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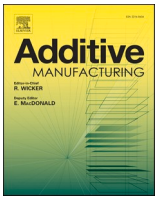

Multimaterial 3D printing of self-assembling smart thermo-responsive polymers into 4D printed objects: A review

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ABSTRACT

The three-dimensional (3D) printing and its extension four-dimensional (4D) printing technique show great promise for advanced additive manufacturing of functional and architected materials with engineered micro- and nanoscale features. The actual usage of additive manufacturing to produce 3D/4D structures is primarily dependent on the improvement of printable polymeric inks. Thermoresponsive polymers (TRPs) show broad application prospects in additive manufacturing since they enable changing the physicochemical properties of the system at a specific temperature. Continuing to progress in the understanding of TRP phenomena enable the design of new feedstocks and their compatibility with fabrication processes. Therefore, increasing the overlap between the fields of fundamental TRPs and application-based research efforts can be important to emerging the technology. In this review, we provide an overview of the functional design of the TRPs, the different classes of TRPs, and their application in 3D printing, ranging from biosensors via advanced self-assembly to a variety of biofabrication, biomedical, biotechnology, and food applications. Basic knowledge of imperative processes like gelation mechanisms of TRPs, bio-based adsorption on the surfaces and adhesion, and fabrication strategies using 3D printing is also provided. For diverse TRPs synthesis and the basic physical and chemical features are described and the mechanism of their TRPs behavior is highlighted. Fabrication methods of TRP surfaces have also been discussed describing several methods in detail.

1. Introduction

Different biological behaviors depend on the response-controlled relations between polypeptides, proteins, and nucleic acids, with the capability to adopt specific conformations to their environments [1–6]. In the same way, the responsive feature is conveyed to the polymers by introducing several types of functional groups, which can be triggered by different stimuli (e.g., temperature, pH, ionic strength, redox reactions, light, shear stress, enzymes, etc.) and change their physical properties [7–12]. Interest in stimuli-responsive polymers has persisted over many decades, and a great deal of work has been dedicated to devising environmentally-sensitive macromolecules that can be crafted into new smart materials in drug delivery, tissue engineering, theragnostic particles, and bio-separation [13–18]. The thermoresponsive polymers (TRPs) can be manufactured as hydrogel, mussel-inspired TRPs, thin film, micro-, and nanoparticles, as well as a micelle. The architecture of TRPs governs their stimuli-responsive properties, which give rise to the design of smart structures for distinct applications. For instance, photo- and pH-responsive features together with temperature sensitivity play an essential role in tissue engineering and drug delivery, respectively [9,19–24]. Therefore, comprehensive information concerning the structure-feature relationship is a necessity to design a smart stimuli-responsive polymer.

The TRPs remain the most widely exploited stimuli in the field of stimuli-responsive materials since the first report of the temperature phase transition property of poly(N-isopropylacrylamide) (PNIPAM) in 1967 by Scarpa et al [25]. According to their temperature-responsive behavior, they are mainly divided into lower critical solution

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temperature (LCST) and upper critical solution temperature (UCST) [26–29]. LCST kind of TRPs can dissolve in aqueous (or organic) solutions at temperatures lower than LCST. Above the LCST, this type becomes hydrophobic because of enhanced polymeric intra- and intermolecular hydrophobic interactions. The obtained reversible solubility alterations have been extensively used in the production of cell-sheet technologies, drug carriers, triggers for self-assembly, model proteins, "on-off" switches for protein activity, sensors, and adsorption compounds [30–33]. In contrast, UCST polymers can dissolve in solvents above the UCST and are insoluble below the UCST. This behavior happens due to some specific interactions, such as hydrogen bonding and electrostatic interactions. UCST polymers are also utilized in several fields, such as biomedical applications protein separations, sensors, and assembled nanomaterials [30,34–36].

In recent years, three-dimensional (3D) printing has emerged as an innovative platform of rapid prototyping to manufacturing complex functional 3D structures in a layer-by-layer fashion. The development of cost-effective costume-designed robust smart materials by additive manufacturing possesses great prospects to use in a broad range of fields [37–39]. However, the 3D printing process of custom-design architectures with 'pristine' polymers lacks essential strength and functionalities to use in multifunctional systems. Therefore, the 3D printing of smart materials including multi-functionalized TRPs is an inevitable path to the effective assembly of functional soft systems through rapid prototyping [37,40]. In 2013, the idea of 4D printing was offered by the Tibbits research group from the Massachusetts Institute of Technology (MIT) [41]. The 4D printing process is the extension of 3D printing, in which the incorporation of a "space-time axis" based on 3D coordinate axis occurs. 4D printing is comparable to 3D printing in the printing process, including a 3D design development and printing of the structure employing a 3D printing system [42]. The main differences between 3D and 4D printing are smart material and smart design, as 4D printed objects can alter shape or function (Fig. 1).

The presence of smart compounds like shape memory alloy supports the utilization of 4D printing technology in the soft robot, aerospace, automobile, electrochemical energy storage, food science, biomedicine, biofabrication, etc. [42–44]. This offers the construction of customized instruments manufactured to fit applications of geometrically complex constructs in any desired 3D shape and dimensions. As an example, the preparation of TRP inks by UCST polymers in energy research brings a robust, flexible, and easily up-scalable method [43,44]. The prepared 3D device is intended to obtain a low resistance interface, improved mechanical performance, electrical features, packing of the reduced chemically modified graphene, and low active material density, while enabling the post-processing of the multi-component 3D printed objects [45]. TRPs also hold great potential in the biomedical field, since they enable the fabrication of cell sheets, in-situ drug delivery, and 3D printing under physiological conditions. In a cell 3D bioprinting process, a suitable bioink is key to the successful construction of a complex tissue structure. The bioinks composed of TRP hydrogels could form a gel by simply varying the external temperature within a physiological range for 3D bioprinting [45].

The traditional 3D architectures featuring static characteristics and behaviors produced by 3D printing cannot serve the requirement to apply in biofabrication, biomedical, biosensor devices, etc. The newly produced 4D printing techniques based on 3D printing including a surrounded capability of shape transformation can address this problem and more precisely imitate the dynamic of the native tissues, electronic devices, etc. For this reason, TRPs can be employed with the 3D printing method to manufacture biologically active objects that can change their shapes during favored stimulation to attain prescribed multifunctionality. There are still several challenges behind the mentioned excessive progress concerning technology, material, and design. First, though 3D printing is friendly to several material kinds, the speed of the printing process is comparatively low and the interface is weak owing to a layer-by-layer fashion. Therefore, the restriction of this 3D printing technique wants to be broken in the future for the development of high-resolution well-defined 4D architectures with greater printing speed. Additionally, the pertinent polymers need more types and more multifunctionalities as a main challenge of 4D printing. The most frequently applied polymers for 4D printing are shape-shifting materials because of their intrinsic shape-changing abilities.

In this review, current progresses in the application of TRPs with different 3D printing methods—such as extrusion-based 3D printing, stereolithography, laser powder bed fusion, and inkjet printing— was highlighted. The state-of-the-art of TRP categories for 3D printing accompanied by their related challenges were also discussed. Furthermore, the potential use of different TRPs, including their potential applications in biofabrication, biomedical, biotechnology, biosensor devices, and food applications was discussed for their ability to attain 4D printing (Fig. 2).

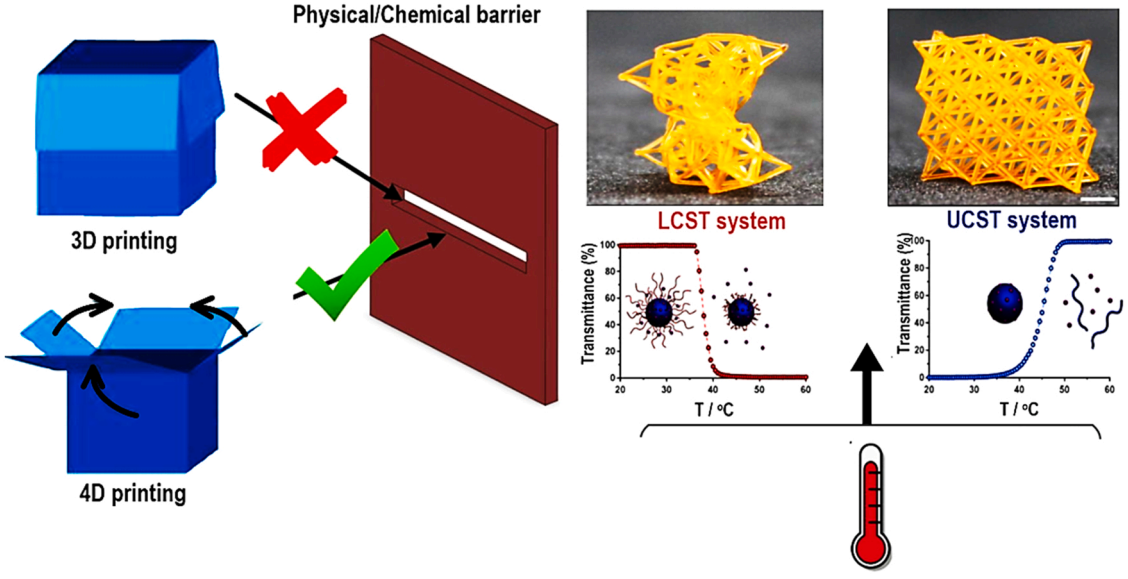

Fig. 1. A schematic diagram of the main differences between 3D and 4D printing.

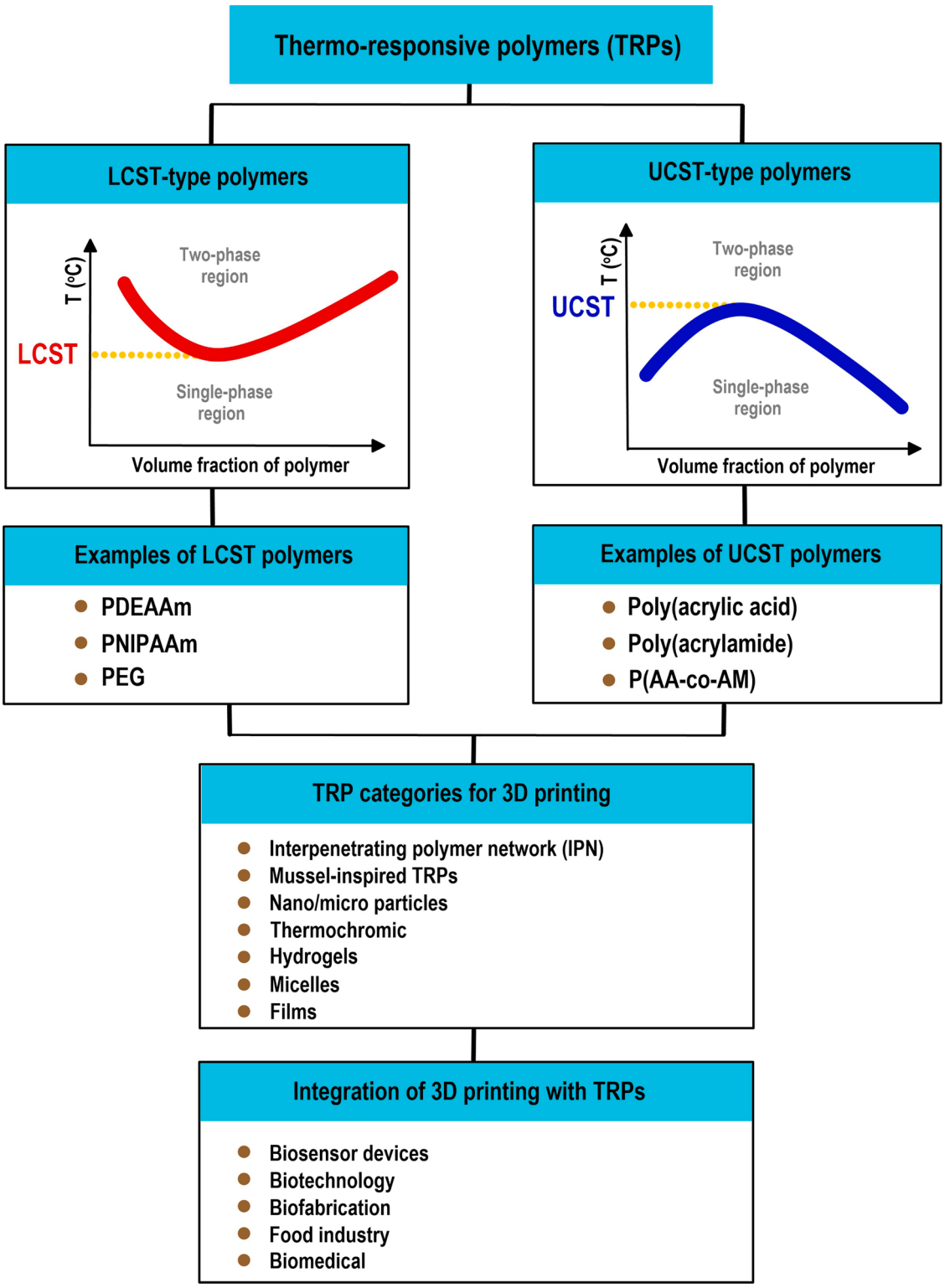

Fig. 2. A summary scheme of mechanisms, examples, and applications of TRPs in 3D printing.

2. TRP behavior and mechanism

The transition temperature of macromolecules in the solution is one of the principal factors to allow considering the application in a certain set of circumstances. For example, a wide range of TRPs described showing possible utilization in biomedical 3D printing offers a transition temperature between ambient temperature and body temperature [1,5,26,27]. Therefore, an insight understanding of the molecular behavior behind the performance of TRPs supports to manufacture of an effective smart 3D structure. The TRP behavior has mainly related to a sudden change in the solubility at either a lower critical solution temperature (LCST) or an upper critical solution temperature (UCST) (Fig. 3). In an aqueous solution, the solubility of polymer is related to several parameters including molecular weight, temperature, presence of a co-solvent or additive, etc [30–33]. The solubility rises slowly as the temperature increases or decreases, and after that so quickly within a narrow

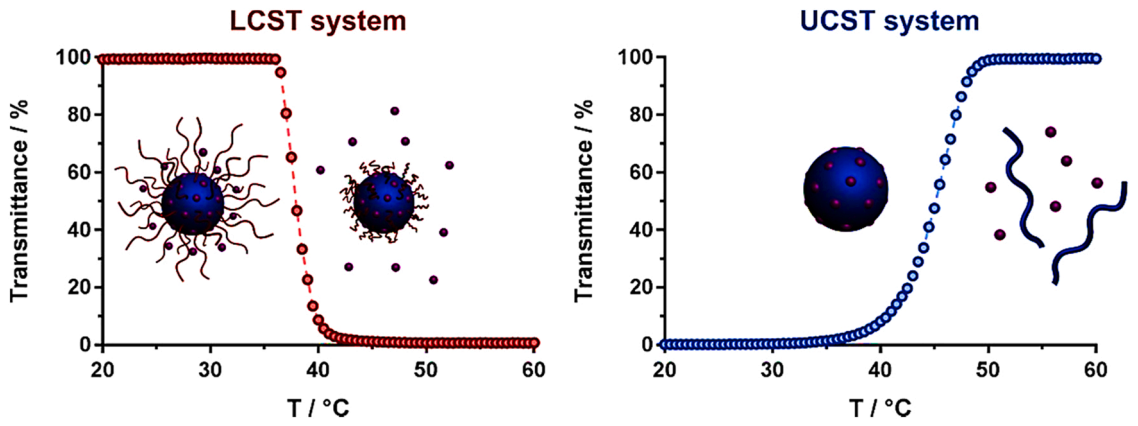

Fig. 3. Schematic perspective on molecular interactions in UCST and LCST systems. Reprinted with permission from ref [48].

temperature range [46]. The temperature at which point a sudden change in the solubility happens is called the critical solution temperature (CST). With increasing temperature, the solubility of the polymer in the solvent increases, which shows a UCST system [25,26,29]. In this case, there is the formation of a homogeneous system above a certain point where the elements are compatible at all concentrations above the UCST. There is a reverse behavior for the LCST system, where the miscible phase is developed below the LCST (liquid-liquid de-mixing upon heating). The occurrence of an LCST system is much less common compared to the presence of UCST, though some cases do exist [47]. Any other transition from soluble to insoluble or vice versa (at a given concentration) should be designated as the transition temperature [48]. However, some macromolecules like PNIPAM present a phase transition, which is nearly independent of the concentration or molecular weight. Therefore, the transition temperature at any certain concentration is almost identical to the LCST [49,50].

All macromolecules with a thermosensitive property show a significant solubility change in dependence on the environmental temperature as this change is commonly accompanied by a conformational alteration in the macromolecule structures [31,33,34]. This behavior is associated with the development of substantial hydrogen linkage interaction with the neighboring water molecules and the presence of limited intra- and intermolecular hydrogen linkages between polymeric molecules [27,29]. Upon heating, there is a disruption process of hydrogen bonding with water, where the intra- and intermolecular hydrogen linkage/hydrophobic interactions prevail, leading to a transition in solubility [26–30]. The LCST systems are simply strengthened by the incorporation of hydrophilic/hydrophobic properties through the copolymerization of hydrophobic/hydrophilic comonomers or end-group transformations [37,38]. An increase in the hydrophilic nature of the macromolecules leads to an improvement in the overall hydrogen linking capacity of the polymers, resulting in greater transition temperature. In contrast, the addition of the hydrophobic compounds depresses the LCST. Besides, the introduction of hydrophobic species causes cleavage of the structure of water around the polymers. This improves the interaction of hydrophobic groups, further simplifying aggregation [2,5,7,19].

The TRPs show a coil-to-globule conformational transition in the aqueous solution mainly through the LCST with a volume change from the hydrophobic to the hydrophilic state [49,50]. The force field parameter has been used for the prediction of the hydrophobic and hydrophilic interactions [51]. There are four kinds of force fields to determine the thermodynamic properties of TRPs, including solvation and hydration-free energy, partition coefficient, and density/heat of vaporization. With increasing temperature, a decrease in the hydration-free energy *per* unit area is observed. This is associated with the reduction in the number of molecules in the first solvation shell around the TRP polar contacts. This case leads to conformational changes via the LCST [26–28].

3. Overview of 3D printing techniques for TRPs

Additive manufacturing techniques have advanced as an innovative technology to build 3D structures layer-by-layer with different geometries and wide-ranging applications. It is proposed that such methods allow the construction of functional objects that cannot be developed with traditional manufacturing techniques. With consideration of quickly manufacturing 3D structures and devices on demand, they have contributed an important improvement to both scientific study and industrial productions. There are seven categories and over 50 kinds of 3D printing techniques currently available for diverse necessities of biomaterials, speed, and precision [37–40]. Owing to this diversity, the rapid prototyping methods have become an adaptable and influential technical platform for forthcoming advanced manufacturing [38,52,53]. Recently, with the growth of matured additive manufacturing techniques, the utilization of TRPs has experienced revolutionary changes [41,42]. Growing scientists from different disciplines have initiated rapid prototyping to develop multifunctional soft devices having high intricacy that can never be attained through traditional manufacturing approaches, which show countless potential to alter human life shortly.

Considering the functionality of TRPs, seven printing techniques are well-established to fabricate 3D printed nanocomposites, including DIW, FDM, SLA, direct energy deposition (DED), laminated object manufacturing (LOM), inkjet printing, and SLS. Actually, a strong relationship exists between 3D printing techniques, mechanical properties, and applications for manufacturing nanocomposites [53].

Extensive surveys on these 3D printing processing technologies can be found in can be found elsewhere [37,53]. There are also some new emerged inspiring high-precision rapid prototyping methods, which are being utilized to develop high-intricacy actually 3D microstructures with a resolution of a few microns or below in a relatively flexible, low-cost and versatile way, including electrohydrodynamic printing, projection micro stereolithography, and two-photon polymerization. Comprehensive and up-to-date reviews regarding utilizing these techniques are available elsewhere, while a detailed review of non-contact micro as well as nano-printing approaches can be found here by Oliveira et al. [54] (Table 1).

In this section, the main 3D printing systems will be overviewed, highlighting the printability, resolution and speed, and requirements on printing ability of TRP, as a recommendation to choose suitable processing approaches for improving printing performance. Next, different types of TRP used for 3D printing methods are discussed. Explicitly, we pay attention to the structure-property-application relationship of diverse 3D printing techniques in each part. Finally, an overview of TRP

Table 1
Examples of 3D printing of TRPs for the development of hierarchical mesostructured architectures.

Technology	State of starting materials	Typical TRPs	Typical nanomaterials	Applications	Benefits	Drawbacks	Ref.
FDM	Filament	Polycaprolactone (PCL), polyurethane (PU), poly(lactic acid) (PLA), acrylonitrile butadiene styrene (ABS), polyethylene (PE)	Ceramic- and carbon-based nanomaterials	Rapid prototyping, advanced composite parts	Low cost, good strength, multi-material capability	Anisotropy, nozzle clogging	[55–58]
Powder bed fusion (SLS, SLM, 3DP)	Compacted fine powders metals, alloys, and limited polymers (SLS or SLM) ceramic and polymers (3DP)	PCL, polyamide, poly(L-lactic acid) (PLLA) powders, poly(ethylene glycol) diacrylate (PEGDA)	Bioactive glass, ceramic- and carbon-based nanomaterials	Biomedical Electronics Aerospace Lightweight structures (lattices) Heat exchangers	Fine resolution High quality	High cost, powdery surface	[59–63]
SLA	Liquid photo-polymer	Photocurable resin (epoxy or acrylate-based resin), poly(N-isopropylacrylamide), gelatin methacryloyl	Ceramic- and carbon-based nanomaterials	Biomedical Prototyping	Fine resolution High quality	Very limited materials Slow printing Expensive	[64–66]
Inkjet printing and contour crafting	A concentrated dispersion of particles in a liquid (ink or paste) Ceramic, concrete, and soil	Thermoset (Poly-iso-butylene), Thermoset (PVA), Thermoset (Polyacrylate), Thermoset (Polyaniline), Thermoplastic (poly(2-methoxyaniline-5-sulfonic acid), Polyethylene glycol	Ceramic- and carbon-based nanomaterials	Biomedical Large structures Buildings	Ability to print large structures Quick printing	Maintaining workability Coarse-resolution Lack of adhesion between layers Layer-by-layer finish	[67–69]

categories (including hydrogels, interpenetrating polymer network, micelles, mussel-inspired TRPs, films, nano/micro particles, and thermochromic) have been provided with emphasis on the principles of functionalization and dispersion of TRPs in well-established and in-house customized 3D printing systems.

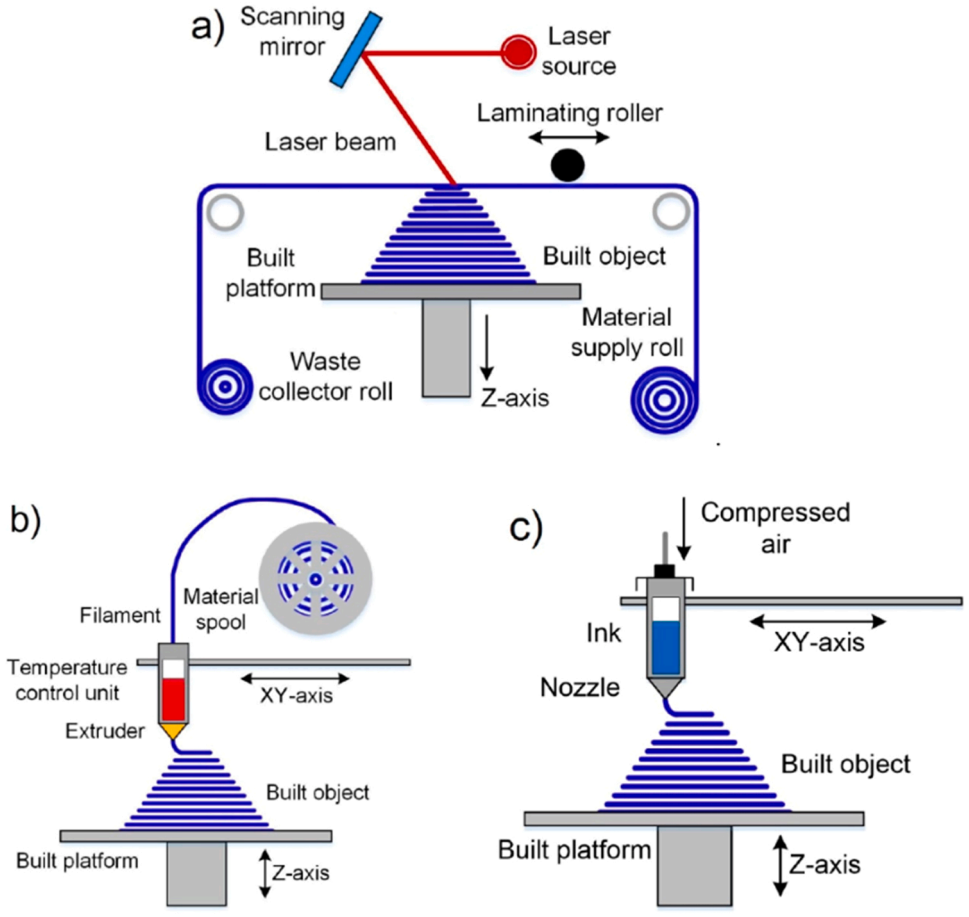

Fig. 4. Schematic illustrations for main methods of bulk solid-based 3D printing technology: (**a**) LOM; (**b**) FDM; (**c**) direct ink writing (DIW). Fig. 4a, b, and c adapted from [73], with permission from Wiley-VCH Verlag GmbH & Co. KgaA, Weinheim, 2018.

3.1. Direct ink writing (DIW)

DIW, also recognized as Robot-Assisted Shape Deposition [70] or Direct Write Fabrication Robocasting [71], is a process associated with the extrusion-based printing method, in which the liquid material inks (such as TRPs) are deposited layer-by-layer on a substrate to form 3D structures. In this technique, the flow properties of TRP-based inks have a critical impact on the resolution of the printed parts and printing performance. Regularly, a high consistency index of inks improves the geometrical capability, albeit the greater risks of nozzle clogging. Therefore, a suitable formulation of TRP-based inks to attain high viscosity (10^3–10^6 mPa s) having *pseudoplasticity* and shear yield stress is an important factor for DIW processing [72] (Fig. 4).

Compared to other 3D printing processes, DIW offers much cheaper and quicker technology to produce 3D 4D hierarchical mesostructured architectures [37]. The distinct utilization of TRP-based inks with proper viscoelastic properties offers the manufacture of 3D printed structures that uphold their unique shape irrespective of a load produced with a newly deposited layer onto them. Normally, the utilized TRP-based inks cause a volume phase transition, offering a biomimetic platform for the enhancement of 3D structures functionality. For this reason, it is likely to construct 3D structures with diverse shapes of an intricated porous scaffold [74], tissue engineering [75], and soft electronics [76]. As an example, the coil-to-globule transitions of TRP-based inks result in a rapid reduction of hydrogel volume, which offers a quick release of solvents and also loaded drugs, followed by a controlled release by more linear diffusion [77]. Furthermore, several researchers have prepared and integrated 3D printing with TRP-based inks to fabricate hierarchical mesostructured starchers loaded with bioactive compounds for controllable drug release [78]. Because of the simplicity and flexibility of the DIW technique, some researchers could implement it to fabricate 3D-printed smart structures for personalized tissue, biomedical tools personalized tissue, bioceramic implants, and lithium-ion battery [79,80]. The inks containing TRP-based inks enhance the physicomechanical [81], thermal [82], and biological features [83] of 3D devices, offering improved multifunctionality for an extensive variety of 3D printing applications. Though, 3D printing TRP-based structures customize shape intricacies, the deficiency of physical integrity and affinity posture hurdle in the additive manufacturing application. Modification methods for the integration of different TRP-based inks into 3D printing need supplementary experiments to overwhelm the mentioned drawbacks [40,84–86]. For example, the modification of gelatin gives the way to produce a preferred 3D object utilizing human body temperature, attaining stable tailored geometry during DIW printing at 37 °C. By using this technique, the 3D-printed objects were successfully printed without using supporting material [87–90]. The results suggested that the printing performance was enhanced with an increasing level of smart-modified gelatin. The final 3D architectures showed good potential in tissue scaffold application, drug delivery, and packaging, because of their intrinsic biodegradability, biocompatibility, and sustainability. Rastin et al [89] introduced a biocompatible printable bioink for 3D bioprinting by incorporation of thermoresponsive methylcellulose and kappa-carrageenan hydrogels into poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) conducting polymer. They claimed that this tertiary multifunctional printable ink showed offers an advantage of conductive polymers in the 3D printing technology [89].

3.2. Fused deposition modeling (FDM)

FDM technique is a very common additive manufacturing process because of its adaptability, low cost, environmentally friendliness, and ease of utilization; furthermore, this method does not need the application of organic solvents [55,56]. In the FDM technique, the thermoplastic filaments are melted and extruded to develop the ultimate 3D structures (Fig. 4b). FDM shows a wide range of applications in different areas of electronics medicine, automotive, and aerospace [91]. By the addition of diverse ranges of TRPs into the filaments, FDM is simply able to print various hierarchical mesostructured architectures [92]. Because of the enhancement progress in FDM methods, particularly an Arburg Plastic Free-forming [93], the selection and application of TRP-based inks have enlarged noticeably to an extensive array for FDM printers [94]. Once applied to the FDM technique, problems encountered with TRP-based inks contain: the printing filaments are simply to disrupt and therefore the process is uneven; the 3D printed structure is simply to twist and therefore it has inadequate strength with poor printing performance [95]. Thus, fillers are regularly introduced into TRP-based inks to improve the flow properties, therefore improving the tensile strength, or enhancing the printability of 3D parts [42].

3.3. Stereolithography (SLA)

As the first used method of 3D printing, SLA is one of the highest precisions (down to 100 nm) of all solid freeform methods for a variety of bioelectronic, biomedical, agriculture, automotive, and applications (Fig. 5) [96,97]. The application of TRP-based inks as smart materials in this technique is a recognized practice, which is regularly introduced into the polymeric/resin matrices to enhance the physical and biological properties of the end-user devices [98] but is also able to improve new features of polymers, including cell viability, electrical characteristics, thermal behavior, etc. Some important points must be considered for the SLA-printed smart materials. The first issue is quickly solidifying the materials through light-induced polymerization that needs a quick debauched light-responsive TRP component. The next issue is an adequate low consistency index to offer for the dipping of polymeric layers, which governs a low level of TRP with a regular distribution [99]. In the SLA technique, diverse kinds of TRPs can be used like poly(N-vinyl caprolactam), pluronic F-127, poly(N-alkylacrylamide)s, and many others [96–99].

In the SLA technique, the flow behavior of the systems is very critical, which has an important effect on the printing performance [97]. Typically, the viscosity of traditional TRP-based inks is varied between 0.5 and 1.5 Pa s, allowing them fluid adequate to redistribute in a tray each time the Z-axis moves [97–99]. It has been reported that the viscosity of inks should have a low value otherwise, the inks would have insufficient time to fill the gaps among layers once the Z-axis moves up, leading to a failure in the printing process [100,101]. The viscosity of inks is related to the particle-solvent and the particle-particle interaction [102]. After converting the TRP-based inks to a colloid system, the unstable particles develop aggregate flocs, in which the viscosity considerably is increased [103]. Furthermore, the aggregate flocs continue to collect in the printing system's vet, which has damaged the printer device or interrupted the oxygen passages through the membranes.

3.4. Laser powder bed fusion (LPBF)

LPBF can be considered a powdery-based additive manufacturing to manufacture functionalized 3D structures, in which powder particles are fused through the application of a highly energized laser (Fig. 6). The process uses sintering a consecutive thin layer of powdery materials that are selectively melted by a CO_2 laser between each powder application. The laser precision makes a simple one-step printing technique with no requirement for pre-processing of materials before 3D printing [104,105] and develops a printed construct of advanced resolution. To sintering the frequently utilized powdery TRP materials, though, there is a severe printing condition including higher temperatures with high-induced energy laser, which have restricted the wide application of LPBF technology in some fields like bioengineering and pharmaceutical areas. For example, the highly energized laser can destroy the bioactive therapeutic components when they are utilized as preliminary formulated materials [106,107]. For this reason, there has been a limitation to using this technique to develop 3D structures in the bioengineering areas

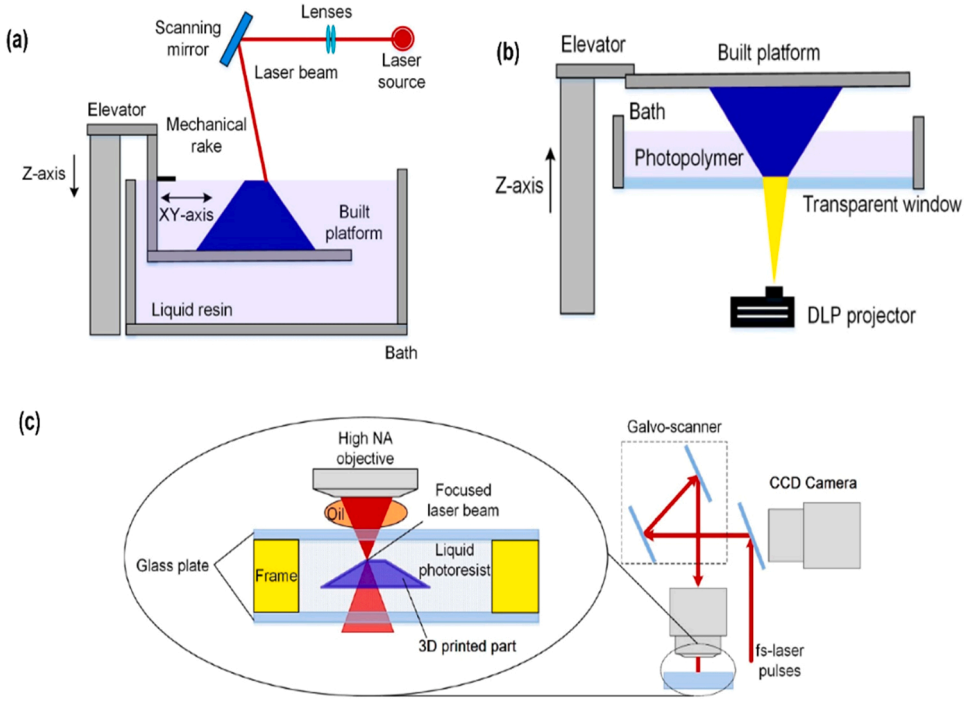

Fig. 5. Schematic diagrams of slurry-based AM technologies' main methods: (**a**) SLA; (**b**) DLP; (**c**) two-photon polymerization (TPP). Fig. 5a,b adapted from [73], with permission from Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2018.

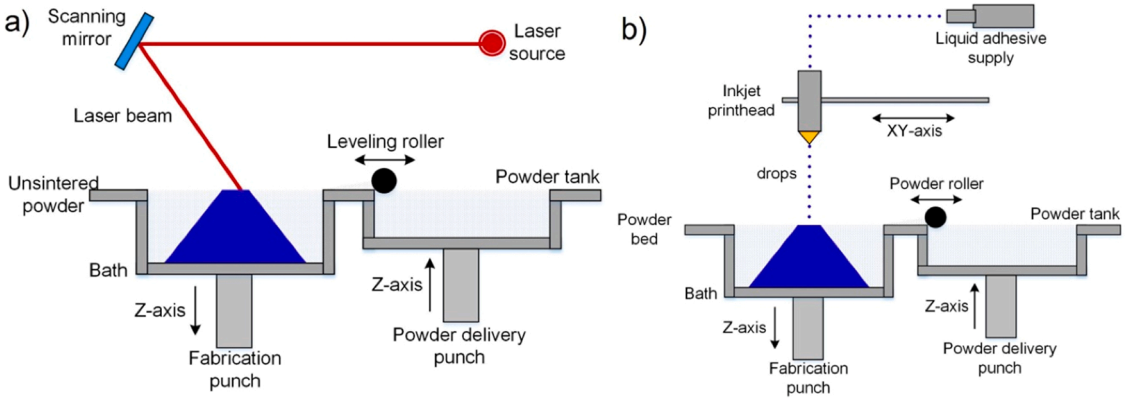

Fig. 6. Schematic diagrams of powder-based additive manufacturing (AM) technologies' main methods: (**a**) SLS and SLM; (**b**) BJ. (a) Adapted from [73], with permission from Wiley-VCH Verlag GmbH and Co. KGaA, Weinheim, 2018.

to either develop tissue scaffolds [108] or medicine delivery devices, in which it is added after completion of the printing process [109,110].

Divers ranges of TRPs are regularly used as feedstock in the 3D printing process. In this respect, some researchers produced a model approach to produce printed soft tissue foam through LPBF [111]. Owing to the detected resistance, some printing factors including holding temperatures and the powers of laser beams should be effectively set, where it is unreasonable to enhance quickly constructed 3D structures' strength via this material.

3.5. Inkjet printing

The inkjet printing technique has a different function compared to other 3D printing methods as it offers drop-on-demand through applicating of different kinds of feedstocks based on colloidal bioinks, hydrogel, and aqueous biopolymers. It includes an ink droplet deposition onto a surface as an act of process curing to detect a 3D model. Two working methods are used in inkjet printing, specifically drop-on-demand inkjet printing and continuous inkjet printing (Fig. 7) [112,113]. Regarding continuous inkjet printing, the ink solutions with shear thinning behavior effectively pass through a jet and alter to the droplet [114]. Alternatively, drop-on-demand methods are the noncontact procedure since the process can be performed through droplet jetted by a thermal actuator. The thermal drop-on-demand printing system uses a heat source for the production of a vapor bubble, which is accountable for the ejection of TRP-based inks. Concerning the piezoelectric type, an electrical stimulus is used for the piezoelectric compounds for manufacturing an acoustic pulse to force the discharge of ink droplets [115,116]. As a whole, inkjet printing methods have been widely used in different areas of bioengineering, bioelectronic applications, and automotive owing to the capability of controlling the droplets' size consistency, and directivity, in addition to the greater printing performance and cost-efficient [117].

The advance in the application of TRP-based inks permits the improvement of bioavailability, solubility, and stability, therefore amending their multifunctionalities [67–69]. Thus, effective approaches

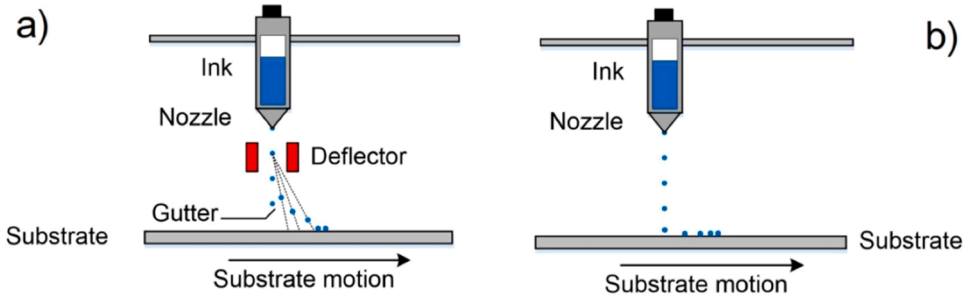

Fig. 7. Schematic diagrams of printing methods used in inkjet printing: (**a**) continuous inkjet (CIJ); (**b**) drop-on-demand (DOD).

to the use of smart materials can be helpful as a promising way to develop 3D multifunctional structures through inkjet printing. The print processing of TRPs was initiated to develop appropriate medicine-loaded TRP-including ink with a low level of particle size < 5 μm, avoiding nozzle blocking. For this reason, a suitable nanosuspension was developed using a high-pressure homogenization to use in an inkjet-type printing technique. In this case, nanosized folic acid particles with a particle size well below 5 μm were developed with a 10% (w/w) active level [118]. A combination of the formulating compensation of inferior soluble drugs as nanosuspension for decreasing the absorption problem through inkjet printing offers efficient treatment for individual patient groups.

4. Selected TRPs from natural and synthetic polymers for 3D printing

In this section, we outline the selected TRPs from natural and synthetic polymers showing the LCST phase separation in aqueous media, and also those whose functionality properties considerably change upon cooling. Owing to a wide range of macromolecules of this type, some polymers, including neutral TRP homopolymers, will not be overviewed here.

4.1. Natural TRPs hydrogels

4.1.1. Gelatin and derivatives

Gelatin is a soluble protein derived from animal byproducts obtained by partial hydrolysis of collagen, the major fibrous protein component in skins, cartilage, and bones [37,87,88]. It has been reported that some inherent features—such as the source, age of the animal, and type of collagen—affect the functionality of the gelatins [37]. Depending on the pretreatment method, there are two types of gelatins commonly used in the 3D printing process type-A gelatin (the isoelectric point at pH ~ 8–9) and type-B gelatin (the isoelectric point at pH ~ 4–5), which are obtained under acid and alkaline pretreatment conditions, respectively. The gelation mechanism of gelatin undergoes a coil-helix mechanism, once the temperature is < 35 °C (upper critical solution temperature, UCST), the random coils transform into the helix structures and the gelation speed goes faster when the temperature is around 4–25 °C [84,85]. Alternatively, the in vitro bioprinting process must be performed at human body temperature (i.e., around 37 °C). But, the application of neat gelatin in the 3D bioprinting process is suffered from poor processability as it turns into a liquid phase at 37 °C. Thus, the modification of gelatin gives the way to produce a favorite 3D structure using human body temperature, reaching stable tailored geometry upon printing at 37 °C [86–89]. Gelatin methacrylate (GelMA) is a common derivative of gelatin, which is obtained by the reaction of gelatin and methacrylate anhydride at around 50 °C under vigorous stirring conditions. GelMA retains numerous main functional properties of gelatin and also simplifies the 3D bioprinting process by controlling the rheological properties of polymeric inks. In the presence of photosensitizers—such as irgacure and Eosin Y—GelMA can gain ultraviolet (UV) photocuring feature and still deliver excellent cell viability [119,120] (Fig. 8).

While pure gelatin lacks enhanced cell viability at 37 °C, the blend of gelatin and GelMA has been applied to manufacture various tissue engineering applications from vascularization to cell patterning [121]. In pertinent work, GelMA was utilized as a sacrificial matrix to keep hydrogel fragments. The method was reported to have an improvement in the application of GelMA to create a 3D complex cell-laden hydrogel structure [122,123] (Fig. 9).

4.1.2. Collagen

Collagen, as an abundant TRP protein, is one of the most frequently used biopolymers in additive manufacturing [37,124]. It is an important element of connective tissue, acting as a structural protein. There are 30 different kinds of collagen that all are in a form of triple-helix tertiary molecular structures [124]. Collagen type I is the most common kind of collagen, which is widely utilized in the bioprinting process [125]. In contrast to gelatins, with a denatured tertiary structure and can be formed as a gel with a simple temperature change, collagen can be frequently obtained in an acidic solution and after that is altered to a hydrogel by both neutralization (increase pH) and thermal gelation [126]. Because of the diverse gelation process, collagen-based hydrogels take extensive time to form a hydrogel (at 37 °C) rather than other TRPs

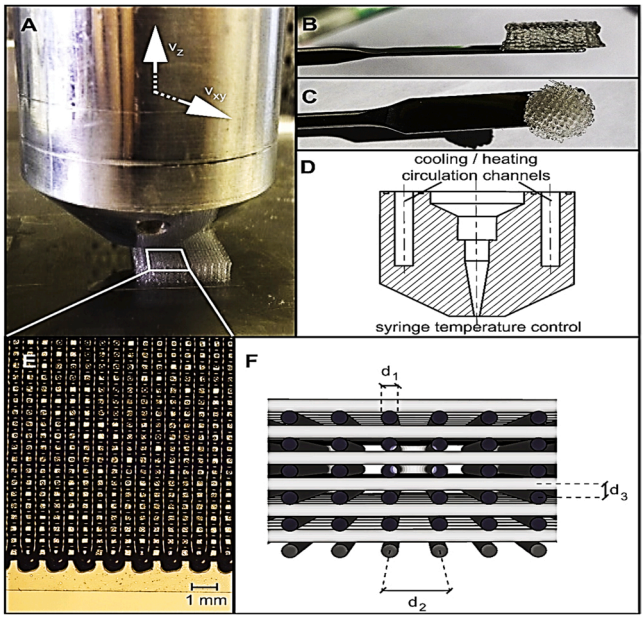

Fig. 8. photos showing a printed object (10 w/v%) (A–C). The heating layers were adjusted till the tip of the dispensing syringe to guarantee a stable process, as shown in the cross-sectional of the layers (D). The Top view photomicrograph represents a porous matrix of printed scaffold (E). A cross-sectional model object dimension and scaffold (F).
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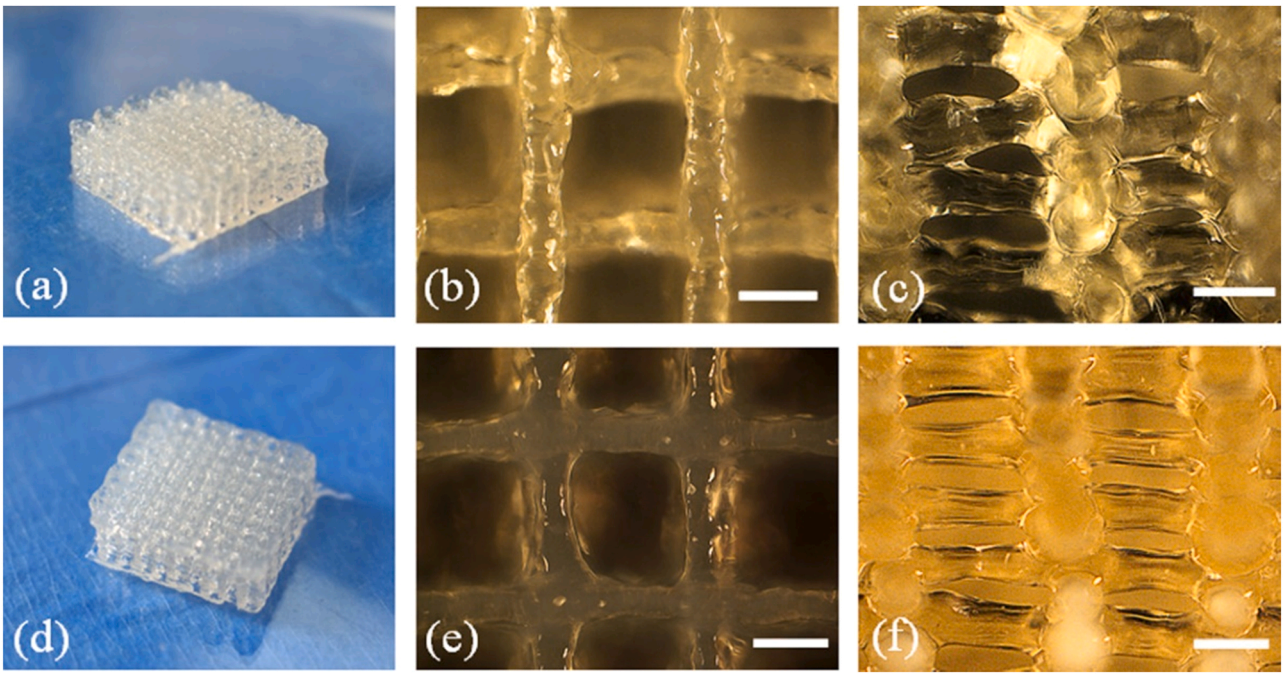

Fig. 9. The photomicrographs of 3D printing lattice assembly ($9 \times 9 \times 5$ mm^3). General shape (a), top (b), and side views (c) of a blend based on gelatin and GelMA scaffolds (a ratio of 5:8%); General shape (d), top (e), and side views (f) of GelMA scaffold (30%). The scalar bar is 500 μm.
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[126]. Collagen hydrogel can be printed using extrusion, inkjet, and bioprinting systems at comparatively low concentrations, 0.1 w/v%, to medium concentrations around 3 w/v% [127,128]. Other biopolymers including alginate, fibrin, and hyaluronan were reported to blend with collagen to enhance its 3D print and stability, which has been applied for numerous biomedical applications—such as wound healing and cartilage tissue engineering [122].

4.1.3. Elastin-like oligo- and polypeptides

Most water-soluble polypeptides are polyelectrolytes, which have some stimuli-responsive properties like thermosensitivity, pH-dependent solubility, and aggregation with oppositely charged biomolecules in vivo. Based on natural amino acids, several side-chain-functionalized nonionic and water-soluble polypeptides have been developed for different applications [129]. Polypeptides can show LCST behavior when hydrophilic and hydrophobic residues are balanced well. For example, a polymer made out of the pentapeptide GVGVP as a repeating unit shows a volume phase transition at 30 °C. Below the phase transition, water molecules are structured around the polymer molecule; the attractive forces weaken upon heating and they finally go into the bulk phase. Above their phase transition temperature, there is the stabilization of the secondary supramolecular structure, i.e., a twisted filament structure of β-spirals, which have type II β-turns [130]. It occurs due to hydrophobic folding and assembly. Some researchers fabricated a double-responsive doxorubicin-polypeptide conjugate for cancer therapy [131]. The LCST behavior of these polymers has been manufactured in a way that the rather higher temperature of the tumor is enough to undergo a phase transition, which means that the conjugate becomes insoluble once it reached the targeted tumor.

Polypeptide-based materials are promising candidates for biofabrication and biomedical applications, principally because of their outstanding biocompatibility, suitable biodegradability, and the versatile side-chain designs of polypeptides [132–136]. Taking advantage of these prominent features, polypeptide-based hydrogels have been broadly used as bioinks for 3D printing [137–139]. The 3D printing of bioinks containing the modified polypeptide, particularly for bioprinting, offers to construct structurally and reproducible intricate scaffolds for tissue regeneration [140], which has already revolutionized the tissue engineering field. Cell printing with the application of polypeptide-based bioink has also been established to develop 3D architectures including viable cells with normal cellular functions [137]. It is an innovative promising printable ink to fabricate a complex 3D tissue-like object in tissue engineering. For example, Li et al [138]. introduced an initial in-situ multilayer 3D printing through a supramolecular polypeptide–DNA hydrogel. The printed bioinks had a fast-healing feature because of the dynamic cross-linking using DNA hybridization (Fig. 10). He et al [141]. fabricated an antibacterial and biocompatible bioink by grafting different amounts of glycidyl methacrylate to ε-poly-L-lysine, as a natural polypeptide. The 3D printed structures showed the highest efficiency of cartilage-like tissue regeneration following 28 days of incubation in vitro, signifying it is a promising antibacterial bioink for 3D bioprinting and tissue engineering applications. In another work, Murphy et al [142] reported a 3D printable responsive crosslinked system based on polypeptides containing glutamic acid. It could potentially provide an innovative thiolyne click chemistry crosslinking device to use in the field of 3D printing, offering extremely stable hydrogel structures. They stated that polypeptide-based self-healing bioinks are likely utilized to construct tissue scaffolds with more 3D printings in the future. Biomedical applications of the prepared polypeptide-based self-healing hydrogels are also a growing research area, and presumptive application in biofabrication and biomedical areas can be attained in the future [142].

4.1.4. Methylcellulose (MC)

Due to the rigid semi-crystalline structure of cellulose, it lacks to dissolve in a wide array of solvents [143]. This makes the cellulose-based inks have poor flow behavior, which accordingly limits their printability. Therefore, pure cellulose can be modified through different physicochemical methods to make the neat cellulose desired to enhance its rheological properties and improve the mechanical features of resulting printed constructs [144,145]. A promising outcome has been obtained when cellulose ether-based hydrogel is produced as printable ink [37,146,147]. The MC has the exclusive feature of reversible thermogelation. In the aqueous solution, it is completely

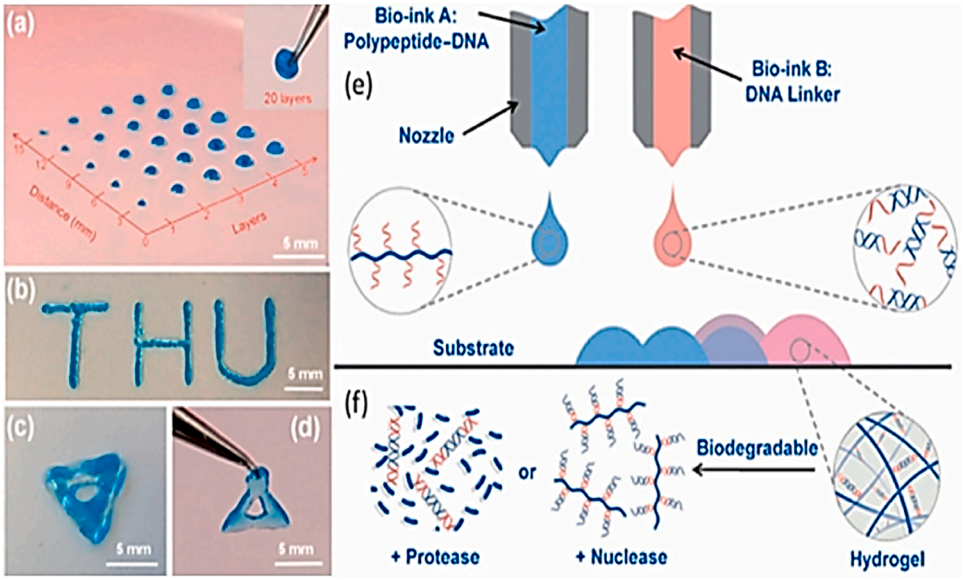

Fig. 10. 3D printing DNA incorporated polypeptide bioink (blue). a) Array of printing droplets with numerous layer numbers (up to 5 layers). Inset: Hydrogel structure with 20 layers. b) the phrase "THU" printed with five layers. c, d) A ten layers triangle printed in 5 min. d) Mechanical strength of the printed structure, e) Bioink A (blue): polypeptide–DNA, and B (red): DNA linker, f) biodegradation structures .
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hydrated and there is little polymer-polymer interaction except for a simple entanglement [148]. With increasing temperature, a considerable reduction of viscosity can be occurred because of a decrease in the hydration water. Upon reaching critical temperature, adequate dehydration happens to induce a biopolymer–biopolymer interaction rather than a biopolymer–solvent interaction. Accordingly, this cellulose ether-based solution starts to form a 3D network structure. With decreasing the temperature, there is a totally reverse gelation process,

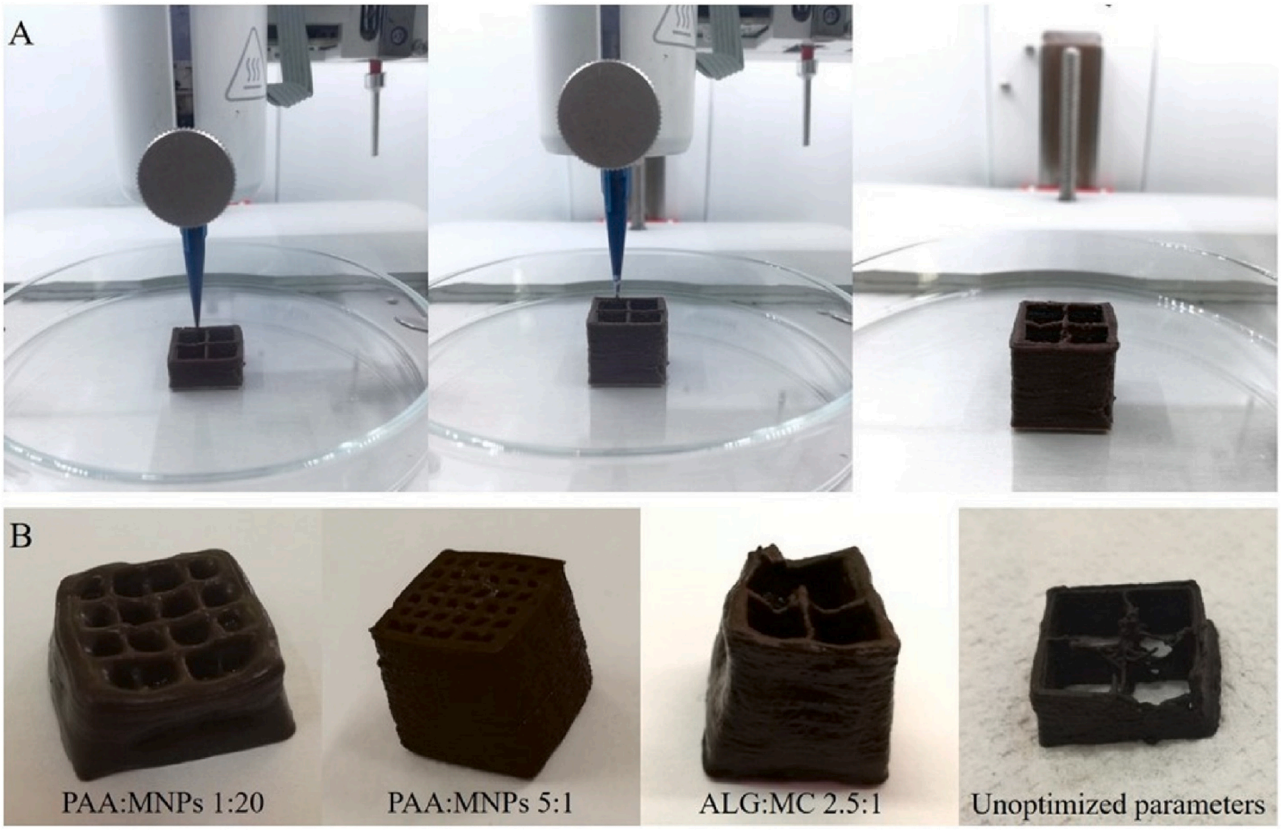

Fig. 11. (A) Direct printing of a hydrogel (1 × 1 × 1 cm^3) based on alginate-methylcellulose-polyacrylic acid magnetic nanoparticles; (B) Images of different 3D printed objects with diverse formulations and printing parameters.
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where the formed 3D network reverts to the sol phase, retrieving its initial viscosity. It should be mentioned that the gelation mechanism of MC is related to the hydrophobic interactions, that is, when the temperature reaches LCST, the hydrophobic parts in the chain become dominant and link with each other to create the gelation network [122]. Among TRP hydrogels, MC is the most desirable material to manufacture 3D complex cell-laden structures as a scaffold-free alternative compound to overcome some of the bioprinting drawbacks associated with the traditional scaffold-based materials in tissue engineering [149–151]. It was reported that MC has been effectively dispensed through a pneumatic extrusion bioprinting system at a level of 4 w/v% to produce a 3D printed complex bone-like tissue [152]. However, MC alone does not show any bioactivity that favors the grafting of adhesion cells. Though, its unique TRPs feature makes MC used as supporting material for the bioprinting process. In this respect, the introduction of other therapeutic biopolymers in a system containing MC is valuable to induce bioactivity for the 3D printing tissue engineering process [153,154] (Fig. 11). Rastin et al [149] produced a multifunctional bioink based on thermoresponsive MC/alginate hydrogel including gallium for skin tissue engineering via removal of the risks related to a bacterial infection. The prepared hydrogel printed out multilayered 3D structures with shape integrity and high resolution, supporting the obtained rheological results of printable bioink. Furthermore, it was detected that the produced bioink supported encapsulated fibroblast cellular functions.

4.1.5. Carrageenan

Carrageenan is a linear, sulfated, hydrophilic polysaccharide with a high molecular weight, consisting of disaccharide repeat units of galactose and (3,6)-anhydrogalactose connected by alternating α-(1,3)- and β-(1,4)-glycosidic links [155,156]. The kappa (κ-) and iota (ι-) carrageenans are derivatives of carrageenan, which can develop a well-defined TRP gel. Carrageenan is then extensively applied to form a stretchable and self-healing double-network hydrogel for 3D printing purposes [37]. Based on the thermoreversible sol-gel transition behavior of κ-carrageenan in water, Liu et al [157] produced a double-network hydrogel by blending a crosslinked κ-carrageenan network with a covalently crosslinked polyacrylamide network. This blend hydrogel showed a TRP feature with excellent recoverability and noteworthy self-healing ability. More appreciably, the blend hydrogel ink of κ-carrageenan/polyacrylamide was effectively employed to print the hydrogel into an intricate 3D object, and the printed hydrogel proved the high mechanical strength after UV exposure (Fig. 12).

Rastin et al [89] introduced a biocompatible thermoresponsive MC/kappa carrageenan and electroconductive PEDOT:PSS bioink, which had favorable rheological properties for the 3D printing process. The ink could manufacture physiological-scale 3D printed objects.

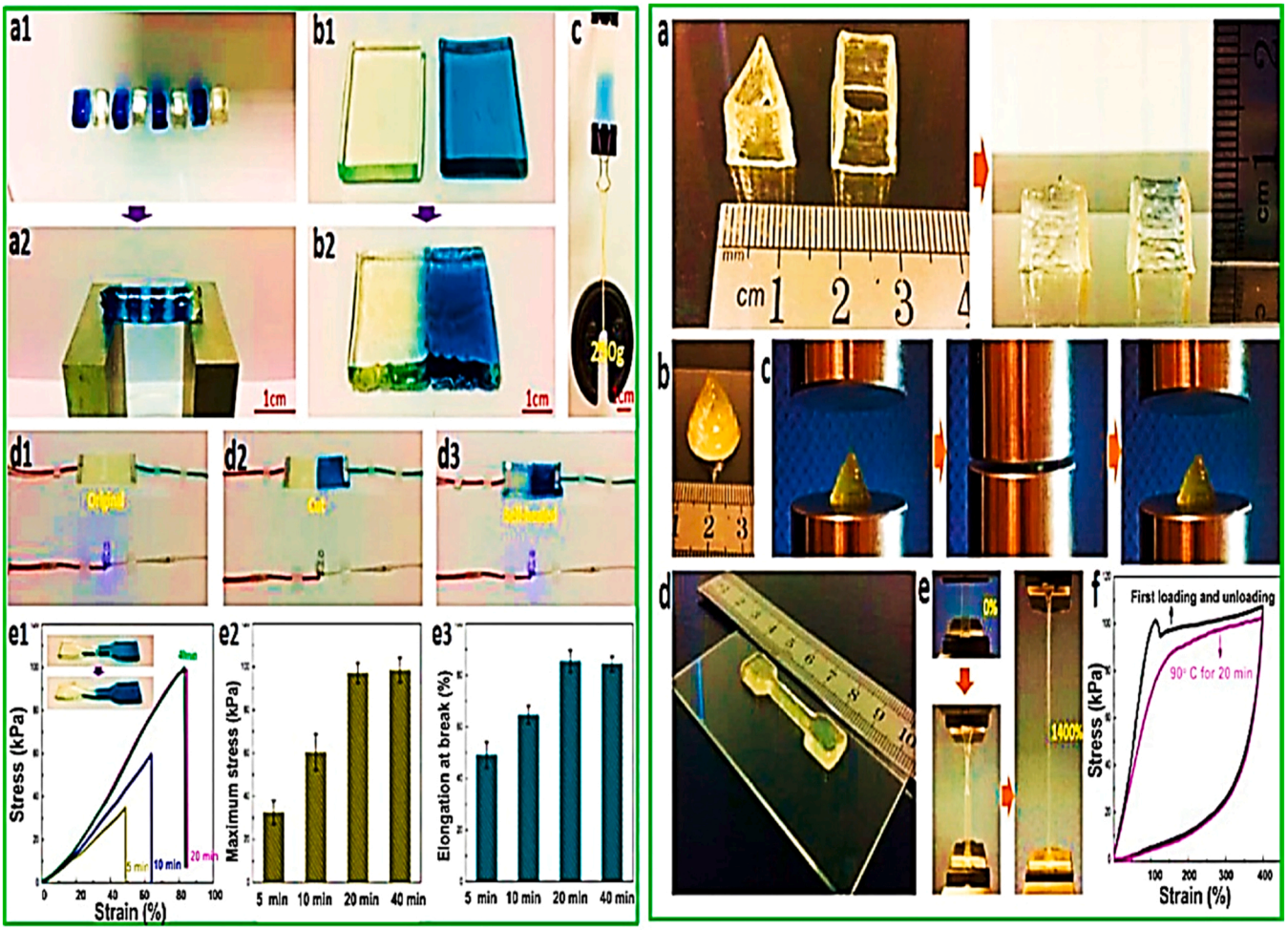

Fig. 12. (Left): (a_1), A small column-formed double network (DN) construct. (a_2), The tubular self-healing DN. (b_1), rectangular-formed DN structure. (b_2), Self-healed rectangular-formed object. (c), A printed construct with self-healing properties upholds 250 g weight. A current comprises the combined LED with pristine (d_1), cut (d_2), and self-healed constructs (d_3). (e_1), storing period influence on tensile strength of the DN structures. (e_2) The changes in the maximum stress. (e_3), elasticity. (Right): (a), The printed DN structures. (b), A cube and cone shape constructs. (c), After applying a pressure force the 3D printed cone recovers its original shape. (d), The preparation of printed dumbbell-shaped objects, and (e) the mechanical test. (f), Stress-strain hysteresis of different printed constructs. Reproduced with permission from [157]. Copyright 2017 American Chemical Society.

Furthermore, the encapsulated human embryonic kidney 293 (HEK-293) cells in this bulk hydrogel followed by 3D bioprinting preserved high cell viability over a week, verifying in vitro biocompatibility of the ink.

4.1.6. Agarose

Agarose is a biocompatible linear polysaccharide extracted from marine algae [158,159], comprising (1,4)-linked (3,6)-anhydro-α-L-galactose and (1,3)-linked β-D-galactose. Agarose shows a thermosensitivity behavior with excellent reversibility, which makes it for cell-encapsulation in tissue engineering applications [160]. The hydrogen linkages from the interaction of the agarose strands propose the development of a 3D network at low temperatures, therefore, it offers a self-gelling feature. On the contrary, a rise in the temperature causes the dissociation of the hydrogen bonds among the agarose strands. It has been reported that the mechanical strength offered by agarose is comparable to that of tissue and is simply manufactured by varying biopolymer concentrations. Once solubilized in water, agarose develops a stable gel with an elastic-like structure, leading to a 3D porous matrix. This offers an appropriate substrate for cell adhesion, spreading, and proliferation [161,162]. The gelation mechanism of agarose is like gelatin, nevertheless, it changes from random coil to double helices once the temperature attains LCST (around 30–40 °C) [50,163]. As a TRP-based polymer, agarose can be utilized in both mechanical- and pneumatic-extrusion bioprinting systems at a low concentration (1–5 w/v%) [152,164]. Agarose has been applied as a sacrificial element to manufacture a mold and pattern rather than printing it with cells directly [164,165]. In this respect, printed agarose was produced as a micro-channel for the vascularization of a tissue engineering architecture [166]. Additionally, agarose has been blended with compatible biopolymers to improve the thermosensitivity of 3D printed soft tissues [167]. Agarose hydrogel also offers a possible application aimed at using bone tissue engineering applications [122].

4.1.7. Hyaluronan and derivatives

Hyaluronic acid (HA) or hyaluronan is a natural glycosaminoglycan comprising a repeating unit of β-(1,4)-D-glucuronic acid and β-(1,3)-N-acetyl-D-glucosamine [168]. In physiological solution, it shows an extremely extended conformation as random coils because of the presence of hydrogen linkages among the disaccharide units, and polyanionic features [169]. To reinforce the mechanical behavior and also thermosensitivity property of HA, a methacrylate group can be grafted onto its backbone to produce methacrylated hyaluronan (MeHA) [37]. This conjugation offers the opportunity for crosslinking and the development of a stable structure, which is stronger than HA alone. In the presence of a photosensitizer, the biopolymer can be crosslinked using a UV polymerization reaction, which produces a 3D network structure [170]. MeHA at a level of 0.1–4 (w/v%), has been used for 3D printing, producing 3D structures with a large range of thermosensitivity, mechanical strength, and extents of biodegradation. MeHA is a promising material for tissue engineering and regenerative medicine purposes. Nevertheless, it is not appropriate alone for printing owing to its low viscosity. Intending to obtain a suitable printable bioink, there are several works dealing with the manufacture of a blend based on neat HA, MeHA, and a range of natural or synthetic polymers [171]. In a relevant investigation, a dual crosslinked TRP bioink was produced consisting of poly(N-isopropylacrylamide) grafted hyaluronan (HA-pNIPAAM) with MeHA to enhance mechanical properties [172]. They first conjugated PAAm onto MeHA to produce a rapidly gelling TRP constituent as temporary support, allowing it proper for 3D bioprinting.

4.2. Synthetic TRPs Hydrogels

4.2.1. Poly(N-alkylacrylamide)s (PNIPAM)

The most broadly studied TRPs in health and bioengineering applications are dedicated to poly(N-isopropylacrylamide) (PNIPAM) [13,84,87]. The brilliant functional properties, including biocompatibility and sharp phase transition in the aqueous solution at 32–33 °C, make it an excellent TRP for 3D printing purposes. The LCST of PNIPAM is independent of concentration and also molecular weight, but it is simply altered upon shifting the hydrophilic/hydrophobic balance. The LCST at the point close to the physiological circumstances offers PNIPAM a promising material for biomedical fields. Thus, there is an increasing interest in to use of PNIPAM in tissue engineering and drug delivery applications, which recently captivated scientists to develop the TRPs for 3D printing [173–175]. Controlling the flow behavior of the TRP suspension is a critical step in the 3D printing process. For example, Wang et al [173] designed a colloidal suspension based on a ceramic powder (Al_2O_3) dispersed with a distinct TRP dispersant, i.e., poly (acrylic acid)–PNIPAM. This suspension experienced an extraordinary fluid-gel transition in response to the thermal stimulus because of the phase transition of the graft chains that is -PNIPAM. They successfully assembled a 3D periodic structure with a fine size of 100 μm by 3D printing. In another related study, Du et al [174] fabricated a 3D printed GelMA micropattern on a PNIPAM-coated interface. They showed that the directed injury-free collective cell migration occurred in parallel and perpendicular directions. After seeding cells, a cell-free space was developed between two 3D printed GelMA micropatterns by lowering the temperature of the PNIPAM interfaces to promote cell detachment. Nizioł et al [175] produced an innovative printable bioink aimed at the 3D printing process to mold thermoresponsive structures. The pintable inks were then loaded by Octenisept® for rendering the therapeutic features and expanding its wound dressing application. Owing to the incorporation of TRPs, the bionics could react to the change of temperatures with the regulation of the swelling and Octenisept® diffusion. The results showed that the printing objects had an excellent temperature-induced shape-transforming feature, and henceforth a promising application as a wound-healing product (Fig. 13).

4.2.2. Pluronic F-127

Pluronics® or poloxamers mostly Pluronic F-127 (PF127) show a sol-gel transition close to the body temperature with an exclusive thermosensitivity, which is broadly used in a wide area of bioengineering and drug delivery applications [176], Pluronic F-127 is readily soluble in nonpolar organic solvents and detected its application in the design of dosage forms. Pluronic F127 shows a diverse aggregate form depending on the molecular weight, blocking size, solvent formulations, temperature, etc. Recently, TRP hydrogels, including those based on Pluronic F127, have been processed by 3D printing systems. Though, the structure of neat Pluronic F127 hydrogel cannot support cells in the long-term owing to high density, limited adhesive moiety, and inadequate nutrient transport [177,178]. Therefore, Pluronic F127 has frequently been employed as a fugitive [179], supporting compounds [180], and deposited in combination with other biopolymers that can be crosslinked in the final phase or develop a robust hydrogel concurrently to their depositions [181,182]. The produced printable ink was a triblock copolymer that transformed into a micelle at elevated temperatures. Lee et al [183], proposed an innovative technique to develop a uniaxially aligned pattern on the struts of the matrix based on poly (ε-caprolactone) or poly(lactic-co-glycolic acid), by taking advantage of the immiscible rheological features and flow-induced force in a dispersed Pluronic F-127 phase (sacrificial materials) and matrix compounds. Their fabricated structures established that the cultured cells have been completely arranged in the direction of the patterned surface.

4.2.3. Poly(N-vinyl caprolactam) [PVCL]

PVCL has not been studied as intensively as e.g., PNIPAM or Pluronic F-127, however, it is another TRPs, exhibiting an LCST as low as 30 °C [184]. It possesses very interesting properties for pharmaceutical excipients and biotechnological applications—such as biocompatibility, solubility in water and organic solvents, and high swelling ratio—along with an effective transition temperature within the settings of these

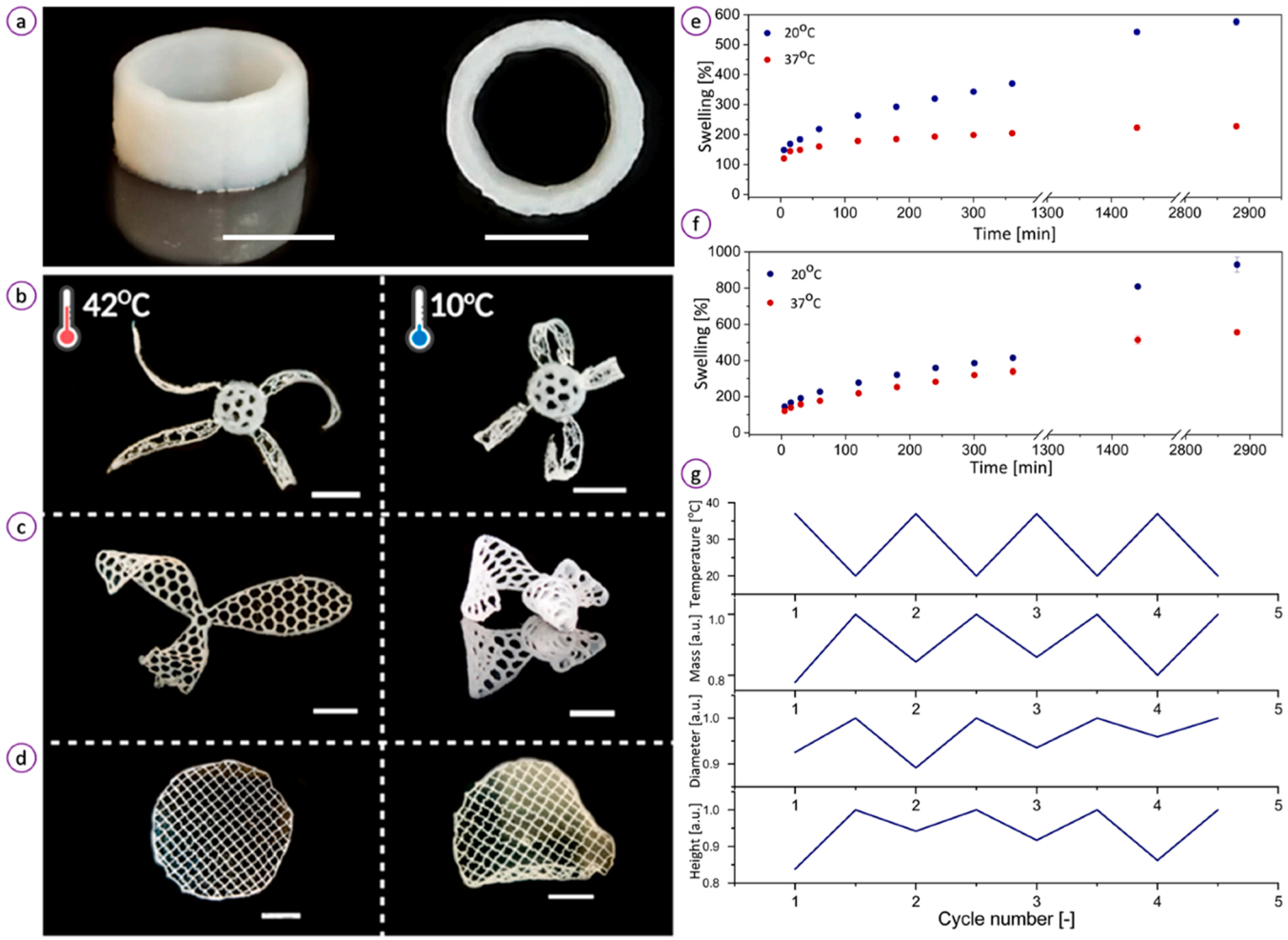

Fig. 13. (a) Images of printed objects containing TRPs with excellent resolution; (b) Flower-like structure including TRPs petals and nonactive cores; (c) Printing TRPs-based propellor; (d) Printing TRPs-based disc. The swelling powers of 3D panted samples at 20 and 37 °C in water (e) and phosphate-buffered saline (f); (g) Temperature-induced swelling (20 °C) and de-swelling (37 °C) phases detected with regard to sample height, diameter, and mass. Reprinted with permission from ref [175].

applications. However, the monomer is difficult to polymerize in a controlled manner. PVCL offers accuracy fabricating of LCST reliant on the pendant chain lengths and end-group. Although, PVCL hydrogels are usually non-porous structures with poor mechanical properties, which makes them inappropriate for the 3D printing process. Therefore, diverse nanomaterials or crosslinkers can be used to enhance the 3D printing performance of PVCL-containing structures. In an investigation, a biocompatible TRP based on PVCL/clay nanocomposite hydrogel was developed with improved mechanical strength. In this respect, a macroporous structure was obtained by introducing an emulsion containing an N-vinyl caprolactam monomer as a template and nonclay sheets as a stabilizer. The TRP 3D printed PVCL/clay nanocomposite exhibited enhanced tensile strength compared to that of 3D printed PVCL without clay nanoparticles. The prepared PVCL nanocomposite showed an appropriate thermosensitivity with a phase transition temperature of 35 °C that allows a long-term cell culture [185].

4.2.4. Poly(2-oxazoline) derivatives

Poly(2-oxazoline) derivatives show a molecular weight- and concentration-dependent LCST in the range of 35–80 °C. In this group, poly(N-ethyl oxazoline) has a transition temperature of around 62 °C, which is too high for any health and bioengineering applications like the drug delivery process. Hence, it should be blended with other TRPs. Rueda et al [186] developed a double TRP system through graft polymerization of EtOx onto a modified PNIPAM backbone. These systems can be explored for their potential in drug delivery applications because they tend to aggregate above the LCST. Poly(2-ethyl-2-oxazoline) (PEtOx) is another interesting class of poly(2-oxazoline) TRPs as a safe food additive. It shows a transition temperature of around 61–69 °C, which can be suitable in the formulation of dosage forms. Considering that fused deposition modeling (FDM) 3D printing has been detected to be a cutting-edge method to manufacture personalized-dose medicines. In this regard, Feng et al [187] fabricated a PEtOx-based solid oral tablet through an FDM 3D printer. This TRP 3D printed tablet has presented an extended-release profile for over 20 h, representing the potential of PEtOx as an innovative extended-release compound to develop a controlled-release drug delivery system by 3D printing.

4.2.5. Poly(methyl vinyl ether) [PMVE]

PMVE offers a transition temperature precisely at 37 °C, which makes it very interesting for biomedical applications [188]. It exhibits a typical type III demixing behavior, which is in contrast to the thermal feature of PNIPAM. PMVE can be produced through cationic polymerization under an inert condition. Nucleophile materials—such as alcoholic compounds or materials with amino groups— cannot be tolerated upon synthesis, which restricts the potential application of PMVE [130]. Recent developments in manufacturing techniques have caused the application of PMVE in bioengineering. Boehm et al [189] employed piezoelectric inkjet printing to manufacture a drug-loaded microneedle based on a blend of PMVE/maleic anhydride with quantum dots. In

another study, Boehm et al [190] coated polyglycolic acid with PMVE in a dimethylsulfoxide solution. Their results revealed that the coated and uncoated of this blend could release within 3 h in the porcine skin of methylene blue dye in the itraconazole layer.

4.2.6. Poly(acrylic acid-co-acrylamide)s [P(AAc-co-AAm)s]

An interpenetrating network of P(AA-*co*-AM) is one of the few TRPs with a UCST behavior in the biomedical application, whose transition temperature is detected to be 25 °C [191]. This UCST behavior is caused by the cooperative effects coming from the hydrogen bonding between AAc and AAm units. In an investigation, a facile approach was performed by producing a 3D gel structure based on highly viscoelastic P(AAc-co-AAm) and poly(acrylic acid-*co*-*N*-isopropyl acrylamide) (P(AAc-*co*-NIPAm)) solutions or their mixtures, which were printed into 3D constructs by using multiple nozzles. The 3D printed gel structure deformed and recovered at a fast speed due to the small diameter of the gel fiber. The four-armed grippers were also fabricated to clamp the plastic ball by substantial holding force, as large as 115 times the weight of the gripper. It was proposed that this method can be appropriate to other rigid hydrogels and widen their applications [192].

5. Different TRP forms used for 3D printing applications

Depending on the aim and the scope of the 3D printing process, various forms of TRPs have been used for rapid prototyping, including hydrogels (for controllable release of drugs), films (for cell-sheet preparation), nanoparticles (for diagnosis of malignant diseases), mussel-inspired materials (for biomedical engineering and soft electronics), interpenetrating polymer networks (for tissue engineering), micelles (for drug delivery systems), and thermochromic polymers (for medical thermography). The micro- or nanostructures of TRPs, developed by grafted copolymers, have been commonly fabricated based on their ultimate applications. For example, TRP injectable hydrogels have been applied for the 3D printing of bone-like materials as a noninvasive technique [193], while a film microstructure has been utilized for the preparation of a cell sheet [194] and a TRP nanocapsule revolutionized drug delivery system [195]. In the upcoming sections, the diverse types of TRPs for the 3D printing process are described separately.

5.1. Hydrogels

Hydrogels are the main forms of macromolecules that have found a wide range of applications in 3D printing [196–198]. Because of the existence of crosslinking between the polymeric chains, hydrogels are capable to absorb a huge level of water without dissolving [199–203]. Therefore, physical junctions (including, chain entanglements, crystallite development, secondary forces, etc.) or chemical crosslinking (like covalent linkages) offer the unique swelling behavior of hydrogels and 3D structures [204]. TRP hydrogels are promising for biomedical applications since they can swell in-situ upon physiological circumstances and deliver the benefit of suitable management. For example, PNIPAM has been crosslinked by *N*,*N*′-methylene-bis-acrylamide or *N*,*N*′-cystamine-bis-acrylamide to develop a TRP hydrogel. As discussed before, PNIPAM has an LCST behavior around 32–33 °C. This temperature range can be adjusted close to the body temperature (37 °C) through various modification methods to achieve a controlled drug release loaded into PNIPAM [205]. Furthermore, its coil-to-globule transitions lead to a quick decrease in the hydrogel volume, which enables the rapid release of the solvents and also the introduced drugs, followed by a controlled release by more linear diffusion [206].

To date, most of the studies have focused on the improvement of the mechanical properties of the hydrogels using numerous energy dissipation methods [37,198–208]. In this respect, the hydrogel assembly approaches still principally relate to the casting and molding, resulting in a restricted shape intricacy with low manufacturing productivity. As aforementioned, additive manufacturing techniques are gaining increasing attention as they provide a more flexible and effective approach to producing complex geometry. One trend in the future is using the TRP hydrogels printing system to create functionalized end-user 3D printed structures, therefore allowing to obtain a versatile shape in tissue engineering, biomedical, energy, and bioengineering applications. For example, 3D printed wound dressings with the therapeutic compound can be fabricated with TRP hydrogels. In a relevant conducted work, Nizioł et al [175] used poly(N-isopropylacrylamide) (PNIPAAm) precursors, sodium alginate, and MC to fabricate a wound healing material. The ink contained laden with a blend of octenidine dihydrochloride and 2-phenoxyethanol (Octenisept®, OCT), which possessed accurate printability and shape fidelity.

5.2. Mussel-inspired TRPs

Since the revolutionary effort by Lee et al [209] mussel-inspired chemistry has emerged as a universal method to functionalize substrates. Mussel-inspired chemistry is inspired by the robust adhesion of mussels toward grit, rock, and ship in seawater. Therefore, it takes advantage of the strong adhesion of mussels to a diverse range of biomaterial surfaces, including metallic elements, biopolymers, and ceramics [97,98,210,211]. On the other hand, the degradation of the hydrogels' structure, once they are printed, can happen because of the existence of shear forces, deteriorating their integrity with losing the printing performance. The biomaterials can be heated to protect the hydrogel structures against this condition, where the host-guest interaction makes noncovalent linkage, hydrogen bonding, and dynamic covalent bonds [212]. This is an innovative tactic inspired by marine mussels. In this matter, self-repairing biopolymers have come into play and are utilized in many research areas adopted by marine mussels [213]. The segregated foot proteins developed by byssus are included in the protein strands that can be adhered to the subaqueous platforms. The self-healing functions of this mussel are related to the reversibility of metallic-catechol coordination [214].

5.3. Interpenetrating polymer network (IPN)

IPNs are a broad class of macromolecule "alloys" that are classically utilized as an alternative route for the fabrication of polymeric-supported reagents. They include two or more intimately blended polymeric networks at least one of them being polymerized or crosslinked in the presence of the other [215–217], with no covalent bonding among them, which cannot be also separated unless the chemical linkages are disrupted [218]. The prepared nontoxic IPN hydrogel systems offer an excellent candidate for 3D printing in pharmaceutics in connection to their super swelling feature and biodegradability. Explicitly, an IPN of alginate-polyacrylamide has developed a tunable elastic and viscoelastic hydrogel that swells above their upper critical solution temperature, specifically UCST. This is due to the formed hydrogen linkages between the two different networks being degraded at higher temperatures allowing the networks to swell. This preliminary work has shown the material properties of 3D printed IPN object was related to those reported in the biomechanics literature for soft tissues like skeletal muscle, cardiac muscle, skin, and subcutaneous tissue [219]. In another work, a mechanically robust and tunable IPN hydrogel was fabricated based on GelMA and silk fibroin through 3D printing, which could be useful for various tissue engineering and regenerative medicine purposes [220].

In contrast to IPNs, semi-IPN architecture has a different structure in terms of the crosslinking matrix as they are not entwined networks, resulting in a two-dimensional analog of the IPN. Concerning the IPN structure, both polymeric strands are crosslinked through two dissimilar paths to inhibit co-network development. While, concerning semi-IPN architecture, only one single polymer can be crosslinked in the presence of the second linear polymer. In addition to their capability to prevent phase separation, semi-IPN material occasionally can combine

the functionality of the two polymers into one single material [221]. As an example, gelatin shows proper flow behavior with TRP features, and alginate crosslinked via calcium ions can make up for its poor mechanical strength. Their blend has formed a robust and high biocompatible semi-IPN hydrogel containing a crosslinked hydrogel and an uncrosslinked hydrogel, which is favorable to 3D extrusion printing [222,223].

5.4. Micelles

Integrating hydrophilic and hydrophobic monomers into block copolymers offers the development of an ordered structure in solution, which can be self-assembled and produce the hydrophobic core around a hydrophilic shell micelle. Micelles are valuable to encapsulate hydrophobic bioactive medicines and delivered them into an aqueous environment [224,225].

Specifically, nanogels are hydrogels formed by connecting nanoscopic micellar networks, which allow the incorporation of the hydrophilic payloads to the exterior of the micellar networks and hydrophobic payloads in the core of the micelles [226]. For example, poly(D, L-lactide-*co*-glycolide)-block-poly(ethylene glycol)-block-poly(D, L-lactide--*co*-glycolide) nanogel has been extensively employed to locally carry the hydrophobic drugs at a slow elution rate. Nanogels delivering a photosensitizer have also been 3D printed to enhance the gelation process or to improve the mechanical properties of the 3D printing hydrogel, which offers local delivery of the therapeutic compounds [227]. Nanogels are also 3D printed in tissue engineering [228]. Pluronic F-127 gel rather mimics the functional properties of natural tissues, nonetheless, it does not last long enough for long-term cell cultures. In this regard, a native Pluronic F-127 was blended with acrylated Pluronic F-127 to produce a robust and stable nanostructured hydrogel through UV grafting [181]. The 3D printed nanogel has also been used as a detoxification device [116,229]. For an instance, a photo-crosslinked poly(ethylene glycol) diacrylate hydrogel as a 3D matrix and a polydiacetylene nanoparticle were chemically tethered through polymerization and installed in a hydrogel matrix [229]. Nanogels are utilized as a filler of the 3D printed external object to improve its mechanical strength and biocompatibility. In this way, Pluronic F-127 nanogel has been used to carry the simvastatin into a 3D printing porous titanium alloy for orthopedic application [230].

5.5. Films

TRP polymeric films enable the development of many functionalities with a switchable interfacial feature. These films could show different trends in biomedical, energy research, and biomedical, in terms of the variations of the bulk (interior) properties against those of the surface properties. For example, multifunctional thin films can be employed as TRP materials for engineering cell sheets, showing a critical area in tissue engineering. A TRP film based on chitosan including polyurethane and PNIPAM was shown as a promising substrate for wound dressing [231].

There was a reduction in the film wetting properties as well as water vapor transmission with increasing temperature, which could be attributed to the LCST properties of PNIPAM and also the repulsion of water molecules at higher temperatures. Although PNIPAM-based TRP film can offer a wide-ranging potential for biofabrication, it still possesses a significant drawback as its lack of biodegradability and not well biocompatible at the elevated temperature when it is hydrophobic [232].

5.6. Particles (nano/micro)

TRP particles have been broadly utilized in 3D printing owing to their several functionalities including drug delivery, protein adsorption, and core/shell-like matrix [233]. Therefore, they can be applied as the treatment or diagnosis of malignant diseases— such as cancers and oral malignant— where TRP particles load and then release the drugs in a controlled manner at the target place by the induced differentiation of the temperature. Therefore, they decrease the side effect of the oncological treatment. One fascinating point of the TRP particles is the response time to a temperature change. It has been stated that the response time is related to the square of the particle radius. This property is imperative as the application of a tiny amount of TRP core-shell particles would offer a decrease in the response time in that application, where a sharp response is required [234].

An innovative fabrication technique, specifically photo-emulsion polymerization, has been introduced for the preparation of monodisperses, i.e., TRP core-shell particles. In the meantime, the core-shell microgel, which includes the hydrophobic cores with the hydrophilic TRPs shells, is promising for researchers as this system can combine the functionality of both the core and the shell [235]. Rapid prototyping through 3D printing of TRP core-shell particles has been used to manufacture micromixers with diverse geometric designs. In a pertinent investigation, a crosslinked alginate microgel was loaded with the antimicrobial peptide polymyxin B in a continuous process. The effectiveness of peptide encapsulation was detected to be much higher for all examined micromixer designs, where the maximum encapsulating effectiveness was detected for the smallest particles produced by microvortex-mediated self-assembly [236]. A porous particle based on PNIPAM as a TRPs particle was also fabricated for the sustained and controllable release of the chemotherapeutic drug, which could demolish cancer and the proposed particles revealed a good performance as an oncoterapeutical device [237].

5.7. Thermochromic polymers

Thermochromic properties are color alterations detected in chromic compounds because of temperature fluctuation, which can be either direct or indirect. Thermochromic polymers are widely applied in temperature sensing systems across numerous fields including packaging, medical thermography, the non-destructive experiments of engineered articles, electric circuits, and the pharmaceutical sector [238]. The liquid crystalline and conjugated biopolymers normally display thermochromic features, where the conjugated π-electrons on the backbone (for example polythiophene) play a thermochromatic [239]. The temperature difference leads to the change of the conjugated lengths of the π-electrons and an alteration in the wavelength of absorption, for which thermochromism is developed. Chen et al [240] fabricated UV curable and thermochromic shape memory polymers that offer color-changeable printing. Thermochromism was imparted by the addition of the thermochromic microcapsule to the system, which endows the printed objects to reversibly change colors upon heating and cooling.

6. Additive manufacturing to produce thermoresponsive multifunctional devices

The functionality of TRPs allows an important control over features of developed 3D constructs produced from such macromolecules through environmental situations, which raise a strong interest in biomedical and biofabrication [182,241–278], biotechnology [279–302], pharmaceutical [303–323], electroconductive and biosensor instruments [324–342], as well as food industries [197–200, 343,344–356]. For example, biofabrication utilization of TRPs typically offers a minor level of stimuli including temperature, pH, ionic strength, redox reactions, light, shear stress, enzymes, etc., which limits their applications because of the fact that protein-based materials can be denatured and cells can be injured if the stimuli being beyond the physiological boundaries. In this section, we summary the application of selected TRPs from natural and synthetic polymers in different fields, which shows the LCST phase separations in the aqueous solution and

also those whose functionality noticeably changes upon cooling.

6.1. 3D printing of TRPs inks for biofabrication

The application of TRPs in biofabrication is promising to develop in vitro models or implantable objects, which simulate the intricacy of a natural tissue [357]. There are two categorized biofabrication methods including bioassembly and bioprinting. Bioassembly can be accomplished based on the development of assembled building blocks into 3D architectures through automated-assembly techniques. The bioprinting methods are applied to manufacture 3D printed architectures based on extrusion and lithography-based printing procedures [358]. Concerning the application of TRPs in biofabrication including bioassembly, a cell-encapsulating TRP was employed as a building block in construction methods [359]. In this way, the fluidic assembly method has been produced using a specific microfluidic channel for controlling the poly (ethylene glycol) diacrylate movement within a printed object. An exterior magnetic field was leveraged for the guidance of a magnetically loaded GelMA nanosized particle and polyethylene glycol within a simpler and complementary replacement for engineering multilayer printed objects [360]. Furthermore, a magnetically responsive microrobot has been also used for controlling the functionality of TRPs for bottom-up tissue engineering of cell-encapsulating printed structures [361]. In another investigation, an acoustic-wave technique has been developed for the manipulation of TRPs to develop 3D printed cell-encapsulating microscale hydrogel structures [362]. TRPs can be also employed to develop a printable bioink to use in extrusion-based bioprinting [363]. Typically, the printable bioink was obtained through both single and double-network gels, and the physicochemical features were reserved homogeneous. Though, the uneven matrix could be favorable to printing an intricate tissue. To solve the mentioned problem, poly(ethylene glycol) (prepared from the microfluidic) has been blended using the printable hydrogels precursor for engineering nanocomposite printable bioinks comprising dissimilar macroscale and microscale situations [364]. The inherent nature of such a system has been shown through encapsulating mesenchymal stem cells in the poly (ethylene glycol)-based bioink, which have been then enclosed with the proangiogenic hydrogels including endothelial cells including fibrin. Additional signs of progress in the biofabrication field could allow the generation of a varied set of functional printable bioinks, where the local micro environment is custom-made to specific encapsulation of cells with one or both bioactive parameters.

6.2. 3D printing of TRP inks for biomedical applications

The TRPs simulate the tissues' behavior as regards an alteration in the physiological situations, especially temperature [364–381] (Fig. 14). This makes the TRPs a suitable material in the fields of additive manufacturing for biomedical applications such as scaffold-based implants [175,248,249,257,377,382–387], intimal thickening [388,389], stabilization of bone implants [383,390–393], diagnostic instruments to artificial tissues [394–398], prosthetic organs [399–404], robotic grippers [405–411], and reducing thrombosis [306,412–417]. TRPs employed in urinary tubes avoid microbial growths on the surfaces, providing slippery and smooth surfaces to enhance biocompatibility. One of the advanced applications of hydrogels reported by Zhang et al [247], successfully printed a thermosensitive bioink based on p (NIPAAm-AA and fibrin as an effective implant for wound healing.

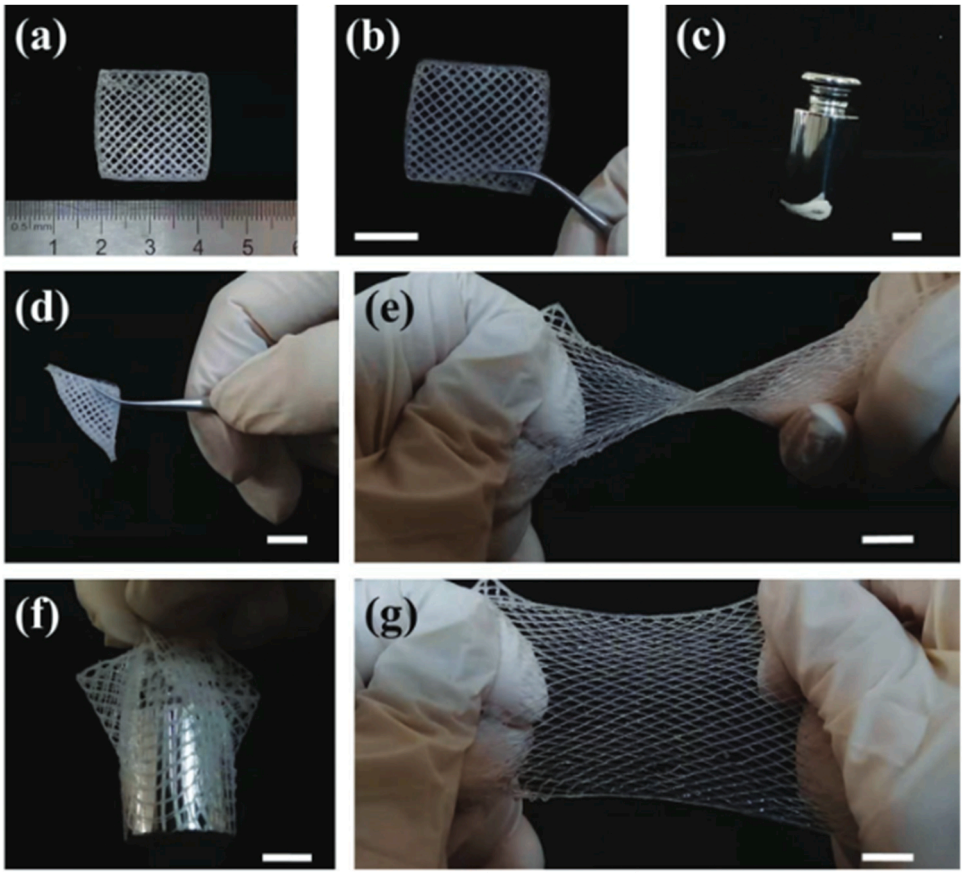

Fig. 14. The photomicrographs of printing poly(N-acryloyl glycinamide) hydrogel constructs. (a): the square lattice holds its (b): own weight, and (c,d): bear different deformations including (c): compression along with (d): bending. The 3D printed construct tolerates the (e): twisting, (f): elongating, (g): and maintains a 0.1 kg weight.
Reprinted with permission from ref [401].

The results showed that comparatively high cell viability regarding endothelial cells, fibroblasts, and keratinocytes has been attained. This was especially more noticeable once the blend of p(NIPAAm-AA) and fibrin bioink including cells was used. It was also found that cell viability was independent of printing speed, cell types, cultivation period, and seeding density.

As a multidisciplinary field, tissue engineering employs a principle of manufacturing and the life sciences to develop biological alternatives that reinstate and enhance tissue functionality [418]. Generally, the TRPs can be used either as a substrate for proliferation and cell growth or as a printable hydrogel for in-situ scaffold development [242,419]. Regarding substrate application, the TRPs capability can be utilized for regulation of the attachment or detachment of a specific cell on the surfaces [370,384,420–430]. Specifically, in relevant work, a 3D printing sacrificial mold through combining thermally induced phase separation has been employed to develop a biomimetic hybrid nanocomposite scaffold. An impregnation process of the obtained printed scaffold into the interpenetrated hybrid networks was detected through hierarchically connected porous structures. The 3D printed thermomechanical and biological responsive scaffolds can be served as an innovative material for personalized clinical rebuilding and regeneration [370]. Another application includes cell microencapsulation within the printed constructs [163,431–433]. The in-situ development of 3D printed scaffolds in comparison with the in-vitro one offers the delivery of encapsulated cells, nutrients, and growth factors for deficiency of different geometries through slightly aggressive methods. Fig. 15 shows a schematic of the elementary hypothesis of the in-situ development. Definitely, the TRPs can be blended at an ambient temperature with a specific cell and next 3D printed to manufacture a cell microcapsule. After injection into the body, because of an increased temperature to 37 °C, which is above the LCST of TRPs, the TRPs can develop a well-defined hydrogel, where the encapsulated cells exist within the 3D structures of the physically developed hydrogel.

6.3. 3D printing of TRP inks for biotechnology applications

Recently, biotechnology and nanobiotechnology have progressed noticeably owing to innovative scientific findings with regard to the application of smart materials in additive manufacturing techniques. One field in the application of TRPs is characterized by the self-assembly methods, because of the simple approach of TRPs to prepare and appropriateness for biotechnology manufacturing custom-made modifications [164,167,181,434–441]. In the upcoming years, considerable utilization of TRPs in biotechnology areas can definitely be in nanobiotechnology, nanomedicine, and pharmaceutical areas. For example, the smart bioactive release domains are currently progressing from micro- to nanoscale features. In this respect, the utilization related to the know-how of TRPs as medicine or ingredients of medicines is a cutting-edge method for improvement of bioavailability, controllable release of drugs, and targeted delivery [442–447]. The TRPs-based capsules prepared with a nanosized scale show a compensation of depolymerization, controllable drug release, and great availability at the targeted places [446–450]. Additionally, TRPs can be utilized in the concentration of a dilute aqueous solution in biomacromolecules solutes such as proteins with no decreasing the enzyme activity through regulating the temperatures/pH of the system dependent on the size and net charge [451–453]. With regard to the reversible swelling/shrinking associated with a minor alteration in the environmental condition, TRPs can be also used as a functional 3D structure in the purification process as a superabsorbent [193,203,454,455]. The adsorbent immobilization within TRPs' matrix such as chitosan, alginate, and agarose hydrogel can be considered an efficient way to avoid the adsorbent fouling through colloidal pollutants. With consideration of altering the swelling features, TRPs were also described to regulate the substrates' reaction with immobilized enzymes [456,457]. Reportedly, steroid changes have been greater in more hydrophobic TRPs because of the high division of water-insoluble steroids [456].

6.3.1. Drug delivery

Because of the protecting features, locally controllable released bioactive compounds, TRPs can be effectively used in 3D printing of drug delivery in pharmaceuticals and growth factors [242,306,385,443,446,458–460]. The application of rapid prototyping in drug delivery overcomes various restrictions of conventional medicine-administration approaches including oral and intravenous methods, which frequently need higher doses and frequent administrations resulting in off-target impacts. Conventionally, TRPs used in the controllable release of drugs were macroscale bulk hydrogel, possibly delivered through marginally aggressive methods [461,462] with controlled-release trends [463]. The TRPs functionality can offer slightly offensive delivery over small catheters and needles [464], and there is no requirement for the definite in-situ modification required for the smart released of bulk hydrogels. Moreover, TRPs are extremely multipurpose since these multifunctional macromolecules are highly compatible with bioactive compounds, which comprise several releasing profiles with multiple degradation behaviors into solitary injections [465]. Therefore, it is valuable to utilize many tissue-repair methods to be compatible with the organic signaling cascade.

6.3.2. Gene delivery

Gene therapy purposes to treat numerous genetic defects since this method can be used to correct imperfect DNA/RNA segments. In this case, the TRPs have been increasingly used in the 3D printing of gene-loaded hydrogel inks, representing an effective method to localize and sustain gene delivery for transplantation and host cells aimed at in-situ orthopedic tissue repairing [466–485]. Definitely, the delivery of

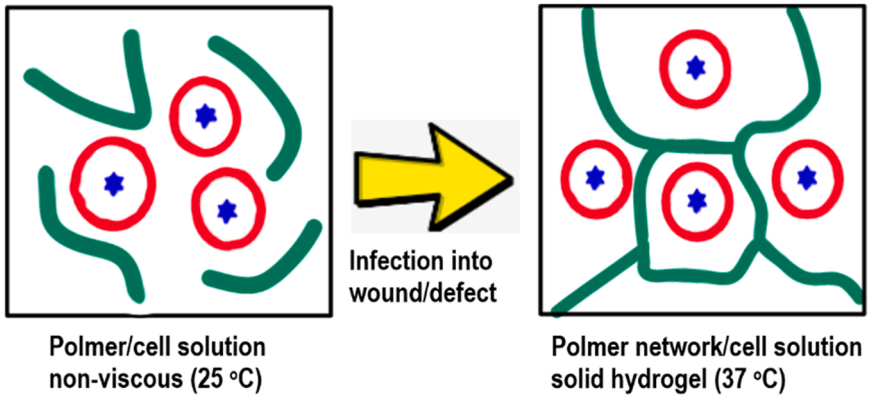

Fig. 15. In-situ formation of 3D printed TRP-based scaffolds in tissue engineering.

suitable DNA segments into a cell that will substitute, control, and repair the imperfect genes causing the diseases are the important phase for gene treatment. As a hydrophilic and negatively charged molecule, the delivery of DNA segments into a cell nucleus with a negatively charged and hydrophobic cell membrane is challenging. In gene delivery investigations through 3D printing, several types of TRPs have been used, including a blend of β-cyclodextrin and PNIPAM [486], chitosan [487], poly(ethyleneimine)/PNIPAM [488], and cellulose nanocrystals/ PCLA [249]. In this regard, the transfection and complexation temperatures have been altered to improve the transfection effectiveness. In the relevant investigations, with the application of random terpolymers of P (NIPAM-*co*-DMAEMA-*co*-BuMA) [489,490] or PNIPAM copolymers [491], only the complexation or incubation temperature differed, whereas the incubation and complexation temperatures have differed via a polyarginine grafted onto PNIPAM [492]. In another fascinating work, the TRPs thermoresponsive have been used in a dissimilar way from the above investigations through [poly(N,N-dimethylamino propyl acrylamide)-*b*-PNIPAM]-*interstellar* macromolecules [493]. The complexations have been accomplished at an ambient temperature below the LCST of macromolecules and next the complexes were positioned at the surface above LCST, in which a cell could be permitted to incubate at human body temperature. Once applying a macromolecule transporter, the key phases of gene delivery can be schematically shown in Fig. 16. The results showed that this in-vitro polymeric-mediated transfection of adipose-derived primary cells could be an efficient tool for sustained transgene expression. It was supposed that the pertinency of this device can be used as deposition transfection in gene treatment.

6.4. 3D printing of TRP inks for electroconductive and biosensor devices

TRPs can be served as instant membrane matrices in biosensors and electroconductive devices with favorite tensile strength, resilience, and discriminating diffusion of refractive and analyte parameters. Electroconductive hydrogels are a wide-ranging type of functional compounds, which have received marvelous attention because of a possible application in soft sensor and actuator devices [494–498], smart patches [385,499–501], in-situ development of the scaffolds in tissue engineering [249,502–507], wound healing materials [175,508–510], and scaffold-based implants [377,382–387,511]. They are a macromolecule-based blend system or polymeric co-network, which combine fundamentally the functionality of conductive electroactive polymeric-based materials with TRPs [327,512–514]. Regarding all cases, they are mutually ionically and electronically conductive, providing the noncytotoxic interface between the instrument and cell culture media or native alive tissues. Electroconductive hydrogels pursue to productively can combine the intrinsic functionality of TRPs to produce a technically pertinent feature for 3D printed parts as the recognition membrane coating in numerous soft sensor and actuator devices. In a relevant work, an electroactive hydrogel with conductivity and customized geometry was synthesized through the integration of rapid prototyping with interfacial polymerization. A printed electroconductive device based on polyethylene glycol diacrylate with interfacial polymerization of polypyrrole was developed. Because of the mentioned phases to form the electroconductive hydrogel, the 3D printed objects showed improved resolution with precisely deposited layers. Regarding the bioprinting of electroconductive hydrogels, cell-laden materials should be processed through a crosslinked fluid development in the aqueous solutions that significantly restricts the selection of TRPs [515]. A nanocomposite blend patch laden containing HCAECs (human coronary artery endothelial cells) with enhanced physicomechanical and electroconductivity was fabricated. In this case, a UV-combined bioprinting method was implemented for the construction of a cardiac patch including carbon nanotubes incorporated with alginate hydrogel and cell-laden methacrylated collagen [516].

6.5. 3D printing of TRP inks for the food industry

The TRPs can be considered a promising material in food applications because of their non-toxic nature and excellent biocompatibility [517–522]. The carbohydrate-based polymers such as agarose, carrageenan, hyaluronan, chitosan, and gellan gum naturally show thermoresponsive features in a binary or tertiary blend form. For example, Lin et al [518] produced a peanut protein composite hydrogel by incorporation of carrageenan or gellan gum. The introduction of these polysaccharides notably improved the physicomechanical properties and thermoresponsivity of the hydrogels. Specifically, they also reported that the prepared hydrogels showed a cold-set behavior, which is promising in 3D food printing applications. The printing process was recyclable because of the excellent thermoreversible cold-set features of carrageenan or gellan gum used, which may support decrease waste and production costs. Some Other polysaccharides can induce thermoresponsivity via chemical modification, such as modified soy [523] and modified starch [524]. Moreover, chitosan-based hydrogel possesses thermoresponsivity in a specified situation. In this case, chitosan dispersion does not show thermoresponsivity, albeit it becomes a thermosensitive gel in the physiological environment upon grafting by glycerophosphate [519]. Numerous researchers have developed innovative biodegradable film/coating for exploiting an 'ecological' benefit of TRPs in food packaging applications. TRPs directly extracted from biomass or obtained by traditional chemical fabrication (i.e., polylactic acid) have been extensively utilized for the development of cutting-edge packaging objects because of low cost, high compatibility, and good biodegradability. Up to now, the most used ways for overcoming the poor mechanical and weak water resistance of TRPs exploited in food packaging include blending native and synthetic macromolecules together or introducing a diverse range of nano-based materials [520]. Recently, the application of TRPs in food packaging captivated scientists to develop intelligent packaging systems based on utilized appropriate materials, as well as simple, small, and low-cost indicators or biosensors. Though, frequently exploited recognition methods including electronic

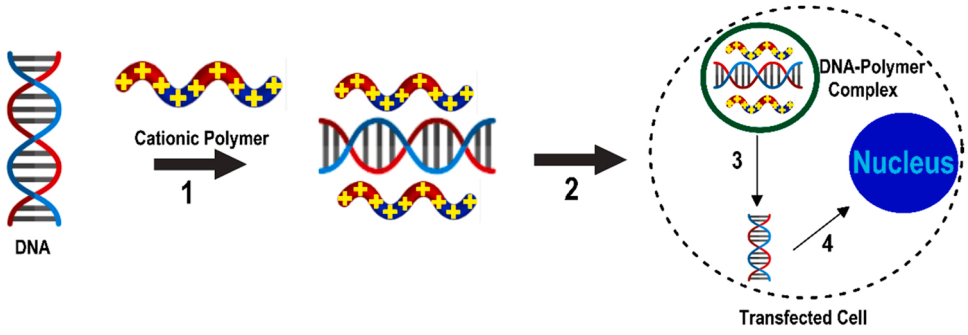

Fig. 16. The key phases of gene delivery through TRPs: DNA complexations (1). Complexes traversing a cell membrane into a cytoplasm (2). DNA is released inside a cytoplasm (3). DNA transfers into a nucleus (4).

tongues and soft sensors are multifaceted and high-cost, limiting their application as detectors toward utilized packaging materials. A soft sensitive recognition technology based on the development of polysaccharide-based biosensors is appropriate to serve in a smart packaging system. Specifically, biosensors depending on the color difference with obvious visual properties, have been employed for effortlessly obtaining data on the nutriment in the food packaging, which is comparatively low-cost than electronic tongues and soft sensors [521]. TRPs have been used for the development of 3D printed nanocomposite-based thin films with therapeutic features. For instance, zinc oxide and clove essential oil were incorporated into gelatin to form a printable nanocomposite-based ink [522]. This class of internal thin film can be considered to use in food packaging applications and also pharmaceutical packaging.

7. Conclusions and future scope

4D printing is still in its infancy phase of research which has developed enormous potential in many areas and produced infinite imagination amongst scientists. In this review, we introduced up-to-date and imperative progress in the application of different types of smart materials in 3D printing in the field of soft robotics, electrochemical energy storage, food science, biomedicine, and biofabrication. Natural and synthetic biomacromolecules have been widely used to simulate natural circumstances. Concepts motivated by nature allow the progress of engineering biomaterials to attain the natural accomplishment of the fabricated materials. The stimulus-sensitive components are identified as the cornerstone of the lesson inspired by nature. In recent years, the research community has been overwhelmed by numerous scientific information associated with thermo-sensitive materials, which act as a game changer in 3D printing usages because of their particular properties in bio-separation, drug delivery, tissue engineering, and theragnostic particles. Moreover, they are valuable for cell-sheet preparation. The combination of excellent properties of thermo-sensitive polymers with 3D printing technology is valuable to produce custom-designed 3D printed architectures with an unprecedented level of functional integration. The thermoresponsive polymers also have offered a biomimetic platform to enhance the functionality of 3D printed structures. As discussed, the thermoresponsive polymers simulate biological conditions and improve their performance. Such materials have been prepared in many forms—such as hydrogels, films, particles (nano/micro), micelles, and IPN. These varieties allow the thermoresponsive to be used in different 3D printing disciplines. Thermoresponsive polymers can be utilized as a delivery carrier for the definite load to a particular field—such as cancer therapy—by a controlled and targeted drug delivery. 3D printed tissue regeneration is another promising field where an injured part of the body is regenerated using biomacromolecules followed by additive manufacturing. The thermoresponsive polymers can be employed as injectable scaffolds that reduce the risk of the surgical process and can be considered a non-invasive technique. Additive manufacturing can enhance the functionality of thermoresponsive and ameliorate performance in various applications. Such materials should be fabricated based on the ultimate application to attain the appropriate functions. The innovation in the material, manufacture, design and modeling in 4D printing will generate additional progress in this field. The integration of smart materials with 3D printing can probably be utilized to design innovative systems, which are not restricted to any specific degree of freedom. Such innovative systems are attained through the replacement of classical mechanical compounds like native cellulose and clay or even motor and gears with appropriate smart materials. The cutting-edge and more effective approaches to introducing smart polymers into multifunctional objects can also result in the development of innovative smart devices. The progress of biocompatible smart polymeric systems can revolutionize different sectors, which is very hard to imagine a future, where 4D printing has a scarce and insignificant influence on the industrial sector. Therefore, to effectively use 4D printing in practical applications, constant development should be performed to overcome the present challenges and only then this technique will bring out its superlative functionality for the future world. We believe in the future, new types of materials applicable for 4D printing and accurate prediction of shape-morphing objects according to the theoretical analysis with the development of printing hardware, which would extend the quick 4D printing progress.

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CRediT authorship contribution statement

Mahdiyar Shahbazi: Investigation, Funding acquisition, Conceptualization, Project administration, Software, Visualization, Writing – original draft, Writing – review & editing. **Henry Jäger:** Supervision, Investigation, Resources, Writing – review & editing. **Rammile Ettelaie:** Investigation, Writing – review & editing. **Adele Mohammadi:** Software, Writing – review & editing. **Peyman Asghartabar Kashi:** Software, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

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