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Soft microorigami: self-folding polymer films

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Fabrication of 3D objects using folding of thin films is novel and very attractive research field. The manuscript overviews recent advances in development and application of polymer films, which are able to fold and form 3D structures.

Introduction

Engineering of complex 3D constructs is highly challenging task for development of materials with novel optical properties, tissue engineering scaffolds, elements of micro and nanoelectronic devices. Three-dimensional materials can be fabricated using a variety of methods including two-photon photolithography, interference lithography, molding (see recent review of D. Gracias [1]). Fabrication of 3D microobjects using controlled folding/bending of thin films – microorigami - is novel and very attractive research field [1-2]. One of the advantages of this approach is the possibility of quick, reversible and reproducible fabrication of 3D hollow objects with controlled chemical properties and morphology of the both exterior and interior. The pioneering works in this field belong to Smella[3] and Jager [4] . They were the first who started to work with self-folding films and demonstrated folding and unfolding of patterned gold films with polypyrole hinges in the response to electric signal. Groups of Oliver Schmidt focused on the design of semiconductor and metal oxide self-rolled tubes and applied them for transport [5], investigation behaviour of cells in confinement [6], nanooptics [7] and energy storage elements. [8] Gracias et al developed approaches for design of metallic self-folding particles and demonstrated their applicability for design of self-assembling microelectronic devices, controlled encapsulation of cells, drugs and design of tissue engineering scaffolds[9-12]. Metallic self-folding thin films are also highly promising for optics [13] and photovoltaic power applications [14].

On the other hand, due to their rigidity, limited biocompatibility and non-biodegradability, application of inorganic self-folding materials for biomedical purposes is limited. Polymers are more suitable for these purposes. First, there are many polymers changing their properties in physiological ranges of pH and temperature as well as polymers sensitive to biochemical process [15]. Second, polymers undergo considerable and reversible changes of volume that allows design of a variety of actively-moving microconstructs [16-17] Third, there are a variety of biocompatible and biodegradable polymers [18] . This paper overviews recent progress in development of polymer films, which are able to fold and form 3D microstructures. The main focus is to summarize polymer-based systems and to classify them with respect to way of fabrication, suitability for design of different 3D objects and applicability for biotechnology.

Bending vs. expansion

Bending is essentially required for design of self-folding materials and allows conversion of semi one-dimensional and two dimensional objects into 2D and 3D ones, respectively. Typically bending is the result of either expansion or contraction of a material caused by change of environmental conditions. In most cases change of conditions, however, results in homogenous expansion or contraction in all directions and does not leads to increase of dimensionality. Bending is produced as a result of inhomogenous expansion/shrinking, which occurs with different magnitudes in different directions. Bending could be achieved either (i) by applying gradients of field to homogenous materials or (ii) by applying non-gradient stimuli to inhomogeneous materials. The example of first case is the bending of polyelectrolyte hydrogel during electrolysis[19]. The examples of the second group are the bending of liquid crystalline films [20], hydrogel with the lateral gradient monomer concentration [21], cantilever sensors[22] and shape-memory polymers [23].

Design of self-folding films

In fact, design of self-folding objects using homogenous materials is technically very complicated because a very complex spatial force gradient must be formed and kept for a considerable period of time. This, for example, can be achieved using surface tension by depositing a water droplet on a thin film [24]. The film folds immediately after the droplet is deposited. The formed 3D object changes its shape during drying of the droplet and unfolds when water is completely evaporated. In physiological buffer environment surface tension effects are, however, weak. Fabrication of self-folding objects using inhomogeneous films is more straightforward. The inhomogeneous films fold due to difference in the properties on constituting materials in pre-programmed manner, which is defined by the film structure/pattern.

To date, three general approaches for design of self-folding polymer films are reported (Figure 1). First approach is based on shape-memory polymers, which are partially liquid crystalline with directional anisotropy of properties (Figure 1a). At low temperature the shape-memory materials are in their temporary shape. The films recover their permanent shape by heating. In second and third approaches two polymers are used. One of the polymers is passive and its properties remain unchanged. Another polymer is active and its volume or shape is changed when stimulus is applied. The second approach is based on use of polymer bilayers (Figure 1b). Active polymer swells or shrinks in response to signal. The swelling in one direction is restricted by the passive polymer. As a result, the bilayer does not uniformly expands/shrinks but folds and unfolds. Third approach is based on use of patterned film of passive polymer with insertion of active one (Figure 1c). Active polymer undergoes shape transition, which might be caused by surface forces, that results in folding of the film.

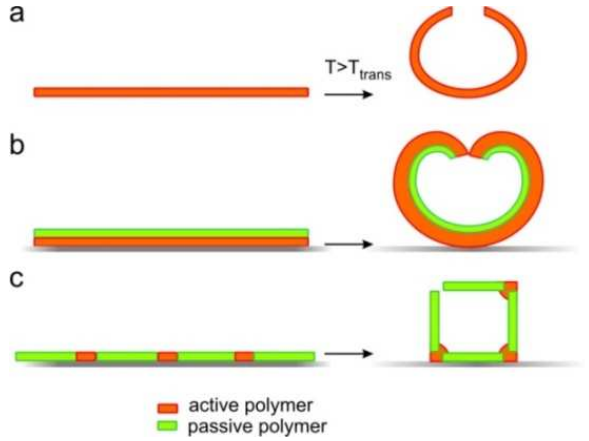

Fig. 1 Approaches for design of self-folding polymer objects (a) relaxation of shape-memory polymers (b) folding of polymer bilayer due to expansion of one of the polymers (b) folding of patterned polymer film caused by shape change of one of polymers.

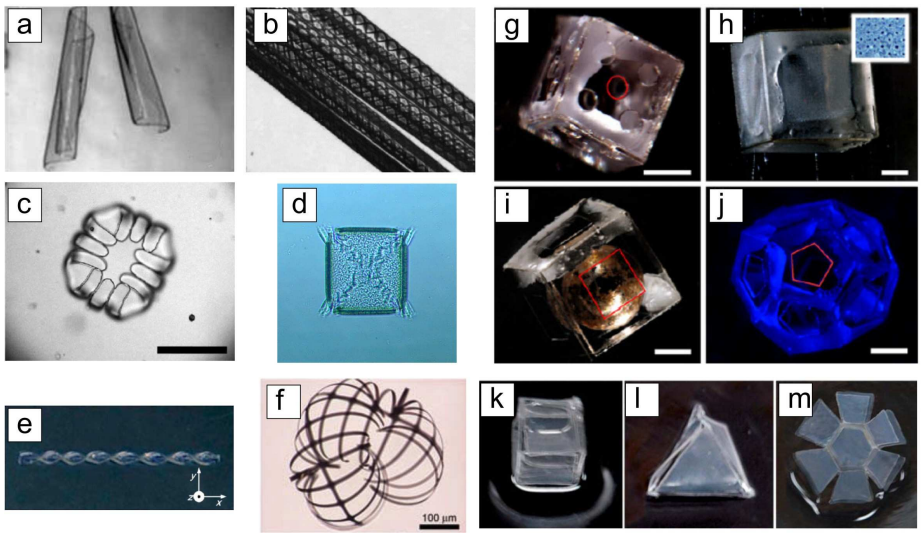

Fig. 2 Examples of self-folding polymer films: tubes [25-26] (a; b , reproduced with permission, Copyright Wiley-VCH Verlag GmbH & Co. KGaA [26]), capsules [27-28] (c, reproduced with permission, Copyright Wiley-VCH Verlag GmbH & Co. KGaA[27]; d Royal Society of Chemistry, Copyright [28]), helix [29] (e), hierarchically-shaped tube [30] (f, reproduced with permission, Copyright Wiley-VCH Verlag GmbH & Co. KGaA [30]), cubes with porous walls [29 31](g,h,I with kind permission from Springer Science+Business Media permission, Copyright [31] ; k, Royal Society of Chemistry, Copyright,[29]), dodecahedron [31] (j, I with kind permission from Springer Science+Business Media permission, Copyright [31]), pyramide [29](l, Royal Society of Chemistry, Copyright,), phlat ball [29] (m, Royal Society of Chemistry, Copyright).

The shape of formed 3D object depends on the shape of the polymer films (Table 1). The simplest case of self-folding object is a tube [25-27, 32-35]. Helixes of different kinds are formed by polymer bilayers with the gradually changing ratio between polymers [29] Envelop-like capsules with rounded corners or nearly spherical ones are formed from the star-like polymer bilayers with four and six arms, respectively [27-28, 35]. Cubes and pyramids are formed by patterned bilayer with the active junction elements [29, 31, 36].

The polymer films with different shape can be obtained either by cutting [25-26, 32], using microwell-like substrates [27, 34-35] or photolithography [28, 31, 33, 36] (Table 1). Cutting allows fabrication of millimetre large species with the rectangular shape, which form the tubes. The main advantage of this method is simplicity and applicability to almost all combinations of crosslinkable polymers. Use of microwell-like substrates is technically more complicated but allows fabrication of polymer layers with different shapes such as rectangles or stars. Photolithography of bilayers allows large scale fabrication of self-folding objects of different shape and size starting from several microns. The formed self-folding objects have rounded corners. The main disadvantage of this approach is necessity to choose proper solvents for polymer deposition in the way that the first polymer is not dissolved during deposition of the second polymer. Fabrication of patterned polymer films (Figure 1c) is the technically most complicated procedure and requires mask alignment during several steps of photolithography. On the other hand, it allows fabrication of the broadest range of shapes of self-folding objects.

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Table 1 Methods for fabrication of self-folding polymer films

Preparation method	Advantage	Disadvantage	Shapes of folded object	Refs
cutting	simple, all crosslikable polymers can be used	limited shapes - mostly rectangular, large objects	tubes	25-26, 32
microwells	all crosslikable polymers can be used, variety of shapes	requires fabrication of microwells	tubes, capsules, helixes	27, 34-35
photolithography of bilayers	simple, large scale fabrication, different sizes and shapes	polymers must be deposited from selective solvents	tubes, capsules	17-18
photolithography of patterned layers	large scale fabrication, different sizes and shapes	complicated, requires special equipment	tubes, capsules, cubes, pyramids	23-25

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Stimuli

Use of polymer sensitive to different signals allows design of self-folding films folding upon immersion in solvent, change of pH, temperature, electric or biochemical signals (Table 2).

pH – responsive. Self-folding films sensitive to pH are commonly designed using weak polyelectrolytes as active polymers. Luchnikov demonstrated that polystyrene-poly(4 vinyl pyridine) bilayer [26] as well as polystyrene-poly(4 vinyl pyridine)-polydimethylsiloxane trilayer [37] are able to roll at low pH when poly(4-vinylpyridine) is protonated and swells in water. Use of layers with two-dimensional gradient of thickness allowed thorough investigation of folding [38]. It was found that rate of rolling increased with the acidity of the solution. Tube diameter and rate of rolling decreased with the increase of the UV exposure time. Moreover, increase of thickness of PS results in increase of the diameter of tube.

Lee et al used pH sensitive poly(methyacrylic acid) - poly(2-hydroxyethyl methacrylate) [34] and poly(methacrylic acid) (PMAA)/ polyEGDMA [35] patterned bilayer which folds in contact with biological fluids. It was not shown that the folding depends on pH. However, since weak polyelectrolyte poly(methacrylic acid) was used, the systems is expected to respond to pH signal. Gracias et al fabricated millimeter large polyethylene glycol / poly-(N-isopropylacrylamide – acrylic acid) bilayers which are able to snap in response to pH signal[36]. One can also expect that this system is thermoresponsive. Huck et al reported pH responsive gold-poly(methacryloxyethyl trimethylammonium chloride) brush patterned films which fold in response to change of pH and salt concentration [30].

Thermoresponsive. Thermoresponsive self-folding films can be designed using continuous thermal expansion, melting, shape-memory transition or polymers which demonstrate LCST (Low Critical Solution Temperature) behaviour in solutions. Kalaitzidou et al used continuous volume expansion with temperature and demonstrated thermoresponsive rolling-unrolling of polydimethylsiloxane - gold bilayers tubes at 60°C- 70°C [25, 32] which is due to different temperature expansion coefficients.

Gracias et al used melting of polymer, which form a droplet and forces patterned polymer films to fold. This was demonstrated on the example of patterned SU-8 photoresist - polycaprolactone film, which irreversibly folds at 60°C [31] due to melting of polycaprolactone (Figure 3). In order to reduce the transition temperature and make film more suitable bio-related applications, Gracais et al used photoresist hinges which are sensitive to temperature around 40°C [39-41]. The metal-polymer grippers irreversibly fold in response to temperature as well.

Lendlein et al demonstrated the possibilities to design thermoresponsive macroscopic self-folding objects using shape-memory polymers based on different poly(ε -caprolactone) [23]. At low temperature the materials are in their temporary shape. The films recover their permanent shape and irreversibly fold by heating, which could be accompanied by a change of transparency. The exact size of the self-folding film as well as temperature of transition was not given.

Polymer bilayers, where active component is thermoresponsive poly-(N-isopropylacrylamide)-based copolymers, are more suitable for encapsulation of cells. In aqueous media, poly-(N-isopropylacrylamide)-based hydrogels reversibly swell and shrink below and above 33 °C. Moreover, the temperature of transition between swollen and shrunk states can be tuned by proper selection of composition of copolymer. As result, poly-(N-isopropylacrylamide)-polycaprolactone patterned bilayers fold and unfold forming tubes of capsules below and above this temperature, respectively (Figure 4). [28, 33]

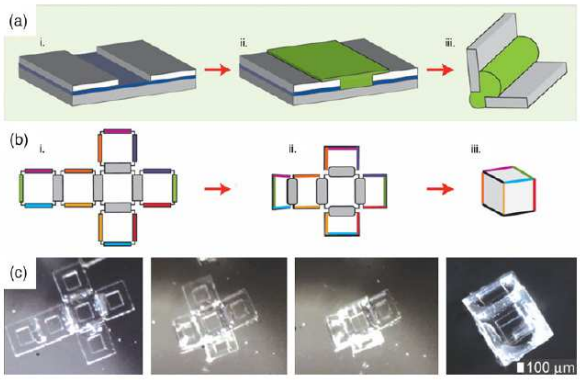

Fig. 3 Thermoresponsive self-folding SU-8- polycaprolcatone thin films. (a) fabrication: (i) A sacrificial layer was spin coated on a clean Si wafer. SU-8 panels were patterned using conventional photolithography. (ii) PCL was deposited in hinge gaps. (iii) 2D templates were lifted off via dissolution of the PVA layer in water and self-assembly occurred on heating above 58°C. (b, i–iii) Schematic demonstrating self-folding of a cubic container. External "locking" hinges are colored in pairs to denote corresponding meeting edges. (c) Video capture sequence (over 15 s) showing a 1 mm sized, six-windowed polymeric container self-folding at 60°C. With kind permission from Springer Science+Business Media permission, Copyright [31]

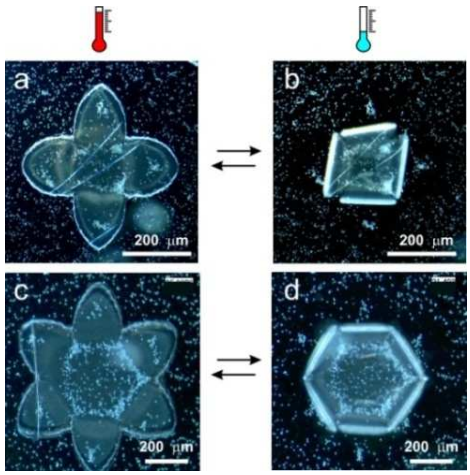

Fig. 4 Encapsulation of yeast cells inside thermoresponsive poly-(N-isopropylacrylamide)-polycaprolactone self-folding capsules. Yeast cells are adsorbed on the polymer bilayer at elevated temperature. Cooling leads to swelling of the thermoresponsive polymer and folding of the capsules. Second heating results in unfolding of the capsules and release of the cells. Royal Society of Chemistry, Copyright [28]

Solvent responsive. Most examples of solvent-responsive self-folding films are the films, which fold upon immersion in aqueous media. Such films contain water-swellable uncharged polymers. Lee fabricated partially biodegradable polyvinyl alcohol-chitosan[27] and chitosan-poly(PEGMA-*co*-PEGDMA) bilayers [35] which folds in water due to swelling of polyvinyl alcohol and polyethyleneglycol, respectively. Jeong and Jang et al developed the approach for fabrication of millimetre size self-folding objects which are able for fold and form different 3D objects such as tube, cube, pyramids and helixes [29] Water-swellable polydimethylsiloxane- polyurethane/2-hydroxyethyl methacrylate complex bilayers and patterned films were used. Since poly(vinyl alcohol), polyethyleneglycol and poly (2-hydroxyethyl methacrylate) and are not polyelectrolytes, the swelling is expected to be independent of pH of aqueous media. These systems immediately fold upon immersion in aqueous media that hampers loading of cells.

Huck reported the example of the system which folds in methanol. This systems is based on poly(glycidyl methacrylate) brush layer grafted to gold patterned films [30].

Other systems. Except for pH-, thermo- and solvent-responsive systems, there are also several examples of systems, which fold in response to other stimuli such as presence of enzymes or applied electric field. Smella[3] and Jager [4] et al, who introduced the self-folding films, demonstrated folding and unfolding of patterned gold film with polypyrole hinges in the response to electric signal. Whilesides et al fabricated electro-responsive self folding bilayer, which consists of polydimethylsiloxane with the aligned cardiomyocytes [42]. The polymer-cell film adopted functional three-dimensional conformations when electric signal is applied. These centimetre-scale constructs perform functions as diverse as gripping, pumping, walking, and swimming with fine spatial and temporal control.

Enzyme-sensitive self-folding films were developed for the first time by Gracias et al. The approach is based on use of self-folding metallic grippers with active polymer hinges, which are sensitive to presence of enzymes [43]. Two kinds of biodegradably polymer were used. The gripper, which is unfolded in initial state, folds when first polymer is degraded after addition of first enzyme. The gripper unfolds when second enzyme is added and second polymer is degraded. As result one circle of folding and unfolding is achieved.

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Table 2 Reported examples of self-folding polymer films

system	stimuli	folding range	biodegradation	reversibility	Ref
pH-responsive					
poly(4 vinyl pyridine) - polystyrene	pH	pH = 2	no	+	26
poly(2-hydroxyethyl methacrylate) poly(methyacrylic acid)	pH	pH = 3 - 7.3	no	+	34
poly(methacrylic acid) - polyethylene glycol	pH	no information	no	+	35
poly-(N-isopropylacrylamide – co- acrylic acid) - polyethylene glycol	pH	pH = 2.5 – 7.5	no	+	36
poly(methacryloxyethyl trimethylammonium chloride) – gold*	pH, salt	not given	no	-	30
metals-photoresist*	acetic acid	> 60%	no	-	44
Solvent-responsive					
polyvinyl alcohol -chitosan	water	immediate folding	partial	-	27
chitosan- polyethylene glycol	water	immediate folding	partial	-	35
polydimethylsiloxane- polyurethane /2-hydroxyethyl methacrylate	water	immediate folding	no	-	29
poly(glycidyl methacrylate) –gold*	methanol	immediate folding	no	-	30
Thermoresponsive					
polydimethylsiloxane – gold*	T	60°-70°C	no	+	25, 32
SU-8 - polycaprolactone	T	60°C	partial	-	31
poly-(N-isopropylacrylamide)- polycaprolactone	T	28°C-30°C	partial	+	28, 33
polycaprolactone	T	unknown	full	-	23
poly(caprolactone-co-pentadecadolactone)	T	unknown	full	-	23
metals-photoresist*	T	40-60°C	no	-	39-41
Other					
polydimethylsiloxane – cardiomyocytes	electric	10 V	partial	+	42
metals- gelatine- carboxymethylcellulose*	enzyme		partial	one circle	43
polypyrrole -gold	electric	1 V	no	+	3-4

*systems with inorganic components are labelled gray

Applications

The main field of application of self-folding polymer thin films is the controlled encapsulation and release of drugs, particles and cells (Figure 5). Kalaitzidou demonstrated reversible adsorption-desorption of fluorescently labelled polyethyleneglycol, which is considered as model drug, inside PDMS-gold tubes at 60-70°C. [32] Gracias et al demonstrated irreversible encapsulation of yeast cells inside self-folding SU8-PCL films upon heating above at 60°C [31]. Poly-(N-isopropylacrylamide)-based self-folding films were also demonstrated to be suitable reversible encapsulation of particles and yeast cells[28, 33]. Cells were encapsulated upon cooling below 30°C and could be released from the film, which is unfolded above 30°C. This encapsulation and release is completely reversible and could be repeated many times (Figure 4).

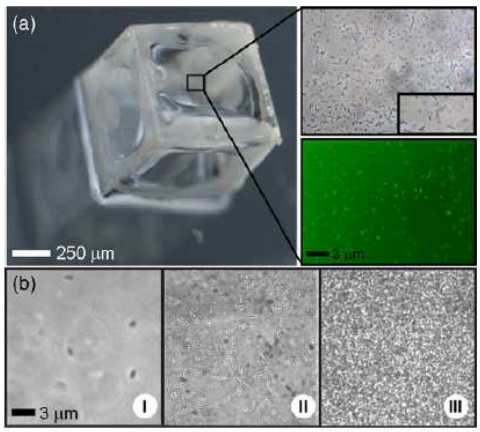

Fig. 5 Bacterial encapsulation using self-folding SU-8-polycaprolactone films. (a) Bright-field and fluorescence images of Syto 9 stained E. coli encapsulated within a polymer container, 24 h after encapsulation. (b) Bright-field timelapse images of bacteria within a polymeric container, taken at intervals of zero, 4 and 15 h following encapsulation by tumbling. Also shown is a plot of the number of bacteria vs. culture time following encapsulation. with kind permission from Springer Science+Business Media permission, Copyright [31]

Self-folding films can also be used as smart plasters. Lee demonstrated this concept on the example of millimerter size poly(methyl methacrylate) - poly(2-hydroxyethyl methacrylate) bilayer with attached mucoadhesive drug layer. The non-swelling PHEMA layer serves as a diffusion barrier, minimizing any drug leakage in the intestine. The resulting unidirectional release provides improved drug transport through the mucosal epithelium

(Figure 6). The functionality of this device is successfully demonstrated in vitro using a porcine small intestine. [34]

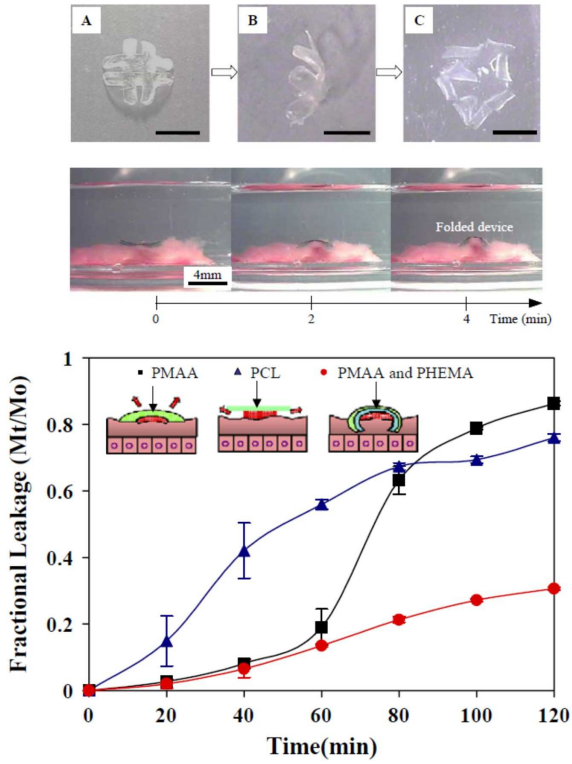

Fig. 6 Self-folding polymer bilayer films as smart plaster. Upper panel - polymer bilayer is undeformed in dry states and folded in aqueous environment. Middle panel – folding of polymer bilayer on the mucus surface. Lower panel - the fractional leakage of drug from the self-folded reservoir with different protection layers is the smallest. (reproduced with permission, Copyright Elsevier [34])

There are several non-biorelated examples of application of self-folding polymer films. Deposition of patterned metal on the polymer bilayer allowed fabrication of self-rolled tubes with patterned conductive inner wall. [26] In another example, pyrolysis of polystyrene-poly(4 vinyl pyridine)-polydimethylsiloxane trilayer [37] were used for fabrication of silica tubes.

Conclusions and Outlook

The self-folding polymeric thin films are emerging field, which only starts to develop. Till now, several examples of the polymer thin films folding due to immersion in aqueous environment, change of pH, temperature, electric signal or presence of enzymes were demonstrated. The self-folding films are potentially very promising for controlled encapsulation and release of drugs and cells. Here, cells are not locked inside amorphous and densely crosslinked matrix, as it happens in the case of hydrogels, but are free to move. This is particularly important for design of tissue engineering scaffolds. The limited applicability of self-folding tubes for design of scaffolds is, one hand, caused by their folding at non-physiological conditions. First, pH is not favourable signal to trigger folding for encapsulation of cells. Use of temperature as stimuli is more suitable, since cells readily withstand temperature variation. On the other hand, most of the reported systems are non-biodegradable. There is only one report about fully-biodegradable self-folding polymer film. In future, these two problems must become the main focus of research in this field.

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The manuscript overviews recent advances in development and application of polymer films, which are able to fold and form 3D structures.

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