Soft Matter

REVIEW



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Reconfigurable and actuating structures from soft materials

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The recent interest in reconfigurable soft materials may lead to the next paradigm in the development of adaptive and actuating materials and structures. Actuating soft materials eventually can be precisely designed to show stimuli-sensing, multi-length scale actuation, tunable transport, programmed shape control and multifunctional orthogonal responses. Herein, we discuss the various advances in the emerging field of reconfigurable soft materials with a focus on the various parameters that can be modulated to control a complex system behavior. In particular, we detail approaches that use either long-range fields (*i.e.* electrical, magnetic) or changes in local thermodynamic parameters (*e.g.*, solvent quality) in order to elicit a precise dimensional and controlled response. The theoretical underpinnings and practical considerations for different approaches are briefly presented alongside several illustrative examples from the recent studies. In the end, we summarize recent accomplishments, critical issues to consider, and give perspectives on the developments of this exciting research field.

1. Introduction

Autonomous biological systems demonstrate how tailored stresses mediated by external stimuli can be utilized in nature to control shape, pattern, appearance, and triggered actuation which are out of reach for current materials designs.^{1,2} Responsive polymeric and hybrid systems, which are sensitive to environmental conditions, are frequently utilized to mimic such active biological structures and serves for biological and chemical sensing, actuation, adaption, and reconfiguration.^{3,4} However, synthetic responsive materials and structures explored to date do not show diverse and sophisticated sensing and actuating properties inherent in autonomous biological systems.

Macromolecular materials such as these have long been recognized as a prospective actuating platform for their unique physical properties resulting from their chain-like flexible structure, an exceptionally high molecular weight, mobile physical entanglements, and weak intermolecular interactions similar to those found in biological materials. Since the recent developments in the field of macromolecular chemistry, tailored responsive polymers have been subjected to intense theoretical treatments which have resulted in the prediction and discovery of many unique and useful quirks in the behavior of polymeric systems. One area of particular interest is the study of the phase separation behavior of polymer solutions, transformation of individual macromolecules, and their aggregates from prospective of their responsive, adaptive, reconfigurable and actuating behavior. Owing to a low entropy of mixing, polymer solutions and blends can be immiscible under certain thermodynamic conditions (*e.g.* temperature and concentration) but show complete miscibility at some critical point (*i.e.* the upper critical solution temperature, or UCST). This result is accounted for under more advanced thermodynamic treatments, most famously the Flory–Huggins solution theory and more recent sophisticated models which have been applied to attempt to explain complex polymeric behavior more completely.⁵

As with most thermodynamic phase boundaries, polymer phase separations can be induced with very slight changes in internal or external thermodynamic parameters. These stimuli alter the overall free energy of the system and methods to alter the entropic term (via temperature and external field) and the enthalpic term (via pH or solvent quality) have been suggested and are widely explored.⁶ From the standpoint of Flory-Huggins theory, the change in solvent will be accounted for in the change in the volume fraction of solvent or in the interaction parameter, depending on the specifics of the solvent alteration. In the former case, the resulting changes in the system will be a consequence of the change of the entropic term from the free energy of mixing. In the latter case, the changes will largely be impacted by the change in the enthalpy term of the free energy of mixing as well, assuming that the solvents used are of molecular weights and are much smaller than the polymer.

In the extreme case of solvent evaporation, that is complete drying of the polymer, the polymer will be exposed to whatever atmosphere is present. While the highly mobile nature of gas molecules means that gases will have a certain degree of solubility in dry polymers, this value has been found to be quite low.⁷ The polymer conformation under this condition can vary considerably due to intra-chain or inter-chain interactions even

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in the solventless cases. In order to account for the influence of nature of atomic bonds as well as the various rotational isomers, a generalized equation may be used to connect global chain dimensions with overall dimensions directly related not only to chain and bond parameters N (number of segments) and l (the length of a segment) but also upon thermodynamic parameters embedded in a conversion factor C which is sensitive to chain environment:⁸

$$\langle R_0^2 \rangle = C_\infty N l^2 \tag{1}$$

Transformation in chain dimensions (as reflected by *C*) can be exploited to create materials that have distinct "response" (change in macromolecular dimensions) to certain external "stimuli" with corresponding abrupt and dramatic changes in macroscopic dimensions and shapes.⁹ An example of this phenomenon can be seen in Fig. 1, which shows the collapse of single macromolecules with dramatic alternation in chain conformation and dimensions as a function of pH conditions as predicted by theories and can be visualized directly with atomic force microscopy.¹⁰



Fig. 1 AFM measurements demonstrating different morphologies of a pH responsive polymer at: (a) pH 3.89 (b) pH 4.04; (c) pH 4.24. Reprinted with permission from ref. 10. Copyright (2005) American Chemical Society.

Cross-linked polymer gels are particularly interesting from practical viewpoint due to the ease of extracting useful work from such responses.11 From a thermodynamic viewpoint, a gel presents an interesting case as the typical thermochemical results are complicated with the addition of the elastic energy stored within a gel under deformation, though simplistic solutions, such as the Flory-Rehner equation,¹² have been developed. When applied to gels, these phase changes and molecular dimension changes are referred to as volume-phase transitions. The response towards a stimulus can be widely varied, and depends on the degree and nature of the crosslinking used. In a system where the crosslinks are robust or permanent (e.g., covalent crosslinks), the response to a stimulus is typically an aforementioned volume-phase transition, i.e. controlled swelling or deswelling with dramatic dimensional (and usually isotropic for regular materials) changes.

Though it is common to alternate a system between two equilibrium thermodynamic states, there have been many successful efforts to use a kinetically metastable state instead. A poignant example of this can be seen in the case of a charge stabilized material (*i.e.* a polyelectrolyte), which collapses¹³ or aggregates¹⁴ with the addition of a charge screening species, commonly a salt. While such cases open the door for the possible range of non-traditional approaches that may be used to produce a responsive system.¹⁵ It is worth to note that responses in these systems can sometimes be irreversible once the material falls out of the kinetically metastable state and into the thermodynamically favored state.

Such a versatile set of phenomena raises the possibility for a range of responsive materials that perform a certain function at an appropriate time or location. In recent years, many complicated designs utilizing responsive polymers have been both proposed and realized. Depending upon design and fabrication conditions a wide variety of individual micro-/nanoparticulated



Fig. 2 Stimuli-responsive polymer materials designs possible in the form of films and micro/nanoparticles. Reprinted from ref. 16. Copyright Nature Materials.



Fig. 3 Modeling of a responsive polymer swimmer. (a) A schematic of the swimmers showing the different flap dimensions. (b) Displacement profiles of the flap motion in each swimmer for a variety of different polymer stiffness, *A*. Reproduced from ref. 17 with permission from The Royal Society of Chemistry.

and film-like materials can be made for various applications as has recently been discussed.¹⁶ A wide range of responsive materials and structures can be designed from linear, crosslinked, and branched polymer chains, as core-shell and continuous structures, as unimolecular micelles and colloidosomes, as thin films and nanoscale coatings, as grafted layers and free-standing composite structures (Fig. 2).¹⁶

In general, there has been much interest into the concept of polymers which can be made to undergo changes in morphology which are controllable, rapid, and reversible, and in the end, allows for fast, repeatable, and complex shape changes, omnidirectional motion as predicted by modeling of stress and stain distribution which might result in complex motion of different elements and corresponding directional move of the whole system (see an example of computer modeling in Fig. 3).¹⁷

While much work has been accomplished in these areas, as fabrication, processing and synthesis techniques all improved, there has been a corresponding increase in the complexity and efficacy of the responsive behavior in more recent polymeric systems with more sophisticated organization. Therefore, the controlled actuating ability in a wide range of spatial, chemical, and time domains can made responsive materials very attractive for use in various fields such as the area of soft robotics, where the material which can replace mechanical joints or piezoceramic is required to undergo a large scale but precise actuation in response to a stimulus.

In this light, the continued work on reconfigurable polymeric and hybrid systems shows great promise in bringing further advancement well beyond traditional field of responsive polymer morphologies, microstructures, and surfaces as discussed in our earlier reviews and original papers.¹⁸⁻²⁰ Indeed, the great interest in research community is stirred by recent exciting examples as will be discussed here.

Therefore, this review focuses on recent achievements in the field responsive complex materials with the variety of stimuli that have been used in readily reconfigurable and actuatable polymeric systems. For the purpose of this rather brief review, we define actuation as a collective, reversible, large scale, abrupt, relatively fast, and directional deformation exhibited by a system after the application of a stimulus. The discussion of these systems will be divided according to two general types of stimulus involved in actuation. In the first section, we discuss the stimuli which act by changing the thermochemical state of the system, including by alternation of solvent, temperature, stress, and addition of chemical species. The second section will cover remote electromagnetic stimuli as applied by external fields (magnetic, electric, and light).

These sections will contain a brief overview of the underlying physical phenomena and corresponding behavior as well as some selected intriguing examples of the actuating systems from recent publications. Considering brevity of this review, little details on specific chemical and morphological features can be provided and a number of selected examples is rather limited by the views of the authors and serve for illustrative purposes and not for comprehensive representation.

2. Thermochemically induced reconfiguration

2.1. Solvent parameter response

The most simplistic method of inducing a response in a polymeric system is to change the solvent conditions of the system (solvent quality or pH of solution by replacing or adding some components). Examples of pH-triggered changes in polymer dimensions and stresses can be explored for controlled changes in overall dimensions of microscopic structures, their physical properties, or functioning of soft matter objects are widely known.^{20–22} Though this is not always feasible in all applications, particularly biological systems, it can be an extremely powerful technique in its own right and will be discussed in greater depth in the following section. While nearly all polymers will display different behaviors in different solvents, this section will focus on the drastic phenomena that are of interest from an actuating behavior point of view.

The change of lengths in individual chains collectively may lead to a large scale deformation in the bulk elastomeric or gel-like polymer: a common theme in many actuating materials using polymers. While this behavior typically leads to an isotropic volume change, polymer gels may be confined in such a way to force anisotropy in the volume change and thus in overall shape of the materials structure and directionality of the actuation behavior unachievable in simple isotropic media. For instance, a recent report from Sun et al.23 demonstrates this concept in the fabrication of a tethered polymeric microwire capable of controlled motion of associated objects (Fig. 4). The microwire was wade from a highly cross-linked butyl methacrylate gel and was suspended between two pillars. In ethanol or hexane, the microwire was in an unswollen state and thus had a relatively low level of extension. Upon exposure to acetone, the wire was able to rapidly expand its length by about 8% but form bending arch. This concept was later shown to be able to drive a miniature moving device. Using the same wire as above, one end of the wire was attached to a fixed block and the other end was attached to a movable block. Upon exposure to a poor solvent (and subsequent deswelling of the polymer), the microwire was able to exert enough force to cause to mobile block to move towards the fixed block.



Fig. 4 Solvent mediated response in a polymer microwire. (a) Schematic of experiment. (b–d) Stretching and contraction occur as the wire is exposed to different solvents. (e) Change in the length of the polymer microwire plotted *versus* the response time with a periodic change in solvent. Reproduced from ref. 23 with permission from The Royal Society of Chemistry.

More complex examples of actuation typically require advanced processing techniques in order to impart a high degree of anisotropy in the finished structure. Oftentimes, these techniques will use a photopolymerization method, as this approach allows for a high degree of spatial control in processing, and also allows for complex actuation and shape control of soft 3D structures. These devices can exhibit drastic and highly directional changes under the swelling or collapse of the gel network. Ultimately, these techniques allow for the fabrication of structures which can be actuated in a predictable and controllable way.

Two recent papers from Fang *et al.*^{24,25} described the fabrication of devices with embedded microfluidic channels in a hydrogel structure. The channels allow for the efficient delivery of a solvent (in this case, water) to the bulk of the polymer gel. Besides allowing for a greater degree of control over the amount and type of solvent entering the gel, this approach greatly enhances the swelling rate of the hydrogels by increasing the surface that is exposed to solvent (which, in turn greatly accelerates the diffusion of water in to the bulk). This setup was first used in the design of a bendable beam, which demonstrated the large deformations possible in hydrogel structures.

Following this study, a number of devices were fabricated using a similar principle, but were made as free standing structures. An example of this jumping behavior can be seen in Fig. 5.²⁵ These devices were shown to exhibit rapid deformations due to a combination of the rapid swelling of the hydrogel and the design of the structures, which takes advantage of a mechanical instability to rapidly release stored elastic energy.

2.2. Chemically induced actuation

Chemical reactions present an interesting method by which one might trigger a response in a polymeric system although a slow response is a common issue. In some cases, a response may be the direct result of a chemical reaction which delivers some amount of usable energy to the system in order to cause some actuation. Alternatively, a chemical species may indirectly trigger a response by reacting with a polymeric species. In this case, the actuation may result from the net motion of the polymer chains under a confined conformational change.



Fig. 5 The rapid actuation of the polymer structure is mediated by a solvent. (1) The initial state of the polymer structure. (2–6) The gradual wetting process causes the structure to open itself up. (7 and 8) The structure rapidly closes itself and achieves a large vertical and horizontal displacement. Reproduced from ref. 24 with permission from The Royal Society of Chemistry.

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In order to induce a rapid response in the system, highly reactive elements in a system can be exploited as miniature fuel supply elements. For example, it is possible to use the evolution of a gaseous species to propel a polymeric sample, which acts in a similar way as traditional rocket propulsion.²⁶ One may, however, use a more subtle effect, such as the diffusion of one chemical species into another, in order to cause a similar propulsion phenomenon. A recent report shows that a polymer soaked in ethanol can be made to propel itself on the surface of water.27 The difference in surface tension between the ethanol and the water causes the polymeric vessel (made from polyacrylamide) to quickly move away from the diffusion front of the alcohol. By adjusting the geometry of the tube, the authors were able to guide the complex trajectory plotted by the bendable tube in a very controlled manner, which can be seen more closely in Fig. 6 where both linear displacement as well as tube curling was periodically tunes in amplitude.

High level of swelling and deswelling of polymer networks in the presence/removal of particular chemical or biological components can be used to initiate actuation of bimorph flexible systems which can be utilized for chemo/biosensing and actuation.²⁸ Bimaterial microbeams which are composed from silicon beams coated with highly swellable polymeric layer with strong interfacial strength can show a high level of actuation due to high interfacial strength developed because of chemically induced swelling of polymers.²⁹



Fig. 7 Optical image of a polymer–silicon microbeam coated bent due to response to hydrazine vapor. Dynamic response of bimorph beam repeated cycles of humidification and desiccation. Reprinted with permission from ref. 30. Copyright (2007) John Wiley and Sons.



Fig. 6 A variety of tube shapes used to create different trajectory profiles. Shown are pictures of the tubing, plotted trajectory paths, and plots of the periodic displacement and rotation of the tubes as a function of time. Reprinted with permission from ref. 27. Copyright (2011) American Chemical Society.

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High stress at the polymer–silicon interface (reaching tens of MPa) facilitates large micron-scale responses to external stimuli, such as polymer swelling and deswelling in various chemical environments. Under certain conditions, the interaction of polymer coated microbeam with analytes might result in such strong interfacial stresses that the silicon microbeams becomes completely and reversibly bent (Fig. 7).^{28,30} Moreover, changes in environment (such as variation of local humidity) may result in corresponding fast (tens of milliseconds response time) actuation of the microbeams (Fig. 7).

The variation of Columbic interactions can greatly affect the conformation of a polymer chain and its interactions with the surrounding media.³¹ When one considers the steady state chain conformation of a polyelectrolyte, the charge carried by the repeat units becomes an important factor to consider. In the case of non zwitterionic homopolymers, the charge of each repeat unit is the same and so an intra-chain repulsive force will occur, causing an expansion of the overall chain dimensions if ion balance would be altered.

For a charged polymer, the repulsive force between repeat units must take into account the effects of the surrounding medium. The polarizability of the medium, composed of solvent and dissolved electrolytes, plays an important role in determining the screening length for the polymer chain segments. Adjusting the polarizability of the solvent (through solvent exchange) may not be practical, but it is generally possible to alter the total dissolved ion concentration in a solvent, and thus the screening length may be affected through addition (or subtraction with an appropriate dialysis setup) of a salt solution. Ultimately, this has the effect of reducing the role of Columbic forces in determining the equilibrium state of the polymer.

Polyelectrolyte materials which are widely used to build various responsive nanostructures³² are commonly divided into two categories: "strong polyelectrolytes" which are fully ionized in solution and "weak polyelectrolytes" which are partially charged according to an equilibrium ratio. While strong polyelectrolytes contain large numbers of charged groups under most experimental conditions, the number of charged groups contained in weak polyelectrolytes may be altered by changing the solvent environment. One of the most ubiquitous methods of controlling the charge contained on a weak polyelectrolyte is through control of the pH of the solution. Many commonly used weak polyelectrolytes are either weak Brønsted acids or bases and thus a critical range of pH values may be obtained from the acid/ base dissociation constants of the repeat units.³³ Knowing this pH range, one can tailor a system that responds to relatively minute changes in pH by virtue of the dissociation of the repeat units.

By varying the pH of the solution, one is able to control the conformation of the polymer chains in the solution. As shown in Fig. 1, the change in polymer conformation and dimensions can be quite dramatic, leading to a large reduction or increase in the pervaded volume of the polymer chains. The volume change of the polymer chains leads to dramatic changes in other physical properties such as viscosity, diffusion rate, and scattering behavior.³⁴ In the case of a polyelectrolyte gel, the swelling of the gel is dependent on the degree of dissociation of the repeat units. As the pH is adjusted, the swelling ratio and thus the volume of the gel will change depending on the pH value and the dissociation constant of the polymer.

As reported by Aizenberg *et al.* pH responsive polymer gels combined with microfabricated arrays can be used as actuatable structures.³⁵ By placing flexible polymeric posts (non pH responsive) in a thin film composed of a pH-responsive polymer (poly(acrylic acid-*co*-acrylamide)), the authors were able to cause a reversible and repeatable large-scale collapse in the pillars under a change in the pH of the solution (Fig. 8). At low pH, the acid group in the polymer film is protonated, which causes a reduction of the affinity of the gel for the solvent. As the water is expelled from the gel, the polymer attempts to collapse, but is bound to the pillars. As the pillars are relatively elastic, they are able to bend in order to relieve the elastic strain in the surrounding gel (Fig. 8). Upon raising the pH of the solution, and the subsequent swelling of the gel, the stored elastic energy in the pillars is released as the gel continue to expand outwards.



Fig. 8 Schematic and proposed mechanism of the pillar actuation. (a and b) The hydrogel pillars contract and extend along with the responsive gel matrix when the surrounding solution is acid and basic, respectively, corresponding to the dissociation of the carboxylic acid side group in the polymer. (c) Overall structure of the device, showing the pillar array embedded into the responsive polymer. Reprinted with permission from ref. 35. Copyright (2013) John Wiley and Sons.



Fig. 9 Composite structure made of 3 different responsive polymer segments. The morphological changes for different conditions are shown for (a) pH = 4 and [NaCl] = 0 M. (b) At pH = 9.5 and [NaCl] = 0 M. (c) At pH = 4 and [NaCl] = 1.5 M Reprinted with permission from ref. 36. Copyright (2013) American Chemical Society.

Through patterning of several different types of polymers (multiphase materials), a more complex actuation response may be garnered. To this end, Kumacheva et al. have reported on the synthesis of a composite gel structure which allows for a number of responses for different stimuli.36 Of particular interest in this report is the design of complex striped ternary composite gel consisting of poly(acrylamide-co-butyl methacrylate), poly(acrylamide-co-butyl methacrylate)/poly(methacrylic acid), and poly(acrylamide-co-butyl methacrylate)/poly(N-isopropylacrylamide). The gels were patterned in a specific way to elicit a particular response under various conditions, as shown in Fig. 9. In this composite structure, the ionic strength and the pH of the solution may be independently controlled and each of these stimuli triggers to the swelling or collapse of one of the responsive elements. Due to the orthogonal response of the different elements, the swelling of one polymer is not directly

hindered by the state of another polymer. Due to the multiphase nature of this structure, the two stimuli can be varied independently, allowing for a wide number of complex morphologies and multistimuli response.

2.3. Thermally responsive systems

The conformation of a polymer chain at equilibrium is driven by the balance of the enthalpy for certain isomers and the entropy of the chain. This process is complicated by the addition of a solvent, and in particular can depend on the quality of the solvent at a given set of experimental conditions, more so when complex interactions exist between the polymer and solvent.³⁷ The free energy of mixing for a solvent and polymer will determine whether a particular polymer solution will be a single-phase or two-phase system.

For certain combinations of solvents and polymers, the free energy of mixing results in different equilibrium phases as the temperature of the solution is varied. These results often manifest in the form of a lower critical solution temperature (LCST) or a UCST which describe the maximum or minimum, respectively, temperatures in which a single phase solution may exist. These temperature transformations represent discrete and abrupt phase transitions, which allows for a high degree of response sensitivity in the region close to the transition temperature.

Poly(*N*-isopropylacrylamide), PNIPAM, is one of the most commonly used thermally responsive polymers due in part to its low temperature LCST (around 32 °C) and high degree of solubility in water at variable temperatures.³⁸ This behavior allows for the creation of thermally responsive devices fabricated from cross-linked PNPAM gels at modestly elevated temperature. Because the LCST represents a phase boundary dividing the swollen and unswollen states of the gel, temperature can be used similar to an on/off switch, meaning that drastic changes in volume may occur due to relatively minor changes in temperature. A recent study demonstrates that a thermally responsive polymer may be combined with a chemically active environment to produce an oscillating system (Fig. 10).³⁹



Fig. 10 Simulation results for a chemical oscillator. (a) Schematic of polymer pillars used in the simulation. (b) Position of the tip of the pillar plotted *versus* the temperature of the tip. The arrows point in the direction of increasing time. (c and d) Plots of the position and temperature off the pillar tips as a function of time. Reprinted with permission from ref. 39. Copyright (2012) Nature Publishing Group.

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In this study, arrays of PNIPAM pillars were fabricated with a catalyst as a cap for each pillar. Intense exothermic reactions were localized at the tips of the pillars, also localizing the increased temperature in this region. Once the temperature reached the LCST, the rods bent into a region of liquid which was designed to contain no reactants, allowing the pillars to cool below the LCST. This caused the pillars to elongate once more and continue the cycle. Simulation results show that such an oscillation is stable at long times, and could thus continue so long as the supply of reagent continued (Fig. 10).

While the use of LCST and UCST behaviors is very common approaches to achieving actuation, there are many more methods that that allow for a thermally induced response. One approach is the use of a mismatch in the coefficient of thermal expansion (CTE) between two materials which can be only effective if a significant difference (orders of magnitude) in materials CTE occurs. When a material with a large CTE is coupled with a material with a small CTE, the materials must strain in order to maintain their bonded interface at elevated temperature.⁴⁰ This strain induces a stress gradient in the materials, and so a macroscale deformation may occur to relax this thermal stress.

A recent study of Dalton *et al.*⁴¹ has found that such an effect can be seen in the case of carbon nanotube (CNT) composites. In this paper, a composites of carbon nanotubes and gel latex particles and deposited onto a silicon substrate, as seen in Fig. 11. Due to the structure of carbon nanotube bonds (rigid



Fig. 11 (a) The mechanisms of the anisotropic swelling behavior in the polymer mediated by the carbon nanotubes. (b) Thermal expansion of the polymer/carbon nanotube composite plotted *versus* the weight fraction of carbon nanotube in the composite. (c) SEM image showing the honeycomb-like structure formed by the nanotubes. Adapted with permission from ref. 41. Copyright (2013) John Wiley and Sons.

single and double bonds), the carbon nanotubes have a much lower CTE than the latex particles. Because of how the nanotubes assemble on the surface (*i.e.* in a honeycomb-like pattern of hexagons) the in-plane expansion of the latex is constrained by the rigid nanotubes. Once the latex has filled the available space between the nanotubes, in order to relieve the strain present in the beads, the polymer will begin to exhibit an increased expansion in the direction perpendicular to the silicon surface. The process forced the polymer material to move upwards through the gaps in the nanotube assembly, achieving enhanced strains (up to 200% greater than nonconfined latex by itself) in the out-of-plane direction.

2.4. Mechanically responsive materials

When a stress is introduced into a material, it can either be stored in the chemical or physical bonding network of the system, or the system will deform in order to relieve the stress. A positive unidirectional stress will typically produce a positive strain along the axis of the stress and a corresponding negative stress along one or both of the orthogonal axes in order to preserve the total volume of the material (assuming incompressibility). A full description of the stress–strain state of the material can be complicated, potentially requiring a 9-element second order tensor (though arguments of symmetry typically reduce the number of elements to 6) in order to fully describe the behavior.⁴² This come in addition to the inhomogeneity of the material which gives a system that has an extremely complex mechanical state.

Because of the potential complexity inherent in a system under a stress, the behavior of the heterogeneous hybrid materials (*e.g.* with incorporated nanostructures) can be much more interesting than a simple linear or isotropic response to a stress. By carefully applying stresses to a mechanically responsive system, a number of interesting strain behaviors may be produced. Further, by introducing another functional material to the mechanically responsive element, the range of possible actuating outcomes may be greatly increased and shape variability can be achieved.

One of the most simplistic uses of a mechanically responsive system is the utilization of a rubbery polymer, such as polydimethylsiloxane (PDMS), as a stretchable, flexible substrate. In recent study, Whitesides *et al.* have demonstrated a range of seemingly complicated soft robots⁴³ based on the selective straining of an elastomer. One recent study demonstrates the development of a prehensile tentacle-like grasping mechanism achieved by forcing pressurized air into several sacs along the length of the tendril. By using two different elastomers, the authors can cause large deformations, while still maintaining a degree of rigidity to the system. As shown in Fig. 12, this can be utilized to allow the tentacle to wrap itself around a variety of complex objects.

While the elasticity of the substrate may hold value on its own, another interesting use of PDMS lies in its ability to change the spacing of adhered substances.⁴⁴ Any particle (or molecule) that is strongly bound to the surface of an elastomer may be made to move in the direction of strain on the polymer substrate. This scenario can be extended to the case of a biaxial stretching, where



Fig. 12 (a) Picture of the internal tubing of the polymer tentacle. (b) Schematic showing a cross-sectional view of the tubing within the tentacle. (c-f) By inflating all three sections simultaneously, the tentacle may be used to hold a number of objects. Reprinted with permission from ref. 43. Copyright (2013) John Wiley and Sons.

the stress is applied in two directions simultaneously, thus giving a large degree of control of a particle's position on the surface of the substrate and thus the overall shape. Of great importance is the fact that groups of particles will typically maintain their local ordering even as the spacing between them changes significantly along with the strain direction and value.

The above mentioned phenomena can be used in systems in which a certain ordering must be conserved, but it is desirous to change the inter-particle spacing. For instance, Park *et al.* show that an array of silicon nanowires may be embedded into a PDMS substrate.⁴⁵ As the silicon nanowires act as a photonic crystal, the spacing between the nanowires will affect the peak resonance of the array, and thus stretching of the substrate may be used to tune the resonance of the system. A similar idea may be applied to tunable plasmonic systems with other metallic nanostructures such as gold nanorods embedded into highly compliant gel matrices.⁴⁶

It is important to note that for these experimental designs computer simulation is critical to predict local and global physical properties of complex materials such as multifunctional responsive behavior, spatial and temporal stress–strain distribution, elastic and viscoelastic response, shape changes, permeability and transport properties. In contrast to traditional molecular modeling, this sophisticated modeling takes into account coarse-scale short- and long-range order effects as well as viscoelastic and permeability properties in order to simulate relevant soft structures.⁴⁷ This advanced approach allows to simulate complex physical phenomena occurring at relatively large time and spatial scales relevant to physical phenomena of



Fig. 13 Computer model of Janus flower structure in neutral and stress-responsive conditions (courtesy of A. Alexeev).

interest, while accurately capturing the essential features of polymer architecture and the important effects associated with the solvent flow and shape changes.⁴⁸ For instance, the selffoldable Janus flower structures constructed from bilayered polymer film demonstrated unique actuating behavior similar to those observed in natural examples and synthetic analogs as will be discussed below (Fig. 13).

It is worth to note that during large deformations buckling can occur due to mechanical instabilities in a material under compressive stresses.⁴⁹ Typically, buckling occurs in a system that exists in a metastable configuration, and under a sufficient perturbation the system may quickly shift to the energetically stable configuration. Buckling modes tend to be more prevalent in system elements which are very slender (thinner in directions perpendicular to stress than in direction parallel to stress). Buckling has been shown to be capable of producing intricate patterns on the surface of the material.⁵⁰ With careful alteration of the topology of a thin film surface, it has been shown that buckling instabilities may be used to develop complex 3D patterning and hierarchical 2D buckling patterns.⁵¹ In very recent study, Aizenberg et al. have shown that a variety of interesting patterns that may be formed in an elastic substrate and shapes can be dramatically re-scaled if organized buckling behavior is utilized.52,53

In another recent study from the same group, a PDMS substrate is pre-stretched to a set degree of strain and exposed to an oxygen plasma, which develops a thin, stiff "skin" on the surface of the PDMS.⁵⁴ Because the modulus of the skin and bulk of the PDMS are drastically different, releasing the stress creates a periodic instability at the interface due to the mismatch in strain. This buckling instability gives rise to complex patterns on the surface which are highly dependent on the stress applied to the system. It was shown that different patterns may be formed by changing the initial degree of prestrain on the PDMS or by increasing the stress on the etched PDMS past a critical value. The different patterns were able to generate scattering sites for light, causing the sample to change in optical properties as a function of the strain on the material.

Precise bending is essentially required for the design of selffolding materials and allows conversion of flat 2D objects into closed and open 3D features with different shapes, which is usually attributed to the mismatched deformation at interfaces caused by changes in environmental conditions, such as thermal expansion, pH variation, light-induced transformations, electric field-responsive, phase-induced strain, swelling or dehydration, osmotic pressure or even magnetic field.⁵⁵ Review



Fig. 14 Surface profile of poly(acrlyic acid) gel with regions of alternating crosslinking density. Reproduced from ref. 57 with permission from The Royal Society of Chemistry.

In a recent report, Santagelo and Hayward demonstrated⁵⁶ a novel method to alter the surface of a polymer through a combination of printing and photopatterning on a surface. This system is combined with PNIPAM in order control swelling though temperature. By changing the local degree of cross-linking, the stiffness of the gel may be altered arbitrarily across the surface of the gel. By deliberately patterning the dots in certain configurations, a macroscale deformation can be formed into a prescribed shape with a high degree in the final curvature of the gel. Recently, a similar strategy has been used with a pH responsive gel to create a rippled structure (Fig. 14).⁵⁷

Related concepts can be found in the phenomena of selfrolling and self-folding materials which are predicted by simple mechanical analysis. Self-rolling is generally defined as the ability of a material to contort itself into a rolled tube under some stimulus. In contrast, self-folding is somewhat vaguely defined in the literature, allowing for a wide range of materials that may qualify. It can be generalized, however, that self-folding materials are those that make a discrete number of folds under some stimulus (as opposed to the smooth, continuous change seen in self-rolling systems, though these terms have sometimes been used interchangeably). To date, it has been demonstrated that self-rolling tubes can be obtained from polymer films exposed to stimuli, such as pH,⁵⁸ temperature,⁵⁹ and solvent.⁶⁰

One of the uses of self-folding materials is in the area of foldable structures such as origami structures.⁶¹ Origami is the known Japanese art of paper folding and is performed by making a number of creases in a sheet of paper until a final three-dimensional shape may be obtained.⁶² A similar methodology is applied in these structures: material elements with slightly different mechanical and thermal properties may be used as the hinges of a shape which cause the material to fold in a prescribed way under some stimulus. In this way, it is possible to rapidly fabricate complex geometric structures under the



Fig. 15 Self-folding of thermally responsive patterned polymer films with different shapes. Reproduced from ref. 63 with permission from The Royal Society of Chemistry.

application of a stimulus which act selectively to different patterned elements.

In a recent study, Ionov *et al.* demonstrated an array of different shapes that may be constructed from such origami structures.⁶³ By incorporating a hinged structure with another class of responsive materials (*e.g.* thermally responsive) the shapes may be caused to fold or unfold reversibly. This effect can be used to capture and release some target with dimensions comparable to the size of the gel structure. As shown in Fig. 15, flower-shaped films could be fabricated which were able to self-fold, bring together all elements and form different enclosed shapes.⁶¹ Moreover, the authors demonstrated that these arrays can encapsulate yeast cells on-demand once brought below a set temperature.

Field induced reconfiguration

3.1. Magnetic fields

Recently, magnetic field has been used in polymeric systems to control the organization of the molecules. The effect of a magnetic field on a material depends strongly on the electronic state of the individual atoms in an atom or molecule.⁶⁴ In general, atoms that have unpaired electrons are paramagnetic and will align their magnetic moment in the direction of the magnetic field, while atoms with no unpaired electrons are diamagnetic and will opposite the direction of the magnetic field. While diamagnetic materials exhibit a weak repulsion under the influence of an external magnetic field, paramagnetic materials generally exhibit an attraction to the source of the magnetic field. Ferromagnetic materials are similar to paramagnetic materials, but contain additional interatomic interactions which allow them to exhibit a permanent magnetic dipole and a higher magnetic susceptibility.⁶⁵

Magnetic fields have been used directly on polymeric substances in order to control alignment. Because magnetic



Fig. 16 Stretching occurs in a highly functionalized hydrogel (60% magnetic nanoparticle). (a) No external magnetic field. (b) Magnetic field is applied. Reprinted with permission from ref. 70. Copyright (2009) John Wiley and Sons.

fields do not tend to alter the chemical state of a system, they can be used in many systems without concern for causing a secondary reaction in the system. In addition, it is possible to tune an external magnetic field to control both the strength of the field and the gradient of the field across the sample.

Because organic materials tend to have magnetic susceptibility values that are too low to allow for a rapid response in a material, proper inorganic "fillers" are often used as a means to add a magnetic functionality to a polymeric material.⁶⁶ This greatly extends the range of magnetic susceptibilities possible in polymeric composites. In addition, controlling the amount of filler can present a strategy to control the degree of magnetic susceptibility in a sample and thus control the responsiveness to an external field.

As alluded to previously, one main attraction in using magnetically responsive materials is the ability to align and position a composite material with a high degree of precision. Magnetically assisted positioning typically requires the presence of a magnetic field gradient in the direction of desired motion. Magnetic orientation, on the other hand, typically requires anisotropy in the material itself such that a preferred axis is present which minimizes the potential energy of the system when aligned parallel/antiparallel with the magnetic field. In a recent study, magnetic nanoparticles were integrated into a polymer brush forming a cylindrical composite structure.⁶⁷ By applying a relatively weak magnetic field, the polymer brush composites can be made to align such that the long axis of the cylinder is parallel to the direction of the magnetic field.

Ferrogels are magnetically active gels and are typically composed of polymeric gels and magnetic nanoparticles.⁶⁸ The ferromagnetic metal or metal oxide (*e.g.* super paramagnetic iron oxide nanoparticles – SPIONs) particles can often be functionalized in a variety of ways to allow the nanoparticle to be covalently bound to the polymer of interest. Once incorporated into the polymer matrix, the nanoparticle endows the results composite with a number of unique properties. As shown in a recent study,⁶⁹ this can be used to cause macroscale deformations. By casting a magnetic nanoparticle (magnetite) into a PDMS gel, the authors were able to make a number of complex magnetically actuating structures. Due to the elasticity of the PDMS, shapes such as a cantilever could be made, which deform under a magnetic field and restore their original shape once the field is removed. An example of actuation in molded ferrogels can be seen in Fig. 16.⁷⁰

As reported previously by our group,⁷¹ it is possible to assemble nickel nanorods into complex ordered arrays (shown in Fig. 17) through a drop cast procedure under an external magnetic field. These arrays can be moved across the surface, and the ordering of the rods inside the array may be adjusting by altering the external field. We have shown that these rods may be encapsulated with adsorbed polymer both before and after the formation of arrays, allowing a highly precise arrangement of the polymer–nanorod arrays on the surface and they monitored bending upon application of the external field. Due to the large spacing between rods in the array, it is possible that surface functionalization of the rods may be possible, allowing for a bottom-up construction of an ordered actuating polymer–ferromagnetic material composites.

While alignment and orientation of polymeric materials is oftentimes the desired outcome of magnetically responsive system, other properties of these systems may also be exploited. One of the most common alternate uses of magnetic nanoparticles is in the development of a hyperthermia-based treatment.⁷² Under a rapidly oscillating magnetic field, a magnetic dipole may be forced to rapidly change orientation. The dipoles quickly return to a position of lower energy, releasing heat in the process. Over time, this heat builds and causes the nanoparticles to rapidly raise the temperature of their surroundings. This temperature rise may be coupled with the thermally responsive materials described previously to fabricate a hybrid responsive system.⁷³

Magnetic self-assembly may be used in tandem with responsive materials, as shown recently by Luzinov and Minko *et al.*⁷⁴ In this report, the authors graft a responsive block copolymer (poly(2-vinylpyridine-*b*-ethylene oxide)) to the surface of iron oxide nanoparticles. Upon application of a magnetic field, the nanoparticles were shown to form into long strings. At pH between 3.5 and 5.5, the assembled strings were stable and persisted even after the removal of the magnet. This stability was attributed to the hydrophobic character of poly(2vinylpyridine) (P2VP) in non-acidic environments. The assemblies could be made to disperse through application of temperature (allowing the particles to cross the requisite energy barrier) or by lowering the pH below 3.5, which protonated the P2VP and caused the swelling of the polymer brushes.

3.2. Electric fields

An electric field may exert a force upon a charged species (*i.e.* ions) or an electric dipole (permanent or induced). This force may cause movement of a species under the influence of the electric field. This force is highly dependent on the polarizability of the species, the strength of the field, and the local environment of the species (*e.g.* charge screening effects). Because placing particles in an electric field has the effect of polarizing particles in a system, these systems can experience a number of particle-particle interactions and result in a number of reconfigurations and local displacements.⁷⁵



Fig. 17 Overview of self-assembly process in nickel nanorods. (a–c) A schematic and SEM, AFM images of the nanorods. (d) The proposed assembly mechanism for the nanorods under a strong magnetic field. (e) Optical microscopy images of the assemblies demonstrating a high degree of order. (f) A schematic of magnetic actuation in nickel nanorods partially bound to a substrate. Reprinted with permission from ref. 71. Copyright (2013) American Chemical Society.

Ionic species can exhibit a concentration profile in a solution due to the competition of the drive towards a homogeneous solution (a minimization of entropy) and the enthalpic drive to remain near an oppositely charged surface. In the case of a polyelectrolyte, the charge of the polymer side groups is screened by the presence of a countercharge, usually from some oppositely charged electrolyte in solution (counter-ions).⁷⁶ Under normal conditions, this phenomenon results in a concentration gradient of the electrolyte species radiating outwards from the polymer chain or particle. Through application of a voltage to the system, the concentration profile will shift and cause some degree of separation of the polyelectrolyte and counterions.⁷⁷

In a bulk polymer system, Maxwell stresses (mechanical stresses due to electrostatic interactions) may be employed to cause a large mechanical deformation under an applied voltage.⁷⁸ Certain polymers, called dielectric elastomers, are often employed due to the large strains generated under an applied voltage, along with an increased stability under these conditions. For instance, a recent report⁷⁹ from Huang *et al.* demonstrated a large areal strain of nearly 500%. This is achieved by using a sheet of a dielectric elastomer under a constant biaxial load (Fig. 18). Under applied voltage, the elastomer was able to stretch even further, ultimately obtaining a very large strain due to a combination of the dielectric properties and the viscoelastic behavior of the polymer gel.

Several studies have been performed to test such polymers as a highly compliant component in an actuator system. A recent report details the usage of an electroactive polymer as a peristaltic pump.⁸⁰ In brief, the authors employ a series of dielectric elastomer segments to form the length of a tube. Upon applying voltage to a segment, the polymer expands and uptakes fluid



Fig. 18 (a and b) Picture and schematic of polymer disk before loading or voltage. (c and d) Picture and schematic of polymer disk after loading but before voltage is applied. Reprinted with permission from ref. 79. Copyright (2012) American Institute of Physics.

from a reservoir. Once the voltage is removed, the polymer is allowed to relax and the elastic force generated by this process forces liquid from the segment. By iterating this process, a preferred flow direction develops along the length of the tube.

Beyond the use of dielectric elastomers, it is possible to elicit a voltage-driven response from a material system through use of ohmic heating. Recent studies report on the polymer (PDMS)/ carbon nanotube composites which act as actuators under an applied electric current.⁸¹ In these studies, the actuation occurs due to a mismatch in the coefficient of thermal expansion between the elements of the composites (around two orders of magnitude difference). Because the carbon nanotubes are much stiffer than the surrounding polymer, it is possible to use a layered structure to drive the actuation in a preferred direction by layering a thin CNT containing polymer region with a region of pure polymer. Further, due to the anisotropy in the coefficient of thermal expansion for CNT, the actuation may be limited to a nearly one-dimensional displacement through proper alignment if the CNT's.

3.3. Photoactive actuating materials

Light illumination has long been used as a source of energy to drive certain chemical reactions and physical transformations. With this in mind, the range of materials which are classified as light-responsive would seem to be nearly limitless. In the context of polymeric systems, however, the term "light-responsive" is typically reserved for materials which undergo a photoisomerization and shape change as a direct result of light



Fig. 19 (a) Pictures of oscillating film with increasing laser intensity. (b) Dual plot of oscillation amplitude and frequency *versus* laser intensity for the polymer film. (c) The amplitude of cantilever deflection as a function of power. Reproduced from ref. 88 with permission from The Royal Society of Chemistry.

exposure. This is often done with the aid of a photoreactive functional group (often containing double bonds) in the polymer backbone or side-chains.⁸² These functional groups may exhibit a change between *cis* and *trans* isomeric states or may react to allow for a ring-opening.⁸³

A common functional group used in photoreactive materials is azobenzene.⁸⁴ Azobenzene compounds consist of two phenyl rings joined by a nitrogen–nitrogen double bond, and is most stable as the *trans* isomer under normal light conditions. The nitrogen–nitrogen double bond may react under UV radiation ($\lambda \sim 320$ nm) to undergo a shift to the *cis* isomer. This transformation causes a reduction in length of about 0.45 nm between the two phenyl rings. Because the *cis* isomer is metastable, the azobenzene may be brought back into the *trans* isomer either through thermal relaxation or by driving the process with blue light ($\lambda \sim 430$ nm). In this way, it is possible to reversibly alter the length of a molecule through use of a light source at 320 and 430 nm.⁸⁵

It has been shown previously that a liquid crystal network containing azobenzene mesogens will bend in a direction that is parallel to the polarization of the incident light.86 This is largely due to a combination of the typical azobenzene trans-cis transformation and the high anisotropy and mobility inherent in the liquid crystal matter.⁸⁷ As one example, Bunning et al. have recently reported⁸⁸ on the fabrication of an fastly actuatable cantilever based on an azobenzene liquid crystal network. In brief, a thin film polymer network containing 4-(6-acryloxy)hexyloxy-4'-ethoxyazobenzene mesogens was exposed to polarized laser light containing several wavelengths (457, 488, 514 nm). As the cantilever passed through the beam of the laser, one face of the cantilever was exposed to the incident beam and was forced to bend (exposing the other face at the same time), as shown in Fig. 19. This setup demonstrates an optically driven oscillator based of the light responsive behavior of polymers.

There also exist a number of functional (light-responsive) groups which react irreversibly under irradiation. Some of the more commonly used moieties include salicylideneaniline, nitrobenzene, and spiropyran.⁸⁹ Salicylideneaniline exists natively in enol form (*i.e.* contains an alcohol group) but may be made to under keto-enol tautomerization⁹⁰ in order to form the



Fig. 20 Gold and silver nanoparticles embedded in a thermally responsive gel. (b and c) Show the normal, swollen state of the gel. In (a) and (d), a laser at 546 nm is used to preferentially heat the part of the gel containing gold nanorods, causing the gel to collapse in these regions. In (c) and (f), a 785 nm laser is used to heat the part of the gel containing gold nanoshells, causing these regions. Reprinted with permission from ref. 95. Copyright (2012) American Chemical Society.

keto product, which is more polar. Furthermore, 2-nitrobenzyl groups are hydrophobic groups which are able to be cleaved (photolysed) from an attached under UV irradiation. This transformation has been shown to allow for a rapid shift in the hydrophilic character of a polymer under irradiation.⁸⁹ Finally, spiropyran is a molecule that undergoes a ring-opening reaction under exposure to UV light.⁹¹ The product of this reaction is much more hydrophilic than its precursor, and thus has been used to drastically change the solubility of an attached polymer.

While light-reactive species remain a popular method to develop a light responsive system, it is possible to utilize thermally responsive polymers or polymer-metal bimorphs to achieve similar results.92 The bimaterial microbeam design can be exploited for large-scale actuation under IR light illumination if bending results from a mismatch in thermal expansion coefficients of the materials.93 The ideal bimaterial properties of these light/thermal sensitive bimorphs include large mismatch of thermal expansion and thermal conductivity between the two materials and one of the materials should absorb in the desired IR range (e.g. because of presence of photoactive groups or nanoparticles). It has recently been demonstrated that trapped residual stress in the plasma polymerized polymer coating can significantly enhance the response of the bimaterial structures and provide for a wide range of actuation amplitude and fast response to incoming illumination.94

The phase transition exhibited in polymers like PNIPAM can be localized in a gel structure through use of a targeted heating system. This relies on a balance between the heat flow into polymer from the source and the heat flow from the polymer to a sink to ensure that the polymer will show a gradient of temperature throughout the device. In recent report,



Fig. 21 (a–f) Photographs taken of polymer sheets loaded with black dye in different locations, and the resulting shapes that form after heating with a light source. Reproduced from ref. 97 with permission from The Royal Society of Chemistry.

Sukhishvili *et al.* have shown that light-driven shape changes may be accomplished through targeted heating of hybrid structures with a light source.⁹⁵ In this study, gold nanoshells and gold nanorods were selectively placed in certain locations in a PNIPAM gel cube using a layer by layer approach and using a microtome to excise the finished cubes (Fig. 20). Gold nanostructures have been found to scatter and absorb light efficiently due to plasmonic resonance in nanoparticles. This behavior of gold nanoparticles is highly dependent on shape, size, and the dielectric constant of the surrounding media.⁹⁶

It was found that the peak scattering positions for the nanoparticles in this study were 550 nm for the nanotubes and 760 nm for the nanoshells, allowing the authors to use different light sources that would be preferentially scattered by either the nanotubes or the nanoshells. As these particles were embedded in a PNIPAM gel matrix, the scattered heat was largely dissipated as heat in a localized fashion near the gold nanorods or nanoshells-rich regions. The resulting temperature gradient caused a deformation in the areas which were heated, which was balanced by the elastic modulus of the gel to give complex morphology, which can be seen in. This process was shown to be reversible after the light source was removed, and the process could be repeated for a number of cycles.

Another approach utilizing targeted heating can be seen from Dickey *et al.*⁹⁷ In this report, a sheet of pre-stretched polystyrene is patterned with black dye. When stretched, the polystyrene may be expected to isotropically contract due to the entropic force from the polystyrene chains. The black dye provides a site of higher light absorption, and thus higher temperature, which causes the polymer sheet to contract preferentially along the lines of dye. Fig. 21 shows a number of the complex 3D enclosed and open shapes formed by this method. Ultimately, this allows for an origami-like structure similar to those seen in a previous section.

4. Conclusions

Overall, it is clear from this brief analysis and discussion that the unique actuating properties of reconfigurable polymeric materials are intimately tied to the intricate workings of the individual macromolecular chains of which they are composed under a variety of external driving forces. An understanding of polymer thermodynamics as well as kinetic of chain transformation can allow one to predict the responsive properties of a reconfigurable polymeric materials with pre-designed chemical composition, molecular organization, chain mobility, stress distribution, and distribution of local physical properties and chemical interactions.

The prospective applications of reconfigurable and actuating soft materials are numerous and might have far-reaching impacts. Reconfigurable soft materials have shown great promise in their potential for incorporation into many different multilength-scale operational mechanical devices such as soft robotic arms to replace simple mechanical joints with limited operational mobility. In addition, the ability to combine multiple compliant transducing matrices and actively responding components together into a single controllably reconfigurable soft (but strong) material structures expands the range of control that can be exerted onto a system and facilitates larger and more rapid continuous shape changes in these systems. This allows for more potent soft actuators in a wide variety of spatial and force scales, a broad range of response time scales, and the potential for multifunctional and orthogonal responsive behavior.

These systems hold great promise for implementation in a number of diverse future applications. The ability to manufacture small, soft responsive microdevices opens the door to biomimetic microrobotics and microfluidic devices: areas of particular importance to the biomedical community and national security. Additionally, the ability of the devices to autonomously respond to a stimulus in a pre-programmed manner means that these systems may be useful for self-configurable mobile sensor arrays. Great inherit advantages of polymer-based responsive and actuating materials as compared to other current choices such as piezoceramic or mechanical actuators are directly related to very basic properties of flexible chain transformations unachievable in hard materials and mechanical joints but common for biopolymers and biomaterials with long-chain building units.

Among most important, from practical viewpoints, fundamental properties are extremely large actuation range which can reach hundreds percent with high precision, combined linear and non-linear responses of soft materials which covers a broad range of forces and time-scales, ability to complex and controlled alternation of dimensions that results in dramatic shape transformations, and a wide spectrum of responses to a wide range of external stimuli including potential ability to cross-stimulus and orthogonal responses. Additional auxiliary properties of these soft materials might include biocompatibility, low cytotoxicity, potentially high toughness, self-healing, variable adhesion, friction, and wettability, and possible biodegradability.

Many challenges still exist in the area of soft matter actuating materials and structures fabricated from synthetic polymers and hybrid materials. While great strides have been made to allow for systems which possess issues of biocompatibility, long term stability, time-dependent creep behavior, and ease of integration are hurdles which must be cleared in order to incorporate such devices into biological systems for biomedical research. Further, while the range of stimuli available is suitable for a number of environments and applications, the ability of actuating systems to respond to a complex, multi-stimuli, reallife environment in an appropriate way remains elusive at the moment. Multifunctionality is often claimed but rarely convincible and unambiguously demonstrated. Another common issue is that a response time is usually slow and is diffusionlimited in gel matrices especially at larger spatial dimensions and low stimulus strengths. Needs of a third component for high mobility (e.g., solvent for gels) or for enhancement of stimulus acts (e.g. metal nanostructures for light absorption) might be a significant limitation for some applications.

However, to finish on a positive note, we suggest that eventually the next generation of reconfigurable and actuating soft materials will be developed which will be based upon computationally preprogrammed material organization and precisely designed stimuli-sensing ability and show efficient spatiallycontrolled actuation, programmed shape control and multifunctional orthogonal responses. In principle, there are no fundamental limitations on a range of changes in soft materials actuating dimensions which can reach 1000%, stresses to be applied or generated which can span a kPa to GPa range, practical times of stimulus response which can extend from milliseconds to hours, the wettability level which can be designed to vary from superhydrophilic to superhydrophobic, external stimuli to be reacted to from chemical potential to magnetic fields, and reconfigurable shape complexity from simple 1D objects to complex 3D open and enclosed soft structures and massive arrays. Future intense work will need to continue and focus on the design and fabrication of complex hybrid materials with "build-in" sensing elements and improved transducing functions and on the introduction of reconfigurable materials that are highly specific to the selected environmental stimuli and their combinations under practical ambient conditions.

Additional information

The authors declare no competing financial interests.

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