

## 11

## Multi-responsive Polymer Actuators by Thermo-reversible Chemistry

Antoniya Toncheva<sup>1,2</sup>, Loïc Blanc<sup>3</sup>, Pierre Lambert<sup>3</sup>, Philippe Dubois<sup>1</sup>, and Jean-Marie Raquez<sup>1</sup>

<sup>1</sup>University of Mons Laboratory of Polymeric and Composite Materials 23 Place du Parc, Mons 7000, Belgium

<sup>2</sup>Bulgarian Academy of Sciences Laboratory of Bioactive Polymers, Institute of Polymers 103A Akademik G. Bonchev Street, Sofia 1113, Bulgaria

<sup>3</sup>Université Libre de Bruxelles Transfers, Interfaces and Processes Department 50 Avenue F.D. Roosevelt CP 165/67, Brussels 1050, Belgium

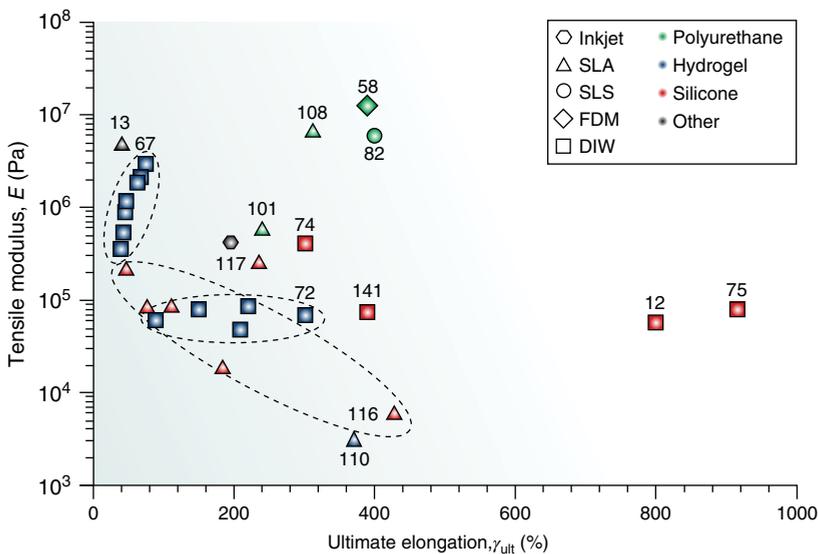
### 11.1 Introduction

From the initial raw materials to the fabrication of a new generation functional polymer devices, chemistry would be playing a crucial role in the discoveries of tomorrow. To define the next wave of innovative directions, material scientists and chemists need to build an efficient collaboration network with various industry partners, process and hardware engineers, and device designers. This network should be well equipped to deal with the transfer from laboratory settings to the industrial scale, in relatively short periods of time, and elevated process yields.

Latest trends in the materials science focus on the design of robotic systems with biomimetic characteristics made from lightweight, low-cost, and high-efficient materials [1]. Generally, such systems must address requirements such as compactness, accuracy, safety, dynamics, and compatibility in specific environments. Naturally, the development of flexible mechanics or soft robotics, where the soft deformable materials being the primary building blocks, are of particular interest [2]. In contrast to conventional robots made of hard materials that limit their ability to elastically deform and adapt their shape to external constraints and obstacles, the soft robots are composed of fluids, gels, functional polymers, and other easily deformable matter. They are also characterized, to large extent, by the same elastic and rheological properties of soft biological matter, allowing the robot to remain operational even as it is stretched and squeezed (e.g. silicone materials). Another advantage of the soft robotic systems is their safety (reduced stress concentration during conformal contacts, continuous motion, and development of low-impact forces), making them safely cooperating with humans and steering through constrained environments [3]. Despite the indisputable advantages (low Young's modulus and high elastic and fatigue resistance values), silicone materials are often produced through molding and casting, and are subject to limit actuating stimuli such as pneumatic

pressure with lack of additional functionalities (self-healing, recyclability, or shape-memory properties), preventing them from becoming true “active matter.” One of the most appropriate candidates for soft robotic fabrication are the polymers due to their high elastic limit to Young’s modulus ratio, lightweight, one- to two-way shape-memory properties, and the possibility to be remotely and reversibly actuated. With the emergence of “smart” polymers, it is becoming easier to convert the chemical energy into mechanical work by enlarging the choice of the actuating stimuli (heat, solvent, humidity, electric-magnetic field, light) [4]. Consequently, the soft actuator deformations (anisotropic shape or volume change) were characterized by reduced friction, wear, and hysteresis, in opposition to the conventional motors (electric motors, combustion engines, and hydraulic pumps) where the motion is generated via changes of relative positions between their components.

Nowadays, polymers are also able to fulfill these requirements while allowing to be printed (Figure 11.1) in devices with complex three-dimensional (3D) geometries and their mechanical characteristics depend directly on the polymer macromolecules architecture (linear, graft, dendrimer-like, etc.). The advantage herein is that by changing the macromolecular architecture it is possible to generate superior supramolecular interactions, explaining why polymers with the same chemical composition can possess variant mechanical properties. However, most of the commercially available polymers cannot respond to any desired structure–processing–property relationship, thus limiting their manufacturing and possible implementation in additive manufacturing (AM) technologies such as 3D printing. A sensible approach toward solving this



**Figure 11.1** General presentation of polymeric materials mechanical properties printed using stereolithography (SLA), selective laser sintering (SLS), fused deposition modeling (FDM), or direct ink write (DIW). Source: Wallin et al. 2018 [2]. Adapted with permission of Springer Nature.

difficulty could be the focus on polymer networks based on thermo-reversible covalent adaptable networks (CANs), for their good processing, recyclability, and actuation upon different environmental stimuli.

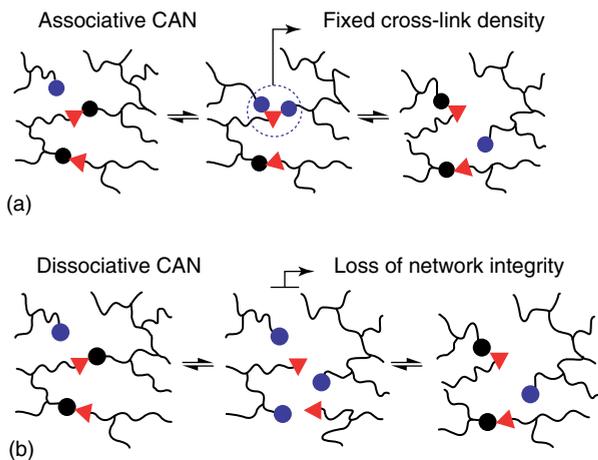
In the present chapter the focus will be on using thermo-reversible CANs as unique strategy for the design and fabrication of smart polymer materials in soft robotics application. A special focus on Diels–Alder (DA) reactions as an excellent way to create the dynamic polymer networks is presented for their high efficiency, selectivity, and versatile approaches in the fabrication of nonconventional polymer architectures and materials topologies. Different aspects in term of materials with shape-memory and self-healing properties, and stimuli-responsiveness have been discussed. A section is dedicated to the latest progress in the field, revealing the great potential of the thermo-reversible chemistry as an elegant solution for fast soft robotics prototyping via 3D printing. At the very end, the reader can find a short list of conclusive remarks on the various trends in the domain, as well as some tips to consider when looking to meet the demands of the constantly evolving AM technologies.

## 11.2 Covalent Adaptive Networks

In the materials world, thermosets find various applications due to their good chemical stability, mechanical properties, and creep resistance. Regardless of these advantages, they cannot be easily reprocessed, reshaped, or recycled, which is limiting their life cycle. To face such a difficulty, scientists proposed a successful approach to increase the materials plasticity through the building of dynamic reversible and exchangeable chemical bonds within the polymer matrix. The advantage here is that such covalent bonds can occur between different locations within the polymer chains, while preserving the material structural integrity and properties. In the literature such polymer networks are known to be defined as CANs [5, 6] and classified into two groups depending on the exchange mechanism: (i) CANs based on associative bond exchange between the macromolecular chains with destruction of the cross-link only when a new covalent bond to another position is build (Figure 11.2a) and (ii) CANs based on dissociative cross-link exchange mechanism, where the cross-link is destroyed and reform at another place (Figure 11.2b).

### 11.2.1 Associative CANs

Generally, in the associative CANs the polymer network is not undergoing depolymerization. The material is maintaining its integrity without any drop of the viscosity state, due to the almost constant level of cross-linking density (the old covalent bonds are only broken when new ones are formed). Such permanent and dynamic state networks were developed at the beginning of 2000s where allyl sulfides were used as photo-mediated free radical reactions [7, 8] or radical generators such as trithiocarbonates [9–11]. Despite of the promising aspects of these networks (flow rate and stress relaxation) their dynamic lifetime is limited mainly because of the radical nature of the involved reactions and the occurrence



**Figure 11.2** Schematic presentation of CAN types, depending on the exchange reactions without or with a temporary net loss of the cross-link density: associative (a) and dissociative (b) CANs. Source: Denissen et al. 2016 [14]. Adapted with permission of RSC.

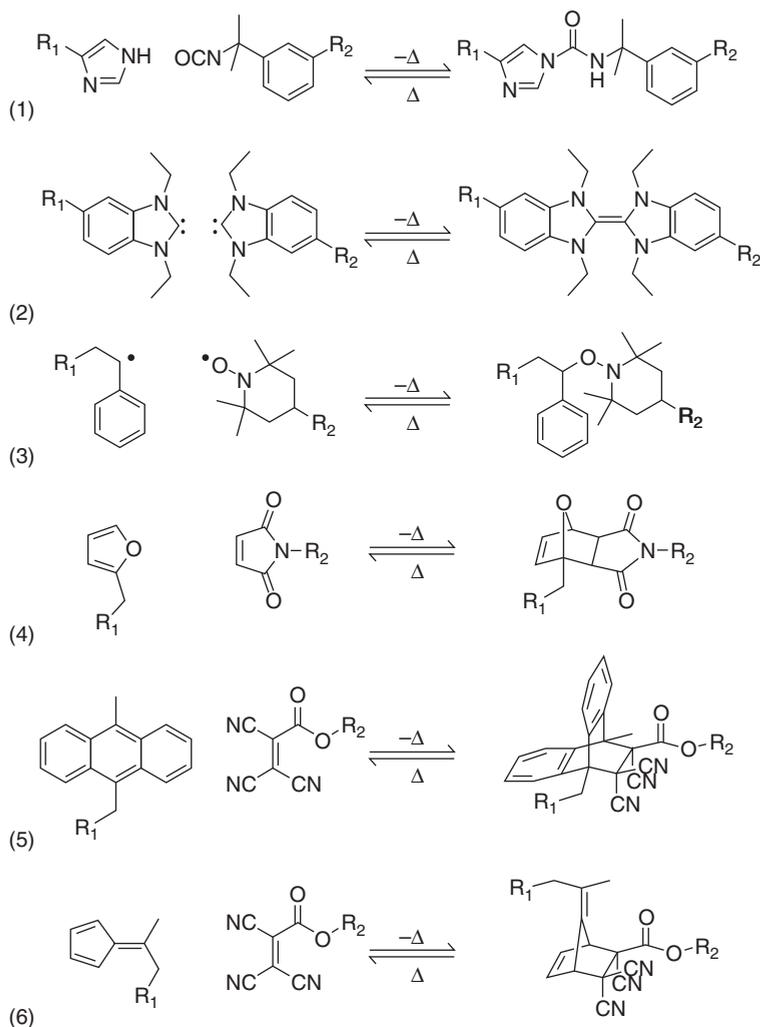
of unavoidable termination reactions. Some efforts were made in the exploration of associative CANs by the development of thermally triggered transesterification catalyst for epoxy/acid or epoxy/anhydride polyester-based networks [12]. Interestingly in the particular case of the permanent polyester/polyol networks a gradual viscosity decrease upon direct heating was observed (Arrhenius law) [13]. This phenomenon gave birth to polymer materials named “vitrimers” [14].

### 11.2.2 Dissociative CANs

Well-explored chemical systems for the design of dissociative CANs are the polymer networks capable of thermo-reversible DA cycloaddition reactions. The thermal reversibility is occurring for temperatures below 50 °C and above 110 °C for complete DA and retro Diels–Alder (rDA) reactions, respectively. DA-based materials easily undergo fast topology rearrangements at high temperatures related to the fast drop in the viscosity values upon heating and the cross-links reform upon cooling while reaching the thermosets characteristics (stiffness and insolubility). Today DA chemistry presents a suitable tool for the development of polymer materials with remarkable dynamic features: shape-memory [15] and self-healing [16] or reconfigurable and recyclable polymer materials [17] with sufficient mechanical properties.

## 11.3 Thermo-reversible Chemistry

In the literature, different thermo-reversible reactions are used as cross-links for the fabrication of dissociative thermo-reversible networks (Figure 11.3). An interesting strategy is the nucleophilic addition reaction (nucleophile with characteristics of good leaving group) for the absence of produced condensate.



**Figure 11.3** A short list of the most applied thermo-reversible reactions for polymer networks production. Source: Kloxin et al. 2010 [5]. Adapted with permission of ACS.

Such systems rely on the reactions of isocyanate with nucleophile (alcohol or amine) under inert conditions (reaction 1 in Figure 11.3) [18]. However, a limitation of these systems is the high moisture sensitivity of the isocyanates restricting the materials practical application. Thermo-reversible reactions can be achieved also by developing ring-opening chemistry – polymer chains carrying maleate [19] or azlactone [20] moieties reacting with bis-alcohol. Somehow, in this case the authors described limited reaction reversibility as a result of the presented various side reactions [21]. In controlled conditions thermally reversible CANs can be produced by a direct dimerization of otherwise oxygen-sensitive carbene (reaction 2 in Figure 11.3) [22]. Active radicals are making also a part of the agents capable of thermo-reversible reactions. One

good candidate is the thermo-reversible homolytic cleavage of the alkoxyamine bond in nitroxide-mediated living/controlled radical polymerizations (reaction 3 in Figure 11.3). This concept was successfully used in studies for networks swollen in monomer solution [23], or to cross-link linear polymers [24]. Here, the main limitation is the bimolecular termination of the active radical, leading to a decrease in the network reversible character.

Thermally reversible CANs can be easily produced by [4+2] cycloaddition (DA cycloaddition reaction) between conjugated diene and an electronically activated compound carrying a double bond (dieneophile). This chemical process might occur in a wide range of temperatures through changes in the macromolecular functional reactivity with relatively low water and oxygen sensibility. Some examples are shown in Figure 11.3 (reactions 4–6), demonstrating the concept of producing thermo-reversible networks from linear or starlike polymers functionalized with bi-, tri-, or more active moieties (e.g. maleimide and furan moieties, cyclopentadiene as cross-linking dimer and others) [25–31]. Practical limitations here are the required high working temperatures to activate the rDA reactions, imparting the formation of irreversible side reactions, as well as the stability of the temperature depending kinetics.

## 11.4 DA Reactions for Thermo-reversible Networks

### 11.4.1 Basic Definitions



**Figure 11.4** General presentation of DA pair involved in thermo-reversible reaction.

Between the previously listed thermo-reversible reactions, DA are among the most common ones used for the synthesis of materials with complex macromolecular architectures and supramolecular interaction. By definition, DA reactions involve [4+2] cycloaddition process between an electron-rich diene (e.g. furan, 1,3 cyclopentadiene, and others) and an electron-poor dienophile (e.g. maleic acid, vinyl ketone, and others) to form a stable cyclohexene adduct (Figure 11.4). The chemical mechanisms were studied in detail by Otto Diels and Kurt Alder who received Nobel Prize in 1950 for their research. DA reactions allow not only the creation of carbon–carbon covalent bonds but also that of heteroatom–heteroatom-type bonds (hetero-Diels–Alder, HDA) widely used synthetically for the preparation of six-membered rings.

### 11.4.2 DA Reactions for Polymer Synthesis

Till date, various strategies have been proposed to produce polymers starting from DA functionalized monomers or oligomers. Some of them deal with the synthesis of homopolymers: (i) linear thermoplastic [32] and thermosetting polymers [33] (polyimides [34–37], polyphenylenes [38–40]); (ii) telechelic polymers [41–43] for macromolecules containing reactive end groups with the capacity to participate in additional polymerization or reactions avoiding

potential cross-linking side reactions; (iii) block copolymers by DA [44] and by HDA [45–47] as an access for more complex macromolecular architectures; (iv) graft copolymers [48]; (v) complex macromolecular architectures applying DA [49, 50] and HDA chemistry [47, 51] for cyclic homo and block copolymers [52]; (vi) dendrimer and dendronized polymers [53, 54]; and (vii) side chain functionalization [55–57] (Figure 11.5). Having in mind all of these possibilities, the idea to build networks based on thermo-reversible DA reaction did not wait to become reality.

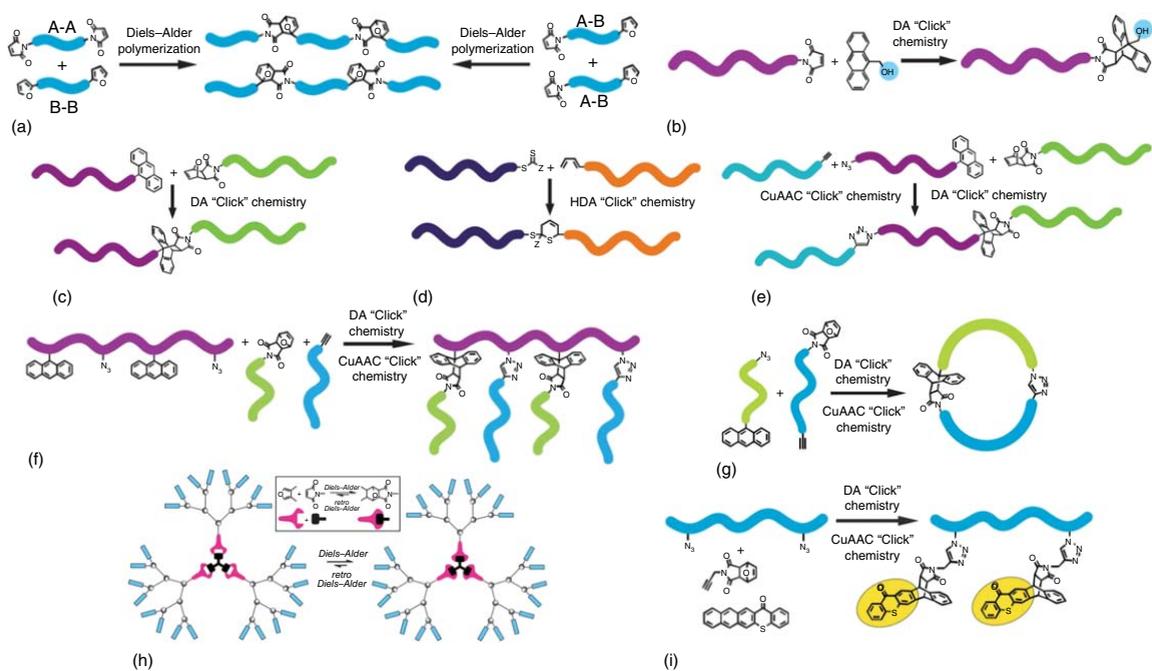
### 11.4.3 DA Reactions for Thermo-reversible Polymer Network

In current materials science, DA reactions have been used as solid tool for the successful synthesis of cross-linked and mendable polymers. Inspired by this progress, smart materials with shape-memory and self-healing properties have been designed with potential applications such as adaptive coatings, actuators, sensors, and devices for soft robotics. Nowadays, three main synthetic strategies are used in the field: (i) direct DA cycloaddition reactions involving multifunctional monomers [35, 59–62], (ii) DA cycloaddition of linear polymers bearing pendant active moieties [25, 29, 31, 63–68], or (iii) cross-linker or initiator containing DA linkage ensuring the polymerization [69, 70] (Figure 11.6). It is precisely the reversible character of the CANs that enables reshaping reversibly the materials to confer them desired initial shapes and to program their life cycle actuation with low degree of fatigue. In the case of the thermo-modulable networks, the rate of the bond rearrangement directly depends on the conversion temperatures situated in the solid-to-liquid transition (static dormant CANs into dynamic activated one) with impact on the time of macromolecules stress relaxation. Taking advantage of these considerations, the focus has been moved to the design of materials with remarkable thermo-adaptive materials exhibiting self-healing properties and biocompatibility (hydrogels).

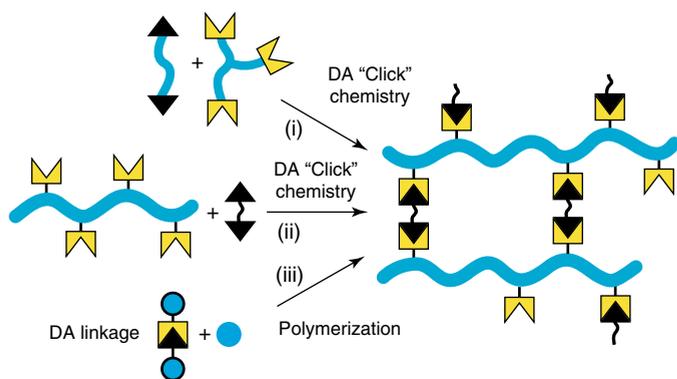
#### 11.4.3.1 Self-healing Materials

From a practical point of view, polymer materials and composites with long lifetime have become a topic of considerable interest inspiring researchers over the world to tackle the problem of restoring damaged materials mechanical properties. Subsequently, two main strategies were defined: (i) production of polymer networks loaded with microcapsules releasing a healing agent upon fracture and (ii) fabrication of reversible CANs activated upon heat, light, or another stimulus.

In the study of Willocq et al. the authors proposed an interesting synthetic pathway for single-component, self-healing polyurethanes (PUs) based on DA chemistry [71]. The polymer matrix was made of thermo-reversible furfuryl and maleimide moieties obtained from 2,2-bis(hydroxymethyl)propionic acid and thermo-responsive monoalcohol coupled with 1,6-hexamethylene diisocyanate and polypropylene glycol. To ensure a good chain mobility for the self-healing processes of importance was the production of amorphous PUs with glass transition temperature ( $T_g$ ) values below the room temperature. The materials demonstrated good post-healing mechanical properties by applying on the samples a load of 250 g representing a shear stress of approximately



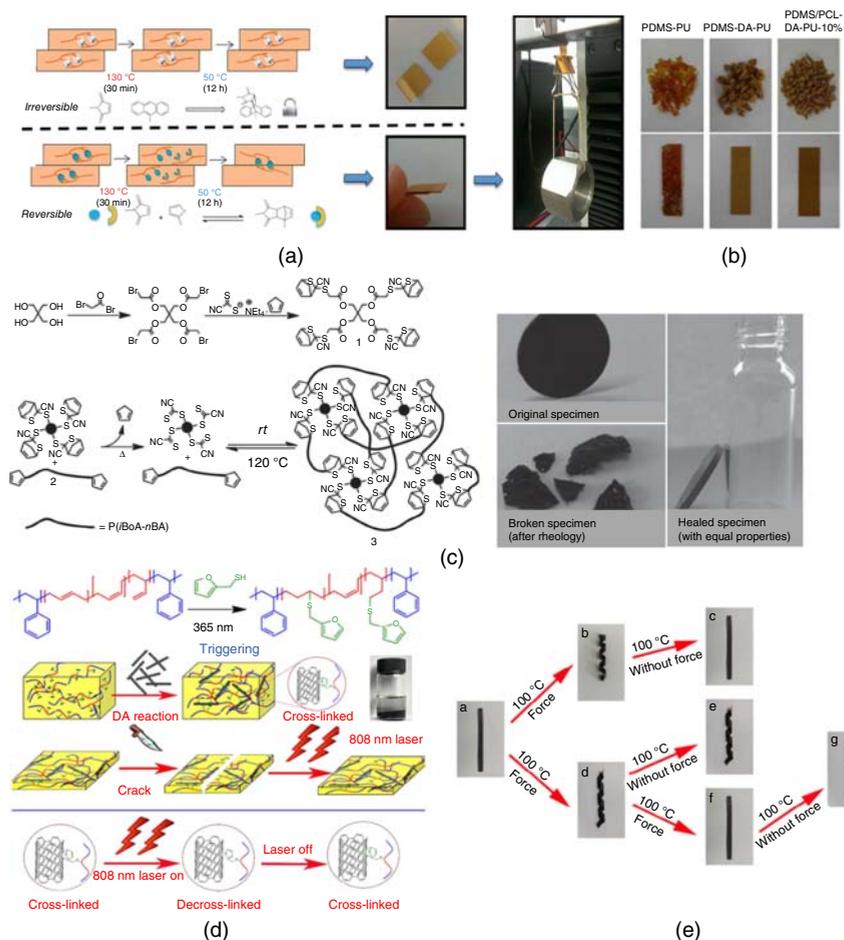
**Figure 11.5** General presentation of the polymerization strategies based on DA chemistry from DA functionalized monomers (a), telechelic polymers (b), DA block copolymers (c), HDA block copolymers (d), triblock copolymers (e), hetero-graft copolymers (f), monomers for cyclic block copolymers (g), dendrimers (h), and side chain DA functionalized polymers (i). Source: Tasdelen et al. 2011 [58]. Adapted with permission of RSC.



**Figure 11.6** Schematic presentation of the generally used strategies for polymer network synthesis by DA cycloaddition reactions. Source: Tasdelen et al. 2011 [58]. Adapted with permission of RSC.

$2.5 \times 10^4$  Pa (Figure 11.7a). It was reported that DA reactions can be used in the improvement of long-time service life of poly(siloxane-urethane) elastomers (PDMS-DA-PU and PDMS/PCL-DA-PU with PCL for poly( $\epsilon$ -caprolactone) and PDMS – polydimethylsiloxane) [72]. In addition, the materials acquired thermal self-healing ability and excellent recyclability, recovering their properties after impact (Figure 11.7b). Despite these advantages, the number of suitable DA pairings occurring at reasonable and at acceptable processable temperatures (below the materials degradation temperature) are barely investigated. Somehow, new directions in this aspect were proposed by Oehlenschlaeger et al., where reversible HDA reactions were developed from activated dithioesters as dienophiles and cyclopentadiene (Cp, slow self-healing kinetics) [73] or cyanodithioester (CDTE, hysteresis-free repetitive cyclability between 40 and 120 °C for less than five minutes) [74]. By combining the CDTE/Cp HDA as multifunctional building blocks it was found that full healing process can be reached in short time at relatively low temperatures. The strategy of the synthesis consists of several steps allowing the protection and deprotection of the C=S-double bond of a tetra-functional linker moiety in order to ensure the DA-based network formation with good healing efficiency and mechanical properties (Figure 11.7c). Such materials can find potential application as adhesives, coatings, or sealants.

The incorporation of nanofillers within the polymer matrix presented also some great perspectives for the generation of multi-responsive materials. Several studies were reported for the synthesis of polymer hybrid materials by DA "click" reactions from organic molecules onto gold nanoparticles [75–77] or tetraethoxysilanes [78, 79]. The cycloaddition reaction between organic and inorganic active moieties was a result of the interactions involving  $\pi$ -electrons of carbon-rich materials (graphene planes of carbon black [80], carbon nanotubes (CNTs) [81–85], or selective modification of fullerenes [46, 86]). For example, CNTs were activated to exhibit DA reactivity within the furan-modified poly(styrene-*block*-butadiene-*block*-styrene) as presented in Figure 11.7d [87].



**Figure 11.7** Polymer systems capable of DA pathways for materials with heat-induced self-healing properties (a), recyclability (b and c), light-induced self-healing (d), and shape memory properties (e). Source: (A) Willocq et al. 2017 [71]. Adapted with permission of RSC. (B) Zhao et al. 2016 [72]. Adapted with permission of RSC. Oehlenschlaeger et al. 2014 [73]. Adapted with permission of John Wiley & Sons. (d and e) Bai and Shi 2017 [87]. Adapted with permission of ACS.

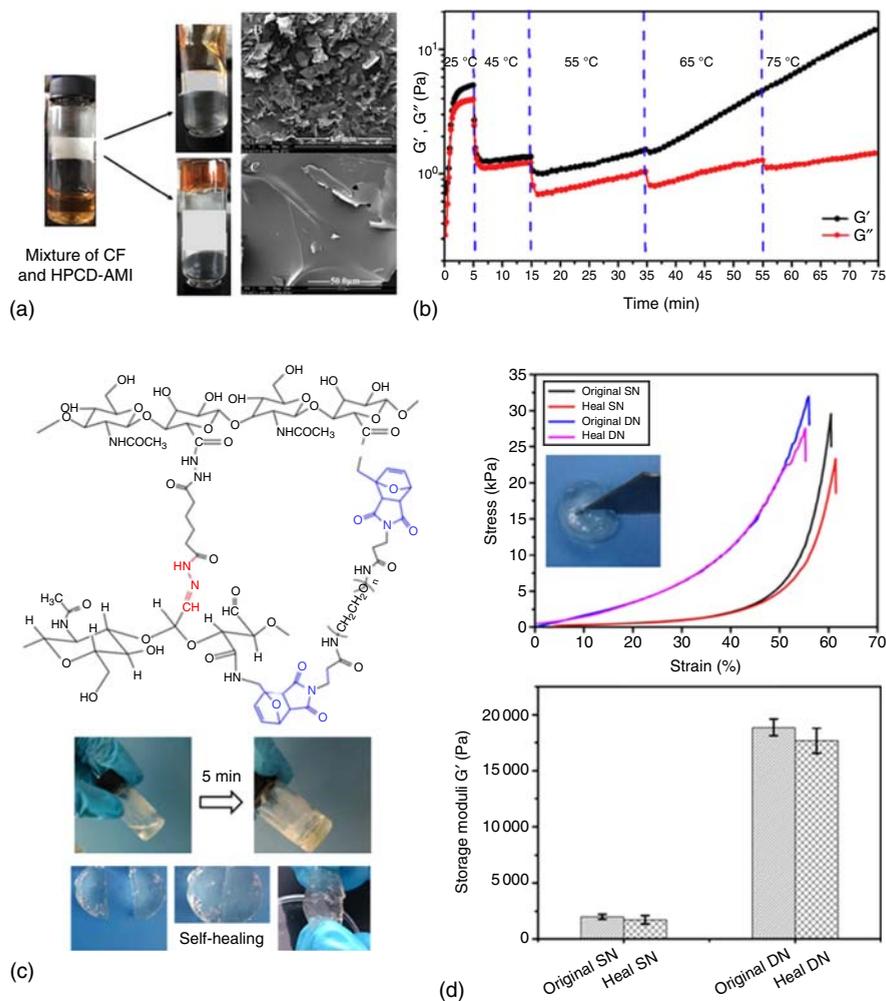
The covalent strategy to incorporate 1 wt% CNT not only increased the materials mechanical properties (16.5 MPa or 9.4 times compared to the stress of the pristine sample) but ensured their homogeneous incorporation resolving the problem with the nanofiller dispersion within the composite material. The system was characterized with excellent recyclability and exhibited self-healing properties. In addition, the nanofiller photothermal effect favor the activation of the rDA by increasing locally the temperature above 200 °C and repairing the surface crack for less than 10 seconds for almost unchanged post-process mechanical properties (Figure 11.7d). Interestingly, this system was subject of successful re-programming offering a possibility to tune locally or remotely the shape-memory effect (Figure 11.7e).

### 11.4.3.2 Hydrogels

Hydrogels, i.e. 3D polymer networks swollen in aqueous solutions, are an interesting type of materials because of their reversible change in volume or shapes upon triggered environmental stimuli such as temperature, pH, and ionic strength [88, 89]. Often, they are made of biocompatible and biodegradable polymers with tunable water absorption and tissue-like architecture. Hydrogels have wide range of applications, such as injectable drug delivery systems, liquid-absorbing wound dressings, scaffolds for tissue engineering, biosensors, food packaging, and many others [90, 91]. Their successful application directly depends on the material cross-linking density, the swelling capacity, mechanical properties, and degradability [92]. Some of the latest progress in this field established that DA cycloaddition reactions are another powerful tool for the hydrogel formation providing mild reaction conditions, absence of initiator or catalyst, tunable gelation rate, and thermal reversibility.

Zhan et al. reported hydrogels-based drug delivery systems from furfural functionalized chitosan and maleimide functionalized hydroxypropyl  $\beta$ -cyclodextrin (CD) as a cross-linker [93]. The CD was used simultaneously as a cross-linking agent and as a key element in the guest–host chemistry for model substances release. The network stability during the gelation process revealed that the  $G'$  and  $G''$  values sharply declined in the mixture and slowly increased in the temperature range between 25 and 45 °C as an evidence of the formation of supramolecular physical hydrogels (Figure 11.8a,b). In contrast, with the increase of the temperature a drop in the elastic modulus with pronounced strength of the hydrogels was noticed due to the formation of the covalent cross-linked network based on the DA reactions. In another study double, cross-linked hydrogel network was prepared by combining DA click reaction and acylhydrazone bond for functional tissue-engineered hydrogel for microenvironment cell survival [94]. The hyaluronic acid networks structural integrity and mechanical strength were maintained by the DA reactions and the dynamic covalent acylhydrazone bond ensured self-healing property by adapting the cross-link density. As presented in Figure 11.8c,d, the materials mechanical properties were well preserved after healing, revealing the effectiveness of the process.

As biomaterials, interesting in vivo injectable thermo-responsive hydrogels were produced from poly(*N,N*-dimethylacrylamide-*co*-furfuryl methacrylate) and *N*-[4-(formyl polyethylene glycol ester)] bismaleimide [95]. The authors underline the possibility to accelerate the DA reactions in aqueous solution and favor the rDA upon immersion of the materials in *N,N*-dimethylformamide. Here, a clear relationship was found between the gelation time and the working temperature: increasing the temperature led to a decrease in the gel fraction. More complex structures were built from starlike polymers. For example, Gregoritz et al. developed hydrogels for controlled antibody delivery by dual approach dealing with both thermal gelation and the DA cross-linking [96]. The starting building blocks were amine-modified four- and eight-armed poloxamines functionalized with maleimide or furyl groups. Once the gel was formed in situ at body temperature the DA reactions gradually took place conferring greater degree of reticulation. Similar cross-linking mechanism were described in the study of Kirchhof et al., where DA reactions were used for the



**Figure 11.8** Examples of hydrogels produced via DA chemistry (a), gel formation procedure upon measuring its mechanical properties (b), hydrogel self-healing properties (c), and post-healing mechanical properties recovery (d). Source: (a and b) Zhang et al. 2018 [93]. Adapted with permission of Elsevier. (c and d) Yu et al. 2015 [94]. Adapted with permission of ACS.

synthesis of four- and eight-arm poly(ethylene glycol)-based hydrogels [92]. The performed rheological tests revealed that the gelation time and mechanical properties depended on the polymer concentration, the branching degree, and the macromonomers molecular weight.

In some cases, the DA-based gelation period is relatively slow (more than 10 minutes) and additional hydrophobic association [97] or branching structures [98] are required. This last point can be easily achieved by using stimuli-responsive polymers activated upon heating exposure, temperature, pH, or ionic strength [98–101]. Such hydrogels forming polymers

are poly(*N*-isopropylacrylamide), poloxamer (Pluronic<sup>®</sup>), and poloxamine (Tetronic<sup>®</sup>) known for their lower critical solution temperature (reduction in solubility above a certain temperature) [102].

While focusing on the advantages of the thermally triggered CANs chemistry and effectiveness of production, another critical consideration must be taken into account regarding their practical application. In general aspect, DA-based CANs should respond simultaneously to sufficient mechanical properties at room temperature and be dynamic in thermal range above 100 °C. This limit the application to only high thermally stable systems. In this aspect, alternative solution can be found in the combination of the shape-memory polymers (SMPs) and the thermo-sensible systems, where CANs will serve as skeleton ensuring the polymers permanent domain. Here the great advantage is that the material  $T_g$  and melting temperature ( $T_m$ ) can be modulated with respect to the network architecture, cross-linking points, and the molar mass of the building oligomers/polymers.

## 11.5 Soft Actuators

In materials science, latest trends show an increased interest in the fabrication of materials with complex deployable structures and functionalities described as actuators. Generally, they are made of materials capable of reversibly changing their shape and size in response to various stimuli. Among potential applications of such actuators, one can mention sensors, artificial muscles, controlled encapsulation/delivery systems, or biomimetic actuating systems as well as soft robots [103]. Basically, the function of an actuator is to provide mechanical energy (force and displacement) along different degrees of freedom (contraction, bending, torsion, expansion, swelling, etc.). It is usually centered on preexisting anisotropic structuration in the material (gradient-like structure, bilayer with different cross-links, and rigidity) responsible for the system expansion, contraction, or bending upon appropriate stimulation (compressed air, remote light irradiation, direct heating, solvent exposure, etc.). The range of actuation depends on the properties of each component with the relative thermal expansion coefficients, swelling abilities, layer thickness, and size. Among many, actuators based on SMPs are very promising, since they are able to memorize their original shape, to acquire a metastable temporary configuration upon deformation (even with large strains), and to revert to the permanent shape when exposed to an appropriate stimulus. The ability of the material to achieve shape recovery from the fixed temporary shape to the initial one is defined as shape-memory effect. This property can be quantified using the shape fixity ratio ( $R_f$ , Eq. (11.1)) or the ability of the material to fix the temporary shape and the shape-recovery ratio ( $R_r$ , Eq. (11.2)), which represents the extent to revert to the original shape.

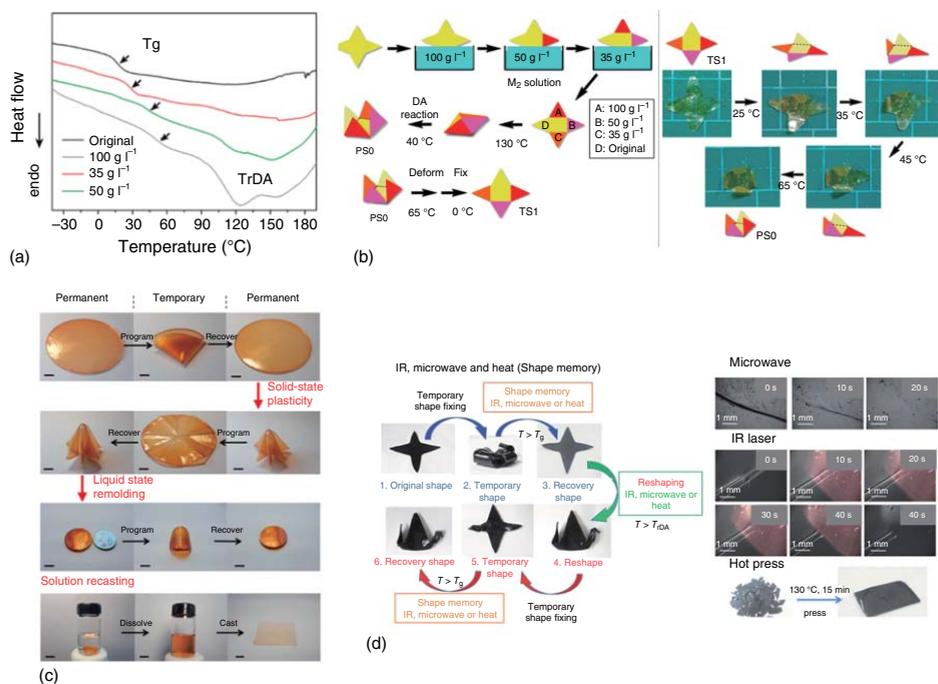
$$R_f = \epsilon_{un} / \epsilon_{ext} \quad (11.1)$$

$$R_r = (\epsilon_{un} - \epsilon_f) / \epsilon_{un} \quad (11.2)$$

where  $\epsilon_{\text{un}}$  is the strain directly obtained before constant loading was released and  $\epsilon_{\text{f}}$  is the strain obtained directly after cooling and unloading, and  $\epsilon_{\text{ext}}$  is the strain after heating in the recovery step.

Usually, the major actuation is directly related to the thermal transitions ( $T_{\text{g}}$  for amorphous regions mobility or  $T_{\text{m}}$  for crystalline phase melting) of the polymeric matrix, but sometimes other stimuli (solvent, vapor, illumination, electro-magnetic field, and others) can be also used after incorporation of nanostructured fillers (cellulose nanocrystals (CNCs), metal oxide nanoparticles (NPs), CNTs, and others). In 2011 Raquez et al. reported the synthesis of thermo-reversible cross-linked PCL-based PU networks by reactive extrusion technology [15, 17]. The proposed solution was characterized by having one- and two-way shape-memory properties as a result of the cycloaddition reaction between furan and maleimide moieties, enabling the final control of the microstructure. The PCL-based PU matrix was made out of linear furfuryl-modified  $\alpha,\omega$ -diol PCL coupled with methylene diphenyl 4,4'-diisocyanate and subsequently subjected to DA reactions with *N,N*-phenylenedimaleimide. A key element was the possibility to modulate the cross-linking density by partially replacing the linear PCL diol with starlike one PCL-tetraol with excellent shape-memory properties. With this it was clear that DA can be used as a versatile way to prepare SMP with controllable cross-link density and multi-shape-memory effects. For this purpose films from poly(2,5-furandimethylene succinate) (PFS) and 1,8-bismaleimidotriethyleneglycol (M2) were produced via DA pathways [104]. The quintuple shape-memory effect was demonstrated by star-shaped like PFS/M2 film with four sections each with distinct  $T_{\text{g}}$  ensuring the number of temporary and recovery steps ( $T_{\text{g}}$  transitions created by different cross-linking degree – the higher the cross-linking density the greater the  $T_{\text{g}}$  values; Figure 11.9a). This highly flexible design capability allowed the fabrication of materials with desired mechanical properties with Young's modulus between 20 and 2000 MPa, while selectively actuating the sections (stepwise increase of the activating temperature from 0 °C to 25, 35, 45, and 65 °C Figure 11.9b).

In most of the studies the DA reaction reversibility is dedicated to the design of thermosets that can be liquefied for reprocessing and self-healing, while neglecting their dynamic equilibrium nature. Going in this direction Zhang et al. [105] demonstrated that in addition to their remoldability at the liquid state (temperatures above 110 °C), such thermo-reversible network can undergo plastic deformation in its solid state at intermediate temperatures (60–100 °C) as a result of the occurred dynamic equilibrium making possible the network topological rearrangement. An example for such transformations are presented in Figure 11.9c: (i) classical SMP behavior with deformation and recovery step at 70 °C followed by (ii) sample plastic deformation (100 °C, 30 minutes) to achieve different umbrella-like permanent shape involved in (iii) next shape-memory cycle at higher temperature (140 °C, part of the material was remolded into a coin while maintaining its shape-memory characteristics). With this concept the liquid state remoldability and solid-state plasticity were studied as two distinct yet complementary mechanisms in the manipulation of the SMP permanent shape opening the door to a variety of future applications.



**Figure 11.9** SMP materials produced via DA chemistry: differential scanning calorimetry (DSC) thermograms revealing the possibility to produce materials with different  $T_g$  (a); films with multistep actuation upon direct heating (b); digital images of shape memory films programming, activating, and recovery (c); and IR, microwave, or thermal activation of graphene-containing materials (d). Source: (a and b) Zeng et al. 2014 [104]. Adapted with permission of ACS. (c) Zhang et al. 2016 [105]. Adapted with permission of ACS. (d) Cai et al. 2018 [106]. Adapted with permission of RSC.

DA chemistry was successfully used for the fabrication of nanocomposite such as cross-linked polyacrylonitrile/graphene nanocomposite for materials with multi-responsiveness (IR light, microwave stimulation, and heat) and enhanced mechanical properties [106]. Here the dispersed graphene sheets (<1 wt%) were used as intrinsic thermal sources by converting absorbed environmental IR light/microwave energy to heat. The main challenge was to trigger the  $T_g$  (elasticity-based shape-memory properties) in addition to the rDA reactions ensuring solid-state plasticity through topological network rearrangement of the materials. Digital images of the healing process for different stimuli and material reprocessing are presented in Figure 11.9d.

## 11.6 DA-based SMPs for Soft Robotics Application

Within its perfection Nature often inspires scientists in the development of bio-inspired robotic structures. As discussed, soft robots are almost entirely made out of flexible soft materials, making them suitable for applications in dynamic task environments, including safe human–robot interactions. However, softness comes at a price: the actuators can be affected by cuts, shears, and perforation while executing complex tasks in unpredictable environments. In a recent study, Terryn et al. [107] proposed an interesting solution for self-healing, soft pneumatic actuators made of Jeffamine-based elastomers capable of DA pathways. The authors demonstrated the successful development of self-healing, soft pneumatic hand, gripper, and artificial muscles model (Figure 11.10a). Of importance for the materials practical application were the mechanical properties after several self-healing cycles (30 cycles), which were found to be slightly changed with contraction force values around 15 N, storage and loss modulus of 10 and 1 MPa, respectively (Figure 11.10b) [108].

In our recent studies, we proposed a simple and straightforward approach to produce solvent, vapor, and IR light actuated materials by reactive extrusion technology [109, 110]. These actuators were based on rigidity gradients created in bilayer architectures of reversibly cross-linked PCL networks (PCL diol and tetraol functionalized with furan and maleimide moieties) into which functional nanofillers, i.e. multi-walled CNTs were incorporated. A key element of the bilayer functionality depended on the good adhesion between the layers. Thereby, the produced material instantaneously swells in an anisotropic way due to the rigidity gradient, resulting in reproducible bending actuations for object grabbing and transportation (Figure 11.10c). Additionally, we designed plasmonic silver nanoparticles (AgNPs) grafted onto CNCs as an efficient plasmonic system for fast and remote actuation. Such CNC-*g*-AgNPs “nanorod-like” structures thereby allowed long-distance and strong coupling plasmonic effect between the NPs. This allowed fast photothermal shape-recovery upon non-invasive IR light illumination (at wavelength 780–1400 nm) by transporting objects 500 times the samples weight (Figure 11.10d). The materials could find applications in the realm of soft robotics for remote object transportation or as smart biomaterials such as self-tightening knots with antibacterial properties.



**Figure 11.10** Soft robotic DA-based thermo-reversible networks with self-healing properties (a and b) and for object catching and transportation upon solvent (c) or remote IR light (d) actuation. Source: (a and b) Terryn et al. 2017 [107]. Adapted with permission of Science Robotics. (c) Toncheva et al. 2017 [109]. Adapted with permission of RSC. (d) Toncheva et al. 2018 [110]. Adapted with permission of ACS.

## 11.7 On the Road to 3D Printing

Recent developments in the field of AM technologies have started a new era in polymer materials fabrication. The technological advancement made possible the fast prototyping process with full control of the object structuration, while conferring it precise environmental responsiveness. There are three main AM technologies using polymeric materials including selective laser sintering (starting materials – powders), stereolithography (SLA), and two-photon polymerization (2PP) (polymer solutions) and fused deposition modeling (FDM; polymer melt). While during the conventional SLA and 2PP methods, the polymer solutions undergo photochemical reactions in the presence of photo-initiator with appropriate absorption wavelength window; in the case of the FDM the polymer thermal properties are the prominent. Up to date, a limited number of studies discuss the building of dual networks by combining

photosensible and thermo-reversible chemistry (DA network containing dissolved multiacrylate monomers) applying SLA (Figure 11.11a,b) [111] or for controlling the photoinitiation and thiol–ene reaction for selective conversion of DA adducts into irreversible cross-links through 2PP (Figure 11.11c,d) [112]. In this section the reader's attention is drawn to the FDM technique, as the more explored, solvent-free, and appropriate 3D printing method to be used in the case of thermoplastic systems.

Generally, during an FDM layer-by-layer deposition, the polymer filament is subjected to direct heating through melting and subsequently exposed to several cooling steps. The use of small molecules, monomers or oligomers, capable of thermo-reversible pathways offered new possibilities to produce polymer networks with desired levels of cross-linking [113, 114]. This is giving the advantage not only to produce complex gradient structures, but also the possibility to increase the interfilamentous adhesion through the creation of DA covalent bonds. With this, one more step forward was made in the improvement of the mechanical properties of the printed devices, avoiding their anisotropic behavior problem (applied stress with respect to the printing direction). These aspects were found to have direct impact on the devices mechanical properties and can be improved by applying some thermo-reversible chemistry strategies, where the networks will “de-polymerize” during the print process and re-polymerizes during the cooling phase, solving the weak welding between the printed filaments.

In a recent study, polylactic acid (PLA)-based actuator was designed for object catching and transportation through the polymerization of maleimide moieties and furan-containing mending agent as cross-linkers (Figure 11.12a) [113]. In this case, the degree of interfilamentous adhesion in the final device was additionally increased and the anisotropic mechanical behavior was prevented (strength and toughness end up being improved with 130% and 460%, respectively along the *z*-axis). Self-healing mechanism have been described by Yang et al., with multi-furan monomer and bismaleimide as initial compounds resulting in more than 95% interlayer adhesion [115]. These approaches ensure a good adhesion between the printed filaments, ensuring the controlled producing of 3D-printed parts with desired design, sufficient mechanical properties, and reproducible functionalities.

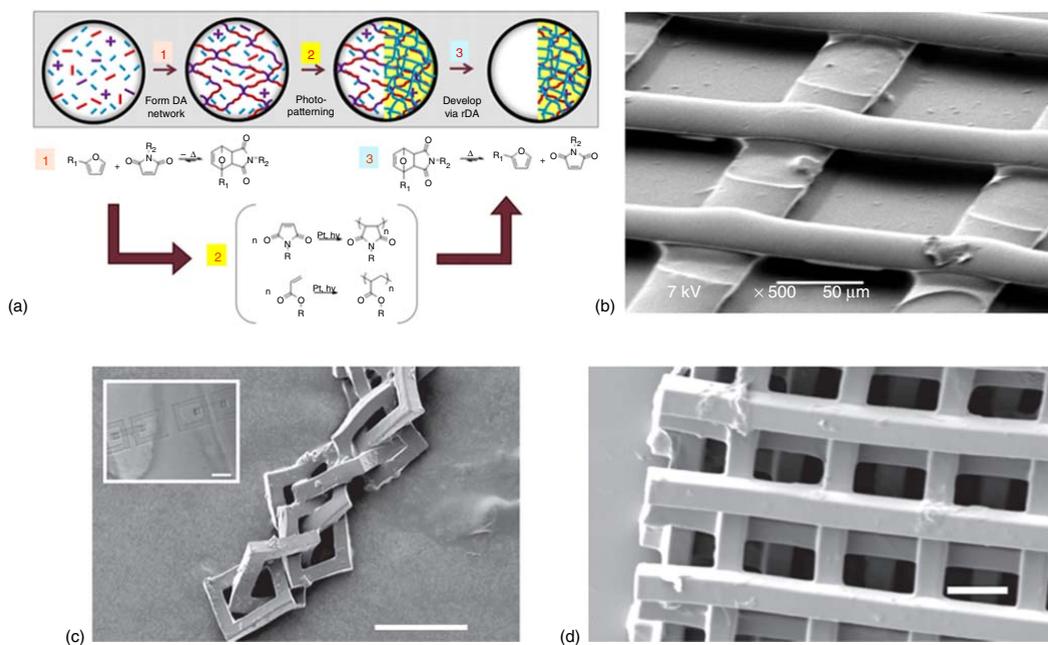
New types of filaments from noncommercially available polymers were also produced from SMP materials. For example, Chen et al. discussed the fabrication of monofilaments from ternary blends between styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene, polyethylene wax, and low-density polyethylene [116]. The smart materials were described with at least three different temporary shapes with specific temperatures (dual, triple, and quadruple heating processes). This gradual shape recovery was explained with the presence of multiple individual melting peaks (heterogeneous microstructuration), offering broad thermally switching transitions. In another study, hydroxyapatite (HA, 15 wt%) was used as nanofiller in 3D SMP filaments [117]. The main role of the HA particles was to reinforce the porous scaffolds acting as nucleation agents on PLA phase, by inhibiting the growth of cracks during compression–heating cycles ensuring the devices self-healing properties. The authors discussed also the feasibility to print personalized scaffolds and implants for self-fitting bone defect replacements

with Rr of 98% and absence of delamination. Additionally, thermally triggered parts can be made from filaments made of an ionomeric thermoplastic SMP-zinc-neutralized poly(ethylene-co-methacrylic acid) [118], by combining two networks: nanodomains with long relaxation times of supramolecular cross-links by ionic bonds (permanent network) and ethylene crystals (temporary network). PU-based filaments ( $T_g$  in the range from 145 to 195 °C) were suitable materials to print parts with complex geometry for actuators capable of catching and transporting objects (Figure 11.12b) [119]. FDM finds also application in the design of light-triggered devices. Therefore, photo-responsive PU-based (nano)composites loaded with carbon black were produced by Yang et al. The materials were characterized with excellent shape-memory properties and photo-thermal conversion efficiency [120]. It was possible to remotely control (light source or sunshine) the printed parts shaped in complex geometric shapes – cubic frame or sunflower-shaped structure (Figure 11.12c). The original shape had a very fast recovery process (within few minutes) due to the excellent photothermal conversion efficiency of the carbon black, revealing the possibility to 3D-print materials as biomimetic solar tracking sensors or smart solar cell systems by FDM.

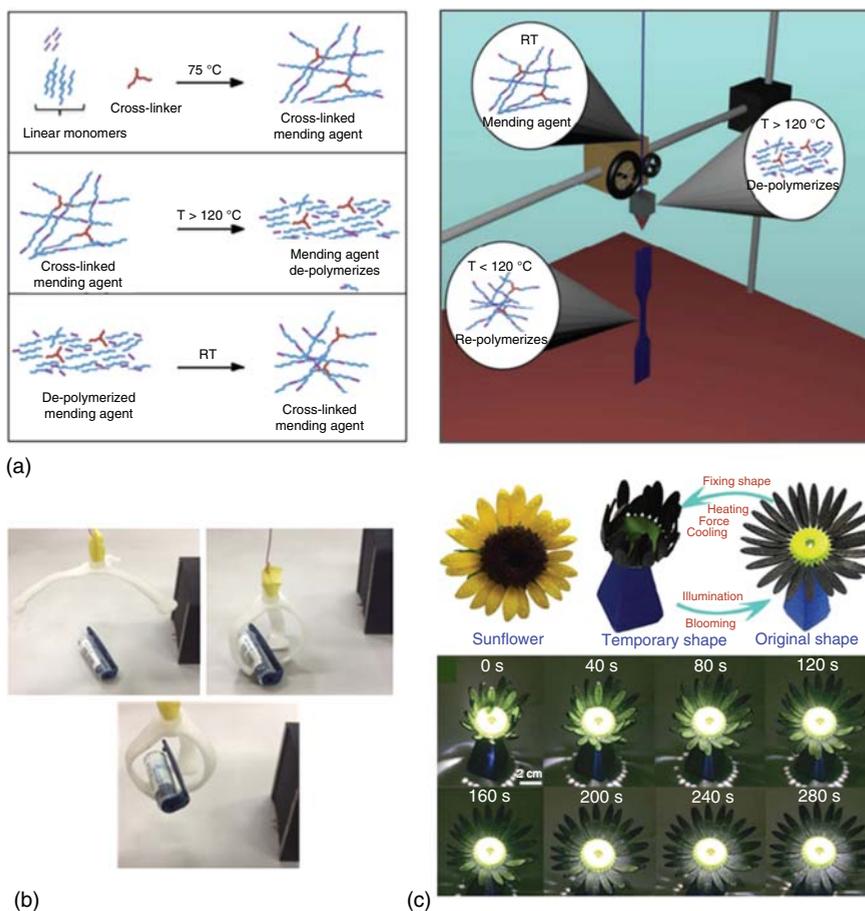
## 11.8 Perspectives and Challenges

Over the past years, DA chemistry has shown significant potential in boosting the creation of the next generation of materials with remarkable macromolecular architectures and composition. Polymer networks with complex geometry, desired mechanical properties, and functionalities (self-healing, recyclability, and stimuli-responsiveness) were therefore produced via 3D printing methodologies. Despite the dynamic perspectives and the already existing applications in soft robotics, some major challenges remain unsolved:

- (i) From a technological point of view, a close collaboration between chemists and mechanical engineers would be crucial for tackling some of the challenges ahead. While currently available 3D printers (particularly FDM) offer the possibility to print commercially available polymers or some custom-made filaments, there are opportunities for improvements in various aspects – the working temperature range, the diameter of the printable filaments, improvement of open source software, increase in printing resolution, increase in the repeatability of the process, and others. For the moment, biomimetic engineering does not always achieve the best technological solution, but it still stimulates scientific curiosity, imagination, and creativity. As the FDM technology is currently showing limitations (the resolution is limited by the size of the nozzle diameter 0.2 mm), the study of smart materials should be extended to other AM technologies.
- (ii) Recently the scientific community released formulas for active inks that can exploit the thermodynamically driven self-assembly of block copolymers and generate the next level of ordered structures. A difficulty to overcome in this field is to maintain the generated assemblies during the 3D printing



**Figure 11.11** DA chemistry for 3D printed objects: dual networks by combining photosensible and thermo-reversible systems applying SLA technique (a) and related SEM micrographs (b). Eight freely rotating rings printed through 2PP (SEM micrographs – 200  $\mu\text{m}$  scale bar, c) and five-layer log pile type structure (40  $\mu\text{m}$  scale bar, d). Source: (a and b) Berg et al. 2014 [111]. Adapted with permission of ACS. (c and d) Adzima et al. 2012 [112]. Adapted with permission of John Wiley & Sons.



**Figure 11.12** Schematic presentation of FDM procedure using DA-activated monomers (a) and digital images of soft robotics devices for object catching and transportation (b) or for light-triggered system (c). Source: (a) Davidson et al. 2016 [113]. Adapted with permission of ACS. (b) Yang et al. [119]. Adapted with permission of Springer Nature. (c) Yang et al. 2017 [120]. Adapted with permission of John Wiley & Sons.

process, as this requires deep understanding of the process thermodynamics, kinetics, phase space, and morphological transitions occurring in the polymer system. On a more practical aspect, during the printing process it is of importance to minimize the occurrence of side reactions and chemical decomposition, while considering the materials application and at acceptable timescale. This creates additional challenges for both chemists and engineers to successfully adjust high temperature activated chemical process for the safety of working environment and protective apparatus conditions. Improvement of the 3D printer parameters in terms of resolution, precise control of the filament melt and multi-head printing (FDM), and greater choice of wavelengths and organic solvents (2PP, SLA,

- bioprinting) will additionally help and inspire the scientific community in the development of new concepts and know-how in the materials making.
- (iii) As discussed in the chapter, DA chemistry has a great potential in solving the problem with the anisotropic mechanical properties of 3D printed parts. However, increasing in situ the interfilamentous adhesion by newly generated covalent bonds might turn out insufficient. Additional posttreatment of the surface by plasma, coatings, nanofillers loading, or solvent vapor exposure could be needed.
  - (iv) Modification of biomolecules via DA “click” chemistry is another possibility that would need further exploration. Some of the studies in this direction are already presenting encouraging results, including increased stability and solubility of the bioconjugates as well as the ability to modulate the protein activity and their bioavailability. The possibility to immobilize oligonucleotides, peptides, and antibodies via DA strategies is also a portal toward interesting therapeutic applications in the field.

## Acknowledgments

A. T. thanks the BEWARE (Belgium Wallonia REsearch, project convention no. 410161) Fellowships Academia program cofunded by the COFUND program of the European Union (FP7-Marie Curie Actions) for financial support. J.-M. R. as a F.R.S.-FNRS research associate and the LPCM thank the Belgian Federal Government Office of Science Policy (SSTC-PAI 6/27) for general support, and LCFM-BIOMAT project is gratefully acknowledged. This work was also supported by the FNRS through an FRIA grant as well as the PREDICTION ARC project between Université Libre de Bruxelles and Université de Mons (2012–17) and FNRS PDR (project convention no. 19471061, 2014–2018). The authors would like to acknowledge Erasmus Mundus EASED (2014–17) for enabling the collaboration with Prof. Kanda in Okayama.

## References

- 1 Momeni, F., Mehdi Hassani, S.M., Liu, X., and Ni, J. (2017). A review of 4D printing. *Mater. Des.* 122: 42–79.
- 2 Wallin, T.J., Pikul, J., and Shepherd, R.F. (2018). 3D printing of soft robotic systems. *Nat. Rev. Mater.* 3 (6): 84–100.
- 3 Polygerinos, P., Wang, Z., Galloway, K.C. et al. (2015). Soft robotic glove for combined assistance and at-home rehabilitation. *Rob. Autom. Syst.* 73: 135–143.
- 4 Pilate, F., Toncheva, A., Dubois, P., and Raquez, J.-M. (2016). Shape-memory polymers for multiple applications in the materials world. *Eur. Polym. J.* 80: 268–294.
- 5 Kloxin, C.J., Scott, T.F., Adzima, B.J., and Bowman, C.N. (2010). Covalent adaptable networks (CANs): a unique paradigm in cross-linked polymers. *Macromolecules* 43 (6): 2643–2653.

- 6 Bowman, C.N. and Kloxin, C.J. (2012). Covalent adaptable networks: reversible bond structures incorporated in polymer networks. *Angew. Chem. Int. Ed.* 51 (18): 4272–4274.
- 7 Scott, T.F., Schneider, A.D., Cook, W.D., and Bowman, C.N. (2005). Photoinduced plasticity in cross-linked polymers. *Science* 308 (5728): 1615–1617.
- 8 Kloxin, C.J., Scott, T.F., Park, H.Y., and Bowman, C.N. (2011). Mechanophotopatterning on a photoresponsive elastomer. *Adv. Mater.* 23 (17): 1977–1981.
- 9 Nicolaÿ, R., Kamada, J., Van Wassen, A., and Matyjaszewski, K. (2010). Responsive gels based on a dynamic covalent trithiocarbonate cross-linker. *Macromolecules* 43 (9): 4355–4361.
- 10 Amamoto, Y., Kamada, J., Otsuka, H. et al. (2011). Repeatable photoinduced self-healing of covalently cross-linked polymers through reshuffling of trithiocarbonate units. *Angew. Chem. Int. Ed.* 50 (7): 1660–1663.
- 11 Amamoto, Y., Otsuka, H., Takahara, A., and Matyjaszewski, K. (2012). Self-healing of covalently cross-linked polymers by reshuffling thiuram disulfide moieties in air under visible light. *Adv. Mater.* 24 (29): 3975–3980.
- 12 Montarnal, D., Capelot, M., Tournilhac, F., and Leibler, L. (2011). Silica-like malleable materials from permanent organic networks. *Science* 334 (6058): 965–968.
- 13 Angell, C.A. (1995). Formation of glasses from liquids and biopolymers. *Science* 267 (5206): 1924–1935.
- 14 Denissen, W., Winne, J.M., and Du Prez, F.E. (2016). Vitrimers: permanent organic networks with glass-like fluidity. *Chem. Sci.* 7 (1): 30–38.
- 15 Raquez, J.-M., Vanderstappen, S., Meyer, F. et al. (2011). Design of cross-linked semicrystalline poly(*ε*-caprolactone)-based networks with one-way and two-way shape-memory properties through Diels–Alder reactions. *Chem. Eur. J.* 17 (36): 10135–10143.
- 16 Willocq, B., Bose, R.K., Khelifa, F. et al. (2016). Healing by the Joule effect of electrically conductive poly(ester-urethane)/carbon nanotube nanocomposites. *J. Mater. Chem. A* 4 (11): 4089–4097.
- 17 Defize, T., Riva, R., Raquez, J.-M. et al. (2011). Thermoreversibly crosslinked poly(*ε*-caprolactone) as recyclable shape-memory polymer network. *Macromol. Rapid Commun.* 32 (16): 1264–1269.
- 18 Chang, J.Y., Do, S.K., and Han, M.J. (2001). A sol–gel reaction of vinyl polymers based on thermally reversible urea linkages. *Polymer* 42 (18): 7589–7594.
- 19 Sun, C.X., van der Mee, M.A.J., Goossens, J.G.P., and van Duin, M. (2006). Thermoreversible cross-linking of maleated ethylene/propylene copolymers using hydrogen-bonding and ionic interactions. *Macromolecules* 39 (9): 3441–3449.
- 20 Wagener, K.B. and Engle, L.P. (1991). Thermally reversible polymer linkages. 3. Covalently crosslinked poly(azlactone). *Macromolecules* 24 (26): 6809–6815.
- 21 van der Mee, M.A.J., Goossens, J.G.P., and van Duin, M. (2008). Thermoreversible covalent crosslinking of maleated ethylene/propylene copolymers with diols. *J. Polym. Sci., Part A: Polym. Chem.* 46 (5): 1810–1825.

- 22 Kamplain, J.W. and Bielawski, C.W. (2006). Dynamic covalent polymers based upon carbene dimerization. *Chem. Commun.* (16): 1727–1729.
- 23 Amamoto, Y., Kikuchi, M., Masunaga, H. et al. (2009). Reorganizable chemical polymer gels based on dynamic covalent exchange and controlled monomer insertion. *Macromolecules* 42 (22): 8733–8738.
- 24 Higaki, Y., Otsuka, H., and Takahara, A. (2006). A thermodynamic polymer cross-linking system based on radically exchangeable covalent bonds. *Macromolecules* 39 (6): 2121–2125.
- 25 Gheneim, R., Perez-Berumen, C., and Gandini, A. (2002). Diels–Alder reactions with novel polymeric dienes and dienophiles: synthesis of reversibly cross-linked elastomers. *Macromolecules* 35 (19): 7246–7253.
- 26 Goiti, E., Heatley, F., Huglin, M.B., and Rego, J.M. (2004). Kinetic aspects of the Diels–Alder reaction between poly(styrene-*co*-furfuryl methacrylate) and bismaleimide. *Eur. Polym. J.* 40 (7): 1451–1460.
- 27 Goiti, E., Huglin, M.B., and Rego, J.M. (2004). Some properties of networks produced by the Diels–Alder reaction between poly(styrene-*co*-furfuryl methacrylate) and bismaleimide. *Eur. Polym. J.* 40 (2): 219–226.
- 28 Liu, Y.-L. and Hsieh, C.-Y. (2006). Crosslinked epoxy materials exhibiting thermal remendability and removability from multifunctional maleimide and furan compounds. *J. Polym. Sci., Part A: Polym. Chem.* 44 (2): 905–913.
- 29 Liu, Y.-L., Hsieh, C.-Y., and Chen, Y.-W. (2006). Thermally reversible cross-linked polyamides and thermo-responsive gels by means of Diels–Alder reaction. *Polymer* 47 (8): 2581–2586.
- 30 Zhang, Y., Broekhuis, A.A., and Picchioni, F. (2009). Thermally self-healing polymeric materials: the next step to recycling thermoset polymers? *Macromolecules* 42 (6): 1906–1912.
- 31 Imai, Y., Itoh, H., Naka, K., and Chujo, Y. (2000). Thermally reversible IPN organic–inorganic polymer hybrids utilizing the Diels–Alder reaction. *Macromolecules* 33 (12): 4343–4346.
- 32 Kennedy, J.P. and Carlson, G.M. (1983). Synthesis, characterization, and Diels–Alder extension of cyclopentadiene telechelic polyisobutylene. IV.  $\alpha,\omega$ -di(3-Cyclopentadienylpropyldimethylsilyl)polyisobutylene. *J. Polym. Sci.: Polym. Chem.* 21 (12): 3551–3561.
- 33 Goodall, G.W. and Hayes, W. (2006). Advances in cycloaddition polymerizations. *Chem. Soc. Rev.* 35 (3): 280–312.
- 34 Mikroyannidis, J.A. (1992). Synthesis and Diels–Alder polymerization of furfurylidene and furfuryl-substituted maleamic acids. *J. Polym. Sci., Part A: Polym. Chem.* 30 (1): 125–132.
- 35 Goussé, C. and Gandini, A. (1999). Diels–Alder polymerization of difurans with bismaleimides. *Polym. Int.* 48 (8): 723–731.
- 36 Kamahori, K., Tada, S., Ito, K., and Itsuno, S. (1999). Optically active polymer synthesis by Diels–Alder polymerization with chirally modified lewis acid catalyst. *Macromolecules* 32 (3): 541–547.
- 37 Mallakpour, S.E., Hajipour, A.-R., Mahdavian, A.-R., and Khoei, S. (2000). Synthesis and characterization of novel optically active and flame-retardant heterocyclic polyimides. *J. Appl. Polym. Sci.* 76 (2): 240–248.

- 38 Schilling, C.L., Reed, J.A., and Stille, J.K. (1969). Diels–Alder polymerization. VI. Phenylated polyphenylenes from bis-2-pyrones and *p*-diethynylbenzene. *Macromolecules* 2 (1): 85–88.
- 39 Stille, J.K., Rakutis, R.O., Mukamal, H., and Harris, F.W. (1968). Diels–Alder polymerizations. IV. Polymers containing short phenylene blocks connected by alkylene units. *Macromolecules* 1 (5): 431–436.
- 40 Mukamal, H., Harris, F.W., and Stille, J.K. (1967). Diels–Alder polymers. III. Polymers containing phenylated phenylene units. *J. Polym. Sci., Part A: Polym. Chem.* 5 (11): 2721–2729.
- 41 Durmaz, H., Karatas, F., Tunca, U., and Hizal, G. (2006). Heteroarm H-shaped terpolymers through the combination of the Diels–Alder reaction and controlled/living radical polymerization techniques. *J. Polym. Sci., Part A: Polym. Chem.* 44 (13): 3947–3957.
- 42 Li, M., De, P., Gondi, S.R., and Sumerlin, B.S. (2008). End group transformations of RAFT-generated polymers with bismaleimides: functional telechelics and modular block copolymers. *J. Polym. Sci., Part A: Polym. Chem.* 46 (15): 5093–5100.
- 43 Akat, H., Gacal, B., Balta, D.K. et al. (2010). Poly(ethylene glycol)-thioxanthone prepared by Diels–Alder click chemistry as one-component polymeric photoinitiator for aqueous free-radical polymerization. *J. Polym. Sci., Part A: Polym. Chem.* 48 (10): 2109–2114.
- 44 Masutani, K., Kawabata, S., Aoki, T., and Kimura, Y. (2010). Efficient formation of stereocomplexes of poly(*L*-lactide) and poly(*D*-lactide) by terminal Diels–Alder coupling. *Polym. Int.* 59 (11): 1526–1530.
- 45 Jørgensen, K.A. (2000). Catalytic asymmetric hetero-Diels–Alder reactions of carbonyl compounds and imines. *Angew. Chem. Int. Ed.* 39 (20): 3558–3588.
- 46 Nebhani, L., Sinnwell, S., Lin, C.Y. et al. (2009). Strongly electron deficient sulfonyldithioformate based RAFT agents for hetero Diels–Alder conjugation: computational design and experimental evaluation. *J. Polym. Sci., Part A: Polym. Chem.* 47 (22): 6053–6071.
- 47 Sinnwell, S., Synatschke, C.V., Junkers, T. et al. (2008). A study into the stability of 3,6-dihydro-2H-thiopyran rings: key linkages in the RAFT hetero-Diels–Alder click concept. *Macromolecules* 41 (21): 7904–7912.
- 48 Bousquet, A., Boyer, C., Davis, T.P., and Stenzel, M.H. (2010). Electrostatic assembly of functional polymer combs onto gold nanoparticle surfaces: combining RAFT, click and LbL to generate new hybrid nanomaterials. *Polym. Chem.* 1 (8): 1186–1195.
- 49 Dag, A., Durmaz, H., Hizal, G., and Tunca, U. (2008). Preparation of 3-arm star polymers (A3) via Diels–Alder click reaction. *J. Polym. Sci., Part A: Polym. Chem.* 46 (1): 302–313.
- 50 Durmaz, H., Karatas, F., Tunca, U., and Hizal, G. (2006). Preparation of ABC miktoarm star terpolymer containing poly(ethylene glycol), polystyrene, and poly(*tert*-butylacrylate) arms by combining Diels–Alder reaction, atom transfer radical, and stable free radical polymerization routes. *J. Polym. Sci., Part A: Polym. Chem.* 44 (1): 499–509.
- 51 Sinnwell, S., Inglis, A.J., Stenzel, M.H., and Barner-Kowollik, C. (2008). Access to three-arm star block copolymers by a consecutive combination

- of the copper(I)-catalyzed azide–alkyne cycloaddition and the RAFT hetero Diels–Alder concept. *Macromol. Rapid Commun.* 29 (12–13): 1090–1096.
- 52 Durmaz, H., Dag, A., Hizal, G., and Tunca, U. (2010). Cyclic homo and block copolymers through sequential double click reactions. *J. Polym. Sci., Part A: Polym. Chem.* 48 (22): 5083–5091.
- 53 Szalai, M.L., McGrath, D.V., Wheeler, D.R. et al. (2007). Dendrimers based on thermally reversible furan–maleimide Diels–Alder adducts. *Macromolecules* 40 (4): 818–823.
- 54 McElhanon, J.R. and Wheeler, D.R. (2001). Thermally responsive dendrons and dendrimers based on reversible furan–maleimide Diels–Alder adducts. *Org. Lett.* 3 (17): 2681–2683.
- 55 Kim, T.-D., Luo, J., Tian, Y. et al. (2006). Diels–Alder “click chemistry” for highly efficient electrooptic polymers. *Macromolecules* 39 (5): 1676–1680.
- 56 Shi, Z., Luo, J., Huang, S. et al. (2009). Controlled Diels–Alder reactions used to incorporate highly efficient polyenic chromophores into maleimide-containing side-chain polymers for electro-optics. *Macromolecules* 42 (7): 2438–2445.
- 57 Gacal, B., Akat, H., Balta, D.K. et al. (2008). Synthesis and characterization of polymeric thioxanthone photoinitiators via double click reactions. *Macromolecules* 41 (7): 2401–2405.
- 58 Tasdelen, M.A. (2011). Diels–Alder “click” reactions: recent applications in polymer and material science. *Polym. Chem.* 2: 2133–2145.
- 59 Ghezzi, F., Smith, D.R., Starr, T.N. et al. (2010). Development and characterization of healable carbon fiber composites with a reversibly cross linked polymer. *J. Compos. Mater.* 44 (13): 1587–1603.
- 60 Inoue, K., Yamashiro, M., and Iji, M. (2009). Recyclable shape-memory polymer: poly(lactic acid) crosslinked by a thermoreversible Diels–Alder reaction. *J. Appl. Polym. Sci.* 112 (2): 876–885.
- 61 Adzima, B.J., Aguirre, H.A., Kloxin, C.J. et al. (2008). Rheological and chemical analysis of reverse gelation in a covalently cross-linked Diels–Alder polymer network. *Macromolecules* 41 (23): 9112–9117.
- 62 Nemoto, T. and Konishi, G.-i. (2008). Synthesis and properties of new organosoluble alkoxyated naphthalene-based novolacs prepared by addition-condensation of mono- or di-alkoxynaphthalene with formaldehyde. *Polym. J.* 40: 651.
- 63 Kavitha, A.A. and Singha, N.K. (2010). Smart “all acrylate” ABA triblock copolymer bearing reactive functionality via atom transfer radical polymerization (ATRP): demonstration of a “click reaction” in thermoreversible property. *Macromolecules* 43 (7): 3193–3205.
- 64 Watanabe, M. and Yoshie, N. (2006). Synthesis and properties of readily recyclable polymers from bisfuranic terminated poly(ethylene adipate) and multi-maleimide linkers. *Polymer* 47 (14): 4946–4952.
- 65 Shi, Z., Liang, W., Luo, J. et al. (2010). Tuning the kinetics and energetics of Diels–Alder cycloaddition reactions to improve poling efficiency and thermal stability of high-temperature cross-linked electro-optic polymers. *Chem. Mater.* 22 (19): 5601–5608.

- 66 Adzima, B.J., Kloxin, C.J., and Bowman, C.N. (2010). Externally triggered healing of a thermoreversible covalent network via self-limited hysteresis heating. *Adv. Mater.* 22 (25): 2784–2787.
- 67 Peterson, A.M., Jensen, R.E., and Palmese, G.R. (2010). Room-temperature healing of a thermosetting polymer using the Diels–Alder reaction. *ACS Appl. Mater. Interfaces* 2 (4): 1141–1149.
- 68 Amalin Kavitha, A. and Singha, N.K. (2007). A tailor-made polymethacrylate bearing a reactive diene in reversible Diels–Alder reaction. *J. Polym. Sci., Part A: Polym. Chem.* 45 (19): 4441–4449.
- 69 Heath, W.H., Palmieri, F., Adams, J.R. et al. (2008). Degradable cross-linkers and strippable imaging materials for step-and-flash imprint lithography. *Macromolecules* 41 (3): 719–726.
- 70 Syrett, J.A., Mantovani, G., Barton, W.R.S. et al. (2010). Self-healing polymers prepared via living radical polymerisation. *Polym. Chem.* 1 (1): 102–106.
- 71 Willocq, B., Khelifa, F., Brancart, J. et al. (2017). One-component Diels–Alder based polyurethanes: a unique way to self-heal. *RSC Adv.* 7 (76): 48047–48053.
- 72 Zhao, J., Xu, R., Luo, G. et al. (2016). Self-healing poly(siloxane-urethane) elastomers with remoldability, shape memory and biocompatibility. *Polym. Chem.* 7 (47): 7278–7286.
- 73 Oehlenschlaeger, K.K., Mueller, J.O., Brandt, J. et al. (2014). Adaptable hetero Diels–Alder networks for fast self-healing under mild conditions. *Adv. Mater.* 26 (21): 3561–3566.
- 74 Oehlenschlaeger, K.K., Guimard, N.K., Brandt, J. et al. (2013). Fast and catalyst-free hetero-Diels–Alder chemistry for on demand cyclable bonding/debonding materials. *Polym. Chem.* 4 (16): 4348–4355.
- 75 Liu, X., Zhu, M., Chen, S. et al. (2008). Organic–inorganic nanohybrids via directly grafting gold nanoparticles onto conjugated copolymers through the Diels–Alder reaction. *Langmuir* 24 (20): 11967–11974.
- 76 Liu, X., Liu, H., Zhou, W. et al. (2010). Thermoreversible covalent self-assembly of oligo(*p*-phenylenevinylene) bridged gold nanoparticles. *Langmuir* 26 (5): 3179–3185.
- 77 Zhu, J., Kell, A.J., and Workentin, M.S. (2006). A retro-Diels–Alder reaction to uncover maleimide-modified surfaces on monolayer-protected nanoparticles for reversible covalent assembly. *Org. Lett.* 8 (22): 4993–4996.
- 78 Gotsmann, B., Duerig, U., Frommer, J., and Hawker, C.J. (2006). Exploiting chemical switching in a Diels–Alder polymer for nanoscale probe lithography and data storage. *Adv. Funct. Mater.* 16 (11): 1499–1505.
- 79 Adachi, K., Achimuthu, A.K., and Chujo, Y. (2004). Synthesis of organic–inorganic polymer hybrids controlled by Diels–Alder reaction. *Macromolecules* 37 (26): 9793–9797.
- 80 Zhou, X., Li, Q., and Wu, C. (2008). Grafting of maleic anhydride onto carbon black surface via ultrasonic irradiation. *Appl. Organomet. Chem.* 22 (2): 78–81.
- 81 Ménard-Moyon, C., Dumas, F., Doris, E., and Mioskowski, C. (2006). Functionalization of single-wall carbon nanotubes by tandem

- high-pressure/Cr(CO)<sub>6</sub> activation of Diels–Alder cycloaddition. *J. Am. Chem. Soc.* 128 (46): 14764–14765.
- 82 Delgado, J.L., de la Cruz, P., Langa, F. et al. (2004). Microwave-assisted sidewall functionalization of single-wall carbon nanotubes by Diels–Alder cycloaddition. *Chem. Commun.* (15): 1734–1735.
- 83 Mercuri, F. and Sgamellotti, A. (2009). First-principles investigations on the functionalization of chiral and non-chiral carbon nanotubes by Diels–Alder cycloaddition reactions. *Phys. Chem. Chem. Phys.* 11 (3): 563–567.
- 84 Hayden, H., Gun'ko, Y.K., and Perova, T.S. (2007). Chemical modification of multi-walled carbon nanotubes using a tetrazine derivative. *Chem. Phys. Lett.* 435 (1): 84–89.
- 85 Chang, C.-M. and Liu, Y.-L. (2009). Functionalization of multi-walled carbon nanotubes with furan and maleimide compounds through Diels–Alder cycloaddition. *Carbon* 47 (13): 3041–3049.
- 86 Vida, Y., Suau, R., Casado, J. et al. (2007). Electropolymerizable terthiophene *S,S*-dioxide-fullerene Diels–Alder adduct for donor/acceptor double-cable polymers. *Macromol. Rapid Commun.* 28 (12): 1345–1349.
- 87 Bai, J. and Shi, Z. (2017). Dynamically cross-linked elastomer hybrids with light-induced rapid and efficient self-healing ability and reprogrammable shape memory behavior. *ACS Appl. Mater. Interfaces* 9 (32): 27213–27222.
- 88 Lim, H.L., Hwang, Y., Kar, M., and Varghese, S. (2014). Smart hydrogels as functional biomimetic systems. *Biomater. Sci.* 2 (5): 603–618.
- 89 Stuart, M.A.C., Huck, W.T.S., Genzer, J. et al. (2010). Emerging applications of stimuli-responsive polymer materials. *Nat. Mater.* 9: 101–113.
- 90 Varaprasad, K., Raghavendra, G.M., Jayaramudu, T. et al. (2017). A mini review on hydrogels classification and recent developments in miscellaneous applications. *Mater. Sci. Eng., C* 79: 958–971.
- 91 Gandini, A. and Lacerda, T.M. (2015). From monomers to polymers from renewable resources: recent advances. *Prog. Polym. Sci.* 48: 1–39.
- 92 Kirchhof, S., Brandl, F.P., Hammer, N., and Goepferich, A.M. (2013). Investigation of the Diels–Alder reaction as a cross-linking mechanism for degradable poly(ethylene glycol) based hydrogels. *J. Mater. Chem. B* 1 (37): 4855–4864.
- 93 Zhang, M., Wang, J., and Jin, Z. (2018). Supramolecular hydrogel formation between chitosan and hydroxypropyl  $\beta$ -cyclodextrin via Diels–Alder reaction and its drug delivery. *Int. J. Biol. Macromol.* 114: 381–391.
- 94 Yu, F., Cao, X., Du, J. et al. (2015). Multifunctional hydrogel with good structure integrity, self-healing, and tissue-adhesive property formed by combining Diels–Alder click reaction and acylhydrazone bond. *ACS Appl. Mater. Interfaces* 7 (43): 24023–24031.
- 95 Wei, H.-L., Yang, J., Chu, H.-J. et al. (2011). Diels–Alder reaction in water for the straightforward preparation of thermoresponsive hydrogels. *J. Appl. Polym. Sci.* 120 (2): 974–980.
- 96 Gregoritz, M., Messmann, V., Abstiens, K. et al. (2017). Controlled anti-body release from degradable thermoresponsive hydrogels cross-linked by Diels–Alder chemistry. *Biomacromolecules* 18 (8): 2410–2418.

- 97 Gregoritza, M., Messmann, V., Goepferich, A.M., and Brandl, F.P. (2016). Design of hydrogels for delayed antibody release utilizing hydrophobic association and Diels–Alder chemistry in tandem. *J. Mater. Chem. B* 4 (19): 3398–3408.
- 98 Kirchof, S., Gregoritza, M., Messmann, V. et al. (2015). Diels–Alder hydrogels with enhanced stability: first step toward controlled release of bevacizumab. *Eur. J. Pharm. Biopharm.* 96: 217–225.
- 99 He, C., Kim, S.W., and Lee, D.S. (2008). In situ gelling stimuli-sensitive block copolymer hydrogels for drug delivery. *J. Controlled Release* 127 (3): 189–207.
- 100 Koetting, M.C., Peters, J.T., Steichen, S.D., and Peppas, N.A. (2015). Stimulus-responsive hydrogels: theory, modern advances, and applications. *Mater. Sci. Eng. R. Rep.* 93: 1–49.
- 101 Qiu, Y. and Park, K. (2001). Environment-sensitive hydrogels for drug delivery. *Adv. Drug Delivery Rev.* 53 (3): 321–339.
- 102 Ruel-Gariépy, E. and Leroux, J.-C. (2004). In situ-forming hydrogels-review of temperature-sensitive systems. *Eur. J. Pharm. Biopharm.* 58 (2): 409–426.
- 103 Lee, C., Kim, M., Kim, Y.J. et al. (2017). Soft robot review. *Int. J. Control Autom. Syst.* 15 (1): 3–15.
- 104 Zeng, C., Seino, H., Ren, J., and Yoshie, N. (2014). Polymers with multishape memory controlled by local glass transition temperature. *ACS Appl. Mater. Interfaces* 6 (4): 2753–2758.
- 105 Zhang, G., Zhao, Q., Yang, L. et al. (2016). Exploring dynamic equilibrium of Diels–Alder reaction for solid state plasticity in remoldable shape memory polymer network. *ACS Macro Lett.* 5 (7): 805–808.
- 106 Cai, C., Zhang, Y., Li, M. et al. (2018). Multiple-responsive shape memory polyacrylonitrile/graphene nanocomposites with rapid self-healing and recycling properties. *RSC Adv.* 8 (3): 1225–1231.
- 107 Terryn, S., Brancart, J., Lefeber, D. et al. (2017). Self-healing soft pneumatic robots. *Sci. Rob.* 2 (9): ean4268.
- 108 Seppe, T., Glenn, M., Joost, B. et al. (2015). Development of a self-healing soft pneumatic actuator: a first concept. *Bioinspiration Biomimetics* 10 (4): 1–17.
- 109 Toncheva, A., Willocq, B., Khelifa, F. et al. (2017). Bilayer solvent and vapor-triggered actuators made of cross-linked polymer architectures via Diels–Alder pathways. *J. Mater. Chem. B* 5 (28): 5556–5563.
- 110 Toncheva, A., Khelifa, F., Paint, Y. et al. (2018). Fast IR-actuated shape-memory polymers using in situ silver nanoparticle-grafted cellulose nanocrystals. *ACS Appl. Mater. Interfaces* 10 (35): 29933–29942.
- 111 Berg, G.J., Gong, T., Fenoli, C.R., and Bowman, C.N. (2014). A dual-cure, solid-state photoresist combining a thermoreversible Diels–Alder network and a chain growth acrylate network. *Macromolecules* 47 (10): 3473–3482.
- 112 Adzima, B.J., Kloxin, C.J., DeForest, C.A. et al. (2012). 3D photofixation lithography in Diels–Alder networks. *Macromol. Rapid Commun.* 33 (24): 2092–2096.

- 113 Davidson, J.R., Appuhamillage, G.A., Thompson, C.M. et al. (2016). Design paradigm utilizing reversible Diels–Alder reactions to enhance the mechanical properties of 3D printed materials. *ACS Appl. Mater. Interfaces* 8 (26): 16961–16966.
- 114 Appuhamillage, G.A., Reagan, J.C., Khorsandi, S. et al. (2017). 3D printed remendable polylactic acid blends with uniform mechanical strength enabled by a dynamic Diels–Alder reaction. *Polym. Chem.* 8 (13): 2087–2092.
- 115 Yang, K., Grant, J.C., Lamey, P. et al. (2017). Diels–Alder reversible thermoset 3D printing: isotropic thermoset polymers via fused filament fabrication. *Adv. Funct. Mater.* 27 (24): 1–11.
- 116 Chen, S., Zhang, Q., and Feng, J. (2017). 3D printing of tunable shape memory polymer blends. *J. Mater. Chem. C* 5 (33): 8361–8365.
- 117 Senatov, F.S., Niaza, K.V., Zadorozhnyy, M.Y. et al. (2016). Mechanical properties and shape memory effect of 3D-printed PLA-based porous scaffolds. *J. Mech. Behav. Biomed. Mater.* 57: 139–148.
- 118 Zhao, Z., Peng, F., Cavicchi, K.A. et al. (2017). Three-dimensional printed shape memory objects based on an olefin ionomer of zinc-neutralized poly(ethylene-co-methacrylic acid). *ACS Appl. Mater. Interfaces* 9 (32): 27239–27249.
- 119 Yang, Y., Chen, Y., Wei, Y., and Li, Y. (2016). 3D printing of shape memory polymer for functional part fabrication. *Int. J. Adv. Manuf. Technol.* 84 (9): 2079–2095.
- 120 Yang, H., Leow, W.R., Wang, T. et al. (2017). 3D Printed photoresponsive devices based on shape memory composites. *Adv. Mater.* 29 (33): 1–7.