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## Featured Letter

## Click polymerizations: Encouraging route for shape memory polymers



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## ABSTRACT

Shape memory polymers (SMPs) exhibit exceptional capability to memorise their original shape from a temporary shape by responding to a suitable external stimuli such as heat, pH, current, moisture and so on. Of late, click polymerizations are being emerged as a promising synthetic route to realize novel SMPs. This short-review discusses the recent growth observed in the field of SMPs based on copper catalysed azide-alkyne, thiol-ene and Diels-Alder polymerization methods. The merits, challenges and future directions are addressed.

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## 1. Introduction

Shape memory polymers (SMPs) are known for their stimuli-sensitive characteristics which enable them to recover original shape from a temporary shape. They display distinctive ability to respond to external stimuli such as heat, pH, moisture, light and electric/magnetic fields [1–4]. As a smart material, they find use as stents, sutures, artificial joints, scaffolds in biomedical field; self-adjustable apparels in textiles; and as self-deployable antennae in aerospace arena [5–8]. SMPs triggered by heat as stimulus are the most common and the key address is their activation temperature ( $T_{act}$ ) which can be glass transition temperature ( $T_g$ ), melting transition ( $T_m$ ) or weak bonds such as hydrogen bonds (supramolecular SMPs). A general classification of SMPs based on their nature of switching unit can be Type I-thermoset SMPs ( $T_g$  based), Type II- thermoplastic SMPs ( $T_m$  based) and Type III-supramolecular SMPs (H-bond based) (Fig. 1). A macromolecular architecture containing a permanent cross-link (chemical/physical) and a switching segment can exhibit shape memory properties [9,10]. The shape memory potential of an SMP is characterised by two parameters viz: extent of shape fixity ( $S_F$  %) and shape recovery ( $S_R$  %) which can be quantified generally by fold-deploy test. Programming (testing) of shape memory comprises four stages (i) heating above  $T_{act}$ , (ii) application of force to obtain a temporary shape, (iii) fixing of temporary shape by lowering the temperature to  $< T_{act}$  and (iv) recovery of original shape from fixed shape by

heating above  $T_{act}$ . During the shape fixing process, stress or strain energy gets stored in the polymer chains and kinetically trapped (entropy is locked). The entropy trapped in polymer chains is released on applying an external stimulus which facilitates the recovery of original shape [11].

In the past, popular chemistries such as epoxy-amine, isocyanate-hydroxyl, radical polymerizations (e.g. SMP from polystyrene) and epoxy-cyanate reactions were employed in quantum to achieve variety of SMPs [12–14]. These routes are highly successful in realizing thermoplastic and low  $T_{act}$  SMPs which are useful mainly for biomedical applications. Currently, applications of SMPs are extended to high-tech areas like aerospace where high  $T_{act}$ , high mechanical properties and low process temperature are indispensable [15–17]. Thermoset SMPs are the suitable candidates (compared to thermoplastic) for these kind of smart-*cum*-structural applications where durability and high strength are also a matter.

Along with the existing routes, click polymerizations have featured a more optimistic sign in the field of SMPs in its entry itself. Click chemistry, introduced by B. Sharpless and co-workers in 2001, comprises organic heteroatom coupling reactions that follow a set of conditions. Click chemistry deals with a group of reactions which can satisfy the conditions such as rapid kinetics, efficiency, versatility, high functional group tolerance, quantitative conversion and no residual by-products. Generally, these reactions can be carried out at relatively milder experimental conditions. [18]. Diels-Alder, thiol-ene and azide-alkyne cycloaddition reactions are the common click reactions broadly employed in polymer chemistry for synthesising functional polymers, new macromolecular architectures, well defined polymers by combining

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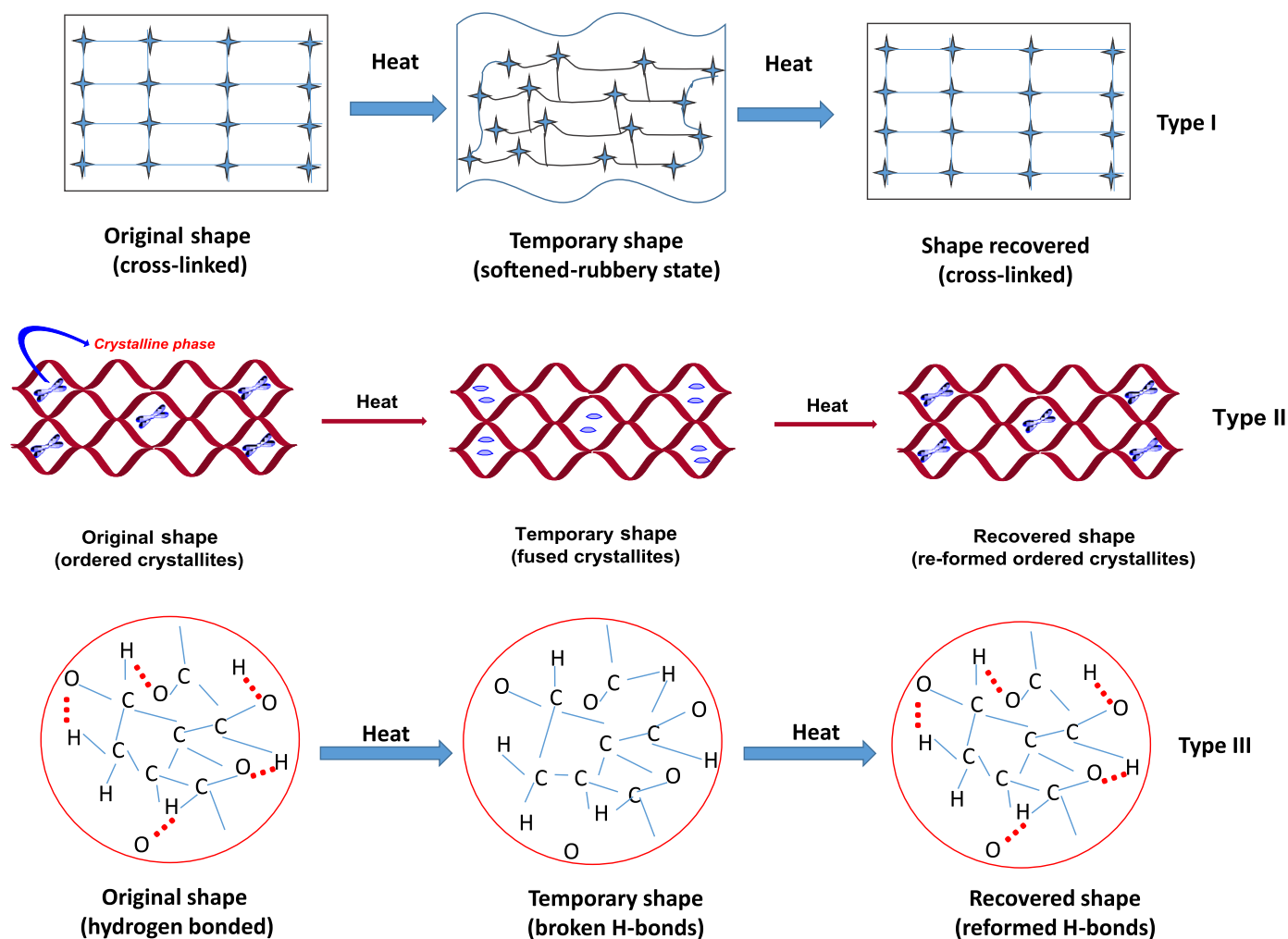


Fig. 1. A general classification of SMPs based on their origin of switching unit; change in macromolecular organization on shape fixing and recovery stages.

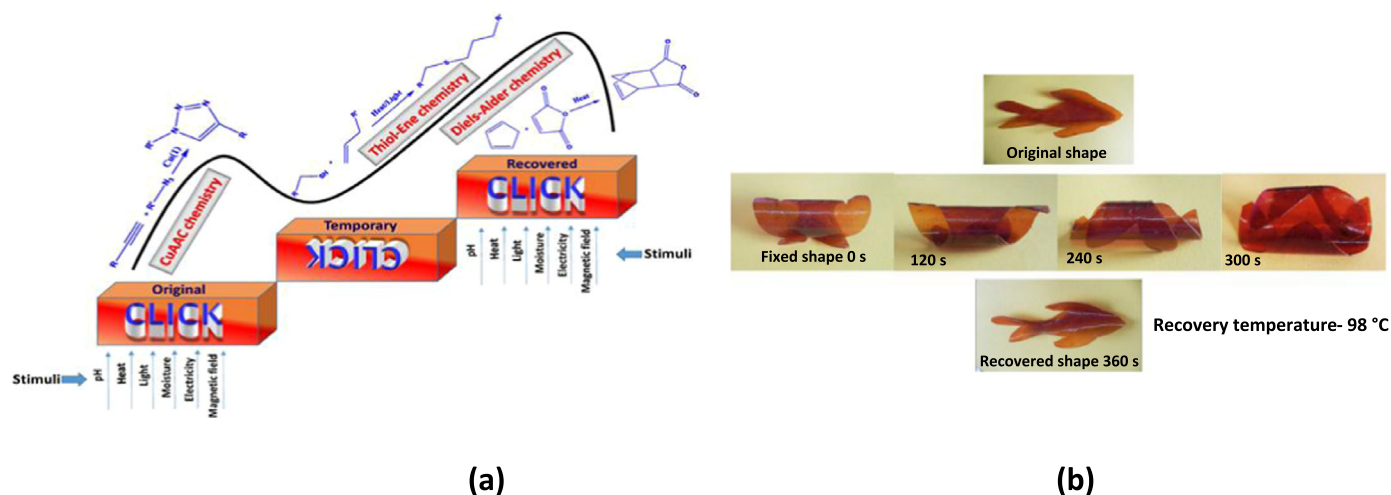


Fig. 2. (a) Typical click polymerizations and schematic representation of shape memory effect (b) shape recovery of an SMP thermoset derived from CuAAC reaction.

atom transfer radical polymerizations (click-ATRP), end-functionalised polymers, smart polymers, surface functionalized polymers, and for coupling polymers [19–27]. Recently, click chemistry is started to utilize for the synthesis of SMPs and this field has witnessed a rapid growth. Rather than coupling different polymers, click monomers are capable to react at moderate polymerization temperature to form cross-linked SMPs. To cite, we

reported an SMP with  $T_{act}$  of 123 °C using copper catalysed azide-alkyne polycycloaddition (CuAAC) where reaction temperature was only about 140 °C [28]. Fig. 2a shows basic click reactions adopted in SMP field and a cartoon of shape memory effect. Fig. 2b demonstrates the shape recovery of an SMP thermoset derived from CuAAC polycycloaddition reaction ( $T_{act}=73$  °C). The well-known Diels-Alder chemistry was the early one utilised for

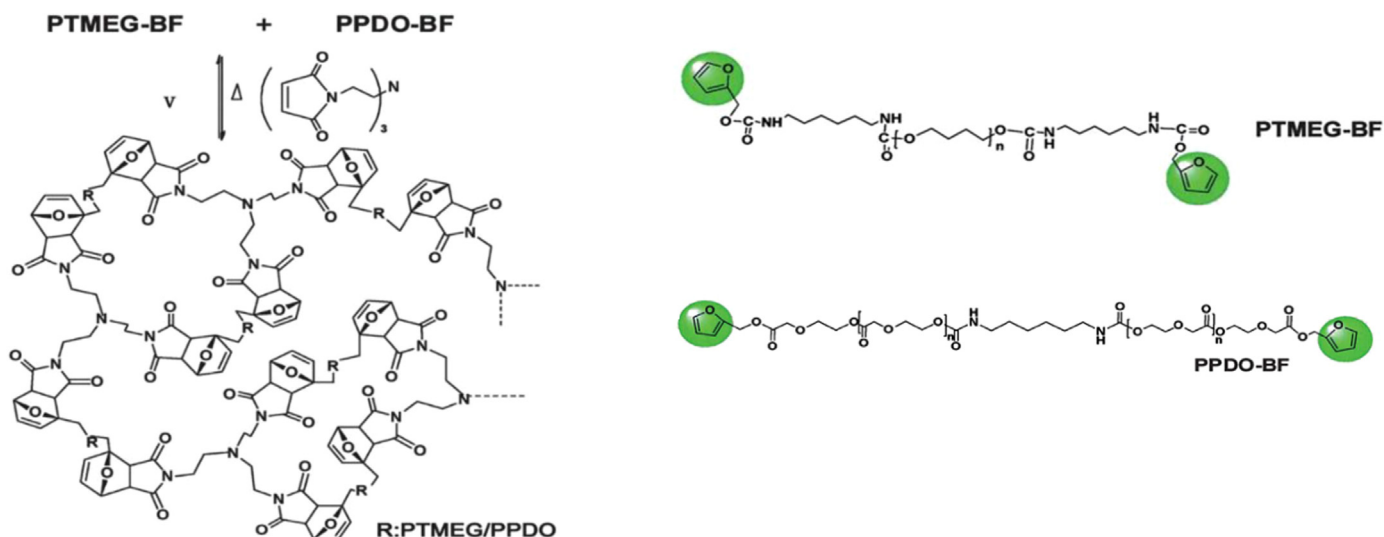


Fig. 3. Triple shape memory with self-healing properties via Diels–Alder chemistry (reproduced with permission from Royal Society of Chemistry, Ref. [34]).

preparing SMPs [29–36]. Later, signature click chemistries *viz*: copper catalysed azide-alkyne (CuAAC) and thiol-ene polymerizations were introduced for designing new SMP architectures [28,37–45].

In this contribution, we present click chemistry as a reliable and efficient route to explore wide variety of SMPs with useful properties. The preparation and shape memory properties of SMPs derived from click methods are reviewed.

## 2. SMPs via Diels-Alder (D-A) polymerizations

Initially, D-A chemistry was used to prepare SMPs. A set of photo-responsive SMPs were prepared by Lendlein and co-workers by using the photo-reversibility of cinnamic acid molecule. The cross-linking and de-chaining of SMP by UV light (above and below 260 nm) conferred shape recovery to polymer [29]. Subsequently, a grafted SMP was prepared from copolymer of *n*-butyl acrylate-hydroxyl ethyl methacrylate and ethylene glycol-1-acrylate-2-cinnamic acid which exhibited shape recovery > 95%, but, a low shape retention capability of < 50% was noticed. Later, furan groups were utilised for generating SMPs *viz*: by crosslinking furan groups of polylactic acid macromonomers (four and six arms) with maleimide moieties,  $T_{act}$  between 50 and 65 °C were achieved. In these SMPs, the shape memory could be erased by heating above 160 °C which is due to retro D-A reaction [30]. The same furan-maleimide cross-linking reaction was carried out on a poly ( $\epsilon$ -caprolactone, PCL) backbone which led to an SMP which was recyclable on account of retro-D-A at 105 °C. The reaction, though was quite easy, the shape retention was low due to the retro D-A even at the shape fixing temperature ( $\sim$ 65 °C). This SMP network displayed shape fixity of 99% (for original and recycled) with memory effect up to four cycles [31]. On comparing the shape memory properties of a star shaped PCL-furan/PCL-maleimide SMP and a star shaped PCL-furan/PCL-anthracene, the former was found to display shape recovery loss in cyclic tests due to the inherent retro-D-A at 65 °C whereas the latter demonstrated good shape recovery due to its thermal stability up to 150 °C [32].

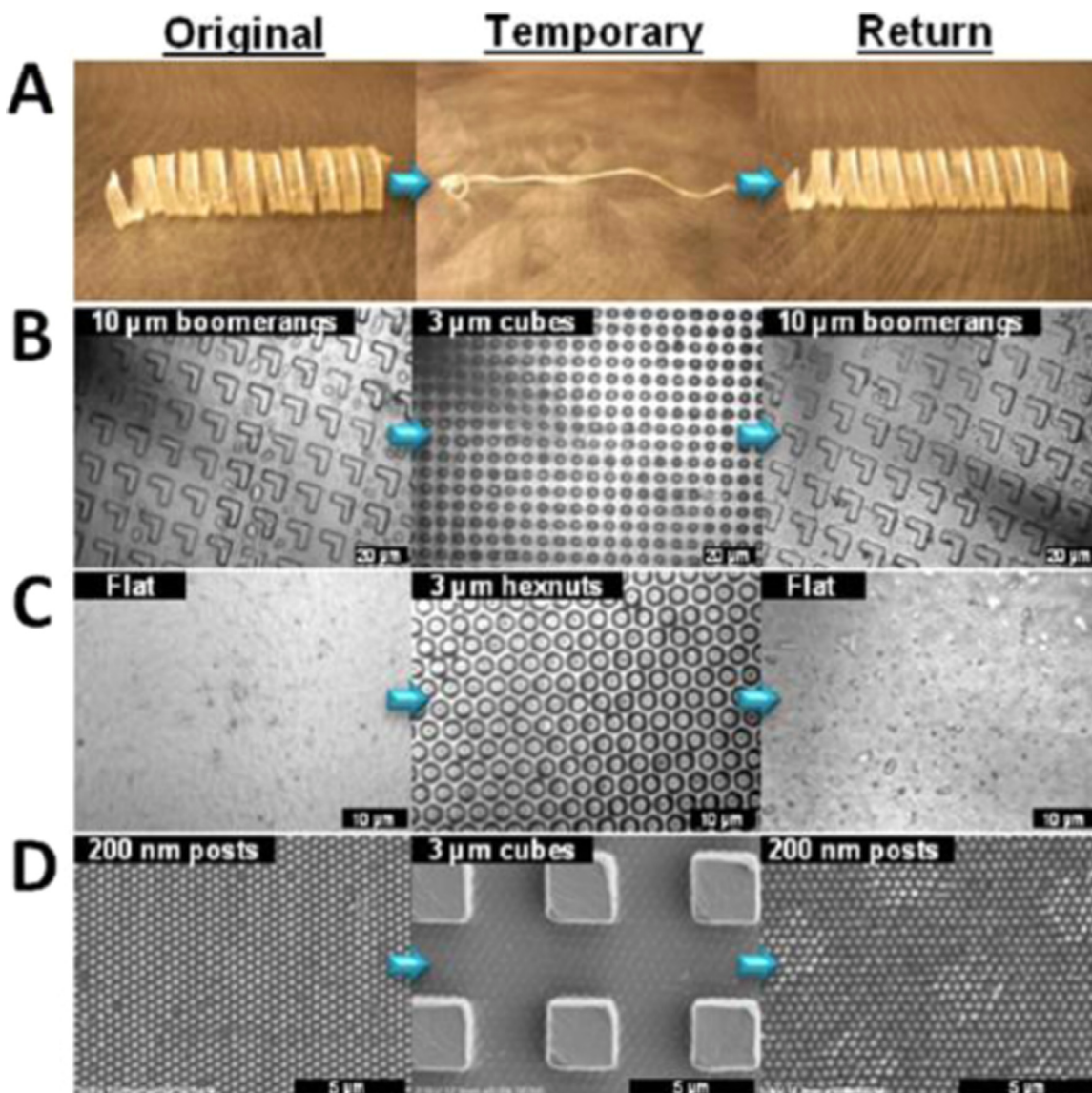
Budhlall et al. prepared biodegradable ABA tri-block SMP by 2+2 polycycloaddition by employing PCL as the central block and cinnamate modified caprolactone as end blocks [33]. This work describes the preparation of SMPs with tunable  $T_{act}$  from 54 °C to human body temperature. These polymers recovered original shape within 44 s with a recovery ratio of 99% and showed a

tensile modulus of 9 MPa with an elongation of  $\sim$ 20%. It is to be noted that, the randomly oriented polymeric architecture of the same backbone could not display any memory properties. In another interesting work, melting  $T_{act}$  was used for designing triple shape memory polymers (TSMs). A mixture of two furan terminated polymers *viz*: bisfuranic terminated poly (tetra methylene oxide) and bisfuranic terminated poly (p-dioxanone) were cross-linked with tris (2-maleimido ethyl) amine at 75 °C which resulted in melting transitions at 25 °C and 103 °C respectively. This SMP exhibited heat-healability owing to retro-D-A at 125 °C, but the healing efficiency was only 75% as indicated in tensile strength studies [34]. The mechanism of this self-healable TSM is shown in Fig. 3. In another work, D-A reaction between poly (furfuryl poly(lactic acid)) and tris (2-maleimidoethyl) amine resulted in a biomass-plastic with recyclable shape memory [35]. As expected, shape memory loss was observed because of retro D-A. Recently, Bettinger and co-workers reported a biodegradable shape memory elastomer from a hyperbranched furan modified polyester precursor which was cross-linked with 1, 1'-methylene (di-4, 1-phenylene) bismaleimide [36]. The actuation temperatures achieved were rather low from –10 to 11.5 °C. This elastomer featured a tensile moduli from 4 to 34 MPa with different degrees of substitution of precursors.

On reviewing the D-A chemistry based SMPs, it is apparent that furan/maleimide cycloaddition system dominates in the literature. We think, SMPs based on D-A chemistry are quite susceptible to reverse D-A reaction in the vicinity of the shape recovery temperature (in most cases) that will eventually reduce the memory retention capability in repeat cycles. These SMPs are highly useful for applications in biomedical field but their high temperature uses are limited.

## 3. SMPs via copper catalysed azide-alkyne (CuAAC) and thiol-ene polymerizations

Though these two click polymerizations were investigated subsequent to D-A, they were utilised extensively for preparing novel SMPs and are highly promising. C.N. Bowman et al. introduced both azide-alkyne and thiol-ene click chemistries to synthesize SMPs for biomedical applications especially to recover shape under physiological conditions. In the first work, they successfully photo polymerised a thiol (trimethylol propane tris 3-mercaptopropionate) and a triene (triallyl-1, 3, 5-triazine-2, 4,

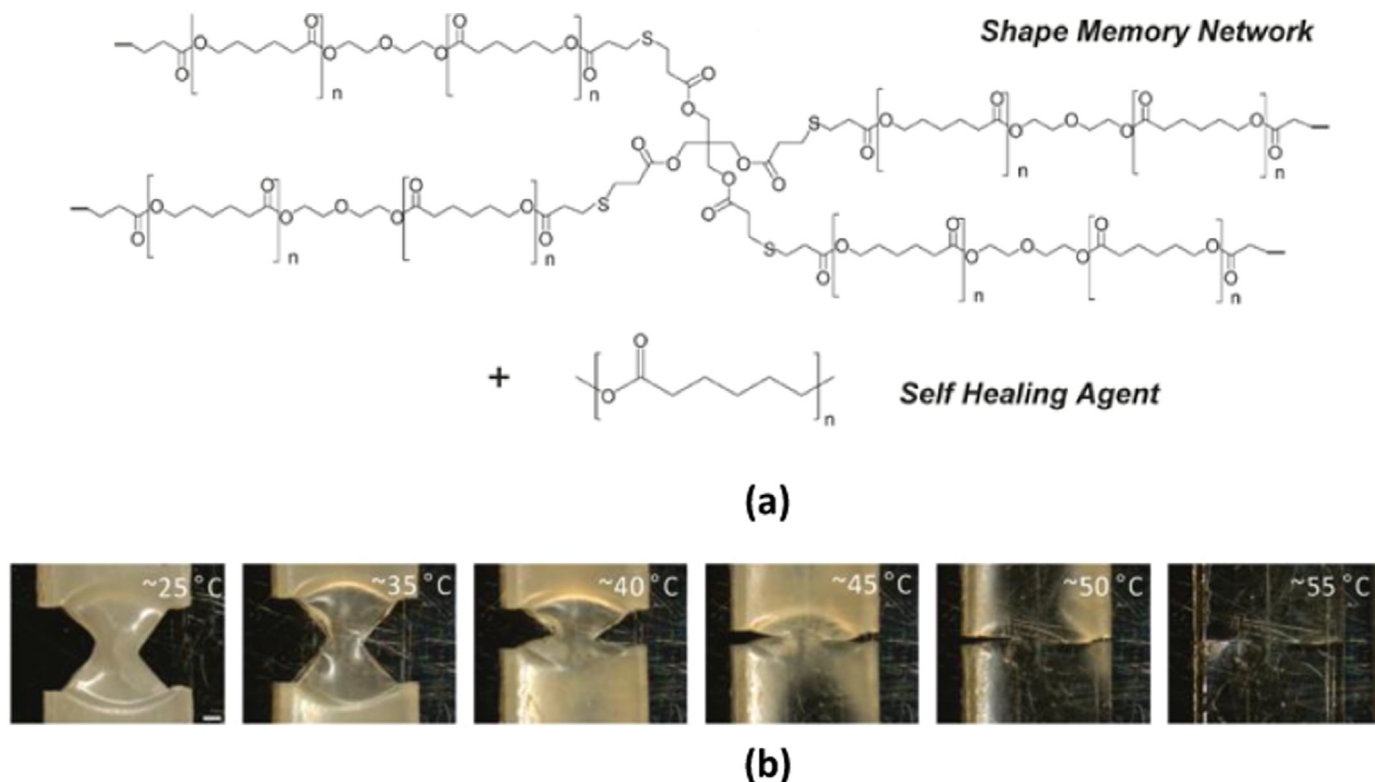


**Fig. 4.** Surface controlled shape memory in azide containing copolyester thermosets (A) Shape recovery of a curly shaped SMP from its wire like temporary shape (3 cm in length, macro-scale shape recovery) (B) micro-scale shape recovery; boomerang shapes to temporary cubes and then back to original boomerangs (C) Flat hexnuts and then return to the flat film (micro-scale shape recovery), and (D) nano-scale shape recovery; SEM images show transition from 200 nm posts to  $3 \times 3 \times 3 \mu\text{m}$  and then back to 200 nm posts (reproduced with permission from American Chemical Society, Ref. no. [39]).

6-trione) via thiol radical - vinyl addition [37]. The resultant SMPs exhibited  $T_{\text{act}}$  between 30 and 40 °C with a glassy moduli between 10 and 63 MPa. They possess unconstrained shape recovery of 96% and constrained recovery of 100%. Our group also carried out CuAAC cross-linking between propargyl novolac oligomer and bisphenol-A (bisazido-hydroxy propyl) ether, which embodied shape memory properties with high elastic ratio (glassy to rubbery modulus) of 34 and  $T_{\text{act}}$  of 73 °C. The rigid triazole rings contribute to shape fixity of > 95% and shape recovery of 90% [38]. Micro/nano level shape memory on surface of SMPs (surface SMPs) was demonstrated by Ashby et al. using click approach [39]. Towards this, functional groups such as propargyl alcohols were attached to the surface via CuAAC and the surface was embossed with different micro/nano shapes. Excellent surface shape recovery was achieved by heating the SMP at  $T_{\text{act}}$  (38 °C). The SEM images also showed high extent of recovery of printed micro/nano structures (Fig. 4). This work demonstrates the capability of click reaction to control the shape memory properties even on surfaces.

Shape memory macrocycles were also developed via click reactions where two different macrocycles were connected by using

a bi-functional click linker like bis (3-azidopropyl) decandioate [40]. The SMP showed shape recovery within minutes after exposure at 40 °C. The physical bonds due to inter- and intra-molecular hydrogen bonding among chains facilitate both shape recovery and retention. The partial breaking of bonds led to folding features at  $T_{\text{act}}$  whereas unbroken physical bonds acted as cross-links. Certainly, these ring polymers are attractive as *inherently self-healing SMPs* (hydrogen bonds can be broken and re-joined on heating). Though the healing efficiency is not so commendable, the study demonstrated well the self-healability of SMPs. Similar to this, shape memory assisted self-healing (SMASH) based on thiol-ene chemistry was demonstrated [41]. Towards that, a polycaprolactone network was embedded with a self-healing agent viz: linear polycaprolactone. At a 50/50 (weight %) composition, the SMP displayed shape recovery of ~92% and shape fixity of ~80%. By heating > 55 °C, the self-healing agent could diffuse into cracks due to the relative movement of polymer chains which eventually healed the cracks (Fig. 5). Recently, we applied CuAAC based cross-linking for preparing polytriazole SMPs using tri-functional azide and bi/tri functional alkyne as monomers. This



**Fig. 5.** (a) Chemical structure of a SMASH polymer where non-reactive poly (caprolactone) was employed as self-healing agent (b) self-healing by thiol-ene polymerization (reproduced with permission from American Chemical Society, Ref. no. [41]).

work illustrates the synthesis of a single cross-linked network containing two independent networks which are bridged well by triazole linkages. The exhibited shape memory was > 95% and repeatable for ten cycles. The hydrogen bonding capability of triazole bridges was also revealed in these SMPs [28].

Bowman et al. developed SMPs with modulus 1.5 GPa by photo-cross-linking acrylate functional polymers via thiol-acrylate polymerization [42]. The shape fixity and shape recovery ratios of all polymer networks were above 95%. Later, a ternary thiol-ene/acrylate thermoset SMP was reported by Taylor Ware et al., which is useful as a substrate for nerve cuff and can undergo shape softening to facilitate shape change in reply to physiological conditions [43]. The polymer recovered original shape at just below 37 °C with a rubbery modulus of 3.6 MPa. The uniqueness of click reactions was illustrated again by synthesising a triple SMP with two  $T_{act}$  segments (at 55 and 10 °C) in one polymeric structure which was prepared by reacting two sets of thiols and acrylates together [44]. They exhibited a storage modulus of 1 GPa and  $S_R$  of 95%. The first shape can be maintained without change at an intermediate temperature (20 °C) for at least 1 h. Very recently, thiol-yne chemistry, a new entrant, shows its potential in generating new SMPs [45]. On polymerizing pentaerythritol tetra-3-mercaptopropionate with bisphenol A di (3-azido-2-hydroxy propan-1-ol) ether (E), an SMP with lower  $T_g$  of 55 °C was achieved whereas  $T_g$  above 100 °C was reached (114 °C) by click reaction between E and 1-(prop-2-ynyloxy)-2,2-bis(prop-2-ynyloxymethyl) butane. The enhanced cross-linking in the SMP facilitated high shape recovery properties too (~ 99%).

The three hallmarking click polymerizations viz: CuAAC, thiol-ene and Diels-Alder were critically discussed. By click route, several SMPs with high shape memory properties, tunable  $T_{act}$  and self-healability have been developed by different research groups. Noting the typical characteristics of the three promising click polymerizations, we believe, CuAAC polyaddition reactions have a

slight edge over other two classes in terms of high functional group tolerance, better thermal stability and hydrogen bonding characteristics of triazole bridges (previously, CuAAC has also been quoted by Sharpless et al. as 'cream of the crop of click chemistries' in the introduction of click chemistry concept).

#### 4. Summary and outlook

The short-review examines the evolution of click chemistry as a powerful tool in the field of shape memory polymers. Click-SMPs inspire the scientific community even with a small fraction of works reported. The shape memory properties, range of actuation temperatures and mechanical properties of click based SMPs are equivalent to forerunner SMPs derived from traditional chemistries. By closely examining the growth of click-SMPs, this route is found to be encouraging as they exhibit low polymerization temperature, wide structure design flexibility and functional group tolerance. The areas such as structure-property relationships, achieving high  $T_{act}$ , high modulus and self-healable SMPs need immediate attention. Other interesting polymers like shape recovery assisted self-peelable adhesives (SRASPA) based on click chemistry can be explored. The authors believe that click polymerizations open new avenues in the field of SMPs and they have to play a vital role in the future.

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