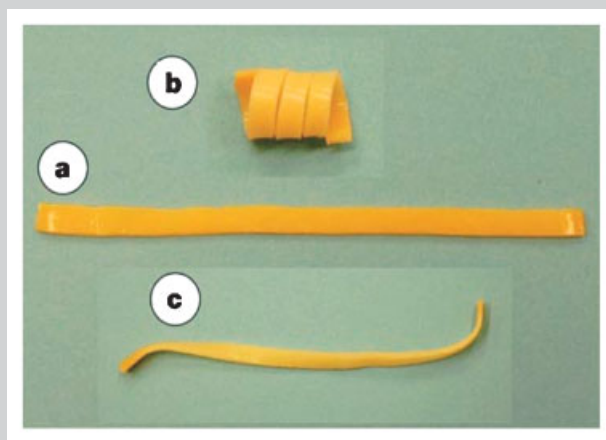


**Summary:** Starting in the 1960s, several kinds of photodeformable polymers have been developed, such as monolayers, polymer gels, solid films and liquid-crystalline elastomers with different photodeformation mechanisms. This field evolved slowly until recently when significant achievements have been made. Most recently, Lendlein and co-workers have put forward another new concept – using photo-crosslinking to prepare deformable polymers with various pre-determined shapes (*Nature* **2005**, *434*, 879). This highlight gives a general introduction into photodeformable polymers and brings forth future challenges.



A polymer film doped with SCAA molecules where (a) is the permanent shape, (b) is the temporary shape and (c) is the recovered shape.

## Photodeformable Polymers: A New Kind of Promising Smart Material for Micro- and Nano-Applications

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### Introduction

Human civilization is profoundly influenced by material technologies whose historical evolution experiences a distinct transition from structural materials to functional materials, and now “smart” materials.<sup>[1]</sup> Smart materials have the capability to select and execute specific functions intelligently, in response to changes in environmental stimuli. Particularly, materials that can sense signals and produce a definite dynamic response in the form of a change in shape or volume are central to developments in various scientific fields.<sup>[2]</sup> Although many materials are under active investigation in this field, polymers play a leading role because they provide such advantages as flexibility, light weight, low cost and quiet operation compliance (thus shock resistance).<sup>[1–4]</sup> To induce deformation, many chemical and physical stimuli have been applied, such as pH,

solvent composition, temperature, electric field, magnetic field and light. Light is a clean energy and can be controlled rapidly, precisely and remotely. Therefore, photodeformable polymers attract increasing attention from researchers.

Starting in the 1960s, several amorphous polymer systems, including monolayers, gels and solid films, have been developed for the research of photoinduced contraction/expansion.<sup>[5–8]</sup> Recently, by using liquid-crystalline elastomers (LCEs), not only photocontraction but also photoinduced bending has been acquired.<sup>[9–18]</sup> In comparison with contraction/expansion which is a two-dimensional action, bending (a three-dimensional movement) should be advantageous for artificial hands and medical microrobots that are capable of completing particular manipulations. Most recently, Lendlein and co-workers reported that polymers containing cinnamic groups can be deformed and fixed into more complicated shapes, such as elongated films

and tubes, arches or spirals, by irradiation with UV light, and they can recover their original shape at ambient temperatures when exposed to UV light of a different wavelength.<sup>[19]</sup> Undoubtedly, this work will stimulate the actual uses of photodeformable smart materials. Here, the purpose of this highlight is to give a general introduction to photodeformable polymers classified by their different deformation mechanisms and to anticipate future developments and challenges in the field.

## Polymer Gels

In 1990, Tanaka and co-workers reported that photosensitive gels incorporated with a leuco derivative swelled in response to UV light irradiation but shrank when the UV light was removed.<sup>[20]</sup> The swelling is caused by an increase in osmotic pressure within the gels due to the appearance of cyanide ions formed by UV light irradiation. Visible light-sensitive gels were prepared by introducing a chromophore (trisodium salt of copper chlorophyllin) to thermosensitive gels. A temperature increase caused by the light absorption of the chromophore altered the swelling behavior of the gels.<sup>[21]</sup> Furthermore, infrared light was also used to elicit a gel response in the absence of the chromophores, since a temperature gradient due to the high infrared light absorptivity of water resulted in deformation.<sup>[22]</sup> In the above cases, the speed of the volume changes is limited by the slow diffusion process.

## Photochromic Amorphous Systems

Most of the photochromic amorphous systems capable of generating photodeformation contain azobenzene chromophores. It is well known that upon alternate irradiation of UV and visible light, azobenzene undergoes reversible *trans-cis* isomerization accompanied by a significant change in molecular length from about 9.0 Å in the *trans* form to 5.5 Å in the *cis* form. Therefore, by incorporation of azobenzene chromophores into polymer backbones or side chains in monolayers, gels and solid films, irradiation at the two different wavelengths produced reversible contraction and expansion of the materials.<sup>[5–7]</sup> On the other hand, it is also known that the *trans*-azobenzene has a small dipole moment of less than 0.5 D, while the dipole moment of the *cis* form is about 3.1 D. Thus, when the azobenzene units in monolayers are free from the water subphase, the monolayers show the opposite photodeformation behavior. They expanded when exposed to UV light and shrank when exposed to visible light. This resulted from the different affinities of the *trans*- and *cis*-azobenzene to the water surface.<sup>[7,8]</sup> From the viewpoint of applications, polymer gels and solid films are of greater interest than monolayers. However, gels have a serious disadvantage in that their response is slow, and the deformation of solid films is too small to be practically utilized.

## Liquid-Crystalline Elastomers

Recently, a new polymer system showing large photocontraction has been developed by Finkelmann and other researchers using azobenzene LCEs (Figure 1).<sup>[9–12]</sup> In these pioneering works, the driving force for the deformation is suggested to arise from the variation of alignment order caused by the well-known photochemical phase transition. Upon UV light irradiation, the azobenzene LCs experience a reduction in alignment order, and even an LC-isotropic phase transition, due to photoisomerization of the azobenzene moieties, because the rod-like *trans*-azobenzene moieties stabilize the LC alignment, whereas the bent *cis* forms lower the LC order parameter. More recently, photoinduced bending in azobenzene LCEs has been achieved,<sup>[13–16]</sup> and even precisely direction-controllable bending has been realized (Figure 2).<sup>[17]</sup> The bending is ascribed to a volume contraction induced by the photochemical phase transition only in the surface region due to the limitation of absorption of photons. Subsequently, an azobenzene-doped LCE sample floating on water was observed to swim away from the light.<sup>[18]</sup>

## Shape-Memory Polymers

Most recently, Lendlein and co-workers reported an excellent study, which adds a new kind of valuable material to the family of photodeformable polymers – photoinduced shape-memory polymers.<sup>[19]</sup> They include two species of photoresponsive polymer networks. One is a grafted polymer incorporated with HEA-CA molecules, and the other is a polymer network doped with SCAA molecules (Figure 3). Similar to thermally induced shape-memory polymers, a photoresponsive polymer film was first stretched by an external force. Then, exposure to UV light longer than

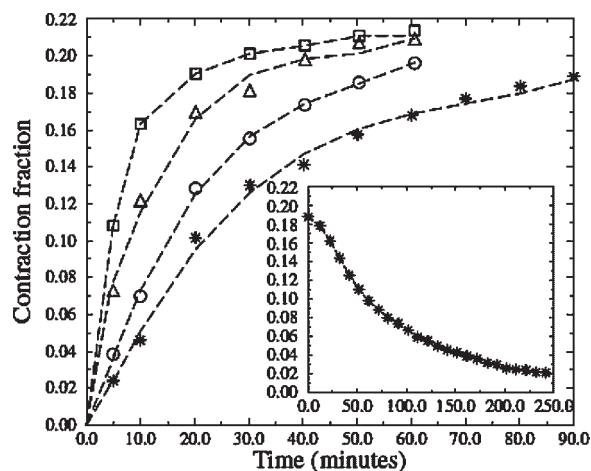


Figure 1. Contraction fraction of an LCE versus the time when the elastomer was exposed to UV light at 298 K (\*), 303 K (O), 308 K (Δ) and 313 K (□). Inset: Recovery of the contracted elastomer at 298 K after irradiation was switched off.<sup>[19]</sup>

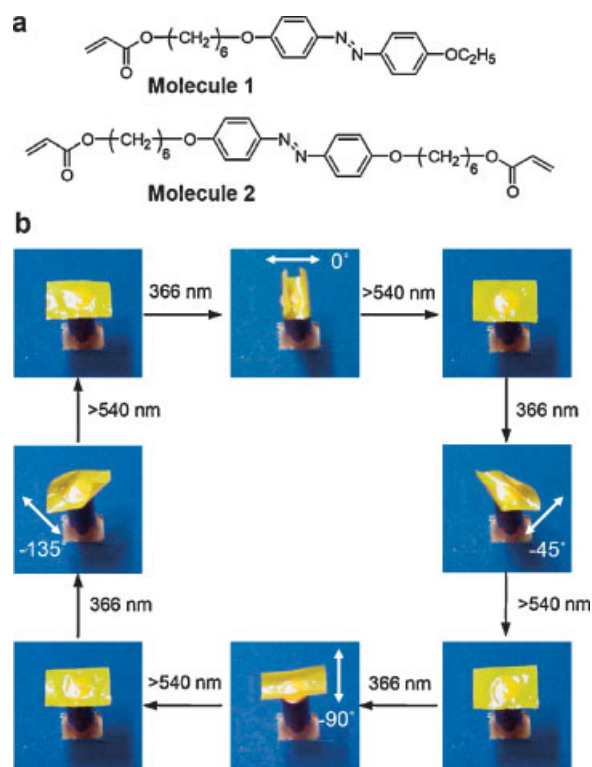


Figure 2. Precise control of the bending direction of an LCE film by linearly polarized light. (a) Chemical structures of the LC monomer (molecule 1) and crosslinker (molecule 2) used for preparation of the film; (b) Photographic frames of the film bending in different directions in response to irradiation by linearly polarized light of different angles of polarization (white arrows) at 366 nm, and being flattened again by visible light at >540 nm.<sup>[17]</sup>

260 nm led to the fixation of the elongated shape due to a photoinduced [2 + 2] cycloaddition reaction. After the external stress was released, the film could stay in an elongated form for a long time. Irradiation of the elongated sample with UV light shorter than 260 nm at ambient temperature brought about the cleaving of the crosslinks and the recovery of the original shape of the film (Figure 3A). Furthermore, when only the top side of a polymer film in a stretched state was irradiated with UV light longer than 260 nm, a corkscrew spiral shape was obtained due to the formation of two layers, in which the elongation is fixed well for the top layer and the bottom layer keeps its elasticity (Figure 3B). For potential specific applications, different original and deformed temporary shapes can be made in a pre-determined manner. The unique characteristics of the above photoinduced shape-memory polymers enable the manipulation of the shape recovery at ambient temperatures by remote activation and the elimination of the temperature constraints for medical and other applications arising from external sample heating.

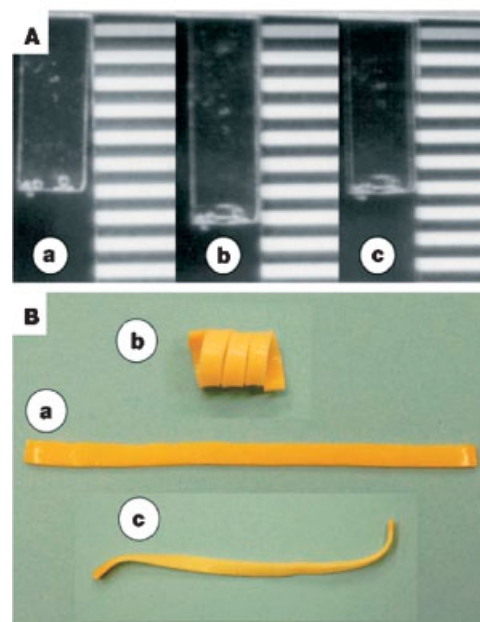
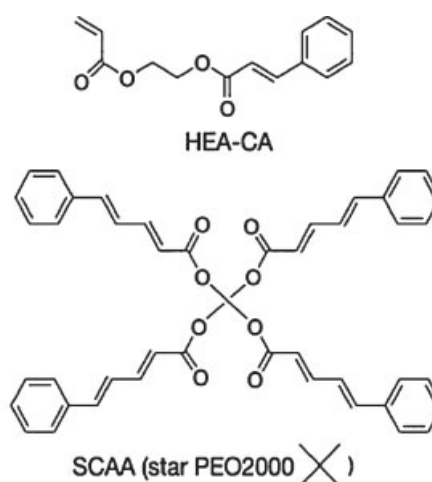


Figure 3. Shape-memory effect of photoresponsive polymer networks. (A) A film of grafted polymer incorporated with HEA-CA molecules; (B) A polymer film doped with SCAA molecules: (a) Permanent shape; (b) temporary shape; (c) recovered shape.<sup>[19]</sup>

## Conclusion and Perspectives

By using the deformations of photodeformable polymers, we can convert light energy into mechanical power directly (photomechanical effects). Moreover, since deformations driven by light require neither batteries nor controlling devices on the materials themselves, it should be simple to miniaturize them for micro- and nano-applications. Although the photodeformable polymers are materials with great potential, the number of significant contributions in the field is still limited. The work published by Lendlein and co-workers constitutes a very important step in the field, since they put forward the concept of using photo-cross-linking to prepare deformable polymers with various

pre-determined shapes.<sup>[19]</sup> For the future, a concerted effort still has to be made in order to study the properties of the various above mentioned photodeformable polymers and their possible applications.

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