** (9),1-34.
- [7] Sauter, T.,Heuchel, M., Kratz, K., Lendlein, A. (2013) Quantifying the shape-memory effect of polymers by cyclic thermomechanical tests. *Polymer Reviews*, **53** (1), 6-40.

- [8] Wong, Y.S, Venkatraman, S.S. (2010) Recovery as a measure of oriented crystalline structure in poly(L-lactide) used as shape memory polymer. *Acta Materialia*, **58** (1), 49–58.
- [9] Ghobadi, E., Heuchel, M., Kratz, K., Lendlein, A. (2013) Influence of the addition of water to amorphous switching domains on the simulated shape-memory properties of poly(L-lactide). *Polymer*, **54** (16), 4204-4211.
- [10] Radjabian, M., Kish, M.H., Mohammadi, N. (2012) Structure–property relationship for poly(lactic acid) (PLA) filaments: physical, thermomechanical and shape memory characterization. *Journal of Polymer Research*, **19**(6), 1-10.
- [11] Karger-Kocsis, J., Shang, P.P., Moskala, E.J. (1999) Effects of deformation rate on the necking of an amorphous copolyester studied by modulated DSC. *Journal of Thermal Analysis and Calorimetry*, **55** (1), 21-28.
- [12] Kanazawa, S. (2008) Development of elastic polylactic acid material using electron beam radiation. *SEI Technical Review*, **66** (April), 50-54.
- [13] Tuba, F., Khumalo, V.M., Karger-Kocsis, J. (2013) Essential work of fracture of poly(ϵ -caprolactone)/boehmite alumina nanocomposites: Effect of surface coating. *Journal of Applied Polymer Science*, **129** (5), 2950-2958.
- [14] Pandini, S., Baldi, F., Paderni, K., Messori, M., Toselli, M., Pilati, F., Gianoncelli, A., Brisotto, M., Bontempi, E., Riccò, T. (2013) One-way and two-way shape memory behaviour of semi-crystalline networks based on sol-gel cross-linked poly(ϵ -caprolactone). *Polymer*, **54** (16), 4253-4265.
- [15] Pandini, S., Passera, S., Messori, M., Paderni, K., Toselli, M., Gianoncelli, A., Bontempi, E., Riccò, T. (2012) Two-way reversible shape memory behaviour of crosslinked poly(ϵ -caprolactone). *Polymer*, **53** (9), 1915-1924.
- [16] Alvarado-Tenorio, B., Romo-Urbe, A., Mather, P.T. (2011) Microstructure and phase behavior of POSS/PCL shape memory nanocomposites. *Macromolecules*, **44**(14), 682–5692.
- [17] Yu, X., Zhou, S., Zheng, X., Xiao, Y., Guo, T. (2009) Influence of in vitro degradation of a biodegradable nanocomposite on its shape memory effect. *The Journal of Physical Chemistry C*, **113** (41), 17630-17635.
- [18] Xiao, Y., Zhou, S., Wang, L., Gong, T. (2010) Electro-active shape memory properties of poly(ϵ -caprolactone)/functionalized multiwalled carbon nanotube nanocomposite. *ACS Applied Materials & Interfaces*, **2** (12), 3506–3514.
- [19] Zhu, G., Liang, G., Xu, Q., Yu, Q. (2003) Shape-memory effects of radiation crosslinked poly(ϵ -caprolactone). *Journal of Applied Polymer Science*, **90** (1), 1589-1595.

- [20] Zhu, G.M., Xu, Q.Y., Liang, G.Z., Zhou, H.F. (2005) Shape-memory behaviors of sensitizing radiation-crosslinked polycaprolactone with polyfunctional poly(ester acrylate). *Journal of Applied Polymer Science*, **95** (3), 634-639.
- [21] Lendlein, A., Schmidt, A.M., Schroeter, M., Langer, R. (2005) Shape-memory polymer networks from oligo(ϵ -caprolactone) dimethacrylates. *Journal of Polymer Science: Part A: Polymer Chemistry*, **43** (7), 1369-1381.
- [22] Inoue, K., Yamashiro, M., Iji, M. (2009) Recyclable shape-memory polymer: poly(lactic acid) crosslinked by a thermoreversible Diels–Alder reaction. *Journal of Applied Polymer Science*, **112** (2), 876-885.
- [23] Defize, T., Riva, R., Raquez, J.M., Dubois, P., Jérôme, C., Alexandre, M. (2011) Thermoreversibly crosslinked poly(ϵ -caprolactone) as recyclable shape-memory polymer network. *Macromolecular Rapid Communications*, **32**(16), 1264–1269.
- [24] Defize, T., Riva, R., Jérôme, C., Alexandre, M. (2012) Multifunctional poly(ϵ -caprolactone)-forming networks by Diels–Alder cycloaddition: Effect of the adduct on the shape-memory properties. *Macromolecular Chemistry and Physics*, **213** (2), 187–197.
- [25] Guo, W., Kang, H., Chen, Y., Guo, B., Zhang, L. (2012) Stronger and faster degradable biobased poly(propylene sebacate) as shape memory polymer by incorporating boehmite nanoplatelets. *ACS Applied Materials & Interfaces*, **4** (8), 4006-4014.
- [26] Rabani, G., Luftmann, H., Kraft, A. (2006) Synthesis and characterization of two shape-memory polymers containing short aramid hard segments and poly(ϵ -caprolactone) soft segments. *Polymer*, **47**(12), 4251–4260.
- [27] Lu, X.L., Cai, W., Gao, Z.Y. (2008) Shape-memory behaviors of biodegradable poly(L-lactide-co- ϵ -caprolactone) copolymers. *Journal of Applied Polymer Science*, **108** (2), 1109-1115.
- [28] Kim, Y.B., Chung C.W., Kim, H.W., Rhee, Y.-H. (2005) Shape memory effect of bacterial poly[(3-hydroxybutyrate)-co-(3-hydroxyvalerate)]. *Macromolecular Rapid Communications*, **26** (13), 1070–1074.
- [29] Yang, J., Liu, F., Yang, L., Li, S. (2010) Hydrolytic and enzymatic degradation of poly(trimethylene carbonate-co-D,L-lactide) random copolymers with shape memory behavior. *European Polymer Journal*, **46**(4), 783–791.
- [30] Zini, E., Scandola, M. (2007) Shape memory behavior of novel (L-lactide-glycolide-trimethylene carbonate) terpolymers. *Biomacromolecules*, **8**(11), 3661-3667.

- [31] Gębarowska, K., Kasperczyk, J., Dobrzyński, P., Scandola, M., Zini, E., Li, S. (2011) NMR analysis of the chain microstructure of biodegradable terpolymers with shape memory properties. *European Polymer Journal*, **47**(6), 1315–1327.
- [32] Yang, D., Huang, W., Yu, J., Jiang J., Zhang, L., Xie, M. (2010) A novel shape memory polynorbornene functionalized with poly(ϵ -caprolactone) side chain and cyano group through ring-opening metathesis polymerization. *Polymer*, **51**(22), 5100-5106.
- [33] Lu, X.-L., Lü, X.-Q., Wang, J.-Y., Sun, Z.-J., Tong, Y.-X. (2013) Preparation and shape memory properties of TiO₂/PLCL biodegradable polymer nanocomposites. *Transactions of Nonferrous Metals Society of China*, **23**(1), 120–127.
- [34] Fejős, M., Karger-Kocsis, J. (2013) Shape memory performance of asymmetrically reinforced epoxy/carbon fibre fabric composites in flexure. *Express Polymer Letters*, **7**(6), 528–534.
- [35] Wang, L.-S., Chen, H.-C., Xiong, Z.-C., Pang, X.-B., Xiong, C.-D. (2010) A completely biodegradable poly[(L-lactide)-co-(ϵ -caprolactone)] elastomer reinforced by in situ poly(glycolic acid) fibrillation: Manufacturing and shape-memory effects. *Macromolecular Materials and Engineering*, **295**(4), 381–385.
- [36] Bhattacharyya, D. and Fakirov, S. (eds) (2012) *Synthetic Polymer-Polymer Composites*, Hanser, Munich.
- [37] Bertmer, M., Buda, A., Blumenkamp-Höfges I., Kelch, S., Lendlein, A. (2005) Biodegradable shape-memory polymer networks: characterization with solid-state NMR. *Macromolecules*, **38**(9), 3793-3799.
- [38] Schmidt, A.M. (2006) Electromagnetic activation of shape memory polymer networks containing magnetic nanoparticles. *Macromolecular Rapid Communications*, **27**(14), 1168-1172.
- [39] Garle, A., Kong, S., Ojha, U., Budhlall, B.M. (2012) Thermoresponsive semicrystalline poly (ϵ -caprolactone) networks: Exploiting cross-linking with cinnamoyl moieties to design polymers with tunable shape memory. *ACS Applied Materials & Interfaces*, **4**(2), 645-657.
- [40] Kumar, U.N., Kratz, K., Behl, M., Lendlein, A. (2012) Shape-memory properties of magnetically active triple-shape nanocomposites based on a grafted polymer network with two crystallizable switching segments. *Express Polymer Letters*, **6**(1), 26-40.
- [41] Nagata, M., Inaki, K. (2011) Biodegradable and photocurable multiblock copolymers with shape-memory properties from poly (ϵ -caprolactone) diol, poly (ethylene glycol), and 5-cinnamoyloxyisophthalic acid. *Journal of Applied Polymer Science*, **120**(6), 3556-3564.

- [42] Nagata, M., Yamamoto, Y. (2009) Synthesis and characterization of photocrosslinked poly(ϵ -caprolactone)s showing shape-memory properties. *Journal of Polymer Science Part A: Polymer Chemistry*, **47** (9), 2422-2433.
- [43] Nagata, M., Yamamoto, Y. (2010) Photocurable shape-memory copolymers of ϵ -caprolactone and L-lactide. *Macromolecular Chemistry and Physics*, **211** (16), 1826-1835.
- [44] Nagata, M., Sato, Y. (2005) Synthesis and properties of photocurable biodegradable multiblock copolymers based on poly(ϵ -caprolactone) and poly(L-lactide) segments. *Journal of Polymer Science Part A: Polymer Chemistry*, **43** (11), 2426-2439.
- [45] Zhang, D., Giese, M.L., Prukop, S.L., Grunlan, M.A. (2011) Poly(ϵ -caprolactone)-based shape memory polymers with variable polydimethylsiloxane soft segment lengths. *Journal of Polymer Science Part A: Polymer Chemistry*, **49** (3), 754-761.
- [46] Guo, B., Chen, Y., Lei, Y., Zhang, L., Zhou, W.Y., Rabie, A.B.M., Zhao, J. (2011) Biobased poly(propylene sebacate) as shape memory polymer with tunable switching temperature for potential biomedical applications. *Biomacromolecules*, **12** (4), 1312-1321.
- [47] Ninh, C., Bettinger, C.J. (2013) Reconfigurable biodegradable shape-memory elastomers via Diels-Alder coupling. *Biomacromolecules*, **14** (7), 2162–2170.
- [48] Ishida, K., Hortensius, R., Luo, X., Mather, P.T. (2012) Soft bacterial polyester-based shape memory nanocomposites featuring reconfigurable nanostructure. *Journal of Polymer Science Part B: Polymer Physics*, **50** (6), 387-393.
- [49] Han, S.-I., Gu, B.H., Nam, K.H., Im, S.J., Kim, S.C., Im, S.S. (2007) Novel copolyester-based ionomer for a shape-memory biodegradable material. *Polymer*, **48** (7), 1830-1834.
- [50] Huang, W.M., Yang, B., and Fu, Y.Q. (eds) (2012). *Polyurethane Shape Memory Polymers*, CRC Press, Boca Raton (FL, USA).
- [51] Sisson, A.L., Ekinici, D., Lendlein, A. (2013) The contemporary role of ϵ -caprolactone chemistry to create advanced polymer architectures. *Polymer*, **54** (17), 4333-4350.
- [52] Ping, P., Wang, W., Chen, X., Jing, X. (2007) The influence of hard-segments on two-phase structure and shape memory properties of PCL-based segmented polyurethanes. *Journal of Polymer Science Part B: Polymer Physics*, **45** (5), 557-570.
- [53] Yan, B., Gu, S., Zhang, Y. (2013) Polylactide-based thermoplastic shape memory polymer nanocomposites. *European Polymer Journal*, **49** (2), 366–378.

- [54] Peponi, L., Navarro-Baena, I., Sonseca, A., Gimenez, E., Marcos-Fernandez, A., Kenny, J.M. (2013) Synthesis and characterization of PCL-PLLA polyurethane with shape memory behavior. *European Polymer Journal*, **49** (4), 893–903.
- [55] Xu, J., Song, J. (2010) High performance shape memory polymer networks based on rigid nanoparticle cores. *Proceedings of the National Academy of Sciences*, **107** (17), 7652-7657.
- [56] Cao, F., Jana, S.C. (2007) Nanoclay-tethered shape memory polyurethane nanocomposites. *Polymer*, **48** (13), 3790-3800.
- [57] Gunes, I.S., Cao, F., Jana, S.C. (2008) Effect of thermal expansion on shape memory behavior of polyurethane and its nanocomposites. *Journal of Polymer Science Part B: Polymer Physics*, **46** (14), 1437-1449.
- [58] Zhu, Y., Hu, J.L., Yeung, K.W., Liu, Y.Q., Liem, H.M. (2006) Influence of ionic groups on the crystallization and melting behavior of segmented polyurethane ionomers. *Journal of Applied Polymer Science*, **100** (6), 4603-4613.
- [59] Madbouly, S.A., Lendlein, A. (2012) Degradable polyurethane/soy protein shape-memory polymer blends prepared via environmentally-friendly aqueous dispersions. *Macromolecular Materials and Engineering*, **297** (12), 1213-1224.
- [60] Yang, S., Yuan, H., Luo, J., Chen, S., Ge, Z., Chen, S., Zheng, J. (2013) Facile preparation of shape memory polyurethanes by polyurethanes blending. *Journal of Applied Polymer Science*, **130**(6), 4047-4053.
- [61] Lai, S.-M., Lan, Y.-C. (2013) Shape memory properties of melt-blended polylactic acid (PLA)/thermoplastic polyurethane (TPU) bio-based blends. *Journal of Polymer Research*, **20** (5), 140 (pp. 1-8).
- [62] Zhang, W., Chen, L., Zhang, Y. (2009) Surprising shape-memory effect of polylactide resulted from toughening by polyamide elastomer. *Polymer*, **50** (5), 1311-1315.
- [63] Raja, M., Ryu, S.H., Shanmugaraj, A.M. (2013) Thermal, mechanical and electroactive shape memory properties of polyurethane (PU)/poly(lactic acid)(PLA)/CNT nanocomposites. *European Polymer Journal*, **49** (11), 3492-3500.
- [64] Amirian, M., Cai, W., Chakoli, A.N., Sui, J., Feng, J. (2010) Shape memory properties of poly(L-lactide)/poly(ϵ -caprolactone) blends and their composites with carbon nanotubes. *Journal of Materials Science and Engineering*, **4** (3), 27-34.
- [65] Luo, H., Liu, Y., Yu, Z., Zhang, S., Li, B. (2008) Novel biodegradable shape memory material based on partial inclusion complex formation between α -cyclodextrin and poly(ϵ -caprolactone). *Biomacromolecules*, **9** (10), 2573-2577.

- [66] Zhang, H., Wang, H., Zhong, W., Du, Q. (2009) A novel type of shape memory polymer blend and the shape memory mechanism. *Polymer*, **50** (6), 1596-1601.
- [67] Du, J., Armstrong, S.R., Baer, E. (2013) Co-extruded multilayer shape memory materials: Comparing layered and blend architectures. *Polymer*, **54** (20), 5399-5407.
- [68] Shen, T., Lu, M., Zhou, D., Liang, L. (2012) Influence of blocked polyisocyanate on thermomechanical, shape memory and biodegradable properties of poly(lactic acid)/poly(ethylene glycol) blends. *Iranian Polymer Journal*, **21** (5), 317-323.
- [69] Li, J., Liu, T., Pan, Y., Xia, S., Zheng, Z., Ding, X., Peng, Y. (2012) A versatile polymer co-network with broadened glass transition showing adjustable multiple-shape memory effect. *Macromolecular Chemistry and Physics*, **213**(21), 2246-2252.
- [70] Erden, N., Jana, S.C. (2013) Synthesis and characterization of shape-memory polyurethane-polybenzoxazine compounds. *Macromolecular Chemistry and Physics*, **214** (11), 1225-1237.
- [71] Lützen, H., Gesing, T.M., Kim, B.K., Hartwig, A. (2012) Novel cationically polymerized epoxy/poly(ϵ -caprolactone) polymers showing a shape memory effect. *Polymer*, **53** (26), 6089-6095.
- [72] Lützen, H., Gesing, T.M., Hartwig, A. (2013) Nucleation as a new concept for morphology adjustment of crystalline thermosetting epoxy polymers. *Reactive and Functional Polymers*, **73** (8), 1038-1045.
- [73] Ratna, D., Karger-Kocsis, J. (2011) Shape memory polymer system of semi-interpenetrating network structure composed of crosslinked poly (methyl methacrylate) and poly (ethylene oxide). *Polymer*, **52** (4), 1063-1070.
- [74] Grishchuk, S., Bonyár, A., Elsässer, J., Wolynski, A., Karger-Kocsis, J., Wetzel, B. (2013) Toward reliable morphology assessment of thermosets via physical etching: Vinyl ester resin as an example. *Express Polymer Letters*, **7**(5), 407-415.
- [75] Rodriguez, E.D., Luo, X., Mather, P.T. (2011) Linear/network poly(ϵ -caprolactone) blends exhibiting shape memory assisted self-healing (SMASH). *ACS Applied Materials & Interfaces*, **3** (2), 152-161.
- [76] Yuan, Y.C., Yin, T., Rong, M.Z., Zhang, M.Q. (2008) Self healing in polymers and polymer composites. Concepts, realization and outlook: A review. *Express Polymer Letters*, **2**(4), 238-250.
- [77] Luo, X., Mather, P.T. (2010) Triple-shape polymeric composites (TSPCs). *Advanced Functional Materials*, **20**(16), 2649-2656.

- [78] Fejős, M., Molnár, K., Karger-Kocsis, J. (2013) Epoxy/polycaprolactone systems with triple-shape memory effect: Electrospun nanoweb with and without graphene versus co-continuous morphology. *Materials*, **6** (10), 4489-4504.
- [79] Zhang, S., Feng, Y., Zhang, L., Sun, J., Xu, X., Xu, Y. (2007) Novel interpenetrating networks with shape-memory properties. *Journal of Polymer Science Part A: Polymer Chemistry*, **45** (5), 768-775.
- [80] Pillai, C.K.S., Sharma, C.P. (2010) Absorbable polymeric surgical sutures: chemistry, production, properties, biodegradability, and performance. *Journal of Biomaterials Applications*, **25**(4), 291-366.
- [81] Ratna, D., Karger-Kocsis, J. (2008) Recent advances in shape memory polymers and composites: A review. *Journal of Materials Science*, **43** (1), 254-269.
- [82] Kwon, D.Y., Kim, J.I., Kim, D.Y., Kang, H.J., Lee, B., Lee, K.W., Kim, M.S. (2012). Biodegradable stent. *Journal of Biomedical Science and Engineering*, **5** (4), 208-216.
- [83] Venkatraman, S.S., Tan, L.P., Joso, J.F.D., Boey, Y.C.F., Wang, X. (2006). Biodegradable stents with elastic memory. *Biomaterials*, **27** (8), 1573-1578.
- [84] Yu, X., Wang, L., Huang, M., Gong, T., Li, W., Cao, Y., Ji, D., Wang, P., Wang, J., Zhou, S. (2012) A shape memory stent of poly(ϵ -caprolactone-co-DL-lactide) copolymer for potential treatment of esophageal stenosis. *Journal of Materials Science: Materials in Medicine*, **23**(2), 581-589.

List of Abbreviations and Symbols

Abbreviations

CL	ϵ -caprolactone
CNT	Carbon nanotubes
DMA	Dynamic mechanical analysis
EP	Epoxy
Fe ₃ O ₄	Magnetite
IPN	Interpenetrating network
kDa	kilo Dalton
LA	L-lactide
MW	Molecular weight
MWCNT	Multiwall carbon nanotubes
PCL	Poly(ϵ -caprolactone)
PEG	Polyethylene glycol
PGA	Poly(glycolic acid)
PHA	Polyhydroxyalkanoates
PHBV	Poly[(3-hydroxybutyrate)-co-(3-hydroxyvalerate)]
PLA	Poly(lactic acid)
PLACL	Poly(L-lactide-co- ϵ -caprolactone)
PLAGA	Poly(L-lactide-co-glycolide)
PLGA	Poly(lactide-co-glycolide)
PLLA	Poly(L-lactic acid)
POSS	Polyhedral silsesquioxane
PTMC	Poly(trimethylene carbonate)
PU	Polyurethane
R&D	Research and development

SM	Shape memory
SMP	Shape memory polymer
SMPs	Shape memory polymers
TiO ₂	Titanium dioxide
wt. %	Weight percentage

Symbols

R _f	[%]	Shape fixity ratio
R _r	[%]	Shape recovery ratio
T _c	[°C]	Crystallization temperature
T _g	[°C]	Glass transition temperature
T _m	[°C]	Melting temperature
T _{trans}	[°C]	Transformation temperature