SHAPE-MEMORY POLYMERS

Introduction

Besides finding high performance materials, material scientists concentrate on designing “intelligent” and “self-repairing materials.” In this context, materials showing a thermally induced shape-memory effect, such as metallic alloys or gels, have been studied intensively, and a class of polymers showing shape-memory behavior has found growing interest (1–5). The relatively easy manufacturing and programming of shape-memory polymers makes these materials a cheap and efficient alternative to well-established metallic alloys. These polymers usually surpass by far the recovery properties of shape-memory alloys, which can recover deformations of 8% at maximum. Taking into consideration the importance of polymeric materials in daily life, a very broad spectrum of possible applications for intelligent polymers opens up, covering an area from minimally invasive surgery to high performance textiles, and to self-repairing plastic components in all kinds of technical devices.

Stimuli-sensitive implant materials have a high potential for applications in minimally invasive surgery. Degradable implants could be inserted into the human body in a compressed (temporary) shape through a small incision where they obtain their shape relevant for the specific application after warming up to body temperature. After a defined time period the implant is degraded. In this case subsequent surgery to remove the implant is not necessary. For applications in biomedicine, it is necessary to have tailor-made shape-memory polymers whose thermal, mechanical, or degradation properties can be varied over a wide range. A substantially new development in this context is polymer systems. These are families of polymers in which macroscopic properties can be controlled by a
specific variation of molecular parameters. In this way shape-memory polymers having a specific combination of properties required for specific applications can be obtained by slight variation of the molecular structure and chemical composition.

Definitions of Shape-Memory Polymer and Related Technical Terms

Shape-memory polymers are stimuli-responsive materials. Upon application of an external stimulus they have the ability to change their shape. A change in shape initiated by a change in temperature is called thermally induced shape-memory effect. The shape-memory effect results from the polymer's structure, that is, its morphology in combination with a certain processing and programming technology. Therefore, shape-memory behavior can be observed for several polymers that may differ significantly in their chemical composition.

The process of programming and recovering the shape of a polymer is shown schematically in Figure 1. The polymer is processed into its permanent shape by conventional methods. Afterwards, it is deformed and the desired temporary shape is fixed. The latter process is called programming. The programming process consists of heating the sample, deforming and cooling the sample, or drawing the sample at a low temperature ("cold drawing"). The permanent shape is now stored while the sample is in the temporary shape. Heating the programmed polymer above a temperature higher than the transition temperature $T_{trans}$ results in activating the shape-memory effect. As a consequence, the recovery of the memorized, permanent shape can be observed. Cooling of the polymer below the transition temperature leads to solidification of the material. However, the polymer sample does not return to its temporary shape. The described effect is called a "one-way" shape-memory effect. The programming process including a mechanical deformation can be repeated. The new temporary shape is not necessarily

![Fig. 1. Schematic demonstration of the thermally induced one-way shape-memory effect. By the programming process the permanent shape is transferred to the temporary shape. Heating up of the sample to a temperature above the switching transition $T_{trans}$ initiates the recovery of the permanent shape. From Ref. 2.](image-url)
The series of photos demonstrates (top–down) the transition from the temporary shape (spiral) to the permanent shape (rod) for a shape-memory network that has been synthesized of poly($\varepsilon$-caprolactone)dimethacrylate and butylacrylate (comonomer content: 50 wt%). The switching temperature of this polymer is 46°C. The recovery process takes 35 s when heated up to 70°C.

supposed to match the temporary shape resulting from the former programming process.

In Figure 2, a photo sequence demonstrates impressively the performance of shape-memory polymers. The permanent shape of the polymer sample is that of a rod. This rod has been deformed to a spiral (temporary shape) during the programming process. Under the influence of hot air having a temperature of 70°C the permanent shape is recovered as soon as
the switching temperature $T_{\text{trans}}$ is reached. With optimized programming conditions the permanent shape can be recovered with an accuracy of more than 99% (1).

**Molecular Mechanism of the Shape-Memory Effect**

All shape-memory polymers discussed henceforth are elastomers. On the molecular level they represent polymer networks consisting of segment chains that are connected by netpoints. The netpoints can be formed by entanglements of the polymer chains or intermolecular interaction of certain polymer blocks. These cross-links are called physical netpoints. Cross-links in the form of covalent bonds form chemical netpoints. An elastomer exhibits a shape-memory functionality if the material can be stabilized in the deformed state in a temperature range that is relevant for the particular application. This can be achieved by using the network chains as a kind of molecular switch. For this purpose, it should be possible to limit the flexibility of the segments as a function of the temperature. This process is supposed to be reversible. The ability to incorporate a control function into the material provides a thermal transition $T_{\text{trans}}$ of the network chains in the temperature range of interest for the particular application. At temperatures above $T_{\text{trans}}$ the chain segments are flexible, whereas the flexibility of the chains below this thermal transition is at least partly limited. In the case of a transition from the rubber-elastic, ie viscous, to the glassy state the flexibility of the entire segment is limited. The molecular mechanism of programming the temporary and recovering the permanent shape is demonstrated schematically in Figure 3 for a linear multiblock copolymer as an example of a thermoplastic shape-memory polymer with a crystalline hard segment.

![Fig. 3. Schematic demonstration of the molecular mechanism of the thermally induced shape-memory effect for a multiblock copolymer, $T_{\text{trans}} = T_m$. If the rise in temperature is higher than $T_{\text{trans}}$ of the switching segments, these segments are flexible (marked red, here) and the polymer can be deformed elastically. The temporary shape is fixed by cooling down below $T_{\text{trans}}$ (marked blue, here). If the polymer is heated up again the permanent shape is recovered.](image-url)
Table 1. Possible Combinations of Hard-Segment- and Switching-Segment-Determining Blocks in Linear, Thermoplastic Block Copolymers with Thermally Induced Shape-Memory Effecta

<table>
<thead>
<tr>
<th>Thermal transition determining the permanent shape at ( T_{\text{perm}} )</th>
<th>Hard-segment-determining block (Block A)</th>
<th>Switching-segment-determining block (Block B)</th>
<th>Phase-separated block copolymers</th>
<th>Possible switching transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point ( T_{\text{perm}} = T_{m,A} )</td>
<td>( T_{m,A} ) ( T_{g,A} )</td>
<td>( T_{m,B} ) ( T_{g,B} )</td>
<td>( T_{m,A} ) ( T_{m,B} ) ( T_{g,A} ) ( T_{g,B} )</td>
<td></td>
</tr>
<tr>
<td>Glass transition ( T_{\text{perm}} = T_{g,A} )</td>
<td>( T_{g,A} ) ( T_{g,A} )</td>
<td>( T_{g,B} ) ( T_{g,B} )</td>
<td>( T_{g,A} ) ( T_{g,B} ) ( T_{g,B} ) ( T_{g,B} )</td>
<td></td>
</tr>
</tbody>
</table>

\( a \)Ref. 2.

The mechanism of the thermally induced shape-memory effect of linear block copolymers is based on the formation of a phase-separated morphology with one phase acting as molecular switch. The phase showing the highest thermal transition \( T_{\text{perm}} \) is by the formation of physical netpoints, on the one hand providing the mechanical strength of the material, especially at \( T < T_{\text{perm}} \), and on the other hand the fixation determining the permanent shape. The materials are divided into two categories according to the thermal transition of the particular switching segment the shape-memory effect is based on. Either the transition temperature \( T_{\text{trans}} \) is a melting temperature \( T_m \) or a glass-transition temperature \( T_g \). In case of a melting temperature one observes a relatively sharp transition in most cases, whereas glass transitions always extend over a broad temperature interval. In case there is no sufficient phase separation between the “hard-segment-determining” block (Block A) and the “switching-segment-determining” block (Block B), mixed glass-transition temperatures \( T_{g,\text{mix}} \) between the glass transitions of the “hard-segment- and the switching-segment-determining” blocks may occur. Mixed glass-transition temperatures are also qualified to act as switching transitions for the thermally induced shape-memory effect. Table 1 gives an overview about possible combinations of “hard-segment- and switching-segment-determining” blocks in linear, thermoplastic shape-memory polymers (2).

In chemically cross-linked shape-memory networks the permanent shape is stabilized by the covalent netpoints. In analogy to linear block copolymers with shape-memory, the temporary shape of covalently cross-linked shape-memory networks can be fixed either by crystallizable segment chains or by a glass transition of the segment chains that is in the temperature range of interest.
Cyclic Thermomechanical Characterization

The shape-memory effect can be quantified by cyclic thermomechanical investigations. Typically, measurements are performed by means of a tensile tester equipped with a thermochamber. During this experiment, different test programs are applied that differ, for example, in the programming procedure (cold drawing at $T < T_{\text{trans}}$ or temporary heating up of the polymer sample to a temperature $T > T_{\text{trans}}$) or in the control parameter of the tensile tester (stress- or strain-controlled). A single cycle includes the programming of the sample and the recovery of its permanent shape.

A typical test program is described in the following: the test piece is heated up to a temperature $T_{\text{high}}$ that is above the switching temperature $T_{\text{trans}}$ and is elongated to the maximum strain $\varepsilon_{m}$. In case of thermoplastics, it is important not to exceed the highest thermal transition $T_{\text{perm}}$; otherwise, the polymer sample would melt. The sample is cooled down below the transition temperature $T_{\text{trans}}$ to a temperature $T_{\text{low}}$ under constant strain $\varepsilon_{m}$. In this way, the temporary shape is fixed. Retracting the clamps of the tensile tester to the original distance of 0% strain causes the sample piece to bend. After increasing the temperature to $T_{\text{high}}$ (> $T_{\text{trans}}$) the sample contracts and the permanent shape is recovered. The cycle can begin again.

The result of such a measurement is usually presented in a tensile stress ($\sigma$)–strain ($\varepsilon$) curve (see Fig. 4a). This is why this test protocol is often called a two-dimensional measurement. Figure 4 schematically represents curves obtained as results from mechanical measurements. If the stretched sample is cooled down (Position 2 in Fig. 4a) different effects can result in changes of the curves' course. Here, differences in the expansion coefficient of the stretched sample at temperatures above and below $T_{\text{trans}}$, as a consequence of the entropy elasticity and volume changes due to crystallization, are inducing changes in mechanical stress $\sigma$. The latter is the case if $T_{\text{trans}}$ is a melting point.

The elastic modulus $E(T_{\text{high}})$ at a temperature $T_{\text{high}}$ can be determined from the initial slope in the program step (Fig. 4a) also the elastic modulus of the stretched sample at a temperature $T_{\text{low}}$ can be determined from the slope of the curve in the program step $9$ (Fig. 4a). Important quantities to be determined describing the shape-memory properties of the material for a certain maximum strain $\varepsilon_{m}$ are the strain recovery rate $R_{r}$ and the strain fixity rate $R_{f}$. Both can be determined according to equations 1 and 3. The strain recovery rate $R_{r}$ quantifies the ability of the material to memorize its permanent shape and is a measure of how far a strain that was applied in the course of the programming, $\varepsilon_{m} - \varepsilon_{p}(N-1)$, is recovered in the following shape-memory transition. For this purpose the change in strain that is applied during programming in the $N$th cycle, $\varepsilon_{m} - \varepsilon_{p}(N-1)$, is compared with the change in strain that occurs with the shape-memory effect, $\varepsilon_{m} - \varepsilon_{p}(N)$:

$$R_{r}(N) = \frac{\varepsilon_{m} - \varepsilon_{p}(N)}{\varepsilon_{m} - \varepsilon_{p}(N-1)}$$  \hspace{1cm} (1)

where $\varepsilon_{p}(N-1)$ and $\varepsilon_{p}(N)$ represent the strain of the sample in two successively passed cycles in the stress-free state before yield stress is applied. The total strain
Fig. 4. Schematic demonstration of the results of the cyclic thermomechanical investigations for two different test programs: (a) $\varepsilon-\sigma$ diagram: ① stretching to $\varepsilon_m$ at $T_{\text{high}}$; ② cooling to $T_{\text{low}}$, while $\varepsilon_m$ is kept constant; ③ clamp distance is driven back; ④ at $\varepsilon = 0\%$ heating up to $T_{\text{high}}$; ⑤ beginning of the second cycle. (b) $\varepsilon-T-\sigma$ diagram: ① stretching to $\varepsilon_m$ at $T_{\text{high}}$; ② cooling down to $T_{\text{low}}$ with cooling rate $k_{\text{cool}} = dT/dt$ while $\sigma_m$ is kept constant; ③ clamp distance is reduced unless stress-free state $\sigma = 0$ MPa is reached; ④ heating up to $T_{\text{high}}$ with a heating rate $k_{\text{heat}} = dT/dt$ at $\sigma = 0$ MPa; ⑤ beginning of the second cycle. From Ref. 2.

Recovery rate $R_{r,\text{tot}}$ is defined as the strain recovery after $N$ passed cycles referred to the original shape of the sample piece:

$$R_{r,\text{tot}}(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m}$$

(2)
The strain fixity rate $R_f$ describes the ability of the switching segment to fix the mechanical deformation which has been applied during the programming process. It describes how exactly the sample can be fixed in the stretched shape after a deformation to $\varepsilon_m$. The resulting temporary shape $\varepsilon_u(N)$ always differs from the shape achieved by deformation.

$$R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_m}$$ (3)

The strain fixity rate $R_f$ is given by the ratio of the strain in the stress-free state after the programming step in the $N$th cycle, $\varepsilon_u(N)$, and the maximum strain $\varepsilon_m$ (1).

As indicated in Figure 4 the first cycles can differ from each other. With an increasing number of cycles the curves become more similar. The process of deformation and recovery of the permanent shape becomes highly reproducible. The changes in the first cycles are attributed to the history of the sample piece. In this respect, processing and storage play an important role. During the first cycles, a reorganization of the polymer on the molecular scale takes place as a reaction on the deformation in a certain direction. Singlepolymer chains arrange in a more favorable way with regard to the deformation direction. Covalent bonds may be broken during this process. An important variable that cannot be determined by a two-dimensional measurement is $T_{\text{trans}}$. In this respect, the “three-dimensional” test record that is given schematically in Figure 4b is interesting. In contrast to the two-dimensional measurement, here, the sample piece is cooled down in a controlled way (constant cooling rate) at a constant tensile stress $\sigma_m$. The change in strain in this program step is influenced by the temperature dependence of the thermal expansion coefficient of the stretched polymer and volume effects, which is based on the thermal transition $T_{\text{trans}}$, e.g., a crystallization process. Having reached $T_{\text{low}}$ the strain is reduced until a stress-free state is reached. The sample is now heated up to $T_{\text{high}}$ at a constant heat rate. During this experiment the tensile stress is kept constant at 0 MPa; this means that the clamps are following the shape change of the test piece. In this way, the shape change caused by the shape-memory effect is recorded as a function of the temperature. From the interpretation of the $\varepsilon$–$T$ plane in the $\varepsilon$–$T$–$\sigma$ diagram not only $T_{\text{trans}}$ but also the temperature interval can be determined in which the shape-memory effect takes place (Fig. 4b).

**Examples for Shape-Memory Polymers**

The following examples show thermally induced shape-memory. The first three examples are exclusively physically cross-linked. These examples are two polyurethanes representing thermoplastic shape-memory polymers with $T_{\text{trans}} = T_m$ or $T_g$, and a high molecular weight, amorphous polynorbornene. Examples of covalently cross-linked shape-memory networks are so-called heat-shrinkable materials and a shape-memory network with a crystallizable switching segment ($T_{\text{trans}} = T_m$) that has been developed for biomedical application.
Polyurethanes with Poly(ε-caprolactone) Switching Segment. Polyesterurethanes with a “hard-segment-determining” block of 4,4′-methylenebis(phenylisocyanate) (MDI) and 1,4-butanediol can be synthesized by the prepolymer method (6–11). The highest thermal transition $T_{\text{perm}}$ corresponding to the melting temperature of the “hard-segment-determining” blocks is found between 200 and 240°C. Poly(ε-caprolactone)diols with a number-average molecular weight ($M_n$) between 1600 and 8000 form the switching segments. The switching temperature for the shape-memory effect can be varied between 44 and 55°C depending on the weight fraction of the switching segments (variation between 50 and 90 wt%) and the molecular weight of the used poly(ε-caprolactone)diols. In polyurethanes with a high molecular weight of the used poly(ε-caprolactone) the “switching-segment-determining” blocks can crystallize optimally and so the temporary shape is set ideally. Moreover, a high weight fraction of “hard-segment-determining” blocks guarantees an optimum stabilization of the permanent shape. As a consequence, polyurethanes that combine a high molecular weight of the used poly(ε-caprolactone) and a high weight fraction of “hard-segment-determining” blocks show the best shape-memory properties. The strain recovery rate comes up to 98% at maximum strains $\varepsilon_m$ of 80%. Nonetheless, the shape-memory properties are strongly influenced by the degree of the applied strain. The strain recovery rates decrease if the applied strains $\varepsilon_m$ are increased from 80 to 250%. Decisive factors influencing the recovery properties are, besides the crystallinity of the switching segments, the formation and stability of the hard-segment-forming domains, especially, in the temperature range above the melting temperature of the switching-segment crystallites. For a content of hard-segment-forming domains below 10 wt% the hard-segment domains are not able to form stable physical cross-links. During the initial three cycles a slight increase in the switching temperature can be observed. This behavior is interpreted in terms of the destruction of weak netpoints, followed by an increasing formation of an ideal elastic network.

Polyurethanes with Poly(tetrahydrofuran) Switching Segment. Materials with a mixed glass-transition temperature $T_{g,\text{mix}}$ are systems with poly(tetrahydrofuran)- (poly(THF)-) switching-segment blocks having number-average molecular weights of 250 and 650 and a hard-segment-forming phase based on MDI and 1,4-butanediol. The hard segment is made using the prepolymer method (12,13). The highest thermal transition $T_{\text{perm}}$ corresponds with the melting temperature of the “hard-segment-determining” blocks. The block copolymers exhibit a $T_{g,\text{mix}}$ between 16 and 54°C in case of the switching segment with $M_n = 250$ depending on the hard-segment content (hardsegment content between 57 and 95 wt%), a $T_{g,\text{mix}}$ between −13 and 38°C for the switching segment with $M_n = 650$ (hard-segment content between 32 and 87 wt%), and a $T_{g,\text{mix}}$ of −36–22°C for the switching segment with $M_n = 1000$ (hard-segment-content between 23 and 81 wt%). If poly(THF)diols with $M_n = 2000$ or 2900 are used one cannot observe a mixed $T_g$ because of the good separation of the different blocks. Here, the occurring glass-transition temperatures are also dependent on the hard-segment content because of the hard segments’ property to hinder the mobility of the switching-segment chains. The shape recovery rate increases with increasing hard-segment content, reaching values up to 99% for the material with a switching segment with
$M_n = 250$ and a hard-segment content of 75 wt%. For materials with a switching segment with $M_n = 650$ complete recovery is not reached until the hard-segment content is 87%. After approximately 100 repetitions a constant shape recovery rate of 95% is reached.

**Polynorbornene.** Norsorex is a linear, amorphous polynorbornene having shape-memory properties. It was developed by the companies CdF Chemie and Nippon Zeon in the late 1970s. The molecular weight of this polynorbornene is about $3 \times 10^6$ (3,14). It is produced by a ring-opening metathesis polymerization of norbornene using a tungsten–alkylidene catalyst. This polynorbornene has a content of 70–80 mol% of trans-linked norbornene units and a glass-transition temperature between 35 and 45°C (14,15). The shape-memory effect of this strictly amorphous material is based on the formation of a physically cross-linked network due to entanglements of the high molecular weight, linear polymer chains. The thermal transition from the glassy state to the rubber-elastic state can be used as switching transition (16). Consequently, upon reaching the glass-transition temperature $T_g$ the material softens abruptly. If the chains are stretched quickly in this state and the material is rapidly cooled down again below $T_g$, as an answer to this, the polynorbornene chains can neither slip off each other rapidly enough nor can entanglements disentangle. By rapid cooling the induced elastic stress can be frozen within the material. After heating up again above $T_g$, because of the thermally induced shape-memory effect a recovery of the material’s shape can be observed. The described Norsorex is not inevitably purely amorphous. There are reports of a high molecular weight polynorbornene with a high content of trans-linked norbornene units showing a tendency toward strain-induced crystallization (14,15). Because of this observation the possibility must not be excluded that crystallites acting as physical netpoints contribute to the shape-memory effect.

**“Heat-Shrinkable” Polymers.** Since the 1960s, polyethylene covalently cross-linked by means of ionizing radiation has found broad application as heat shrink foil or tubing especially for the insulation of electric wires or as protection against corrosion of pipe lines (17–22). These materials are marketed under the term heat-shrinkable materials. The mechanism of the heat-shrinking process corresponds to the thermally induced shape-memory effect. The permanent shape is fixed by covalent cross-links. The switching process is controlled by the melting temperature of the polyethylene crystallites.

**Biodegradable Polymer Networks with Shape-Memory.** Based on oligo($\varepsilon$-caprolactone)diol representing the component to form a crystallizable switching segment, a polymer system with an AB-polymer network structure has been developed (1). For this purpose oligo($\varepsilon$-caprolactone)diols have been functionalized with methacrylate end groups that can undergo a polymerization reaction. The comonomer of choice is $n$-butyl acrylate because of the low $T_g$ (−55°C) of pure poly($n$-butyl acrylate); this supposedly determines the amorphous network chains of the expected network. The molecular weight of the used oligo($\varepsilon$-caprolactone)dimethacrylate cross-linking agent and the content of the comonomer butyl acrylate represent the molecular parameters controlling crystallinity, eg $T_{trans}$, and mechanical properties. The number-average molecular weights of the oligo($\varepsilon$-caprolactone)dimethacrylates used were 2000 and 10,000. The cross-link density in the case of the oligo($\varepsilon$-caprolactone)dimethacrylate
Section 1: Material Preparation and Investigation

(M_n = 2000) was varied by addition of 11–90 wt% butyl acrylate and for the oligo(ε-caprolactone)dimethacrylate (M_n = 10,000) by addition of 20–71 wt% butyl acrylate. The cross-link density increases with decreasing content of butyl acrylate. The butyl acrylate content influences the thermal properties of the formed AB network, especially for the oligo(ε-caprolactone)dimethacrylate with M_n 2000. Here, only in the case of a very low content of butyl acrylate of 11 wt%, a melting point at a T_m = 25°C can be observed. The corresponding homonetwork of oligo(ε-caprolactone) dimethacrylate has a melting point at T_m = 32°C. All other networks of this series were found to be completely amorphous. For the networks of butyl acrylate and oligo(ε-caprolactone)dimethacrylate with M_n 10,000 the melting point decreases from 51 to 44°C with increasing butyl acrylate content. With increasing butyl acrylate content the mechanical properties of both materials with oligo(ε-caprolactone) segments with M_n = 2000 and 10,000 change in such a way that the values of the elastic modulus (E), the tensile strength (σ_max), and the tensile stress at break (σ_R) decrease for about an order of magnitude. The absolute values are an order of magnitude higher for the series with oligo(ε-caprolactone) segments with M_n = 10,000. In cyclic thermomechanical tensile tests for the network with oligo(ε-caprolactone) segments (M_n = 10,000), strain fixity rates between 95 and 85% and strain recovery rates from 98 to 93% could be obtained. After three thermocycles all materials reached a constant strain recovery rate of 99%. In in vitro tests these shape-memory networks appear to be promising in their biocompatibility.

BIBLIOGRAPHY

5. U.S. Pat. 6,160,084 (2000), R. S. Langer and co-workers (to MIT).

ANDREAS LENDLEIN
STEFFEN KELCH
Deutsches Wollforschungsinstitut