# Review of progress in shape-memory polymers

C. Liu,[a] H. Qin[b] and P. T. Mather*[b]

Shape-memory polymers (SMPs) have attracted significant attention from both industrial and academic researchers due to their useful and fascinating functionality. This review thoroughly examines progress in shape-memory polymers, including the very recent past, achieved by numerous groups around the world and our own research group. Considering all of the shape-memory polymers reviewed, we identify a classification scheme wherein nearly all SMPs may be associated with one of four classes in accordance with their shape fixing and recovering mechanisms and as dictated by macromolecular details. We discuss how the described shape-memory polymers show great potential for diverse applications, including in the medical arena, sensors, and actuators.

## 1. Introduction

### 1.1. Definitions and mechanisms

Shape-memory materials are those materials that have the ability to "memorize" a macroscopic (permanent) shape, be manipulated and "fixed" to a temporary and dormant shape under specific conditions of temperature and stress, and then later relax to the original, stress-free condition under thermal, electrical, or environmental command. This relaxation is associated with elastic deformation stored during prior manipulation.[1] Shape-memory materials have aroused great attention from scientists and engineers due to their capacity to remember two shapes at different conditions. This gives materials great potential for application in sensors, actuators, smart devices, and media recorders. Previously, Irie,[2] Lendlein and Kelch,[3] and V.A. Beloshenko et al.[4] provided excellent reviews of SMPs based on results reported before 2004. The

recent review by V.A. Beloshenko et al. further classified shape-memory polymers based on their microstructures (glassy, crystalline, composites, and gels). That review focused significantly on how thermal treatment affects the physical responses of polymers, such as shrinkage stress, stress relaxation, and strain recovery rates, among other aspects, while no attention was given to the chemistry of the materials involved. More recently, Lendlein has provided an update on work from his group, especially in the areas of SMP biomaterials and a light-induced shape-memory effect.[5] The present review adopts a somewhat distinct perspective, including a new classification scheme, and discusses more recent work in the context of a comprehensive review, revealing trends in this dynamic field.

The most prominent and widely used shape-memory materials currently are shape-memory alloys (SMAs). Their shape-memory effect stems from the existence in such materials of two stable crystal structures: a high temperature-favored *austenitic* phase and a low temperature-favored (and "yield-able") *martensitic* phase. Deformations of the low temperature phase, occurring above a critical stress, are recovered completely during the solid–solid transformation to the high temperature phase. This shape-memory effect

[a]Department of Chemical Engineering, University of Connecticut, Storrs, CT 06268, USA
[b]Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, USA.
E-mail: patrick.mather@case.edu

**Changdeng Liu**

*Changdeng Liu obtained his PhD from the Chemical Engineering Department of the University of Connecticut in 2004. Under the supervision of P. T. Mather, Dr Liu has worked on shape-memory polymers since 1999 and has applied for 9 patents on shape-memory polymer compositions and their applications. He currently works for Ethicon, Inc.*



**Haihu Qin**

*Haihu Qin obtained his PhD in polymers from University of Connecticut in 2004, under the supervision of P. T. Mather, where his research focused on new thermosetting polymers ranging from liquid-crystalline networks to hyperbranched polymers. After that, Dr. Qin joined P. T. Mather at Case Western Reserve University as a postdoctoral researcher, where he pursued inorganic–organic hybrid biodegradable polymers. He currently works for Lubrizol Corporation.*

witnessed by SMAs is considered to have been first observed in a AuCd alloy by Chang and Read in 1951.[6] However, the discovery of the shape-memory effect in the equiatomic nickel–titanium alloy (NiTi, Nitinol®) in 1963 led to greatly enhanced interest towards commercial applications due to the combination of a desirable transition temperature close to body temperature, superelasticity, biocompatability, and a so-called two-way shape-memory capability.[7–10] These materials were then investigated thoroughly and have found their way to commercialization in a variety of fields over the past 40 years.[8,11–18] Despite the demonstrated merits, SMAs also show some downsides that limit their application, such as limited recoverable strains of less than 8%, inherently high stiffness, high cost, a comparatively inflexible transition temperature, and demanding processing and training conditions. Such limitations have provided motivation for the development of alternative materials, especially polymeric shape-memory materials.

Polymeric materials are intrinsically capable of a shape-memory effect, although the mechanisms responsible differ dramatically from those of metal alloys. In SMAs, pseudo-plastic fixing is possible through the martensitic de-twinning

**Patrick T. Mather**

*Patrick T. Mather received his BS degree in engineering science (1989) and MS degree in engineering mechanics (1990) from Penn State University. He then pursued a PhD in materials from U.C. Santa Barbara, where he studied flow behavior of liquid crystals with Dale S. Pearson, graduating in 1994. Mather then undertook a civilian position in the Air Force Research Lab, first at Edwards Air Force Base (California) and then at Wright Patterson Air Force Base (Ohio). During this time, Pat undertook the study of hybrid inorganic–organic polymers and became interested in shape-memory polymers. In 1999, he joined the Faculty of Chemical Engineering and Polymer Science at University of Connecticut, attaining tenure in 2003. Then, in 2004, Mather joined the faculty of Macromolecular Science and Engineering at Case Western Reserve University as an Associate Professor, where he currently pursues research in the area of functional polymers, ranging from shape-memory polymers, to fuel-cell membranes, and to self-healing thermosets. Prof. Mather is the author of over 70 peer-reviewed articles, 2 edited books, 4 US patents (14 pending), and has delivered over 70 invited lectures around the world. Mather has been honored with several awards including the Rogers Corporation Award for Outstanding Teacher in Chemical Engineering (UConn) in 2003, an SPE Medical Plastics Division, ANTEC 2002 Best Paper Award in 2002, a School of Engineering Outstanding Junior Faculty Award (UConn) in 2001, and an NSF CAREER Award for ''Orientational Dynamics in Flows of Thermotropic Polymers'' for 2001–2006. He recently won the outstanding teaching award (2005–06) for engineering from Case's Undergraduate Student Government.*

mechanism, while recovery is triggered by the martensite–austenite phase transition. Thus, fixing of a temporary shape is accomplished at a single temperature, normally slightly below room temperature, and recovery occurs upon heating beyond the martensitic transformation temperature. In contrast, shape-memory polymers achieve temporary strain fixing and recovery through a variety of physical means, the underlying very large extensibility being derived from the intrinsic elasticity of polymeric networks.

Polymers that are cross-linked, whether covalently or physically (through, *e.g.* microphase separation), are elastic to large strains above either $T_g$ (amorphous cases) or $T_m$ (crystalline cases) of the bulk material. The associated modulus of elasticity is dictated by configurational entropy reduction that occurs with deformation of the constituent chains and is therefore often termed "entropy elasticity". For $T > T_{crit}$ ($T_g$, $T_m$ or other), polymer networks exhibit "superelasticity" wherein the polymer chain segments between cross-link points can deform quite freely and are prone to being twisted randomly, *via* rotations about backbone bonds, maintaining a maximum entropy ($S = k_B \ln \Omega$, $k_B$ being Boltzmann's constant and $\Omega$ being the number of configurations) and minimum internal energy as macroscopic deformation occurs. The classic prediction from rubber elasticity theory[19] is that the resulting elastic shear modulus, $G$, is proportional to both cross-link density and temperature, or:

$$G = \nu K_B T = \rho R T / M_c \qquad (1)$$

where $\nu$ is the number density of network chains, $\rho$ is the mass density, $R$ is the universal gas constant, and $M_c$ is the molecular weight between cross-links. A rubber usually has a tensile storage (elastic) modulus of several MPa ($10^6$ N m$^{-2}$), a state that is very flexible and allows easy deformation under external force. This can be compared to the much larger stress plateau of pseudoplastic martensite de-twinning of shape-memory alloys, discussed below, of approximately 200 MPa.[20]

From a macroscopic viewpoint, the shape-memory effect in polymers can be graphically depicted in the form of measured tensile elongation *vs.* temperature and tensile stress, a form particularly suitable for characterization under conditions of controlled stress, as in a common dynamic mechanical analyzer. Shown in Fig. 1 is the response of a SMP rubber to a simple thermomechanical cycle, represented as a 3-D plot of strain *vs.* temperature and force (Fig. 1), beginning at the star. Elevated temperature deformations caused by applied load can be "fixed" during cooling, as witnessed by the horizontal unloading curve at room temperature. Thus, the work performed on the sample can be stored as latent strain energy if the recovery of the polymer chains is prohibited by vitrification, crystallization, or other means[21] (Fig. 1, cooling and fixing). Note that the shape fixing (Fig. 1, fixing) in this plot is achieved during cooling under fixed stress, but not fixed strain as is the case in many publications. In general, release of stress during the fixing stage will also lead to a slight strain decrease (Fig. 1, unloading), depending on the extent of fixing. This non-equilibrium "fixed" state is stable for long times. Upon subsequent heating above the critical transition temperature, either $T_g$ or $T_m$, the stored strain energy can be
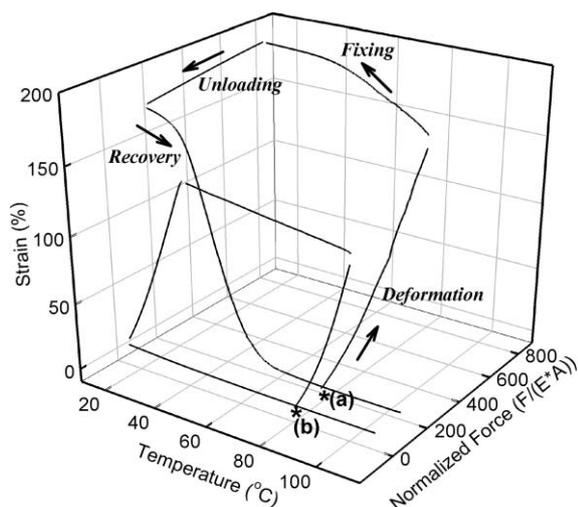
**Fig. 1** 3-D plot of the shape-memory cycle for (a) a shape-memory polymer and (b) natural rubber. The star indicates the start of the experiment (initial sample dimensions, temperature, and load). Both the SMP and the rubber were deformed under constant loading rate at constant temperature. The deformation step was then followed by a cooling step under constant load. At low temperature, the load was removed and shape fixing was observed for the SMP, but an instant recovery was seen for natural rubber. Shape recovery of the primary equilibrium shape was obtained by heating the SMP. The plot is adapted with permission from reference 21.

released as the polymer chains are liberated (Fig. 1, recovery). The strain or shape that the sample returns to is the "primary" or equilibrium shape dictated during cross-linking, whether chemical (covalent bonds) or physical (associations). The rigidity of the rubber and the work that will be saved during deformation, dictated by the shear ($G'$) or tensile ($E'$) storage modulus, can be tuned by controlling the extent of curing; that is, the cross-link density (eqn (1)). The vitrification or crystallization of the rubber component controls the "locking" of the polymer chains and therefore allows setting of an arbitrary secondary shape. Fig. 1(b) shows the response of a material *without* fixing capacity in the temperature range examined (natural rubber) to the same thermomechanical cycle. Clearly, unloading at low temperature returns the sample to it's equilibrium strain.

According to this shape-memory mechanism description, the features of a polymer that allow for good shape-memory behavior include: 1) a sharp transition that can be used to promptly fix the secondary shape at low temperatures and trigger shape recovery at high temperatures; 2) superelasticity (low loss modulus, high deformability) above the transition temperature that leads the shape recovery and avoids residual strain (permanent deformation); and 3) complete and rapid fixing of the temporary shape by immobilizing the polymeric chains without creep thereafter.

## 1.2. Advantages of shape-memory polymers

Compared with shape-memory alloys, polymeric shape-memory materials possess the advantages of high elastic deformation (strain up to more than 200% for most of the materials), low cost, low density, and potential biocompatibility and biodegradability. They also have a broad range of application temperatures that can be tailored, tunable stiffness, and are easily processed. These two materials (polymers and metal alloys) also possess distinct applications due to their intrinsic differences in mechanical, viscoelastic, and optical properties. A comparison of the different characteristics of SMPs and SMAs is summarized in Table 1.

## 1.3. A quick history of shape-memory polymers

To our knowledge, the first publication mentioning "shape-memory" effects in polymers is due to L. B. Vernon in 1941 in a United States patent,[22] who claimed a dental material made of methacrylic acid ester resin having "elastic memory" that could resume its original shape upon heating. This report appeared even earlier than the appearance of the first shape-memory alloy in 1951.[6] Despite this early discovery, recognition of the importance of shape-memory polymers did not occur until the 1960s, when covalently cross-linked polyethylene found its way into heat shrinkable tubing and films.[23–27] Significant efforts began in the late 1980s and this trend continues to grow as shown by the number of publications appearing yearly, which is summarized in Fig. 2. To date, dozens of other polymers have been designed and synthesized to demonstrate shape-memory properties for diverse applications.[2,3,15] Interestingly, approximately 40% of these have been published or patented by Japanese researchers,

**Table 1**  Comparison of the properties of shape-memory alloys with shape-memory polymers

|  | Shape-memory polymers | Shape-memory alloys |
|---|---|---|
| Density/g cm$^{-3}$ | 0.9–1.1 | 6–8 |
| Extent of deformation (%) | Up to 800% | <8% |
| Young's modulus at $T < T_{tran}$/GPa | 0.01–3 | 83 (NiTi) |
| Young's modulus at $T > T_{tran}$/GPa | $(0.1–10) \times 10^{-3}$ | 28–41 |
| Stress required for deformation/MPa | 1–3 | 50–200 |
| Stress generated during recovery/MPa | 1–3 | 150–300 |
| Critical temperatures/°C | −10–100 | −10–100 |
| Transition breath/°C | 10–50 | 5–30 |
| Recovery speeds | <1 s–several min. | <1 s |
| Thermal conductivity/W m$^{-1}$ K$^{-1}$ | 0.15–0.30 | 18 (NiTi) |
| Biocompatibility and biodegradability | Can be biocompatible and/or biodegradable | Some are biocompatible (*i.e.* Nitinol), not biodegradable |
| Processing conditions | <200 °C, low pressure | High temperature (>1000 °C) and high pressure required |
| Corrosion performance | Excellent | Excellent |
| Cost | <$10 per lb | ~$250 per lb |

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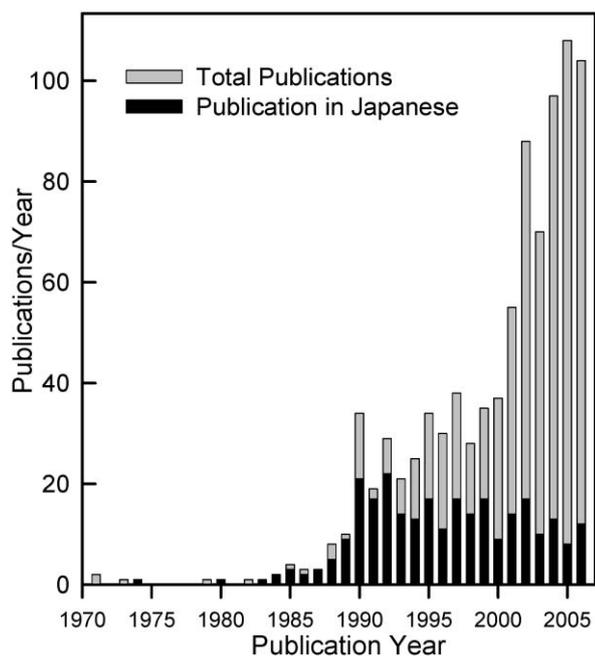*J. Mater. Chem.*, 2007, **17**, 1543–1558 | 1545

**Fig. 2** Publication history of SMPs from 1970 to 2006.

according to a literature search conducted in December 2006 (Fig. 2), including the representative materials that were frequently cited and will be discussed later, such as polynorbornene, poly(*trans*-isoprene), styrene–butadiene copolymers, and some polyurethane elastomers.[2,3,15,28] Fig. 2 also reveals that research in this area accelerated in the 1990s and has kept growing since then, especially the total publication numbers. It bears mentioning that publications coming from Japan showed a peak in the early 1990s and the numbers have been declining since then.

Earlier works in shape-memory polymers were mainly in industrial fields and the main focus was preparation of these new materials for various end-applications. Not much fundamental inquiry was involved and few thermomechanical properties were tuned. Recently, these materials have aroused interests in academia for more tailored applications. Several groups have been actively working on shape-memory polymers with tailored properties for specific requirements. The main research groups include those of A. Lendlein (biopolymers),[5,29–35] R. C. Larock (natural sources),[36–39] K. A. Gall (composites and simulation),[40–43] Y. Osada (hydrogels),[44–48] T. S. Wilson (medical devices),[49,50] F. Kremer[51] and Banahalli R. Ratna (liquid-crystal elastomers),[52] and our own group (various),[1,21,53–58] among many others. In our group, we have been studying shape-memory polymers with quite different thermomechanical responses and tailored properties for medical and other applications. This review is based on the work done primarily in our group, but also major works from other researchers. According to our experiences and literature research, the reported SMPs can be divided into four categories differentiated by their differences in fixing mechanism and origin of ''permanent'' shape elasticity (Fig. 3).[56] This review focuses on the recent progress of shape-memory polymers with discussion based on the four categories defined in Fig. 3, with each graph of this figure being described at that point.

## 2. Developments of shape-memory polymers

### 2.1. Covalently cross-linked glassy thermoset networks as SMPs (class I)

The simplest type of shape-memory polymer is a cross-linked glassy polymer featuring a sharp $T_g$ at the temperature of interest and rubbery elasticity above $T_g$ derived from covalent cross-links. This class of materials has attractive characteristics that include excellent degree of shape recovery afforded by rubbery elasticity due to the nature of permanent (or near permanent) cross-linking, tunable work capacity during recovery garnered by a rubbery modulus that can be adjusted through the extent of covalent cross-linking, and an absence of molecular slippage between chains due to strong chemical cross-linking. However, since the primary shape is covalently fixed, once processed (casting or molding) these materials are difficult to reshape thereafter. An example of this class is a chemically cross-linked vinylidene random copolymer consisting of two vinylidene monomers (one being methyl methacrylate and the other butyl methacrylate) whose homopolymers show two very different $T_g$ values of 110 °C and 20 °C, respectively.[55] The random copolymer itself gives a single, sharp $T_g$ that is tunable between the two $T_g$ values of the homopolymers by varying the composition. The work capacity, dictated by the rubbery modulus, is precisely adjustable to accommodate each particular application by varying the extent of cross-linking, in this case achieved by copolymerization with a tetraethylene glycol dimethacrylate. This thermoset shows complete shape fixing and fast, complete shape recovery in hot water at the stress-free stage (Fig. 4). In addition, this polymer has the advantage of being castable and optically transparent.

Prof. Larock's group worked on copolymerization and chemical cross-linking of renewable natural oils, having a high degree of unsaturation, with styrene and divinylbenzene to obtain random copolymer networks. These networks show tunable glass transitions and rubbery properties upon varying the monomer ratio.[36–38] In this work, broad glass-transition spans were observed for all of the copolymers and this, in turn, apparently slowed the shape-recovery speed, though no shape-recovery speed data was shown. Complete shape fixing and shape recovery were observed at high temperatures. However, due to the broad glass-transition span and the coexistence of rigid, glassy fragments and soft, elastic rubbery segments, incomplete shape recovery occurs at these transition ranges. While attractive in their unique composition, an unfavorably broad $T_g$ might limit the materials as SMPs.

Besides the *chemically* cross-linked polymers, polymers with $T_g$ > room temperature and with ultra-high molecular weight, >10^6 g mol^{-1}, may also be included in this category due to their lack of flow above $T_g$ and good shape fixing by vitrification. Such polymers feature a significant number of entanglements per chain (>25) and these entanglements function as physical cross-links on the time scale of typical deformations (1 s < $t$ < 10 s). Such physical cross-linking forms a three dimensional network that gives excellent elasticity above the glass transition, but makes thermal processing difficult; instead solvent-based processing may be required. These characteristics make the polymers essentially behave like the thermoset shape-memory polymers just discussed. The
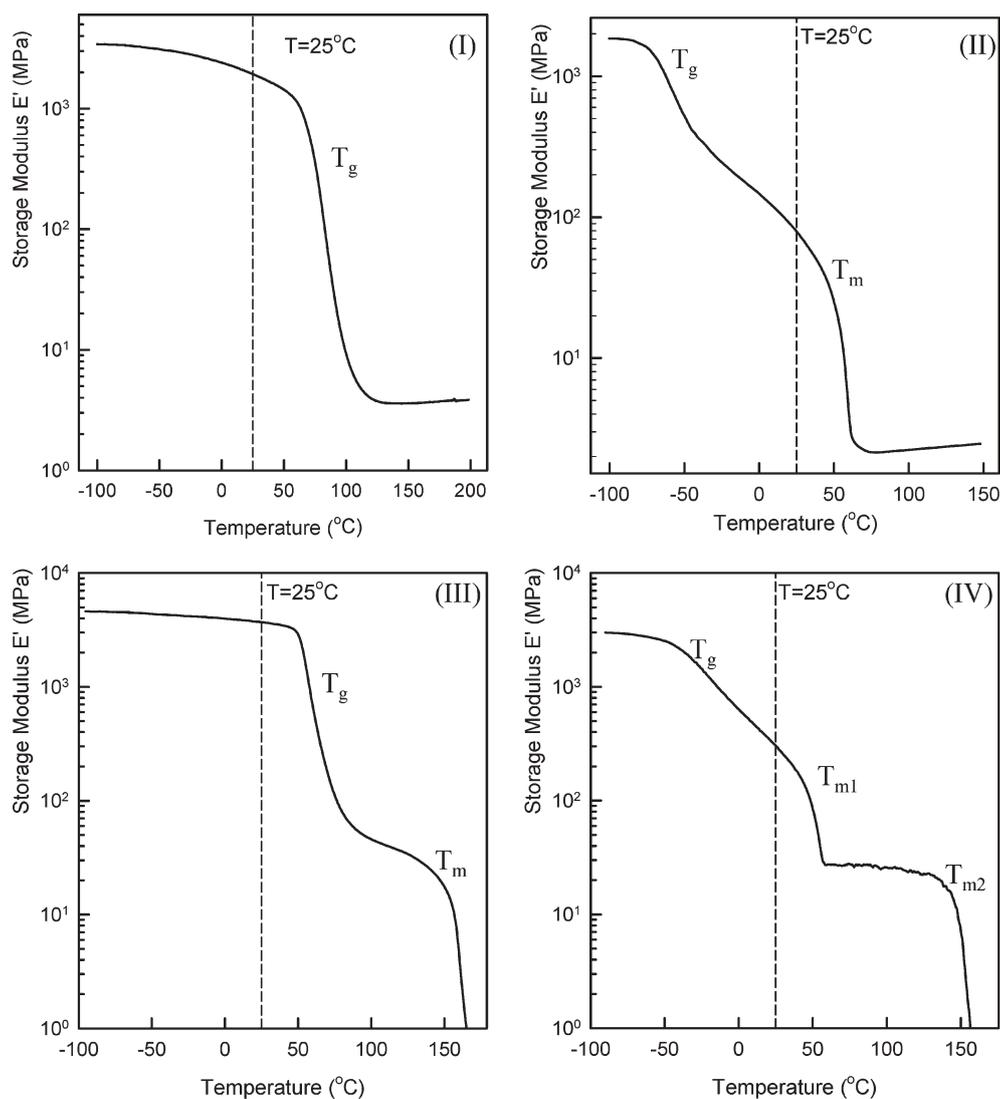
**Fig. 3** Definition of four types of shape-memory polymers with different shape-fixing and shape-recovery mechanisms depicted as a function of their dynamic mechanical behaviour. Plotted is the tensile storage modulus *vs.* temperature as measured using a small oscillatory deformation at 1 Hz for: (I) chemically cross-linked glassy thermosets; (II) chemically cross-linked semi-crystalline rubbers; (III) physically cross-linked thermoplastics; and (IV) physically cross-linked block copolymers. (See text for details on actual materials.)

most widely known materials with these characteristics include polynorbornene (PN, Norsorex®),[53,54,61–63] with $T_g \approx 40$ °C, and high molecular weight poly(methyl methacrylate) PMMA,[2,64,65] with $T_g \approx 105$ °C. An external force applied above the $T_g$ causes deformation to a secondary shape that can be fixed when cooled below $T_g$, which stores the elastic energy exerted during deformation. The decrease in mobility of PN molecules at $T < T_g$ maintains the secondary shape. The recovery of the original shape can be accomplished by reheating above its $T_g$, releasing the stored energy. Such polymers show quite complete shape fixing when vitrified and demonstrate fast and complete shape recovery due to the sharp glass-transition temperature (sharper for polynorbornene than for PMMA) and high entanglement density that forms a three dimensional network, evidenced by a flat rubbery plateau measured rheologically. However, the disadvantages of such materials are: 1) the transition temperature cannot be easily varied; 2) the modulus plateau, which controls the energy

stored when deforming, is low ($\approx 1$MPa) and also hard to change; 3) the polymer will creep under stress at high temperature due to the finite lifetime of the entanglements; and 4) difficulty of processing because of the high viscosity associated with high molecular weight polymers. Thus, the processing of such materials is limited to solvent casting instead of more desirable thermal processing, such as extrusion, injection molding, or compression molding.

In addition to the examples given above, other materials are reported to be shape-memory materials based on the same mechanism, such as poly(alkyl methacrylate) copolymers,[59,69] polystyrene copolymers,[74] filler-modified epoxy networks,[40,41,65,70] chemically cross-linked amorphous polyurethanes,[75,76] poly((methyl methacrylate)-*co*-(*N*-vinyl-2-pyrrolidone))–PEG semi-IPNs,[66] HDI–HPED–TEA network,[50] and biodegradable copolyester–urethane networks.[31] A list of shape-memory polymers based on glassy thermosets, along with references, is summarized in Table 2.
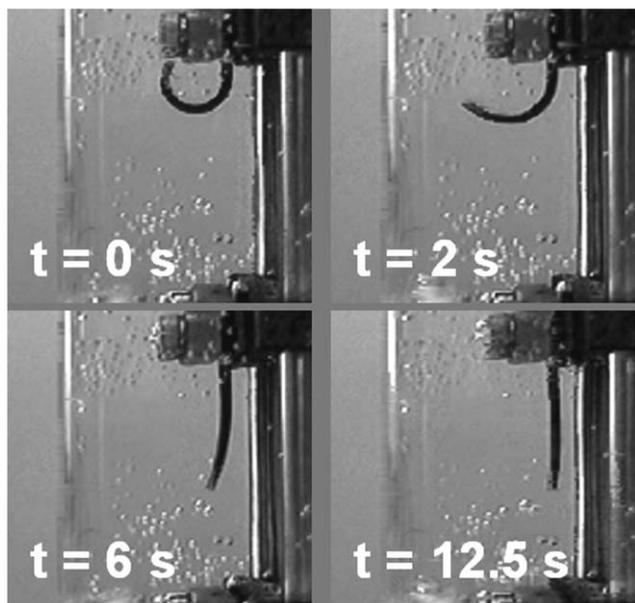
**Fig. 4** Strain recovery of a cross-linked, castable shape-memory polymer (class I) upon rapid exposure to a water bath at $T = 80\ °C$. Adapted from reference 59 with permission of Society of Plastics Engineers, copyright 2002.

## 2.2. Covalently cross-linked semi-crystalline networks as shape-memory polymers (class II)

Aside from the glass transition as a critical temperature, the melting transition of semi-crystalline networks can also be employed to trigger shape recovery, typically giving a sharper recovery event. Here, the secondary shapes are fixed by crystallization instead of being fixed by vitrification. Similar to the first class, the permanent shapes are established by chemical cross-linking and cannot be reshaped after processing. Compared with glassy materials, this class of materials is generally more compliant below the critical temperature, with a stiffness that is sensitive to the degree of crystallinity, and thus indirectly to the extent of cross-linking. Shape-recovery speeds are also faster for this first-order transition with an often sharper transition zone. This class of materials includes bulk polymers, such as semi-crystalline rubbers and

**Table 3** Summary of the semi-crystalline shape-memory thermosets with shape recovery triggered using their melting temperatures

| Materials | Transition temperature/°C | Special features | Reference |
|---|---|---|---|
| Poly-caprolactone | 54–58 | Room temperature gamma radiation cross-linking | 84,85 |
| EVA + nitrile rubber | 85 | — | 86 |
| PE | ∼120 | E-beam cross-linking | 26,87,88 |
| Poly-cyclooctene | 45 | Fast shape recovery | 78,1 |
| PCO–CPE blend | 58 | Selective cross-linking of rubber | 89 |
| PCL–BA copolymer | 45 | UV polymerization | 29 |
| Poly(ODVE)-co-BA | 42 | Sharp transition | 90 |
| EVA + CSM | ∼80 | Flame retardant | 91 |
| Poly-caprolactone | 54–58 | No chain scission | 92 |

liquid-crystal elastomers (LCEs), and hydrogels with phase separated crystalline microdomains. Table 3 provides a summary of materials and associated characteristics for this SMP class.

Semi-crystalline rubbers have been favored as shape-memory materials as a result of their superelastic rheological characteristics, fast shape recovery, and flexible modulus at the fixed stage. One classic material of this family of SMPs is chemically cross-linked *trans*-polyisoprene (TIP),[2] which is a semi-crystalline polymer having a melting point ($T_m$) of 67 °C and a degree of crystallinity around 40%, giving a stiffness of about 100 MPa at room temperature. TIP was chemically cross-linked by peroxides at 145 °C for 30 minutes to form a three dimensional network, thus establishing the permanent (primary) shape and creating the superelastic property required for shape recovery above its melting temperature. Thermal instability inhibits the end-application of this material due to the high density of unsaturated double bonds.

In our group, we have successfully developed a chemically cross-linked, semi-crystalline *trans*-polyoctenamer (polycyclooctene, PCO) with a *trans* content of 80%, a $T_g$ of −70 °C, a $T_m$ of 58 °C, and much better thermal stability, for shape-memory applications.[1] When cooling a strained sample to below $T_m$, crystalline domains begin to form and ultimately percolate the sample, at that point establishing strain fixing. When heated above $T_m$, for instance, $T = 80\ °C$, the crystals

**Table 2** Summary of shape-memory thermosets with the shape recovery triggered by their glass-transition temperatures

| Materials | Transition temperature/°C | Special features | Reference |
|---|---|---|---|
| P(MMA-co-VP)–PEG semi-IPNs | 65 | Semi-IPN | 66 |
| Copolyester | 48–66 | Biodegradable | 31 |
| P(AA-co-MMA)–PEG | 60 | Broad transition | 67 |
| Corn oil copolymer | 0–90 | Biomaterial | 39 |
| PMMA–PBMA copolymers | 20–110 | Optically transparent | 59,68,69 |
| Epoxy | 50–80 | Filled reinforced | 40,41,65,70 |
| Fish oil copolymers | 30–109 | Biodegradable | 36 |
| PET-PEG copolymer | Up to 80 | — | 71 |
| P(MA-co-MMA)–PEG | 50–90 | — | 72 |
| Soybean oil copolymers with styrene and DVB | 30–110 | Biomaterial | 37,73 |
| Styrene copolymer | — | Optically transparent | 74 |
| Thermosetting PU | Up to 56 | Water swollen | 75 |
| Thermosetting PU | 0–150 | Ester type | 76 |
| Dehydrochlorinated cross-linked PVC | 80 | — | 77 |
| Polynorbornene | 40 | Sharp $T_g$ | 61,62 |
| High $M_w$ PMMA | 105 | Deformable below $T_g$ | 2,64 |
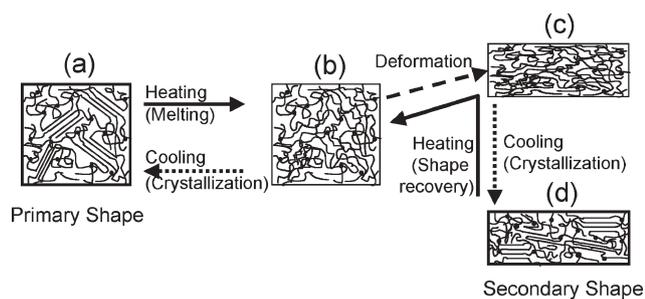
**Fig. 5** Schematic depiction of shape fixing and recovery mechanisms of semi-crystalline shape-memory rubbers. (a) As-cross-linked shape at semi-crystalline stage (low temperature); (b) melted sample at stress-free stage (high temperature); (c) deformed shape at melt stage (high temperature) and; (d) crystal-frozen deformed shape (low temperature). Adapted with permission from reference 1.

melt to an amorphous, homogenous phase with high mobility, leaving the chemical cross-links to re-establish the primary shape. PCO, cross-linked as mentioned above, has elasticity similar to rubber at temperatures above $T_m$ and can be deformed easily with external force to make a new, secondary shape. The secondary shape can be fixed by crystallization during the subsequent cooling process to a temperature below the melting point. The material will maintain this temporary shape (though possibly subject to prolonged warpage) as long as the crystals are not destroyed at the temperature below the melting transition ($T_m$). The deformed shape can return to the primary shape promptly upon reheating above its melting point, where the fixing phase is eliminated. A shape-memory mechanism was proposed in a publication (Fig. 5) based on the above description that will eventually illustrate most of this class of materials. By design, the room-temperature stiffness, transition temperatures, and rubbery modulus can be tuned independently by blending with rubbery (yielding "shape-memory rubber") or solid components, manipulating the tacticity of PCO, and/or controlling the cross-linking degree.[78] Crystallization kinetics and thermal conductivity along with their effects on shape fixing and recovery properties were fully investigated.[79,80] Besides thermal heating, recovery in this material was successfully triggered using an electric current at a very low voltage.[56] Similarly, polyethylene has been modified to feature shape memory by radiation cross-linking and used as heat shrinkable tubes, though the melting point is inconveniently high ($110 < T_m < 150 \,°C$)[26,27] for many applications.

Using an analogous concept, A. Lendlein and co-workers have developed shape-memory polymers having biodegradable properties by synthesizing and copolymerizing a narrowly dispersed, oligomeric poly(ε-caprolactone) dimethacrylate with n-butyl acrylate under UV radiation to yield a multiblock structure.[29] The polycaprolactone segments form a crystalline structure to fix a secondary shape at low temperature, leaving the melting points of the PCL segments to control the shape-recovery temperature. Meanwhile, the amorphous n-butyl acrylate main chains, together with the PCL dimethacrylate as cross-linker, form a network that gives rise to the permanent shape and prompts the shape recovery by a softening effect with its low glass-transition temperature ($T_g = -55 \,°C$). The

merit of this material lies with the very sharp melt transition, due to the uniformity of the crystals caused by PCL segments having almost identical molecular length, though no data to this effect was reported. A sharp transition would assure sharp and fast shape recovery. Despite this promise, the report shows that this SMP recovers to its primary shape with a characteristic time of 20 seconds on a hot plate at 70 °C. However, such a slow recovery might have been because the sample was not uniformly and effectively heated. An additional contribution of this article is the application of a photo-cure method to quickly fabricate shape-memory polymers directly to their permanent shapes. Recently, other synthetic methods based on radiation cross-linking were also proposed to construct biodegradable polycaprolactone networks exhibiting excellent shape-memory properties.[33,81–83]

Cross-linking a semi-crystalline material impedes crystal formation and, hence, might cause a lesser degree of crystallinity, broader crystal-size distribution, and a lower and broader melting-transition temperature span. Efforts are undertaken to specifically cross-link the amorphous fraction but not the crystalline fraction so as to keep a sharp transition and avoid a drop in the transition temperature due to cross-linking. Successful implementation of this approach was reported recently for a *blend* composition composed of a semi-crystalline polymer acting as the reversible phase and a specially functionallized, co-continuous rubber matrix as the permanent phase. Special curing techniques were performed to only cross-link the rubber matrix, leaving the semi-crystalline phase unaffected.[89]

Liquid-crystalline polymers can also be used for this purpose. In our lab, a main smectic chain LCE was synthesized and the shape-memory properties characterized using a shape-memory cycle test. This LCE features a sharp transition close to body temperature, a low modulus comparable to muscle, and optical clarity, all suggesting potential for biomedical applications.[21] Interestingly, by careful preparation, similar LCEs can also show two way (reversible) shape-memory properties. This is exclusively discussed separately in section 2.5.2.

## 2.3. Physically cross-linked glassy copolymers as shape-memory polymers (class III)

Ease of processing has been an issue for technological advancement of shape-memory polymers. To some extent, class III SMPs (summarized in Table 4) display rheological characteristics amenable to facile processing with conventional thermoplastics technology. The example for this class shown in Fig. 3 is that of a melt-miscible blend of poly(vinyl acetate) (PVAc) and poly(lactic acid) (PLA). In this SMP class, crystalline or rigid amorphous domains in thermoplastics may serve as physical cross-links affording the super-$T_g$ elasticity required for shape memory to be developed, mainly in the form of phase-separated block copolymers. When the temperature surpasses the $T_m$ or $T_g$ (symbolized as $T_{high}$) of these discrete physical domains, the material will flow and can be processed and reshaped. Another continuous phase, having a lower $T_m$ or $T_g$ (symbolized as $T_{low}$), exists which softens to a rubbery state at $T_{low} < T < T_{high}$ and fixes a secondary shape on cooling to $T < T_{low}$. For some block copolymers and

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**Table 4** Summary of physically cross-linked block copolymers and blends as shape-memory polymers

| Materials | Hard segments | Soft segments | Shape fixing/°C | Reference |
|---|---|---|---|---|
| POSS telechelic | POSS domain | PEG | $T_m = 55$ | 115,116 |
| PLAGC multiblock copolymer | PLLA crystalline domain | Copolymer amorphous $T_g$ | $T_g = 40$–$50$ | 96 |
| Aramid/PCL | Aramid | PCL or polyTHF | $T_m = 0$–$35$ | 117 |
| PVDF/PVAc Blends | PVDF crystals | PVDF/PVAc amorphous regions | $T_g = 20$–$35$ | 95,118 |
| Poly(ketone-$co$-alcohol) | Micro-crystalline segments | Amorphous polyketone E-P/CO | $T_g$ | 119 |
| PCL-$b$-ODX | ODX(oligo($p$-dioxanone) diol) | PCL | $T_m$ | 30 |
| PLA/PVAc blends | PLA crystals | PLA/PVAc amorphous region | $T_g$ | 57,118 |
| Poly(1-hexadecene)-$co$-PP | PP crystals | PHD crystals | $T_m$ | 120 |
| PE-$co$-PMCP | Polyethylene | Poly(methylene-1,3-cyclopentane) | $T_m$ | 121 |
| POSS–PN block copolymer | POSS domain | PN | $T_g$ | 53,54 |
| PA–PCL | Polyamide (nylon 6/6,6) | Polycaprolactone | $T_m$ | 122 |
| PET-$co$-PEO | PET crystals | PEO crystals | $T_m$ | 123–125 |
| PE-$co$-Nylon 6 | Nylon 6 | PE | $T_m$ | 110,122 |
| PS–TPB | Polystyrene | Polybutadiene | $T_m$ | 126,127 |

polyurethanes, the soft domain shows a sharp glass-transition that can be tuned to be useful for shape memory.[93,94] Although the room-temperature stiffness of these materials is similar to the first class, their being only *physically* cross-linked yields the advantage of being processable above $T_{high}$ of the hard domains. An example of this material is a miscible blend of a thermoplastic polyurethane with phenoxy resin, in which the soft segment of the polyurethane is PCL.[94] In this system, a single glass-transition ($T_g > RT$) forms and is tunable by varying the ratio between the phenoxy resin and the PCL segments. In another system of this class, norbornene was copolymerized with a polyhedral oligosilsesquioxane (norbornenyl–POSS) hybrid monomer, yielding a microphase-separated copolymer with fewer repeating units in the back-bone[53] than commercial polynorbornene. Such a composition also improved the thermal processability and suppressed high temperature yielding of polynorbornene homopolymer. Both the critical temperatures and the stored energy during deformation (rubbery modulus) were enhanced, while the $T_g$ of the copolymer broadened somewhat, which slightly retarded the shape-recovery speed.

This SMP class further includes some low crystallinity, semi-crystalline homopolymers, or melt-miscible polymer blends that are compatible in the molten and amorphous states, but have at least one semi-crystalline component.[57] In such a system, the crystals serve as physical cross-links (or hard domains) and the composition-dependent $T_g$ of the amorphous region functions as the transition temperature. For these miscible blends, the glass-transition temperature of the amorphous phase and the work output during shape recovery can be easily tuned by changing the blend composition, analogous to the copolymer thermosets as in class I.

We have worked on two miscible blend systems: poly(vinyl acetate) (PVAc) with poly(lactic acid) (PLA) and PVAc or PMMA with poly(vinyldiene fluoride) (PVDF).[57,95] Both systems are melt miscible for all blend ratios, with the PVAc and PMMA being totally amorphous. PLA and PVDF each show semi-crystalline features and have a degree of crystallinity of about 50%, individually. The degree of crystallinity of the blends varies from 0 to 50% according to the blend ratio, with crystals serving as physical cross-links and the crystallinity controlling the rubbery modulus. The $T_g$ of the amorphous phase works as a transition temperature and can

be tailored between the $T_g$ values of the two homopolymers. Recently, a multiblock copolymer, PLA-$co$-poly(glycolide-$co$-caprolactone), and PLA–HA composites were also developed to show desirable shape-memory properties.[96,97]

Besides crystalline and glassy domains, other physical cross-linking techniques can also help to set the network. Examples include hydrogen bonding [110] or ionic clusters [109] within the hard domains. The existence of these interactions strengthens the hard domains by decreasing chain slippage during deformation and therefore increases the extent of shape recovery. Ionomers themselves can be very strong in setting a network, giving elasticity similar to chemically cross-linked materials.[111] However, shape-memory polymers based on pure ionomers have not been reported so far.

Given the diversity in selection of soft domains, hydrophilic oligomers can be used to construct multiblock copolymers with shape-memory properties. For these materials, besides heat-triggered shape recovery, moisture can be used to plasticize the soft domain and lower its glass transition below ambient temperature to activate shape recovery.[112,113] Generally, slow recovery results given the comparatively slow speed of water diffusion.

Due to the easy processing nature of this class, electrospinning technology was used to fabricate shape-memory fibers.[114] A relatively low shape recovery was observed compared with bulk polymers. However, improvements in weaving technology could resolve this problem.

## 2.4. Physically cross-linked semi-crystalline block copolymers as shape-memory polymers (class IV)

For some block copolymers, the soft domain will crystallize and, instead of $T_g$, their $T_m$ values function as shape-memory transition temperatures and the secondary shapes are thus fixed by crystallization of the soft domains. The example for this class, shown in Fig. 3, is that of a multiblock polyurethane featuring PEO as a soft segment.[60] As another example, styrene–$trans$-butadiene–styrene (STBS) triblock copolymers feature SMP behavior that is afforded by this mechanism.[128] STBS is a strongly segregated ABA-type triblock copolymer with a minor component of polystyrene (PS) segments, *ca.* 10–30 volume percent, serving as A-domains at each end of the macromolecular chains, and a major component of semi-crystalline poly($trans$-butadiene) (TPB) segments as B-domains

in the middle block. Due to the immiscibility between PS and TPB blocks, the copolymer phase separates and PS blocks form discontinuous, amorphous micro-domains having $T_g$ = 93 °C. TPB blocks form a semi-crystalline, comparatively compliant matrix having a $T_m$ of 68 °C and a $T_g$ far below room temperature, at −90 °C. The rigid PS microdomains remain rigid up to 90 °C and thus serve as physical cross-links whose configuration set the permanent shape. When heated to 68 < T < 90 °C, the material becomes flexible and rubbery ($E \sim 1$ MPa) due to the melting of the TPB crystals in the matrix, but does not flow due to the rigid PS microdomains, maintaining a stress-free permanent shape. At this stage, the materials have a storage modulus resembling rubber and dictated by the TPB molecular weight. When cooled below 40 °C, the TPB matrix crystallizes so that a secondary (deformed) shape can be "fixed" by those crystals. The energy exerted during deformation is then "frozen" into the material. The shape can return to the permanent shape upon melting of TPB. The STBS block copolymer, and other class IV materials, has the advantage of having a permanent shape that can be reprocessed by thermal processing above 100 °C, when both domains flow. As a possible disadvantage, the "hard" microdomains may creep under stress when setting the temporary shape near $T_g$, limiting the level of recoverable strain.

As a similar approach, thermoplastic segmented polyurethanes with semi-crystalline flexible segments have also been investigated for shape-memory effects.[129–132] Table 5 summarizes this class of SMPs. Conventionally, polyurethanes are multiblock copolymers consisting of alternating oligomeric sequences of hard and soft segments. The hard segments form physical cross-links by way of polar interaction, hydrogen bonding, or crystallization, with such cross-links being able to withstand moderately high temperatures without being destroyed. Meanwhile, crystallizable soft segments (e.g. oligo-caprolactone) form the thermally reversible phase and the crystallization of these soft segments governs the secondary shape. Polyurethanes feature the advantage of easily tuning the room-temperature stiffness, transition temperature, and work-output ability by manipulating their compositions, with some being potentially biocompatible. Also, polyurethanes can easily be foamed, as with the foamed shape-memory material

CHEM, which was successfully manufactured and brought to application.[133]

We have designed, synthesized, and fully characterized a series of novel multiblock polyurethane copolymers for shape-memory applications using the POSS hybrid monomer in the hard domains and various polyols, either amorphous or semi-crystalline, as soft domains.[98,115,134–136] The POSS units drive segregation from the soft domain and crystallize, with a relatively low melting temperature of around 110 °C. Above its melting temperature, the polyurethane can be thermally processed. The rubbery properties can be tuned by manipulating the hard/soft domain ratio, while the transition temperature can be controlled by separate tailoring of the melting temperature or the glass transition of the soft domains. Additionally, the materials may also be designed to be biocompatible and biodegradable. Hydrophilic polyols, such as PEG, have been incorporated as soft domains, allowing the potential for strain recovery to be triggered by water vapor while broadening the potential applications to polymeric surfactants by hydrophilic–hydrophobic balance.[134,137,138] Additionally, an advantage of this material is the low hard-domain melting temperature ($T_m \sim 110$ °C), which is much lower than that of conventional TPUs and amenable to thermal processing, but high enough to have a broad processing window for shape-recovery triggering.

### 2.5. Two-way actuation polymeric materials

**2.5.1 Hydrogels.** Besides the aforementioned *bulk* (solvent-free) shape-memory polymers, another class of polymers possessing shape-memory properties are shape-memory gels. These materials are usually more flexible than shape-memory rubber and are best represented by Y. Osada's work from Hokkaido University in Japan.[44–48] Analogous to shape-memory rubber, a typical shape-memory gel is a cross-linked material having a hydrophilic fraction that can be swelled in water and hydrophobic sections with reversible order–disorder structures controlled by temperature. While cross-linking sets the permanent (high temperature) shape, the ordered structure that forms at temperatures, $T < T_{critical}$, can be used to fix secondary shapes established by deformations at higher temperature, $T > T_{critical}$. Heating above $T_{critical}$ then triggers quite complete shape recovery. One example is a water-swollen

**Table 5** Summary of physically cross-linked polyurethane multiblock copolymers as shape-memory polymers

| Chain extenders | Soft segments | Di-isocyanate | Shape fixing/°C | Reference |
|---|---|---|---|---|
| POSS | PDLA-*co*-PCL | MDI | $T_g$ = 45 | 98 |
| 4,4′-Dihydroxybiphenyl (DHBP) | PCL blend with phenoxy resin or PVC | Hexamethylene diisocyanate (HDI) | $T_g$ = −50–66 | 94,99 |
| 1,6-HD | HDI–1,2-BD | 4,4′-MDI | 40–53 | 100 |
| 1,4-Butanediol | Poly(ethylene adipate), 300, 600, 1000 Da | MDI | $T_g$ = 10–50 | 101 |
| 1,4-Butane glycol, ethylene glycol bis(2-hydroxyethyl) hydroquinone, bisphenol A + ethylene oxide, bisphenol A + propylene oxide | Polypropylene glycol, 1,4-butaneglycol adipate, polytetramethylene glycol, polyethylene glycol, bisphenol A + propylene oxide | 2,4-Toluene diisocyanate, 4,4′-diphenyl-methane diisocyanate, hexamethylene diisocyanate | $T_m$ = up to 50 | 102 |
| 1,4-BD | Poly(tetramethylene glycol) (PTMG) | MDI | $T_m$ = 25 | 103 |
| 1,4-BD | PCL diol | MDI | $T_m$ = 57–63 | 104,105 |
| BEBP or BHBP | PCL diol | MDI | $T_m$ = 40 | 106 |
| DHBP | PCL diol, 4000 Da | HDI | $T_m$ = 38–60 | 107 |
| 1,4-BD | Poly(tetramethylene oxide) glycol (PTMO) | MDI | $T_m$ = 0–46 | 108 |
| BD + DMPA | PCL diol, 2000, 4000, 8000 Da | MDI | $T_m$ = 50 | 109 |

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hydrogel from a chemically cross-linked copolymer of acrylic acid (AA, hydrophilic section) that swells in water, and stearyl acrylate (SA, hydrophobic and crystallizable) that acts as the fixing phase when crystallized at $T < T_m$, even when the material is highly water-swollen.[44,46] The stiffness of this gel will change dramatically from 10 to 0.1 MPa over a narrow 10 °C temperature span and can be tuned by varying the cross-link density. Interestingly, the transition temperature itself can be altered by varying the monomer compositions. Other ordered aggregates, including 12-acryloyldodecanoic acid (ADA) and 16-acryloylhexadecanoic acid (AHA), were also incorporated for the same purpose.[48,139]

In addition to shape-memory gels fixed and triggered by constant volume order–disorder transitions, Hu has elaborated on another class of "shape-memory gels" consisting of modulated gel macro-assemblies.[140] Portions of such assemblies witness a volume phase-transition wherein the gel changes its volume (albeit slowly) by three orders of magnitude in response to external stimulation, such as temperature, solvent, pH, electrical current, or light. The underlying mechanism is the hydrogel's lower critical solution temperature (LCST) phase behavior. In one demonstration,[140] Hu *et al.* constructed a bi-gel strip by first synthesizing an *N*-isopropylacrylamide (NIPA) gel slab that will swell in water below the LCST and collapse drastically at 39 °C with an enormous volume change (up to 3 order of magnitude). Next, another polyacrylamide (PAAM) gel slab was synthesized, with one side of the slab in contact with the previously prepared NIPA gel slab and allowing some of the AAM monomers to diffuse into the NIPA surface before polymerization to chemically weld them together. When the temperature is raised to 39 °C, the NIPA layer of the bi-gel strip will deswell and shrink, while the PAAM maintains its dimensions, so that the bi-gel strip will curve towards the NIPA side and change its shape. When cooled below the transition temperature, the NIPA gel slab will swell and expand, and the bi-gel strip will recover. The shape changes are reversible, similar to two-way shape-memory alloys, but have a much larger deformation.

**2.5.2 Reversible shape-memory elastomers.** As interest increases in smart materials for applications such as reversible actuators, especially for artificial muscles, a requirement of highly *reversible* strains up to 30%, substantial stress of 350 kPa, and fast actuation up to 5–10 Hz emerges.[52,141] Indeed, a wide range of materials has been investigated for potential two-way shape-memory properties to varying degrees of success, including the modulated gel technique discussed above, electroactive polymers,[142–144] conducting polymers,[145–148] and liquid-crystalline elastomers (LCEs).[51,52,141,149,150] Among these candidates, LCEs have shown the best potential based on their fast actuation speed and mechanical properties that can be tuned and optimized to mimic skeletal muscle.

The mechanism of the two-way shape-memory effect intrinsic in LCEs stems from their anisotropic polymer-chain conformation.[151] The constituent polymer chains are prolate in the direction of the liquid-crystalline director for temperatures in the liquid-crystalline state, while in the isotropic phase the polymer chains are spherical, existing as Gaussian coils.[19]

Traversing the clearing transition from the liquid-crystalline phase to the isotropic rubber phase, the polymer chains can spontaneously contract from a prolate to a spherical configuration. The reverse is true upon cooling. In the case of monodomain LCEs, this microscopic deformation can accumulate into a macroscopic one in the direction of the liquid-crystalline director.

Compared with two-way shape-memory alloys, LCEs are capable of much larger recoverable strains, up to 300%. In 2001, by the hydrosilation reaction between poly(methylhydrogensiloxane), vinyl functionalized liquid-crystalline mesogen, and cross-linker, a class of monodomain nematic LCEs were prepared by Finkelmann's group.[152] Under a small preload stress of 6 kPa, a recoverable strain as high as 300% was observed through the nematic–isotropic transition ($T_{NI}$). Furthermore, more than 90% of the total strain sharply recovered in a narrow temperature range of $0.95 < T_{red} < 1$, where $T_{red}$ is defined as $T/T_{NI}$. Indeed, in such a sharp transition, the rate of recovery/deformation is determined more by thermal conductivity than other factors. In the case of thin samples, the response rate of this kind of nematic LCEs can match that of natural muscles.

In addition to the thermally triggered two-way shape-memory materials, LCEs stimulated by photo-illumination[153,154] and electrical fields[51] were also investigated. For those triggered by photo-illumination, the photo-isomerizable azo group was incorporated into the liquid-crystalline mesogens. Upon UV irradiation, the azo group isomerized from the *trans* to the *cis* configuration and sharply bent the mesogens, hampering the nematic ordering. Correspondingly, the material underwent a photo-induced nematic–isotropic transition, accompanied with a large shape change. For example, Finkelmann *et al.*[153] showed that, under UV irradiation at 365 nm, a contraction of 24% strain was generated in a time of about one hour.

A photo-triggered LCE with much faster reaction time was fabricated by doping azo dye molecules into the LCE matrix without covalent attachment.[154] Upon irradiation, the sample bent to more than 60° in only 80 ms. Nevertheless, the mechanism of this kind of actuation has not yet been elucidated. It is possibly due to heating upon absorption, reduction in the orientation order by the isomerization of the dye molecules, or both.

## 2.6. Quantitative analysis of the shape-memory ability by a fill factor

Though some researchers have tried to quantify the shape fixing and shape recovery for their systems, most of the quantifications are limited to the percentage of shape fixing and extent of shape recovery, although some have endeavored to assess the speed of shape recovery. However, no standard method has been published on the overall performance of shape-memory polymers for comparison of one system to the next. Here, we introduce a shape-memory cycle analysis method to characterize and compare the shape-fixing and shape-recovery ability in a standard way.[155] A schematic shape memory cycle is shown in Fig. 6, which is a projection from a three dimensional, length–temperature–force plot of Fig. 1.
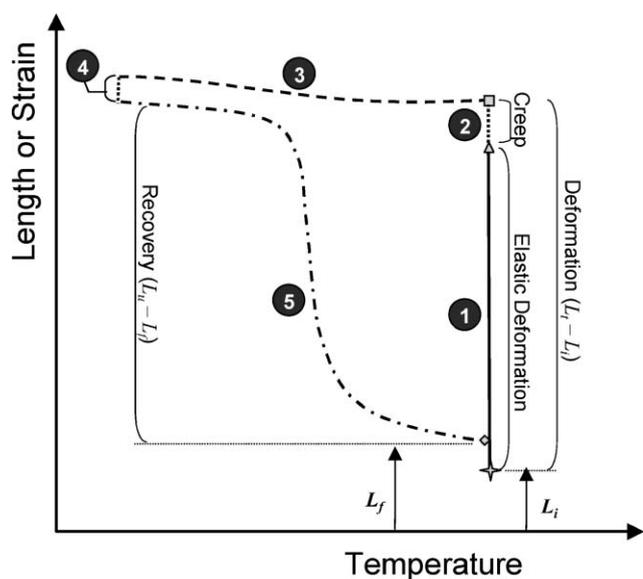
Fig. 6 Anatomy of a shape-memory plot. $L_i$ = initial length, $L_t$ = temporary length, $L_u$ = unloaded length, and $L_f$ = final recovered length. In step 1, a sample is stretched to a certain stress at a constant stress rate and a temperature of $T_{\text{Tran}} + 20\ ^\circ C$. In step 2, the sample is kept at the stress for a time to reveal any creep. In step 3, the stretched sample is then fixed by cooling down to $T_{\text{Tran}} - 20\ ^\circ C$, at a constant cooling rate under constant stress. In step 4, the stress is released and a length shrinkage observed. In step 5, the sample is finally heated to $T_{\text{Tran}} + 20\ ^\circ C$ at a constant heating rate of $2\ ^\circ C\ \text{min}^{-1}$ and prescribed stress and the shape recovery with the heating profile recorded.

Beginning at the point denoted with a star, a sample is first loaded from a small preload to certain stress at a constant stress rate and a temperature of $T_{\text{tran}} + 20\ ^\circ C$. This is indicated by (1) in Fig. 6. The sample is then kept at this stress for a period of time until equilibrium to reveal any creep ((2) in the graph). The stretched sample is then cooled down to $T_{\text{tran}} - 20\ ^\circ C$, at a constant cooling rate, (3), under the stress. Following equilibration, the stress is then released, (4), and a length shrinkage (if any) is observed. The sample is finally heated to $T_{\text{Tran}} + 20\ ^\circ C$ at a constant heating rate (we recommend $2\ ^\circ C\ \text{min}^{-1}$) and the prescribed stress (usually negligible compared with the maximum stress) and shape-recovery profile upon heating recorded, (5). Besides conventional visual comparison of the shape fixing and shape-recovery extents by inspection, we define shape fixing with reference to Fig. 6 as:

$$R_f = (L_u - L_i)/(L_t - L_i) \times 100\% \qquad (2)$$

and shape recovery as:

$$R_r = (L_u - L_f)/(L_t - L_i) \times 100\% \qquad (3)$$

where $L_i$ = initial length, $L_t$ = temporary length, $L_u$ = unloaded length, and $L_f$ = final recovered length.

Besides defining the extent of fixing and recovery, each being its own figure-of-merit, we also define a more inclusive figure-of-merit, termed "shape-memory fill-factor", allowing classification of shape-memory materials into five types,
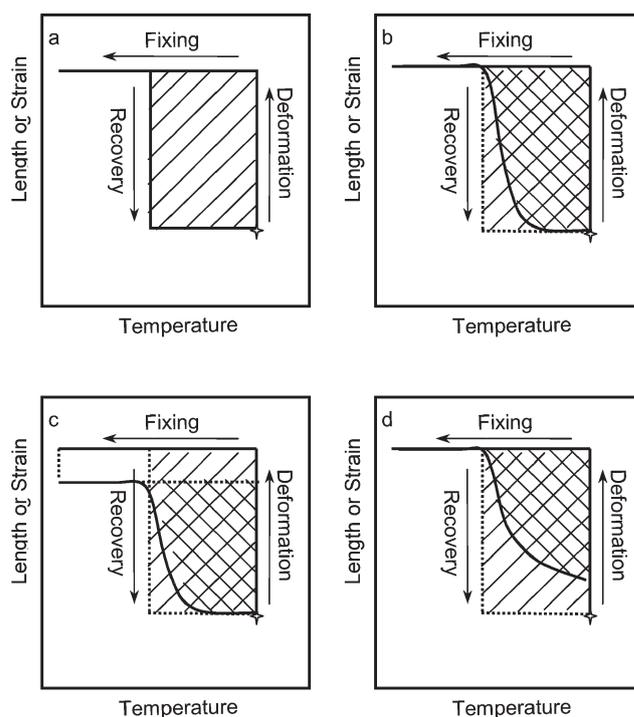


Fig. 7 Classifications of shape-memory polymers by their shape-fixing and shape-recovery abilities. (a) Ideal shape-memory material; (b) shape-memory material with excellent shape fixing and shape recovery; (c) shape-memory material with excellent shape recovery but poor shape fixing; (d) shape-memory material with attractive shape fixing but poor shape recovery. The fill factor is defined as: $f_{\text{sm}} = A_{\text{cross-hatch}}/A_{\text{ideal}}$.

according to performance, as shown in Fig. 7. The five classes of shape-memory materials are: (a) ideal shape-memory material; (b) shape-memory material with excellent shape fixing and shape recovery but finite sharpness; (c) shape-memory material with excellent shape recovery but poor shape fixing; (d) shape-memory material with attractive shape fixing but poor shape recovery; and (e) shape-memory material with both poor shape fixing and shape recovery (Figure not shown). We define a fill factor, $f_m$, as the ratio of the cross-hatched $L$–$T$ (or strain-$T$) areas to the hatched $L$–$T$ area of the ideal (a) case as an overall figure of merit for shape-memory materials. An ideal shape-memory polymer, with the same work ability as work input, thus has a $f_m \equiv 1.0$, while an extremely poorly fixed sample, such as a rubber band without any shape-fixing ability and hence no shape recovery occurring later, has a $f_m \equiv 0$. A realistic "good" shape-memory polymer demonstrates a fill factor of about 0.5. Several points bear mentioning at this stage. First, measurements of $f_m$ are sensitive to selection of temperature limits and care should be taken to do so consistently. Second, a higher fill factor is not necessarily a better solution for a particular application of SMPs. For example, if a slow, prolonged recovery event is needed then the response shown schematically in Fig. 7(b) would be better than that of Fig. 7(a), i.e. a lower $f_m$ would be better.

As a demonstration of shape-memory fill-factor analysis, the shape-memory cycle of a class I shape-memory polymer[59] was performed as indicated in the experimental section (Fig. 8). At
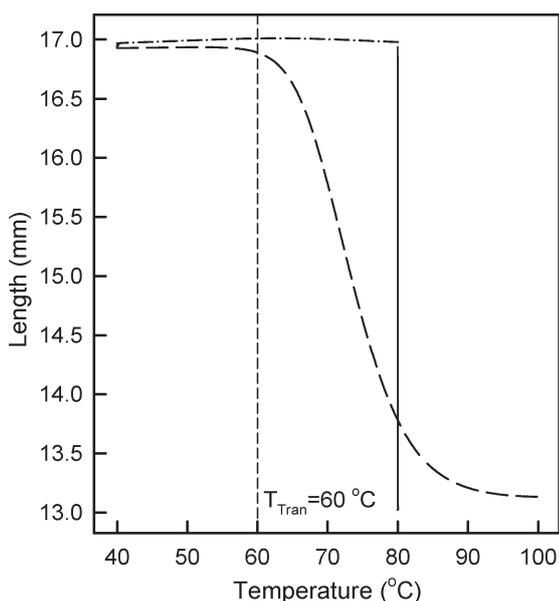
**Fig. 8** Shape-memory cycle of a class I shape-memory polymer. This SMP has excellent shape fixing and shape recovery, but has a slow recovery speed. Its fill factor calculated using the above equation is 0.344.

80 °C ($T_{\text{Tran}}$ + 20 °C), the sample was loaded to a stress of 300 MPa at a constant stress rate of 0.01 MPa min$^{-1}$, leading to a strain of 31%. An almost linear stress–strain relationship was obtained, indicating good elasticity of the material. Isostress holding at the maximum load led only to a slightly higher strain (1%), which is commonly observed for "real" elastomers. Cooling at the rubbery stage leads to some shrinkage under constant stress, probably due to an increase of the rubbery modulus.

Subsequently unloading at 40 °C ($T_{\text{tran}}$ − 20 °C) led to no observable strain loss, indicating that the shape fixing is complete when fully vitrified below the glass transition. The subsequent heating to 80 °C at a heating rate of 2 °C min$^{-1}$ leads to a broad shape recovery beginning at 60 °C, with the recovery being somewhat sluggish and not complete at 80 °C. The fill factor was calculated according to Fig. 6 and the result is 0.344. Further heating to $T = 100$ °C led to quite complete shape recovery. By comparison, a shape-memory elastomer with a demonstrated high shape recovery speed of within 1 s in hot water ($T = 70$ °C), as illustrated in our previous paper,[1] shows a relatively high fill factor of 0.647.

The concept of fill factor provides an additional and more quantitative way to distinguish the performance of shape-memory polymers. However, in this concept, slow recovery was not well differentiated from incomplete recovery. The former could be misinterpreted as the latter if data acquisition stopped at deformation temperature, that is, $T_{\text{tran}}$ + 20 °C. Care must be taken when utilizing this concept to evaluate a SMP whose shape recovery speed is not a concern, or slow shape recovery is preferred. Another factor that might affect the fill factor is the strain; similar strains are essential for meaningful comparison, since different strains usually yield different extent and speed of shape recovery.

## 3. Applications of shape-memory polymers

Since shape-memory effects in polymeric materials were first discovered, many applications have been developed for these unique materials that allow triggered responses. Besides traditional applications such as heat shrinkable tapes and tubes made with radiation-cross-linked polyethylene, these materials have also been used for information storage that can allow thermally reversible recording,[157–160] temperature sensors,[161–164] and actuators.[165–168] However, our literature search found that recent applications are mainly focused on medical areas, such as biodegradable sutures,[30,156] actuators,[43,49,50,166,169] catheters, and smart stents.[42,170] We have elaborated orthodontic applications[171,172] of class I and class II SMPs, focusing on devices that simplify ligation and other time-intensive orthodontic procedures. The medical applications of shape-memory polymers are of great interest due to a combination of biocompatibility with their wide range of tunable stiffness ($0.01 < E < 3$ GPa), tailorable transition temperatures with sharp transition zones, fast actuation, large shape deformation and complete recovery, and elastic properties of the materials. A. Lendlein and R. Langer fabricated a self-tightenable biodegradable suture from a biodegradable shape-memory thermoplastic monofilament fiber.[156] This fiber was extruded through a 1 mm rod die, prestretched above the critical temperature, and fixed to a stretched temporary shape by cooling below its critical temperature. When used, the suture can be loosely connected and then heated above critical temperature to trigger the shape recovery and tighten the suture. A series of snapshots were presented in their paper, showing that at 40 °C, only 20 s were required to completely tighten this suture (Fig. 9a). An additional set of experiments was performed to test the feasibility of this concept by extruding some monofilaments out of this material, sterilizing them, stretching under sterile conditions at controlled stress, and subsequent thermal quenching to fix the temporary shape. Such programmed sutures were then loosely stitched through incized rat belly tissue and the abdominal muscle. When heated to 41 °C, shape recovery was triggered and the suture tightened by itself (Fig. 9b). The authors claim that when stretched to 200%, an impressive force of 1.6 N could be generated upon shape recovery. Another example of a biomedical application is a microactuator made from an injection-molded shape-memory thermoset polyurethane that was used to remove blood vessel clots.[166] The permanent shape of the SMP microactuator was a cone-shape coil, which could be elongated to a straight wire and fixed before surgery. The wire was then delivered distally to an occlusion through a catheter, where triggering the shape recovery using optical heating restored the original coil shape. After thermal triggering, both the microactuator and the thrombus could be removed from the vessel, restoring the blood flow. Further work on new materials and experimental models have appeared recently.[49,50] In our own group, we are also constructing medical devices and implants with shape-memory abilities and enjoying significant progress in collaboration with industrial research sponsors and support of the US federal funding agencies. Further work is being directed toward biocompatibility testing and commercialization.
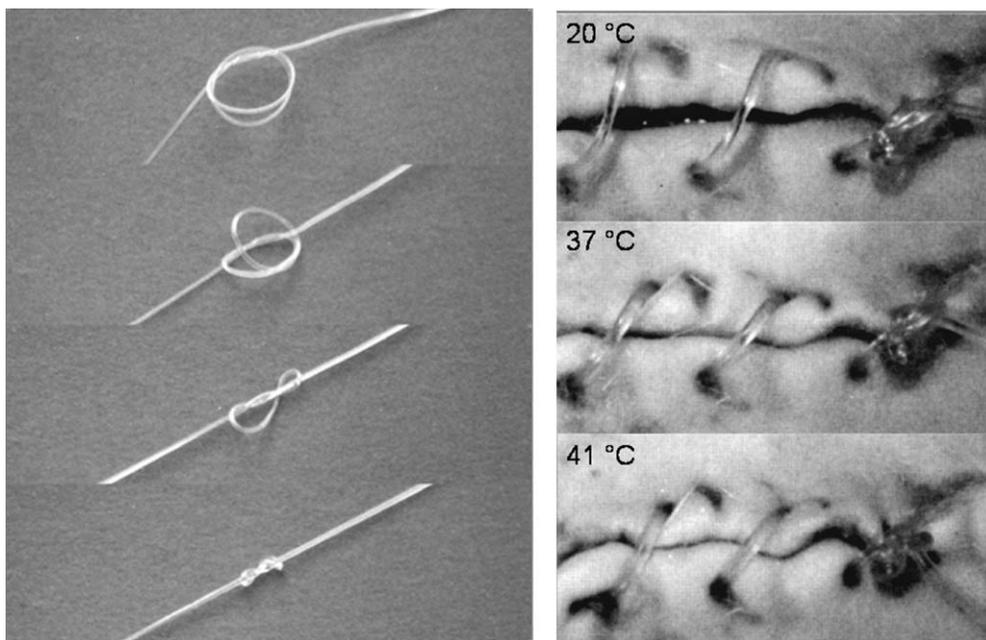
**Fig. 9** (a) A smart surgical suture self-tightening at elevated temperatures (left). A thermoplastic shape-memory polymer fiber was programmed by stretching to about 200% at a high temperature and fixing the temporary shape by cooling. After forming a loose knot, both ends of the suture were fixed. The photo series shows, from top to bottom, how the knot tightened in 20 s when heated to 40°C. (b) Degradable shape-memory suture for wound closure (right). The photo series from the animal experiment shows (top to bottom) the shrinkage of the fiber while the temperature increases from 20 to 41 °C. Adapted with permission from reference 156.

## 4. Future outlook

The research regarding shape-memory polymers continues its rapid growth, with present efforts divided between enabling technologies (materials, processes, and techniques) and application identification and prototyping. On the enabling front, there are an increasing number of reports discovering novel recovery trigger mechanisms other than external heating. Examples include photo,[35,153,154,173] magnetic[174] and humidity.[112,175] In another example, one of us has conceived a mechanically-activated shape-memory device,[176] where the exothermic heat from crystallization of a supercooled liquid held within a SMP container is transferred to the SMP to stimulate shape recovery. While some of these non-traditional shape-memory approaches are actually still thermally triggered, for example by heat from irradiation or magnetic fields, some are triggered by a change in material properties caused either by the photo-isomerization of the constituent molecules or a plasticizing effect after the material is swollen in water or other media.

Aside from alternative triggering mechanisms, there is also an emerging interest in shape-memory polymers capable of memorizing two or more temporary shapes. At different temperature stages, this kind of SMP can recover in a tandem manner from one shape to another and finally to its original shape. This class of SMP, called ''tandem shape-memory polymer''[177] or "polymeric triple-shape materials"[178] are expected to be capable of providing more complex actuation events and potential for application in biomedical devices or deployable structures.

Driven by their utility in the area of self-actuating biomedical devices, there are an increasing number of research studies focused on the development of biodegradable and/or drug-eluting SMPs. Compared to conventional shape-memory devices, a biodegradable SMP device can negate the need for a consequential surgery to remove the device and a drug-eluting SMP can provide enhanced functionality, such as a significant reduction of restenosis in applications with endovascular stents. Challenges exist, however, mainly with how to incorporate the shape-memory properties, biodegradability, and drug-eluting properties into one material to fulfill the multi-dimensional requirements in modulus, triggering/fixing condition, degree of fixing/recovery, biocompatibility/bio-degradability, drug-eluting kinetics and many other aspects.

Another active SMP application area for the future concerns deployable structures for aircraft and spacecraft applications. Of interest to NASA and the US Air Force Research Laboratory, deployable SMP devices are preferred over their SMA peers due to their light weight. An example of this sort of application could include the hinges of a satellite structure bearing enormous photovoltaic arrays or deployable thin-film structures. These arrays are folded to save storage space during launch and then opened to their full span once deployed into space by shape recovery of the hinges. Compared to other cases, this application demands a steady and well controlled recovery process since an overly fast recovery may vibrate the satellite in space, causing damage. Clearly, the future for SMPs is broad and only limited by the creativity of materials chemists and engineers.

## 5. Summary

This review summarizes the recent developments of the shape-memory polymers in our group and other major research

groups, along with their applications in the medical field. In this paper, a new classification scheme has been adopted based on the mechanisms of shape fixing and shape recovery, and this is further used to organize the review. Also, a new method towards the quantification of the shape-memory ability was proposed, and applications and future outlook of SMPs described.

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