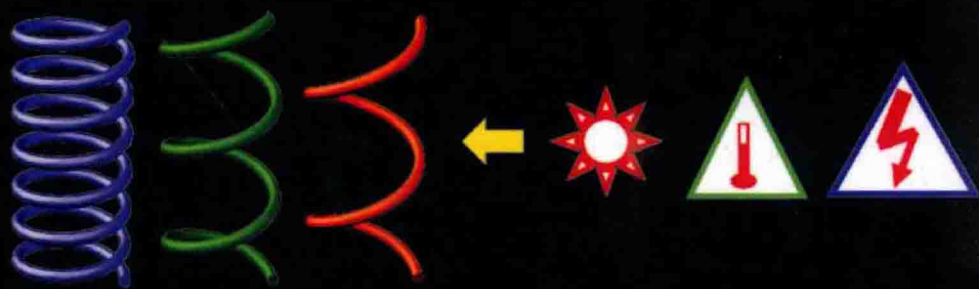


Intelligent Stimuli-Responsive Materials

From Well-Defined Nanostructures to Applications

Edited by *Quan Li*



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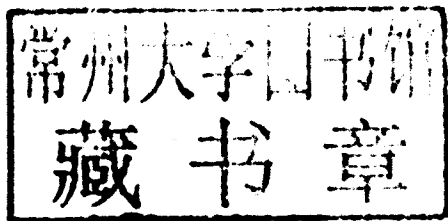
INTELLIGENT STIMULI-RESPONSIVE MATERIALS

**From Well-Defined Nanostructures
to Applications**

Edited by

QUAN LI

*Liquid Crystal Institute
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**INTELLIGENT
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PREFACE

Nature around us is vibrant and colorful. We are able to enjoy and admire its beauty because we can see and distinguish the objects around us by the differences in color and contrast. Behind our ability to see objects, there operates a natural process known as photoisomerization of the retinal, thereby enabling vision. However, this is just one example of Mother Nature's numerous reversible stimuli-responsive activities that accomplish the desired tasks smoothly and elegantly. Inspired by such elegant and efficient activities of nature, the scientific community has embarked to develop artificial materials and systems to mimic and understand the natural stimuli-responsive activities, and eventually use them for the benefit of human beings. Furthermore, the rapidly developing field of nanotechnology has provided a strong impetus for the development of smart stimuli-responsive materials that can be designed from a wide range of functional molecular or macromolecular building blocks. The functionalities and macroscopic properties of these materials embrace many disciplines, including nanotechnology, materials science, polymer science, organic chemistry, inorganic chemistry, biochemistry, medicine, engineering, etc. Stimuli-responsive materials have been designed such that the changes of the individual subunits are additive, and thus produce a measurable coherent response to an external stimulus such as light, heat, pH, metal ion, solvent polarity, electric field, magnetic field, redox, and chemical reaction. Over the years, several strategies have been developed in order to achieve such characteristics. The combination of the bottom-up approach in molecular design and external and internal triggering shows great promise for the development of intelligent materials. Practical stimuli-responsive materials must meet a combination of attributes which would lead to high response efficiency, material processability and long-term stability. Thus, the focus of this book will be on the basic design principles of intelligent stimuli-responsive materials, their performance,

and the major challenges still to be accomplished in order to achieve materials with appropriate characteristics for industrial applications. Furthermore, the possibilities of programmed and controlled variations in the properties and characteristics leading to their practical applications will be emphasized.

This book does not intend to exhaustively cover the field of stimuli-responsive materials as it is extremely difficult to do so within a single book. Instead, the book focuses on the recent developments of the most fascinating theme about intelligent stimuli-responsive materials: from well-defined nanostructures to applications. The chapters span the following topics: nature-inspired stimuli-responsive self-folding materials (Chapter 1), stimuli-responsive nanostructures (Chapter 2), stimuli-directed alignment control of semiconducting discotic liquid crystalline nanostructures (Chapter 3), anion-driven supramolecular self-assembled materials (Chapter 4), photoreponsive cholesteric liquid crystals (Chapter 5), electric- and light-responsive bent-core liquid crystals: from molecular architecture and supramolecular nanostructures to applications (Chapter 6), photomechanical liquid crystalline polymers: motion in response to light (Chapter 7), responsive nanoporous silica colloidal films and membranes (Chapter 8), stimuli-responsive smart organic hybrid metal nanoparticles (Chapter 9), biologically stimuli-responsive hydrogels (Chapter 10), biomimetic self-oscillating polymer gels (Chapter 11), stimuli-responsive surfaces in biomedical applications (Chapter 12), and stimuli-responsive conjugated polymers: from electronic noses to artificial muscles (Chapter 13). In each chapter, the state of the art, along with future potentials in the respective fields, is discussed and highlighted by the leading experts.

I hope the reader will find this book professionally valuable and intellectually stimulating in the rapidly emerging area of stimuli-responsive materials. It has been organized to be accessible to undergraduate and graduate students, as well as researchers in both academia and industry in the fields of organic chemistry, polymer science, liquid crystals, materials science, materials engineering, electrical engineering, chemical engineering, photonics, optoelectronics, nanotechnology, medicine, and renewable energy. For young scientists, this book would provide a flavor of the diverse opportunities in this exciting area. For the scientific community, it is anticipated to serve as a ready reference and act as a catalyst to spark creative ideas.

Finally, I would like to express my gratitude to Jonathan Rose at Wiley for inviting us to bring this exciting field of research to a wider audience, and to all our distinguished contributors for their dedicated efforts. Also I am indebted to my wife Changshu, my sons Daniel and Songqiao for their great support and encouragement.

QUAN LI

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NATURE-INSPIRED STIMULI-RESPONSIVE SELF-FOLDING MATERIALS

LEONID IONOV

1.1 INTRODUCTION

Engineering of complex 3D constructs is a highly challenging task for the development of materials with novel optical properties, tissue engineering scaffolds, and elements of micro and nanoelectronic devices. Three-dimensional materials can be fabricated using a variety of methods including two-photon photolithography, interference lithography, molding [1]. The applicability of these methods is, however, substantially limited. For example, interference photolithography allows fabrication of 3D structures with limited thickness. Two-photon photolithography, which allows nanoscale resolution, is very slow and highly expensive. Assembling of 3D structures by stacking of 2D ones is time-consuming and does not allow fabrication of fine hollow structures.

Fabrication of 3D microobjects using controlled folding/bending of thin films—self-folding films—is novel and a very attractive research field [1, 2]. Self-folding films are the examples of biomimetic materials [1]. Such films, on the one hand, mimic movement mechanisms of plants [3] and, on the other hand, are able to self-organize and form complex 3D structures. The self-folding films consist of two materials with different properties. At least one of these materials, active one, can change its volume. Because of the non-equal expansion of the materials, the self-folding films are able to form a tubes-, capsules- or more complex-structure. Similar to origami, the self-folding films provide unique possibilities for the straightforward

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fabrication of highly complex 3D micro-structures with patterned inner and outer walls that cannot be achieved using other currently available technologies. The self-folded micro-objects can be assembled into sophisticated, hierarchically organized 3D super-constructs with structural anisotropy and highly complex surface patterns. Until now most of the efforts were focused on the design of inorganic self-folding films [4]. 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 [5]. Second, polymers undergo considerable and reversible changes of volume that allows the design of a variety of actively moving microconstructs [6]. Third, there are a variety of biocompatible and biodegradable polymers [7]. This chapter overviews recent progress in development of the polymer films which are able to fold and form 3D microstructures.

1.2 DESIGN OF SELF-FOLDING FILMS

Bending is essentially required for design of self-folding films 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 lead to increase of dimensionality. Bending is produced as a result of inhomogeneous 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 the first case is the bending of polyelectrolyte hydrogel during electrolysis [8]. The examples of the second case are the bending of liquid crystalline films [9], hydrogel with the lateral gradient monomer concentration [10], cantilever sensors [11], and shape-memory polymers [12].

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. For example, this can be achieved using surface tension by depositing a water droplet on a thin film [13]. 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 using inhomogeneous materials are reported (Fig. 1.1). First approach is based on shape-memory polymers, which are partially liquid crystalline with directional anisotropy of properties (Fig. 1.1a). At low temperature, the shape-memory materials are in their temporary shape. The films recover their permanent shape by heating. In second

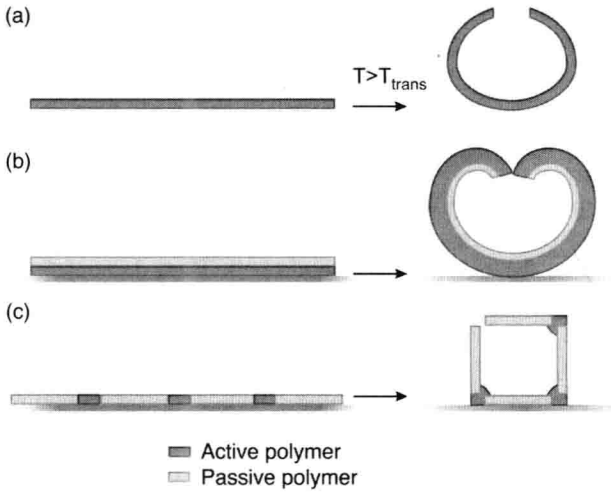


FIGURE 1.1 Approaches for design of self-folding polymer objects (a) relaxation of shape-memory polymers (b) folding of polymer bilayer due to expansion of one of the polymers (c) folding of patterned polymer film caused by shape change of one of polymers. Reproduced from Reference 14, with kind permission from Royal Society of Chemistry. Copyright 2011.

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 the use of polymer bilayers (Fig. 1.1b). 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 expand/shrink but it does fold and unfold. Third approach is based on the use of patterned film of passive polymer with insertion of the active one (Fig. 1.1c). Active polymer undergoes shape transition, which might be caused by surface forces, that results in folding of the film.

1.3 MECHANISM OF FOLDING

Timoshenko [15] was the first who investigated bending of bilayer, which consist of two materials with different expansion coefficients. He assumed that the bilayer can bend in only one direction and results in a bilayer with uniform curvature

$$\frac{1}{\rho} = \frac{6(\varepsilon_2 - \varepsilon_1)(1+m)^2}{h \left(3(1+m)^2 + (1+mn) \left(m^2 + \frac{1}{mn} \right) \right)} \quad (1.1)$$

$$\frac{E_1}{E_2} = n \quad (1.2)$$

$$\frac{a_1}{a_2} = m \quad (1.3)$$

where E are the elasticity modulus, a are the thickness of the layers, h is the total thickness ($h = a_1 + a_2$), ϵ is the stress of the films, ρ is the radius of curvature. As it comes from the Equations (1.3), radius of curvature is inversely proportional to film stress. Moreover, radius of curvature first decrease and then increase with the increase of m . The resultant curvature is not very sensitive to the difference in stiffness between the two layers, and is mainly controlled by the actuation strain and the layer thickness. The Timoshenko equation applies to a beam bending in only one direction and does not predict the folding direction. Moreover, Timoshenko equation considers elastic deformations, the polymers and hydrogels often demonstrate viscoelastic properties.

More recent models have considered complex bending of bilayer in two dimensions. Mansfield found analytical solutions for large deflections of circular [16] and elliptical [17] plates having lenticular cross sections with a temperature gradient through the thickness. For small gradients, the plates formed spherical caps, curved equally in all directions. At a critical gradient, a configuration with greater curvature in one direction became more favorable. Because of the lens-shaped thickness profile, even though the elliptical plate had a major axis it showed no preferred direction for bending even for large deflections. Freund determined the strain at which the spherical cap, formed by circular bilayer of uniform thickness, becomes unstable using low order polynomial solutions and finite element simulations [18].

Later, Smela et al. showed that short-side rolling was preferred in the case of free homogeneous actuation and that this preference increased with aspect ratio (ratio of length to width of rectangular pattern) [19]. Li et al. [20] and Schmidt [21] experimentally demonstrated the opposite scenario, namely a preference for long-side rolling, in the case where bilayers are progressively etched from a substrate. They observed that when the tube circumference was much larger than the width or the aspect ratio of the rectangle was high, rolling always occurred from the long side. When the tube circumference was much smaller than the width and the aspect ratio of the membrane pattern was not very high, the rolling resulted in a mixed yield of long- and short-side rolling, as well as a “dead-locked turnover” shape. Short-side rolling occurred at small aspect ratios when the deformed circumference is close to the width. In these self-rolling systems, the active component undergoes relatively small volume changes or actuation strains, which are nearly homogenous over the whole sample. Control of rolling/folding direction is very important for programmed folding. For example, Schmidt demonstrated that introduction of wrinkles allows switching to short-side rolling [21].

In inorganic self-rolling systems, the active component undergoes relatively small volume changes or actuation strains, which are nearly homogenous over the whole sample. Hydrogels, however, demonstrate considerably different properties. First, hydrogels undergo large volume changes (up to 10 times) upon swelling and contraction. Second, the swelling of a hydrogel is often kinetically limited: due to slow diffusion of water through hydrogel, the parts which are closer to the edges swell first while the parts which are closer to the center of the films swell later. Stoychev et al. investigated the folding of rectangular stimuli-responsive hydrogel-based polymer bilayers with different aspect ratios and relative thicknesses placed on a substrate

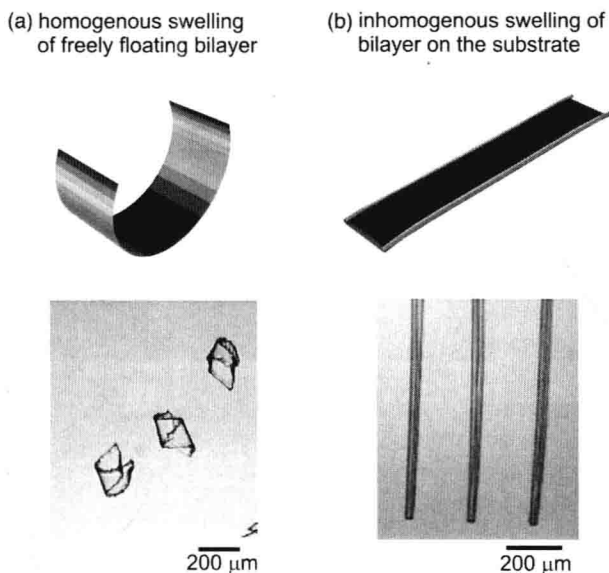


FIGURE 1.2 Simulation and experimentally observed folding of rectangular bilayers at different conditions: (a) freely floating rectangular bilayer (homogeneous swelling) (b) rectangular bilayer on substrate (inhomogeneous swelling) Reproduced from Reference 23, with kind permission from American Chemical Society. Copyright 2012.

and freely floating is fluid [22]. The polymer bilayer with homogeneous actuation which freely floats in aqueous medium undergoes short-side rolling leading to the formation of scrolls (Fig. 1.2a). In the case of bilayer placed on a substrate, it was found that long-side rolling dominates at high aspect ratios (ratio of length to width) when the width is comparable to the circumference of the formed tubes, which corresponds to a small actuation strain (Fig. 1.2b). Rolling from all sides occurs for a higher actuation strain, namely when the width and length considerably exceed the deformed circumference. In the case of moderate actuation, when the width and length are comparable to the deformed circumference, diagonal rolling is observed. Short-side rolling was observed very rarely and in combination with diagonal rolling. Based on the experimental observations, finite-element modeling as well as energetic considerations, it was argued that bilayers placed on a substrate start to roll from corners due to quicker diffusion of water. Rolling from the long side starts later but dominates at high aspect ratios in agreement with energetic considerations. It was showed experimentally and by modeling that the main reasons causing a variety of rolling scenarios are (i) non-homogeneous swelling due to the presence of the substrate and (ii) adhesion of the polymer to the substrate.

There are many parameters which determine folded shape. For example, the shape of formed 3D object depends on the shape of the polymer films (Fig. 1.3). The simplest case of self-folding object is a tube which is formed by rectangular bilayers [24]. Helixes of different kinds are formed by polymer bilayers with the gradually

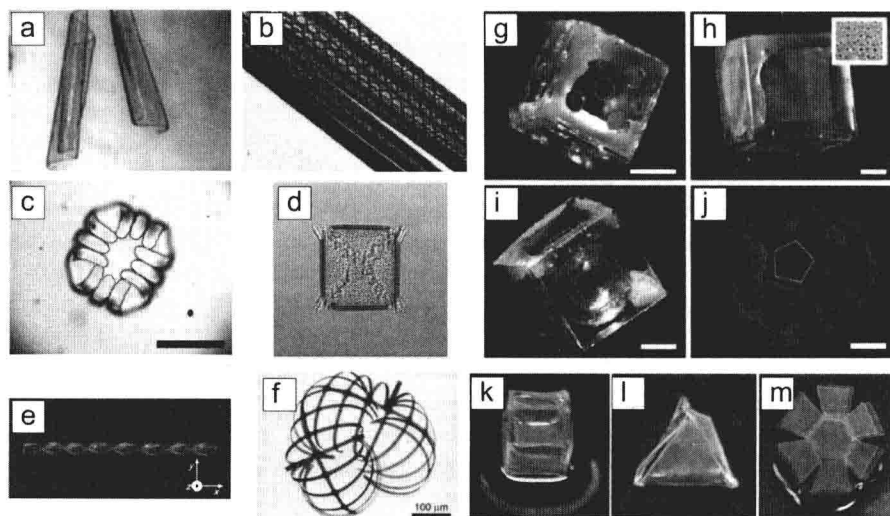


FIGURE 1.3 Examples of self-folding polymer films: (a), (b) tubes. Reproduced from References 24b, with permission from RSC, Copyright 2010, 24c, with permission from Wiley, Copyright 2005. (c,d) capsules. Reproduced from References 24f, 26, with permission from Wiley-VCH Verlag GmbH & Co. KGaA. Copyright 2011. (e) helix. Reproduced from References 25, 26, with permission from Royal Society of Chemistry, Copyright 2011. (f) hierarchically shaped tube. Reproduced from Reference 28, with permission from Royal Society of Chemistry. Copyright 2011. Reproduced from Reference 28, with permission from Wiley-VCH Verlag GmbH & Co. KGaA. Copyright 2011 (g), (h), (i), (k) cubes with porous walls. Reproduced from References 25, 27b, with kind permission from Springer Science & Business Media. Copyright 2010. (j) dodecahedron. Reproduced from Reference 27b, with kind permission from Springer Science & Business Media. Copyright 2010. (k) Reproduced from Reference 25, with permission from Royal Society of Chemistry. Copyright 2011. (l) pyramid. Reproduced from Reference 25, with permission from Royal Society of Chemistry. Copyright 2011. (m) phlat ball. Reproduced from Reference 25, with permission from Royal Society of Chemistry. Copyright 2011.

changing ratio between polymers [25]. Envelope-like capsules with rounded corners or nearly spherical ones are formed the star-like polymer bilayers with four and six arms, respectively [24f, 24g, 26]. In these examples, simple rounded figures based on different combinations of fully or semi-folded tubes are formed. Moreover, because of the isotropy of mechanical properties of the bilayer, formation of hinges during folding of bilayers is considered to be impossible. Objects with sharp edges are formed patterned bilayer where active component is deposited locally. The active component can either swell/shrink or change its shape due to melting. In this way, cubes and pyramids are formed by patterned bilayer with the active junction elements [25, 27]. Important, in all reported cases, folding runs in one step—active polymer changes its volume that results in simple bending.

1.4 FABRICATION OF SELF-FOLDING FILMS

The polymer films with different shape can be obtained either by cutting [24a–c], using microwell-like substrates [24e–g] or photolithography [24d, 26, 27]. Cutting allows fabrication of millimeter 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 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.

1.5 STIMULI-RESPONSIVE PROPERTIES OF SELF-FOLDING FILMS

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.

1.5.1 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 [24c] as well as polystyrene-poly(4 vinyl pyridine)-polydimethylsiloxane trilayer [29] are able to roll at low pH when poly(4-vinylpyridine) is protonated and swells in water. Use of layers with 2D gradient of thickness allowed thorough investigation of folding [30]. 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(methacrylic acid)-poly(2-hydroxyethyl methacrylate) [24e] and poly(methacrylic acid) (PMAA)/polyEGDMA [24g] 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 are 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 [27a]. 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 [28].