

Stimuli responsive materials: new avenues toward smart organic devices

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“Smart” patternable polymer-based materials that can be designed from various molecular building blocks show great potential, as they may be used in many fields, including nanotechnology, biochemistry, organic and physical chemistry, and materials science. The focus of this highlight will be on the basic design characteristics of practical Stimuli Responsive Materials (SRMs), the wide range of potential applications and the challenges to be accomplished in this rapidly expanding area. In particular, recent developments are described which are related to two of the many fundamental aspects of stimuli triggered responses: those that are photo-triggered and those that are solvent triggered. These selected state-of-the-art examples demonstrate the large scope and diversity in terms of activation mechanism, response time and property control.

Introduction

The rapidly developing field of nanotechnology has provided a strong impetus for the development of “smart” polymer-based materials that can be designed from a wide range of functional molecular building blocks.^{1,2} The functionality of individual molecular units and the macroscopic properties of Stimuli Responsive Materials (SRMs)

places many fields, including nanotechnology, biochemistry, organic and physical chemistry, and materials science, in an ever close proximity. Recent developments in this area have demonstrated that patternable SRMs on a micro- or even submicro-meter scale show great promise,³ as they may be used, for example, in drug-release systems and memory elements. The development of photo- and electrochemically active mesoscopic polymeric materials is expected to play a major role in nanoscale applications. Molecular structures which can be externally triggered to contract or expand, in a controlled fashion, are expected to become key components in prototype “all-organic”

devices and may find eventually applications ranging from artificial muscles, targeted drug delivery or sensing materials to robotics and molecular electronics.⁴ These materials are often designed so that the conformational changes of the individual subunits are additive, and thus produce a measurable coherent mechanical response to an external stimulus (e.g. light, heat, pH, metal ions, solvent polarity, electric field).

Several strategies were developed by Tanaka *et al.*,⁴ Hoffman *et al.*,⁶ Chilkoti *et al.*,⁷ Lopez *et al.*⁸ and many others^{9–14} in order to achieve such characteristics. While many studies are focused on the relationship between the shape and the kinematic properties of the materials,

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the main focus here will be on the basic design characteristics of such SRMs and the major challenges still to be accomplished in order to achieve SRMs with appropriate characteristics for industrial applications. Practical SRMs must meet a combination of criteria, which may lead to a trade-off between mechanical response efficiency, material processability and long-term stability. The conditions at which many conventional devices operate and which are induced in processing require often patternable materials with long-term chemical, photochemical, mechanical, thermal and temporal stability. Electro-optical (EO) polymers are an excellent example of a class of SRMs that has made significant progress during the last five years in terms of the above-mentioned requirements.^{1e,2d,13,14} Optical computation and telecommunication require high speed conversion of electrical to optical signals at low cost. The electrical-to-optical data conversion can be accomplished with materials that exhibit nonlinear optical (NLO) properties. These SRMs undergo a small, reversible change in the index of refraction upon applying an electric field. The formation of EO polymers requires a high-voltage induced poling process to

align the chromophore building blocks at elevated temperatures. The poling process might be circumvented as there are several alternative processes available including the formation of intrinsically acentric materials by solution-based layer-by-layer assembly and vapor-phase deposition.¹³ Major problems such as chromophore–chromophore interactions and polymer stability under processing and operating conditions have been addressed^{1e,2d,14} and several prototype light-modulators and switches have already been reported (Fig. 1).^{1e,2d,13a,b,d,e} Optical absorption losses are still problematic especially in large device structures. However, C–H groups may be replaced by C–F and/or C–D moieties to increase optical transparency of the SRM at the typical telecommunication wavelengths (1.3 μm and 1.55 μm).

In general, a modulator consist of an EO-active film ($>1\ \mu\text{m}$ thickness) through which light is passed while a modulated electric field is applied. Several modulators based on organic SRMs have been demonstrated to operate even at $<1\ \text{V}$ and are likely to become an alternative to expensive single-crystal lithium niobate (LiNbO_3) based systems.^{2d}

It is clear that the growing area of organic SRMs is very broad, therefore, we will discuss here recent developments relating specifically to two fundamental aspects of stimuli triggered responses: those that are photo-triggered and those that are solvent triggered. These examples demonstrate the large scope and diversity in terms of activation mechanism, response time and property control. The response of the material can take the form of mechanical work, as the example by Hugel *et al.* shows,^{10b} or it can change the wettability of a surface by phase-segregation as demonstrated in the work by Minko *et al.*,^{11a} or a photo-response can be tuned on/off, as shown by the work of Beck and Rowan.¹² Patterning of SRMs will be highlighted as well as this direction offers a wide range of novel materials that can respond in a selective manner to an external trigger. From the examples chosen, the wide range of potential applications is undoubtedly apparent.

Photo-induced mechanical work

Azobenzene-based polymers are excellent vehicles for photoinduced processes.¹⁰



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study of polymeric electroactive materials derived from biomolecules. After studying at the Heinrich-Heine Universität Düsseldorf and the University of Kent at Canterbury, he received his Ph.D. from the University of Calgary and carried out postdoctoral work in organometallic chemistry at the University of Maryland, College Park, and the Weizmann Institute of Science. He worked as an assistant Research Officer at the Steacie Institute of Science, Ottawa and in 1998 he joined the Department of Chemistry at The University of Saskatchewan. He received a PetroCanada Young Innovator Award in 2001 and since January 2002 has been the Canada Research Chair in Biomaterials.

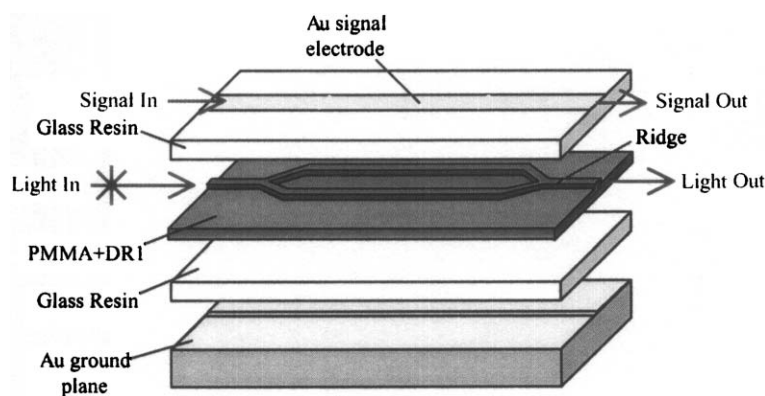


Fig. 1 Example of a poled-polymer based electrooptic modulator. The spin-coated polymer layers are cured up to 200 °C. The distance between the two arms of the ridge waveguide is 8 μm . The width of the top electrode is 30 μm .^{13e} The commercially available azobenzene disperse red-1 (DR1) and polymethylmethacrylate (PMMA) are used as the electrooptical material. (Reprinted with permission from *Science*, 2002, **298**, 1401. Copyright 2002, AAAS).

An excellent example from Wang *et al.* recently described the photoinduced deformation of azo polymer colloids.^{10a} The colloid morphology changes from spheres to “spindles”, and from “spindles” to “rods”. Hugel *et al.* reported on a photo-triggered polymer, which contains azobenzene units as part of the main polymer backbone.^{10b} This key study demonstrates an opto-mechanical cycle using a single azobenzene polymer molecule (Fig. 2), representing the first experimental work using opto-mechanical energy conversion in a single-molecule device, in which a

polymer is covalently coupled to an AFM tip and a glass slide. The polymer's azobenzene units are reversibly switched at two distinctly different wavelengths between an extended *trans* and a contracted *cis* configuration. Applying focused UV light ($\lambda = 420 \text{ nm}$) to the glass substrate having the polymer bound to it results in stretching of the polymer since its conformation is switched to the all-*trans* state. Subsequent illumination with light of $\lambda_{\text{max}} = 356 \text{ nm}$ causes relaxation of the polymer and conversion to the all-*cis* conformation. The material can be repeatedly cycled between these

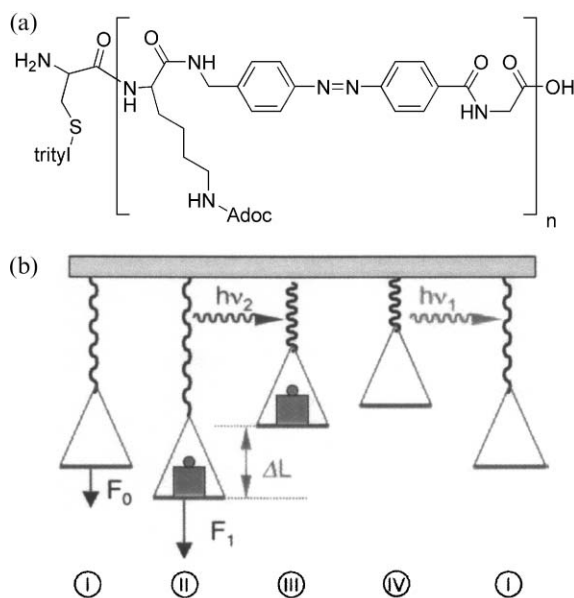


Fig. 2 a) Precursor of a polyazobenzene peptide conjugates used in the study by Hugel *et al.*; b) the four states (I–IV) of a work cycle based on a single molecule. (Reprinted with permission from *Science*, 2002, **296**, 1103–1106. Copyright 2002 AAAS.)

two states, even when an external load is put on the AFM tip. Thus, this photo-induced conformational transition is able to generate mechanical work. This can be the basis of a wide range of new SRMs designed to incorporate such azobenzene-based building blocks.

Patterning of SRMs

Substantial efforts have been devoted to the design of patterning of stimuli-responsive polymer films.¹¹ For example, Feringa and coworkers reported recently on light driven dynamic pattern formation in a sol-gel system by using an optically addressable molecular building block.^{11b} Chemically patterned SRM will selectively respond to an external trigger paving the road towards the formation of smart surfaces. Minko and coworkers recently reported a novel strategy making use of a mixed-brush of poly(2-vinylpyridine) and poly-isoprene, which allows the permanent storage or writing of a pattern.^{11a} This pattern is then reversibly developed and erased upon exposure to the appropriate environment, such as solvent, pH, and temperature. Initially a Si wafer is functionalized with a glycidoxypyril trimethoxysilane layer, which is followed by spin-coating of carboxylic acid terminated poly-isoprene (up to a thickness of 2.6 nm), followed by grafting of poly(2-vinylpyridine) to give a total surface thickness of about 5 nm. Remarkably, *the resulting surface wettability can readily be switched from hydrophobic to hydrophilic*. Exposure to toluene will give a hydrophobic surface, whereas exposure to water (pH = 2) will give rise to a hydrophilic surface, causes by phase segregation of the two polymers. The contact angles change accordingly from 80° for a toluene-treated surface to 42° for a surface treated with acidic water. A change in the nature of the solvent will change the solvation of the surface, forcing a change in the surface composition. The importance of this approach lies in the ability to fix the properties and state of the film by causing subsequent irreversible polymerization, without destruction of the polymer. For instance, a mask is applied to the surface, followed by UV treatment causing polymerization in areas that were exposed to the light, thereby fixing the surface morphology,

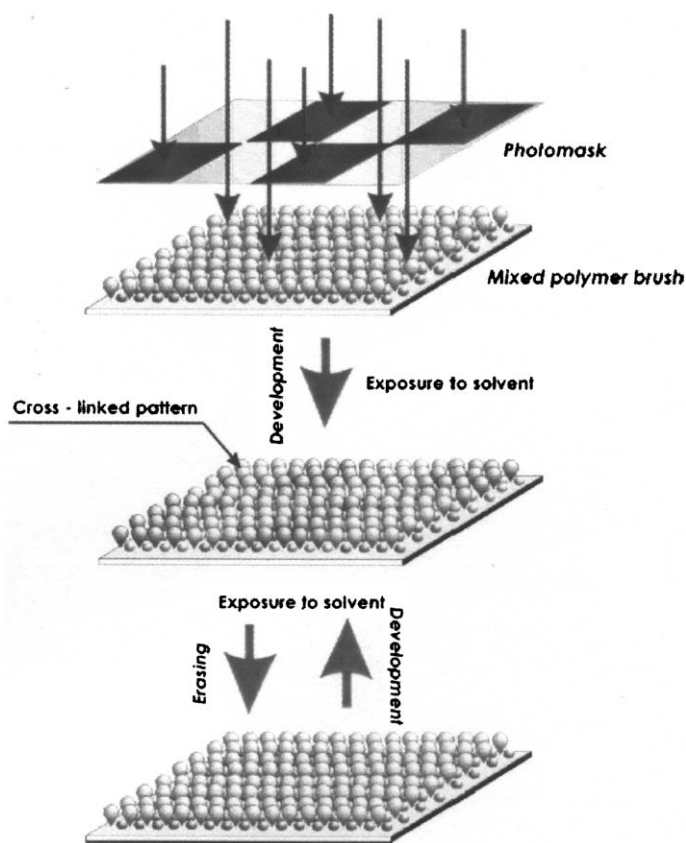


Fig. 3 Schematic representation of the photolithographic process using mixed polymer brushes (reproduced with permission from *J. Am. Soc. Chem.* 2003, **125**, 8302–8306. Copyright 2003 Am. Chem. Soc.).

preventing phase segregation of the polymers. The aqueous contact angle in the irradiated polymerized areas is independent on the solvent conditions (69°). The non-irradiated areas retain their ability to respond to external stimuli. For example, after exposure to ethanol, both irradiated and non-irradiated areas have the same wetting properties. However, upon treatment with acidic water, the non-irradiated areas are more

hydrophilic than the irradiated ones, allowing this approach to be used for patterning as is illustrated in Fig. 3 and 4.

The utility of this approach to produce prototype SRMs-based devices was demonstrated by patterning a switchable micro-channel in which the channel can be opened and closed by external stimuli—in this case, pH or temperature. The irradiated areas become the walls of the channel and lose their switching

ability. The bottom of the channel is hydrophilic and water can flow. However, if the pH increases, or the temperature is raised, the bottom changes to a hydrophobic state, thereby closing the channel. It is notable that drug-release research has focused on controlled release from polymeric matrices triggered by light, ultrasound, enzymes, pH, temperature, magnetic or electrical fields. The rapidly emerging field of microfabrication technology is becoming an alternative approach as it includes already micro-meter-scale devices that can deliver liquids *via* a combination of sophisticated pumps and channels. Integration of SRMs and microfabrication technology is likely to become of much increasing academic and industrial importance in the coming decade.

Minko and coworkers also introduced an advanced patterning method by using two-level structured surfaces, which are capable of reversible switching from hydrophilic to ultra-hydrophobic states upon external stimuli.^{11a} Again, solvents, acidity, and temperature were used as the external triggers. The polymer brush was prepared by spin-coating and annealing of carboxy-terminated poly(styrene-*co*-2,3,4,5,6-pentafluorostyrene) onto poly-fluoroethylene, followed by spin-coating and annealing of carboxyl-terminated poly(2-vinylpyridine). The initially smooth polymer surface is then exposed to radiofrequency oxygen plasma etching, which generates a rough polymer surface, with large 1–2 μm -size features as shown in Fig. 5. The two polymers form a uniform but compositionally segregated surface in which nanometer-sized domains of the two polymers are present with an overall even surface composition, as judged by ATR-IR and XPS measurements. Upon exposure to a solvent that solvates one of the two polymers preferentially, the surface characteristics change dramatically. For example, on exposure of the surface to toluene, the poly(2-vinylpyridine) forms round domains within the polystyrene matrix, while exposure to water at pH = 3 causes the polystyrene to be buried within the surface. 1,4-Dioxane gives lamellar-type structures on the surface. This had dramatic effects on the wettability of the surface. While exposure to toluene causes water to roll off the surface, exposure of the surface to acidic

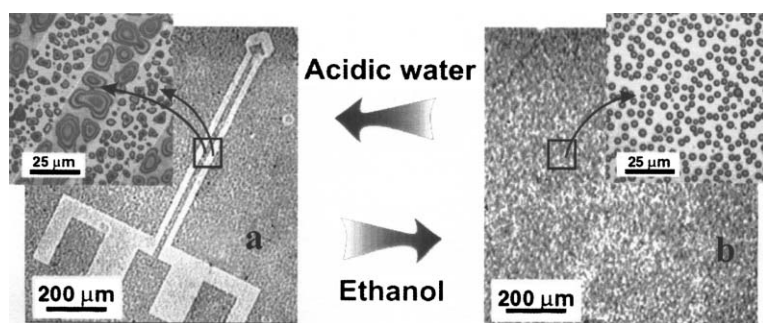


Fig. 4 The images show the adsorption of water drops on the polymer brush with developed (a) and erased (b) patterns (reproduced with permission from *J. Am. Soc. Chem.* 2003, **125**, 8302–8306. Copyright 2003 Am. Chem. Soc.).

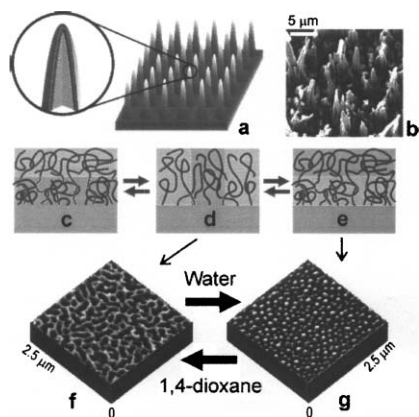


Fig. 5 a) Schematic representation of the two-level structure of self-adaptive PTFE surfaces showing a needle-like morphology; b) shows the SEM image of the etched PTFE film; c–e) each needle is covered by a covalently grafted mixed brush that consists of hydrophobic and hydrophilic polymers; f) the AFM image shows the surface morphology after exposure to 1,4-dioxane; g) shows the AFM of the surface after exposure to water (reproduced with permission from *J. Am. Soc. Chem.*, 2003, **125**, 3896–3900. Copyright 2003 Am. Chem. Soc.).

water causes a wicking effect, and the water drop spreads out attesting to the hydrophilic nature of the surface.

Supramolecular polymers

Supramolecular polymers are composed of monomeric units held together by directional and reversible non-covalent interactions such as hydrogen bonding and π – π interactions. The structure and

stability of such polymeric systems is in nature highly dependent on external stimuli, including solvent and temperature. Takeshita and others reported very recently an elegant example of a photo-reversible supramolecular polymer system that is based on switching on and off the intermolecular multiple hydrogen bonding by use of a photoswitchable dithienylethene unit (Fig. 6).^{15a}

UV irradiation with $\lambda = 366$ nm of a colorless solution of the open form in CHCl_3 resulted in the formation of the closed photoisomer as indicated by the appearance of a characteristic violet color. Visible irradiation ($\lambda = 540$ nm) reversed the supramolecular polymer formation.

A family of supramolecular polymers are held together by metal–ligand interactions and are not considered as classical supramolecular polymers as they often do not exhibit dynamic properties but rather static ones. The vast majority of metal-coordination based supramolecular polymers have been characterized in the solid state. Although many structures have been identified, well-characterized linear systems in solution are relatively rare.¹⁶ A recent example of a solvent or temperature triggered optical response in a metallo-supramolecular SRM was reported by Beck and Rowan,¹² which is based on a coordination polymer of a ditopic nitrogen-based ligand with transition metals Co^{II} and Zn^{II} as shown in Fig. 7. Under these conditions, the ditopic ligand chelates to the transition metal ions, forming a

linear polymer. However, in the presence of lanthanide ions (La^{III} or Eu^{III}), highly cross-linked gels are obtained. These polymer gels exhibit thermoresponsive behavior at 100°C in MeCN undergoing a gel–sol transition, which is caused by de-coordination of the ligand from the lanthanide, thereby reducing the amount of cross-linking. After cooling, the gel is reformed. The potential application lies in their use as photo- or electroluminescent materials that can be reversibly solvent or temperature triggered. For example, the Zn/Eu polymer exhibits Eu centered emissions at 581, 594, 616, and 652 nm, as well as a ligand-based emission at 397 nm. Heating this material results in a significant reduction of the Eu-based emissions without reducing the ligand-based emission. A solvent response is observed upon addition of formic acid, which will chelate the Eu^{III} and displace the nitrogen-based ligand, causing complete quenching of the Eu^{III} emission. This behavior can be reversed by drying of the material, followed by re-swelling in acetonitrile. It is clear from this work that other metal-based functionalities can be introduced into a coordination polymer by choosing the appropriate molecular building blocks.

Opto-control of biological activity

An important driving force to generate SRMs is for medical and biotechnological control of biological processes

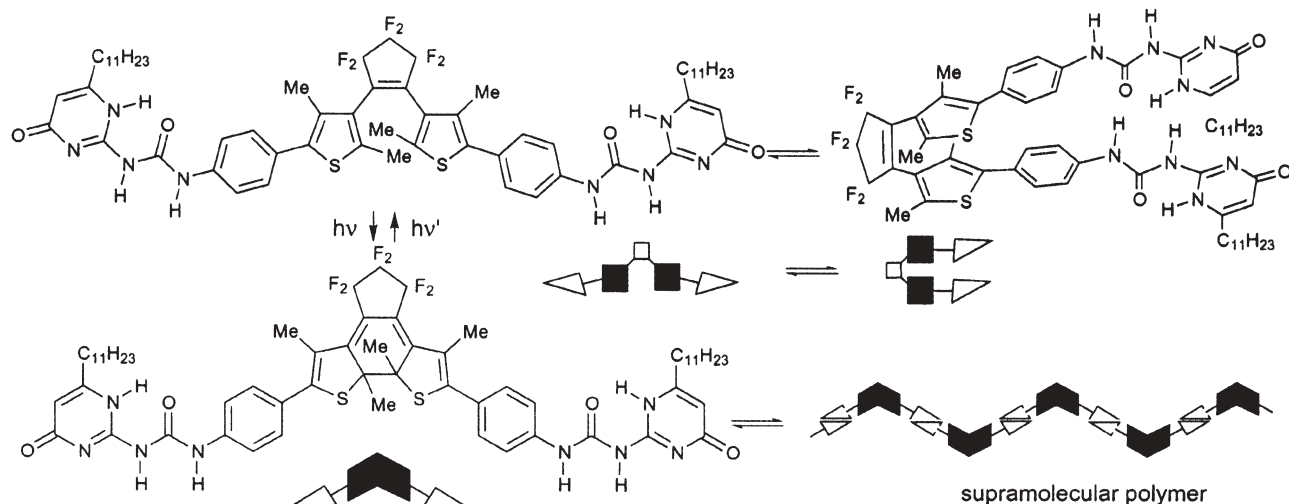


Fig. 6 Example of a photoresponsive supramolecular polymer. The polymer unit has two terminal ureidopyrimidinone groups for hydrogen bonding and a photochromic dithienylethene unit^{15a} reproduced from *Chem. Commun.* 2005, 761. Copyright The Royal Society of Chemistry 2005

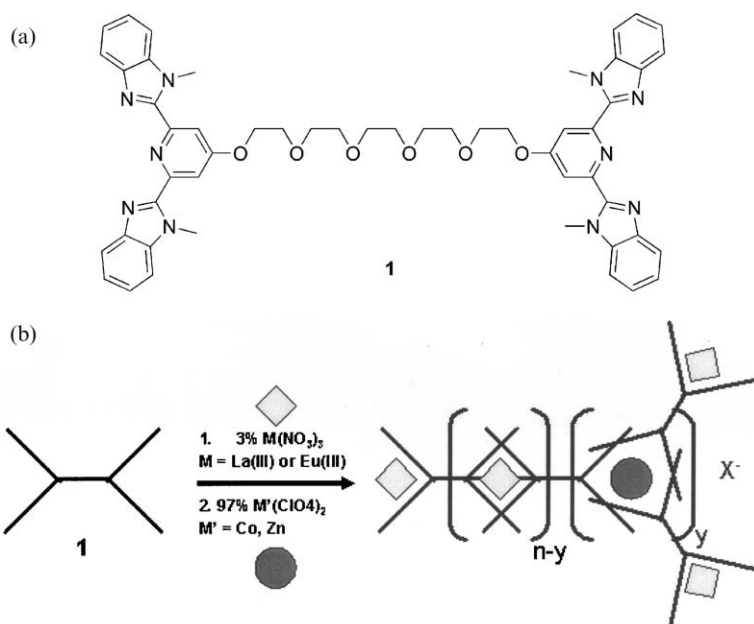


Fig. 7 Schematic representation of the formation of a metallo-supramolecular gel-like material using a combination of lanthanide and transition metal ions mixed with monomer **1** (reproduced with permission from *J. Am. Chem. Soc.* 2003, **125**, 13922–13923. Copyright 2003 Am. Chem. Soc.).

ranging from protein–ligand recognition, protein purification, immobilization of peptides to photoresponsive polymer–enzyme switchable systems.^{6c,d,7c,9a,c} The latter system is of particular interest for regulating enzymatic activities using light in microfluidic devices. The multifunctional photoresponsive polymers shown in Fig. 8 has azobenzene units as light sensitive probes and serve as an actuator to control the activity of enzyme endoglucanase 12A (EG 12A).^{6c} The terminal vinylsulfone moiety allows conjugation to a sulfhydryl group of a protein. EG 12A is an efficient catalyst for the internal β linkages of cellulose and is of commercial importance. *o*-Nitrophenyl- β -D-cellobioside was used as a model substrate as it is hydrolyzed by EG 12A to *o*-nitrophenol.

The photoswitching can be cycled between the active state and the off state as shown in Fig. 9 with a response time <1 min. Both states are stable for several hours. Interestingly, the N55C-DMA-*co*-4-phenylazophenyl acrylate (DMAA) conjugate is active when exposed to UV light and turned off under VIS light, whereas the N55C-(DMA-*co*-*N*-4-phenylazophenyl acrylamide) DMAAm system is activated with VIS light and switched off under UV light. These opposite enzyme activity responses are in line

with the different photoinduced phase transitions of the conjugated polymers. The DMAA polymer forms an extended coil under far UV illumination ($\lambda = 350$ nm) and changes into a compact system under VIS illumination ($\lambda = 420$ nm). The DMAAm polymer

switches between these two states in the opposite way. The photoresponsive SRM-EG 12A system can be immobilized on magnetic beads which may lead to pro-drug therapeutic applications where the enzyme will be activated by light when a specific target is within reach.

Summary and outlook

The combination of a bottom-up approach expressed in the molecular design of SRMs combined with chemical patterning and external triggering shows great promise for the development of smart materials. Although there have been major advancements in various fields of nanotechnology and chemistry of materials, there are still today gaps in the ability to couple the microscopic and macroscopic phenomena. The studies highlighted here^{10–12,15} and recent work by many others^{1–9,13,14} show significant advances in the design of new SRMs with specific responses. However, it is clear that although the state-of-the-art of SRMs has advanced considerably during the past decade in terms of mechanical response efficiency, reversibility, and stability, this area still poses tremendous challenges and is highly intriguing. At present there are

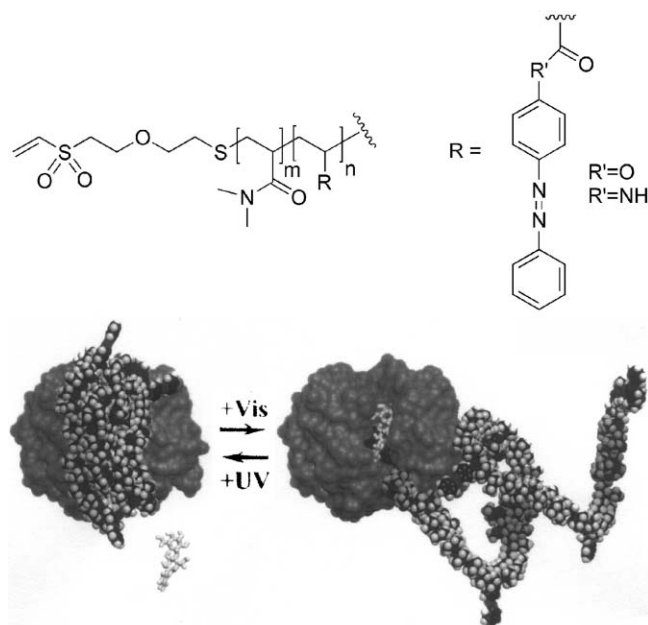


Fig. 8 a) Photoresponsive copolymer compositions with vinyl sulfone terminus for thiol-specific conjugations. b) Example of a photoresponsive enzyme switch based on the photoresponsive copolymer and EG 12A.^{6c} (Reprinted with permission from *Proc. Natl. Acad. Sci. USA*, 202, **99**, 16592. Copyright *Proceedings of the National Academy of Sciences USA*).

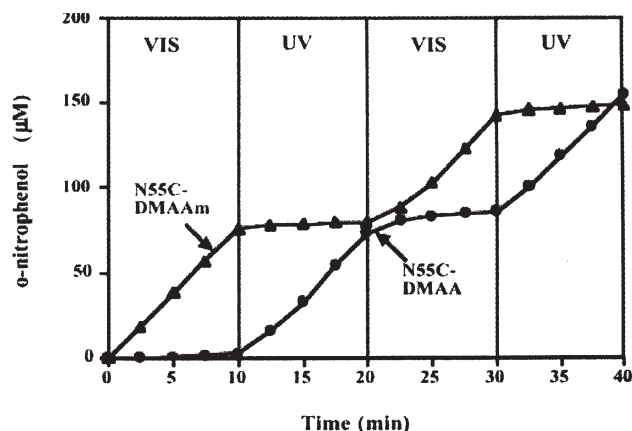


Fig. 9 Demonstration of photoswitching of the activity of the EG 12A mutant N55C DMA-co-4-phenylazophenyl acrylate (DMAA) and DMA-co-N-4-phenylazophenyl acrylamide (DMAAm) conjugates. The *o*-nitrophenol concentration was measured for 100 nM conjugates with free polymer present, using ammonium sulfate, *o*-nitrophenyl- β -D-cellobioside (8 mM) as a substrate at 45 °C in a 50 mM sodium acetate buffer with pH 5.5.^{6c} (Reprinted with permission from *Proc. Natl. Acad. Sci. USA*, 202, **99**, 16592. Copyright *Proceedings of the National Academy of Sciences USA*).

still various fundamental issues to be addressed. In particular, the design of SRMs with exceptional robustness and the ability to withstand fast continuous cycling with a fast response time are highly desirable targets. However, it is important to realize that significant advances in the design of new SRMs with substantially advanced characteristics will most likely require the design at the molecular and the mesoscopic scales. The design of smart and stable materials that encompass the individual molecular response and allow a collective molecular contribution to generate a concerted macroscopic phenomenon is highly desirable and an intriguing task. Ideally, the overall material response should preserve the individual molecular responses. In particular, the design of molecule-based structures featuring an interrelating collection of components that has the ability to store energy in a reversible molecular conformation is highly desired. Subsequently, the stored energy can be converted into a mechanical motion for performing work or dynamically controlling a micro or macroscopic material property. Further optimization and fine-tuning of these parameters by applying novel approaches based on recent findings such as highlighted here to robust polymeric systems that can be readily processed is a distinct possibility for generating series of device-quality “smart” polymers. An example is the successful introduction of dendrimers

for the formation of highly efficient electrooptic poled polymers.^{1e,14} It is noteworthy that poly(*N*-isopropylacrylamide) (poly(NIPAAm)) is the workhorse for many researchers in the SRM field, however, the wide range of readily available polymeric materials allows fine-tuning of the material properties for a given task. Chemical or photolithographic patterning of SRMs to create areas of (multifunctional) substrate surfaces that respond to external stimulus is an exciting development as they can be used for information storage and the formation of microdevices. Important progress on the realization of reversible photopatterned 2D and 3D data storage has been reported recently by demonstrating repeated “recording–erasing” processes using thermally robust photochromic compounds.¹⁷ Equally important is the use of polymeric materials as substrates for the construction of SRM-based microdevices using conventional patterning techniques. For instance, poly(methyl methacrylate) (PMMA) and related substrate surfaces can be chemically modified to afford a reactive (e.g., amine, hydroxyl, carboxyl groups) terminated surfaces that can be functionalized with SRMs. Applicable SRM-based devices may soon become a reality, with the photo-triggered and photopatterned SRMs begins a valuable entry for the formation of a variety of nano-level devices, memory elements, or molecular machines.

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