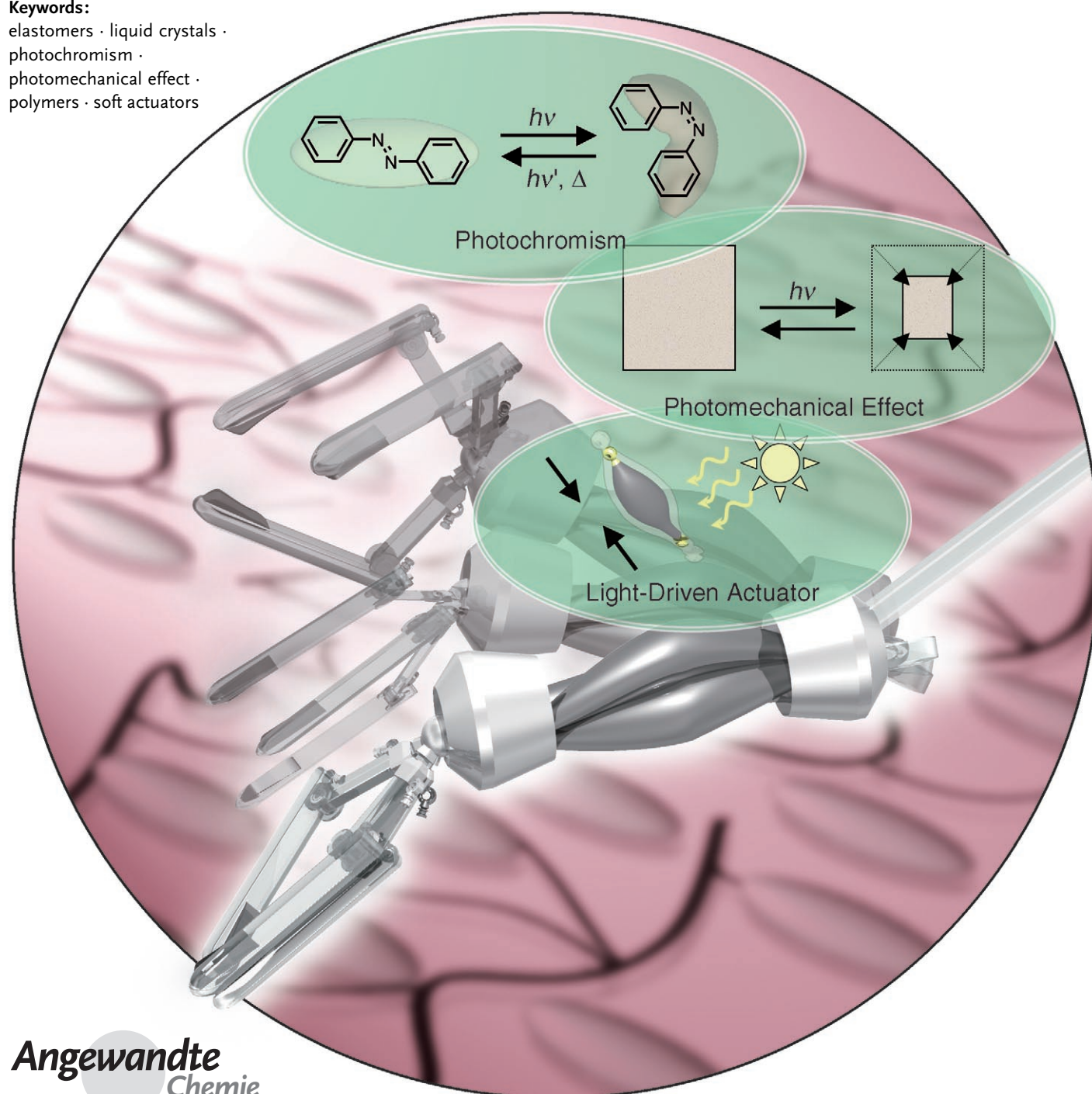


Photomechanics of Liquid-Crystalline Elastomers and Other Polymers**

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Muscle is a transducer that can convert chemical energy into mechanical motion. To construct artificial muscles, it is desirable to use soft materials with high mechanical flexibility and durability rather than hard materials such as metals. For effective muscle-like actuation, materials with stratified structures and high molecular orders are necessary. Liquid-crystalline elastomers (LCEs) are superior soft materials that possess both the order of liquid crystals and the elasticity of elastomers (as they contain polymer networks). With the aid of LCEs, it is possible to convert small amounts of external energy into macroscopic amounts of mechanical energy. In this Review, we focus on light as an energy source and describe the recent progress in the area of soft materials that can convert light energy into mechanical energy directly (photomechanical effect), especially the photomechanical effects of LCEs with a view to applications for light-driven LCE actuators.

1. Introduction

Many studies on actuators for the construction of artificial muscles have been performed recently. An actuator is an energy transducer that can convert input energies of a variety of forms into mechanical quantities such as displacement, strain, velocity, and stress. Many types of materials have already been developed as actuator materials, including inorganic materials such as shape-memory alloys and electrostrictive and piezoelectric materials. However, to realize muscle-like movements in artificial actuators, these should be soft and deform in response to external stimuli such as changes in electric field or temperature.^[1] Polymers are one of the most promising materials for artificial muscles because of their advantageous properties, such as their high processability, softness, easy fabrication characteristics, high corrosion resistance, and low manufacturing costs. Many actuators that respond to various external stimuli have been developed using polymers as base materials: polymer gels,^[2–4] conducting polymers,^[5–7] carbon nanotubes,^[8–11] and dielectric elastomers.^[12] Among these materials, polymer gels have attracted much attention as artificial muscles because polymer gels contain fluid in their three-dimensional network structures, which provides softness as well as high biocompatibility; moreover, large deformations are produced with only a small stress. In particular, electric-field-responsive polymer gels are superior to other materials in view of their high sensitivity to electric fields and the large amount of mechanical energy produced by an electric field. However, polymer gels have some disadvantages: they swell in fluids and require cycles of swelling and shrinking to induce their deformation, which could in general result in slow response times and low fatigue resistance. From this point of view, dry actuators are advantageous. Shape-memory materials consisting of cross-linked polymers function by the combination of cross-linking reactions and polymer crystallization, which fix the shape of the polymers.^[13] Furthermore, a variety of external stimuli that produce effective responses have been examined, for

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example, heat, light, electric field, magnetic field, and concentration of fluids.

Studies on photoinduced deformation (contraction and expansion) of amorphous polymers have been performed intensively since the 1960s.^[14–17] Light as an external stimulus enables the remote control and rapid deformation of materials. Furthermore, no wires or connections are necessary to use light as a stimulus, which enables easy fabrication of the devices and reduces the weight. Light-driven polymer actuators, therefore, are promising in a wide range of micro- and macroscale devices. However, in these amorphous polymer materials, the deformation in response to external stimuli takes place in an isotropic way; there is no preferential direction for the deformation. Also the degree of the deformation is in general small. If the materials possess any anisotropy, their deformation in response to external stimuli could be induced in an anisotropic way with preferential direction of the deformation, which could produce a much larger deformation than that observed in amorphous materials.

Liquid-crystalline elastomers (LCEs) are a new type of material that have properties of both liquid crystals (LCs) and elastomers; the elastomer properties arise from polymer networks. LCEs contain mesogens, which, because of their LC properties, are aligned; this alignment of the mesogens is coupled with polymer network structures and gives rise to the characteristic properties of LCEs. Depending on the mode of alignment of the mesogens, LCEs are classified into nematic LCEs, smectic LCEs, cholesteric LCEs, and so on. If a

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nematic LCE film is heated toward the nematic–isotropic phase-transition temperature, the nematic order decreases, and the mesogens become disordered when the temperature exceeds the phase-transition temperature. With this phase transition, the LCE films in general show contraction along the alignment direction of the mesogens; if the temperature is lowered below the phase-transition temperature, the LCE films revert to their original size (expansion). This anisotropic deformation of the LCE films is sometimes very large, which makes the LCE materials promising as artificial muscles.^[18,19] The incorporation of photochromic moieties into LCEs can induce a reduction in the nematic order (and in extreme cases conversion into the isotropic phase) and causes a contraction of the films upon exposure to UV light as a result of a photochemical reaction of the photochromic moiety.^[20–22] Furthermore, three-dimensional movement (bending) of LCE films was observed by incorporation of photochromic moieties into LCEs.^[23,24] Light-driven actuators based on LCE materials are a topic of recent intensive studies, and a variety of actuation modes have been developed.

In this Review, we describe photomechanical effects observed in many kinds of materials, focusing our attention on light-driven LCE actuators. In Section 2, we summarize the photomechanical effects in monolayers, gels, and polymers. In Section 3, we describe LCEs, their preparation and general properties, and their responses to various external stimuli other than light. In the final section of this Review, we discuss the photoresponsive behavior of LCEs, focusing on recent progress in this field.

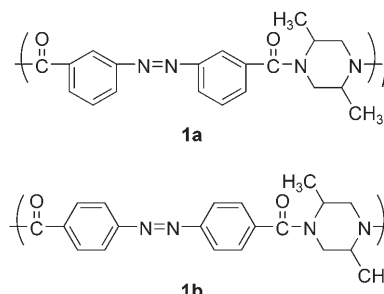
2. Photomechanical Effects in Various Systems

2.1. Monolayers

Azobenzene is a classical photochromic molecule that has been used by many researchers to incorporate photoresponsive properties into materials: its *trans*–*cis* photoisomerization produces a variety of changes in physicochemical properties of the materials, such as molecular length and polarity. The introduction of azobenzene functions to polymers also leads to fascinating photoresponsive systems. Monolayers of the azobenzene polymers are easily prepared at air/water interfaces. In a monolayer, changes in the

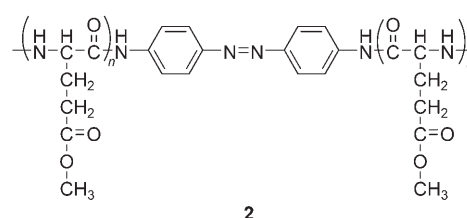
molecular shape and orientation can be directly related to the film properties, such as area and surface pressure. The molecular motion of azobenzene moieties in polymers at a monolayer interface is transferred and amplified to a macroscopic level of the materials.

Photomechanical effects of a monolayer consisting of polyamide with azobenzene moieties in the main chain (**1**)



were first reported by Blair et al.^[25,26] A decrease in stress at the air/water interface was observed upon irradiation of the monolayer with UV light, thus indicating contraction of the monolayer. When the monolayer was in darkness, the stress increased again; this cycle could be repeated many times. For these main-chain type monolayers, the azobenzene moieties are considered to lie flat on the water surface. The photomechanical effects are due to the *trans*–*cis* isomerization of the azobenzene moieties, which occupy a larger area at the interface when they are in the more-linear *trans* form than in the *cis* form.

Higuchi et al. prepared a polypeptide monolayer composed of two α -helical poly(γ -methyl L-glutamate) rods linked by an azobenzene moiety (**2**).^[27] The *trans*–*cis* photoisomerization and the consequent variation in geometry of



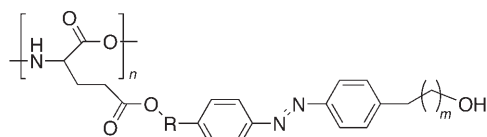
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the azobenzene moiety led to bending of the main chain of the molecule and a decrease in the limiting area per molecule. It was estimated that the bending angle between the two α -helical rods, produced by irradiation with UV light, was about 140° . The photoinduced bent structure of **2** resulted in a decrease of the molecular area of **2** at the air/water interface owing to a decrease in the distance between the ends of the molecule. An important finding was that the photoinduced changes in the area of the monolayer of **2** occurred more slowly than the spectral changes of the azobenzene moieties. The photoinduced changes in the surface area may arise from rearrangement of the bent molecules of **2** induced by photoisomerization of the azobenzene moieties in the main chain. The intermolecular interaction of **2** in the solid condensed monolayer may serve to slow down the rate of their rearrangement.

The photoresponsive behavior of related polypeptides in which the side chains contain azobenzene functions were investigated by Menzel et al.^[28] They prepared poly(L-glutamate)s with azobenzene-containing side chains coupled to the backbone through alkyl spacers (**3**). The monolayers showed



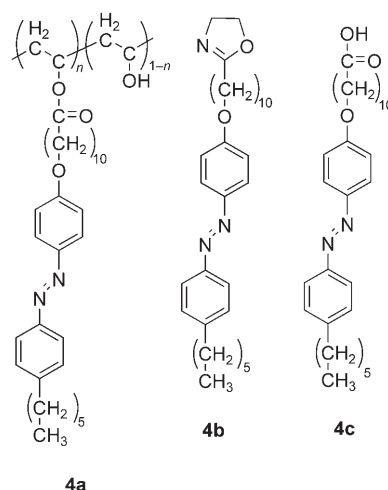
3a: R = C₆H₁₂, m = 2

3b: R = C₂H₄, m = 6

3c: R = C₆H₁₂, m = 6

photoresponsive behavior that was opposite to that of the above-mentioned systems. The monolayers expanded when exposed to UV light and shrank when exposed to visible light. The *trans*-*cis* photoisomerization of the azobenzene moiety upon irradiation with UV light leads to a large increase in the dipole moment of this unit, and this part gains a high affinity for a water surface.^[29]

Seki and co-workers prepared poly(vinyl alcohol)s (**4**) containing azobenzene side chains and observed photoinduced changes in their areas on a water surface.^[29–38] The



4a

4b

4c

monolayers at the air/water interface exhibited a threefold expansion in area upon irradiation with UV light and reversibly shrank by irradiation with visible light (Figure 1).

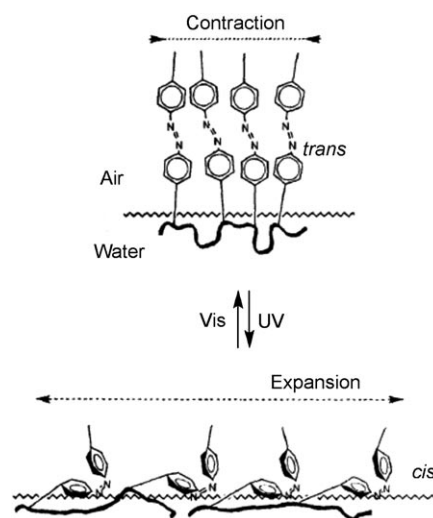
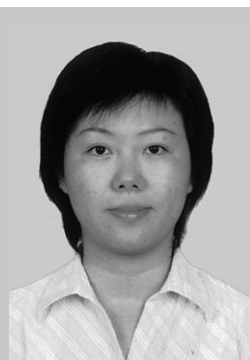


Figure 1. UV- and visible-light-induced deformation of a polymer monolayer containing azobenzene side chains at the air/water interface.

The mechanism of the photoinduced changes in area was interpreted in terms of the change in polarity of the azobenzene moiety: the *trans*-*cis* photoisomerization leads to an increase in dipole moment, thus bringing about a higher affinity of the *cis*-azobenzene for the water surface and the expansion of the monolayers. The *cis*-*trans* back-isomerization by irradiation with visible light leads to the recovery of the monolayers in the initial structure. The XRD data show that the monolayer of the *trans* isomer is thicker than that of the *cis* isomer. The change in thickness by 0.2–0.3 nm as a result of the *trans*-*cis* isomerization in the hydrophobic side chain is observed in situ on the water surface.^[35]

These results indicate that the photoinduced deformations of the azobenzene-containing monolayers strongly depend on the location of the azobenzene moieties in the dark: when the



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